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# Spectroscopic Signatures of Nitrogen-Substituted Zeolites

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## Abstract

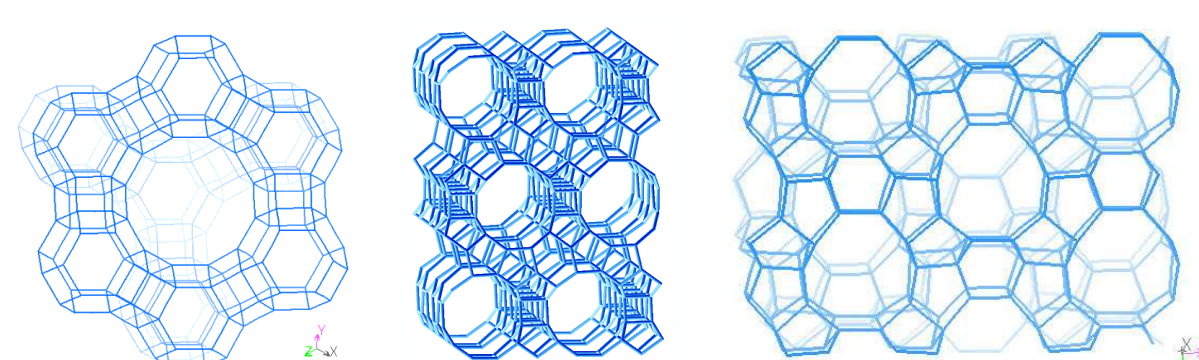
- Zeolites are crystalline microporous materials
  - Zeolites are typically acids
  - Treating zeolites with amines at high temperatures has been shown to produce basic (alkaline) catalysts in which nitrogen is substituted for oxygen
  - Goal: Find a way to characterize nitrogen substituted zeolites

### Methods

- Experiment: nuclear magnetic resonance spectroscopy, infrared spectroscopy, Raman spectroscopy, X-ray diffraction, physical adsorption
- Calculations: cluster models, Reaction energies, chemical shielding/chemical shifts (NMR), quadrupolar NMR, vibrational spectra (infrared/Raman).

### Materials of interest

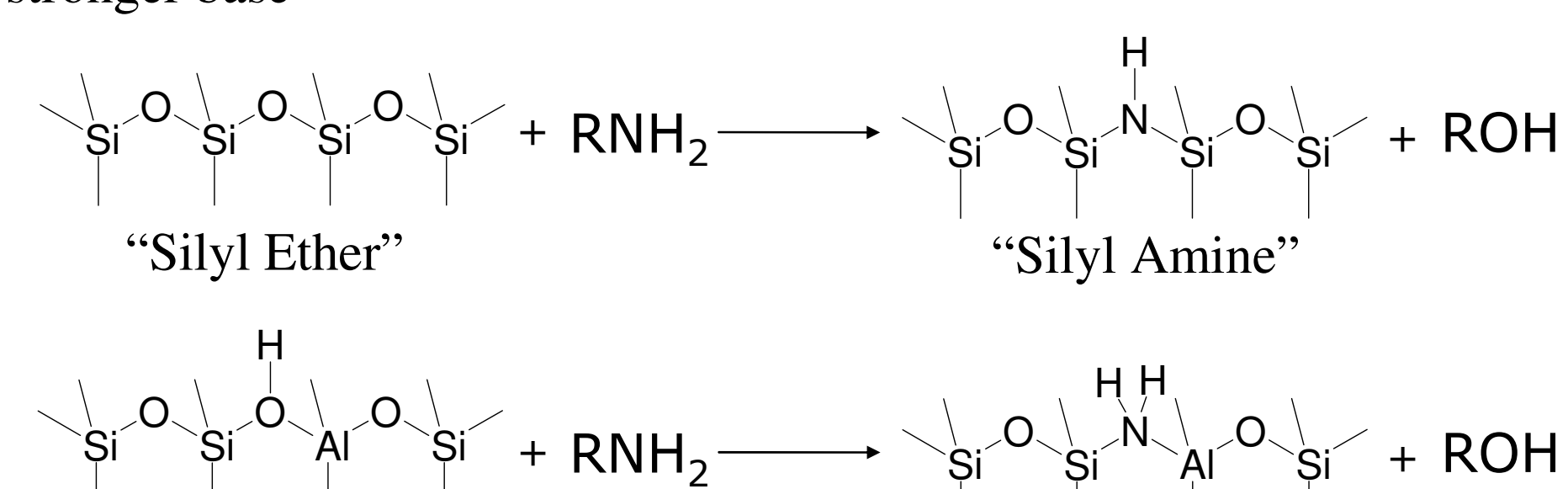
- Y zeolite (FAU structure)
- Beta zeolite (BEA structure)
- ZSM-5 (MFI structure)



We find compelling evidence from experiments and simulations that nitrogen incorporates into zeolite frameworks. Questions remain of the stability of these materials.

