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A molecular dynamics approach to simulate Raman and IR spectra of silicon nanowires

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Introduction

- Raman/IR spectroscopy is one of the mayor methods to characterize nanostructures
- Raman spectra need to be interpreted → input from theory needed
- Calculations of Raman spectra with density functional theory is straightforward for small systems
- Many nanostructures are much too big for these methods

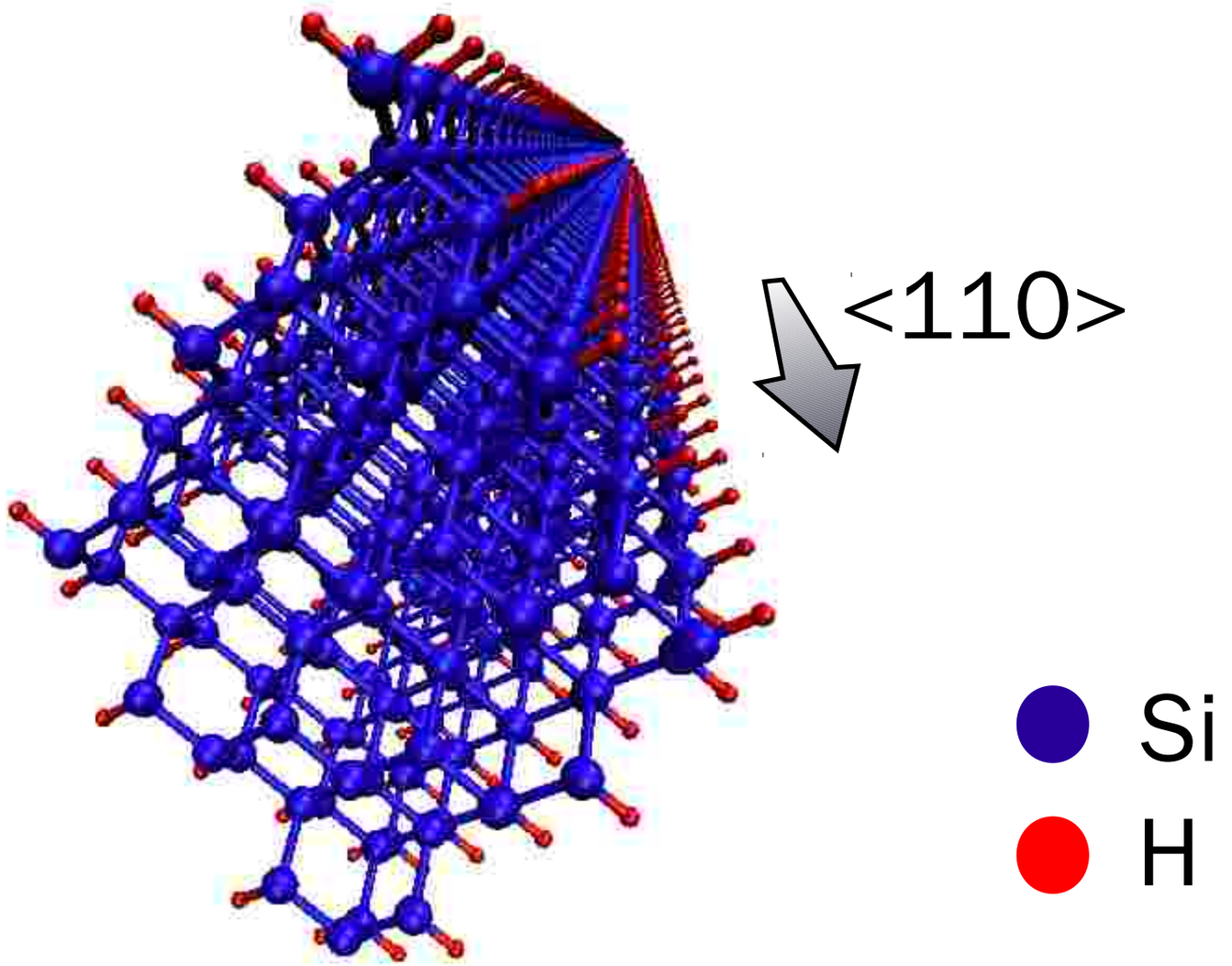
Task: **Simulate the Raman spectrum of nanostructures and interpret the spectrum in terms of phonon modes.**

Calculational Method

1. Model the geometry of the nanostructure
2. Do a **molecular dynamics simulation** of the nanostructure
   → trajectories
3. **Decompose** the trajectories into phonon modes and **filter** out the
   - Raman active phonon modes
   - IR active phonon modes
4. Calculate the spectral function = Fourier transform of the **Velocity Autocorrelation Function**

Calculational Method

1. Geometry of a silicon nanowire



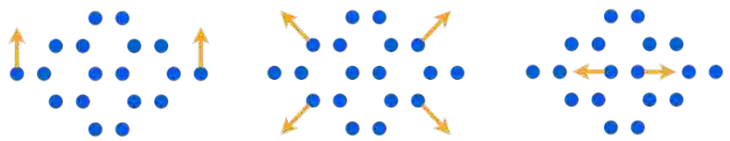
Calculational Method

2. Molecular Dynamics Simulations

- Density Functional Tight Binding (DFTB) method
  semi-empirical quantum mechanical method; fast; quite accurate for silicon

3. Decomposition of MD trajectories into phonon modes

- use **crystal symmetry analysis** to find
  - all possible phonon displacements vectors (polarizations) at the Γ-point
  - Raman/IR active modes



etc. : $\vec{\epsilon}_j \ , \quad j = 1...3N$

- Filter out a particular phonon from the MD trajectories by projection

$$v_j(t) = \vec{\epsilon}_j \cdot \vec{v}(t)$$

Calculational Method

4. Calculate the spectral function