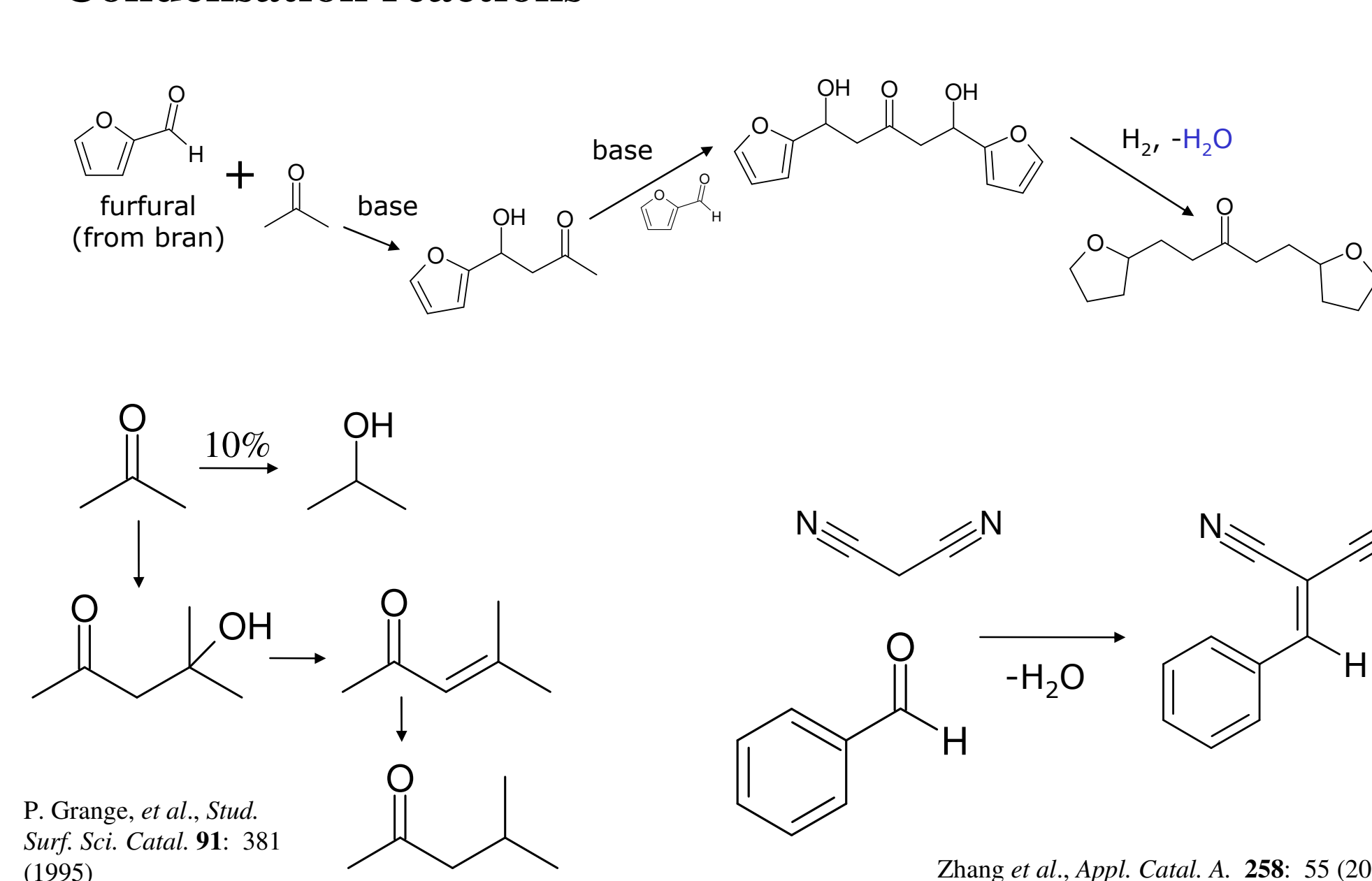
## Zeolites as Acid/Base Catalysts

- Zeolites are usually strongly acidic
  - Low-aluminum zeolites are stronger acids
  - High-aluminum zeolites are weak(er) acids
- The alkaline or alkaline-earth forms are weakly basic: NaY, CsX, K-ZSM-5
  - Low-aluminum zeolites (e.g. K-ZSM-5) are very weak bases
  - High-aluminum zeolites (e.g. CsX) are merely weak bases
- IDEA: Replace some oxygen in the zeolite with nitrogen to produce a stronger base



## Examples of Uses for Zeolitic Base Catalysts

### Condensation reactions

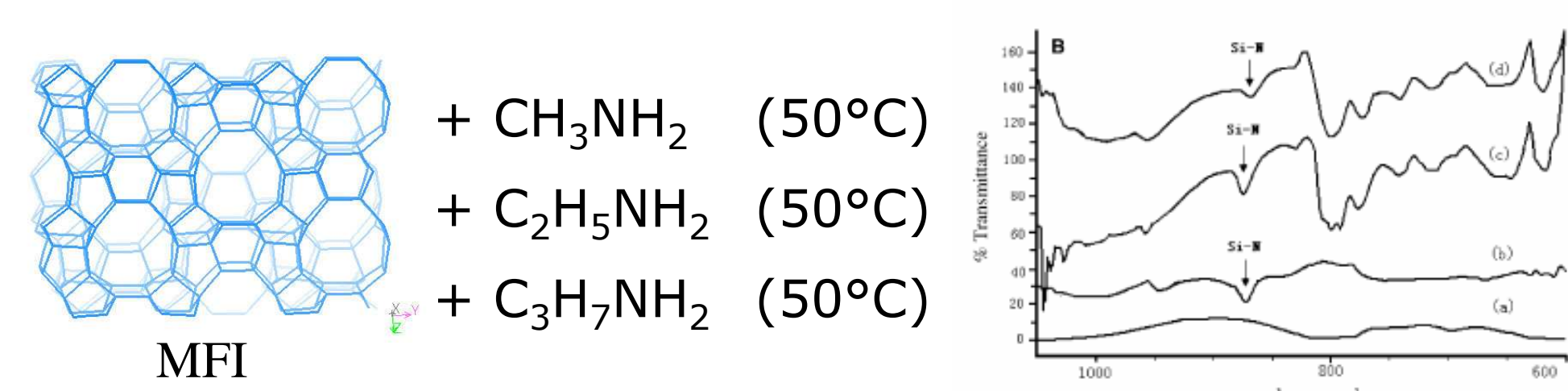
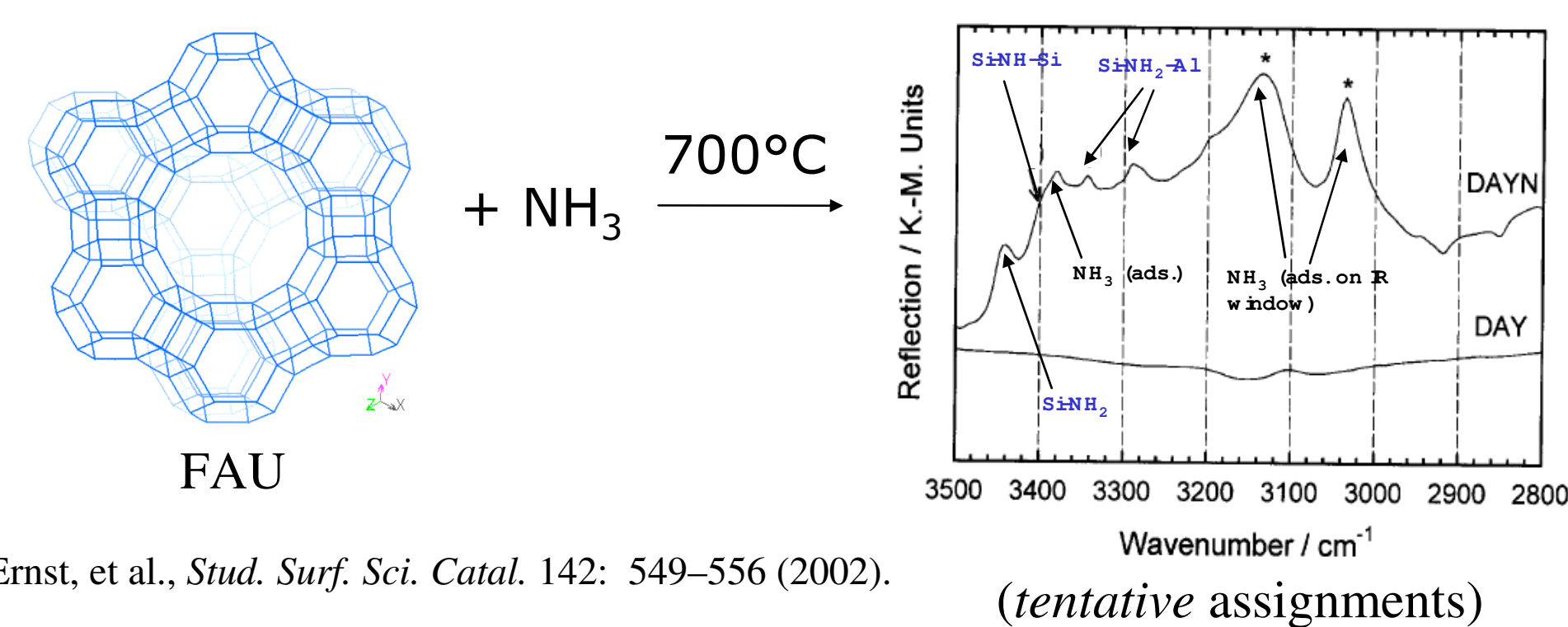


## How to Make Zeolites into Bases

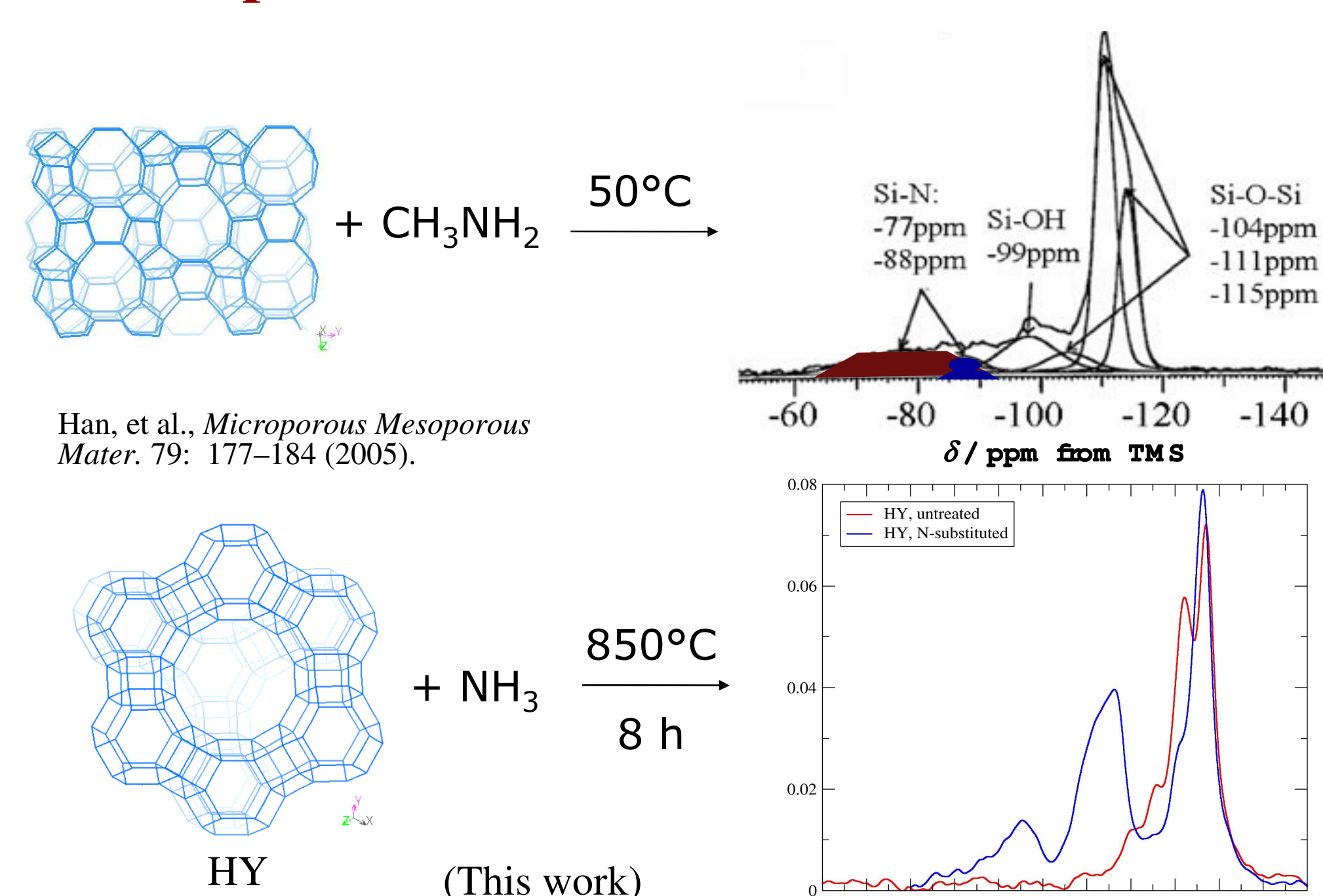
- Step 1: Heat
  - Removes water
  - Removes some hydroxides on surface
- Step 2: Expose to a nitrogen source:
  - Ammonia (NH<sub>3</sub>)
  - Alkylamines (CH<sub>3</sub>NH<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub>, etc.)
  - Others: Polysilazane (SiCl<sub>4</sub>+NH<sub>3</sub> deposited and pyrolyzed), Silicon nitride (Si<sub>3</sub>N<sub>4</sub>), Azides (NaN<sub>3</sub>, etc.), Nitrogen gas (N<sub>2</sub>)



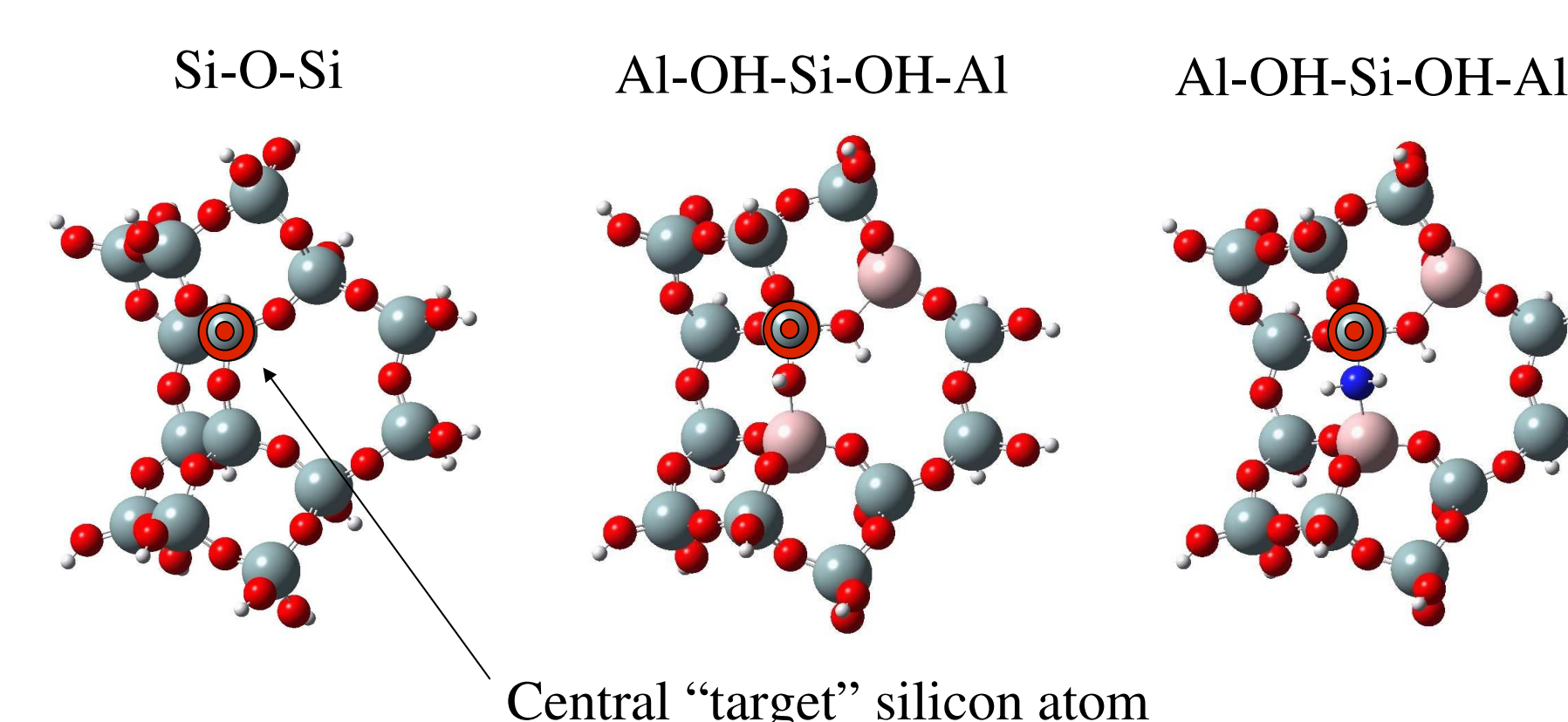
## Experimental Characterization: Infrared



## Experimental Characterization: NMR



## Cluster Calculations



- Things to vary from cluster to cluster:
- Aluminum atoms nearby
  - Placement of hydrogen
  - Number of nearby nitrogen vs. oxygen atoms

## Chemical Shift Calculations

$$\Delta E = \hbar \gamma \Delta I (1 - \sigma) B$$

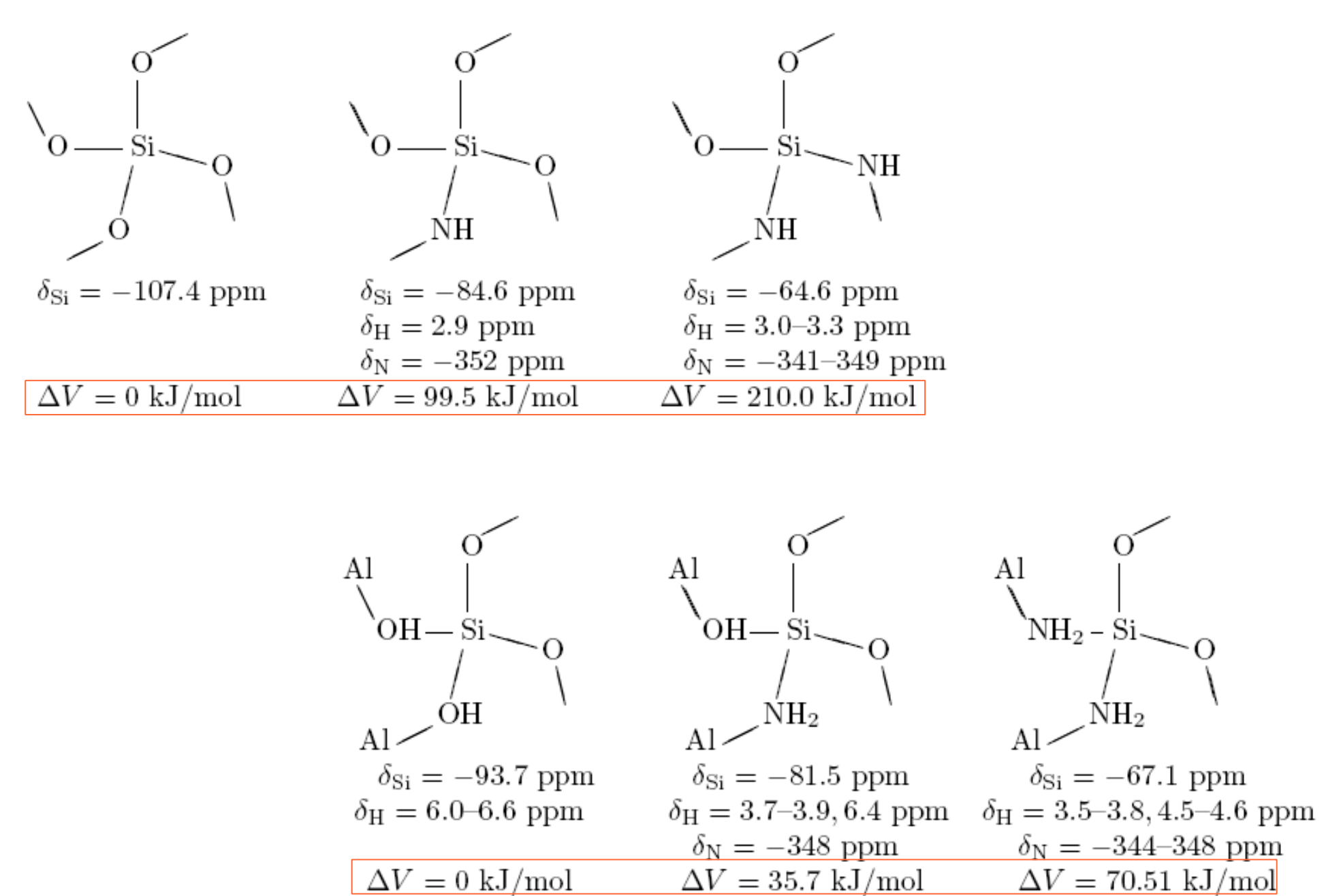
Change in magnetic moment (constant for each nucleus)

External magnetic field (constant)

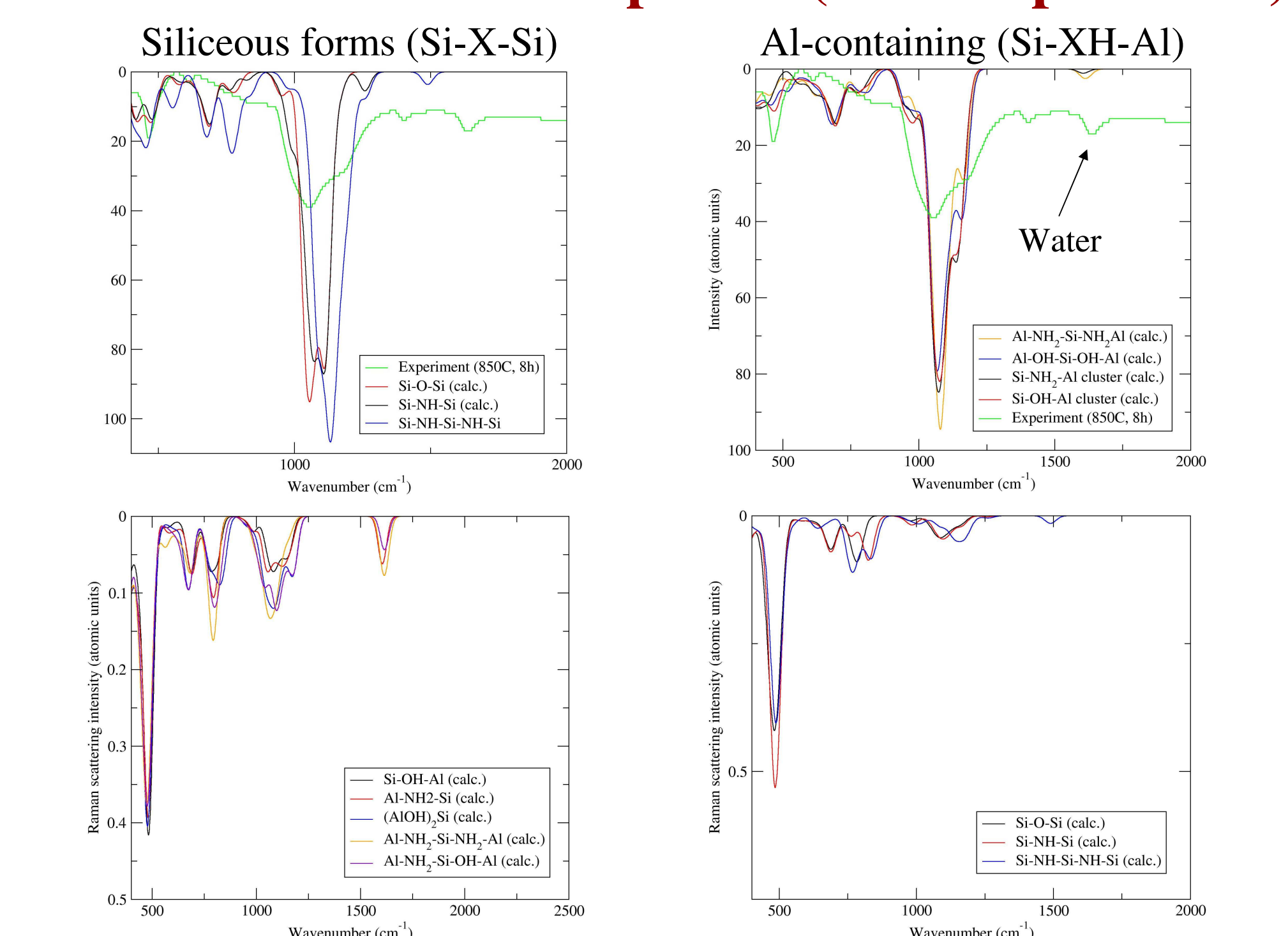
Shielding constant (function of electron density)

$$\delta = \frac{\Delta E - \Delta E_{\text{ref}}}{\Delta E_{\text{ref}}} = \frac{V - V_{\text{ref}}}{V_{\text{ref}}} = \frac{\sigma_{\text{ref}} - \sigma}{1 - \sigma_{\text{ref}}} \approx \sigma_{\text{ref}} - \sigma$$

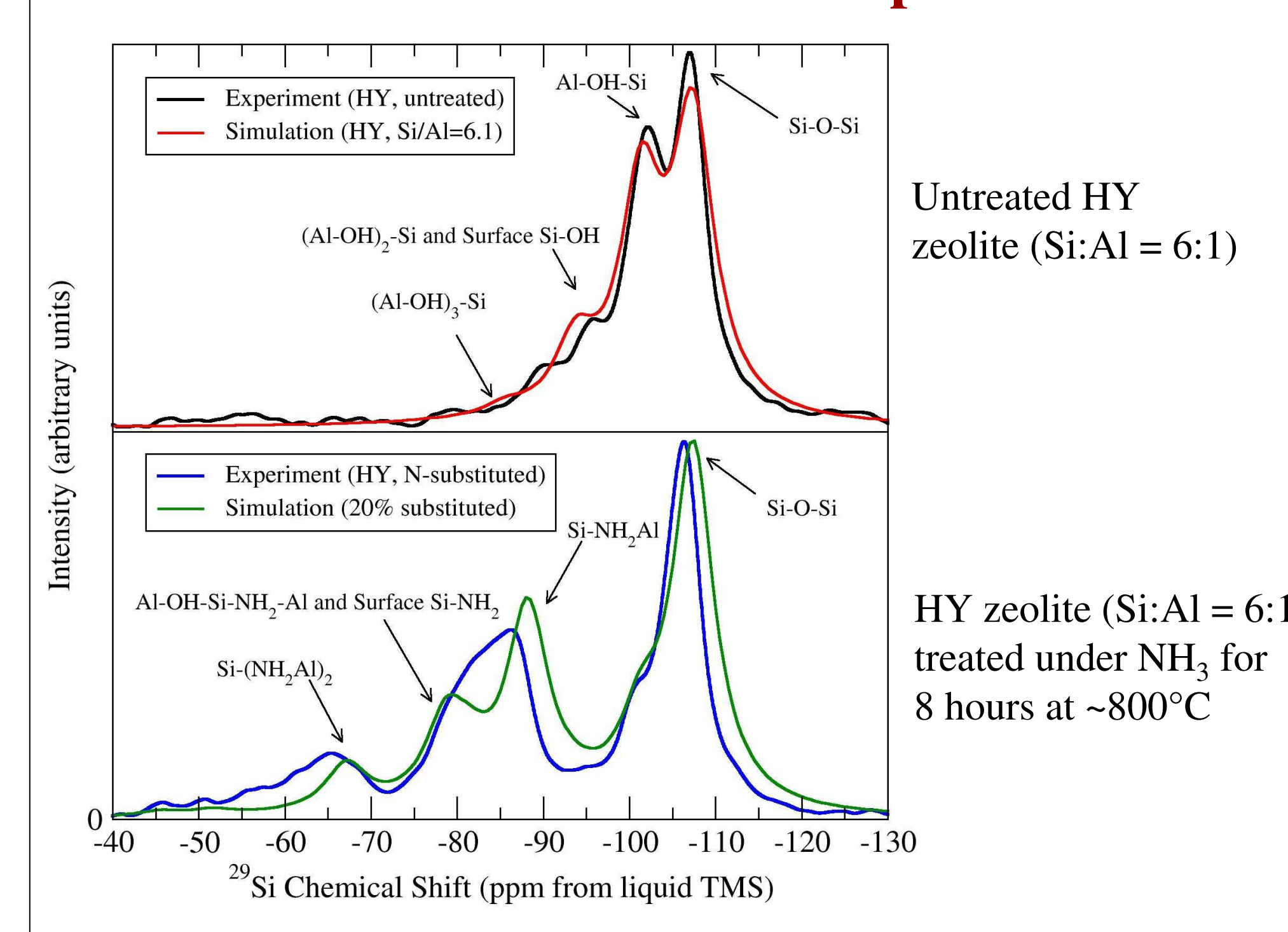
## Calculated Energies of Amine Substitutions



## Calculated Infrared Spectra (with Experiment)



## Calculated 29Si NMR Spectrum



## Conclusions and Future Work

- Nitrogen prefers to substitute between Si and Al, not between Si and Si
- Approximately 20% of total oxygens are substituted for nitrogen after 8 hours of treatment. Of those, 87% take place inside the framework
- Current/Future Work:
  - High-resolution physical adsorption
  - Stability of treated zeolites
  - Extraframework aluminum simulations
  - Non-silicon NMR spectroscopy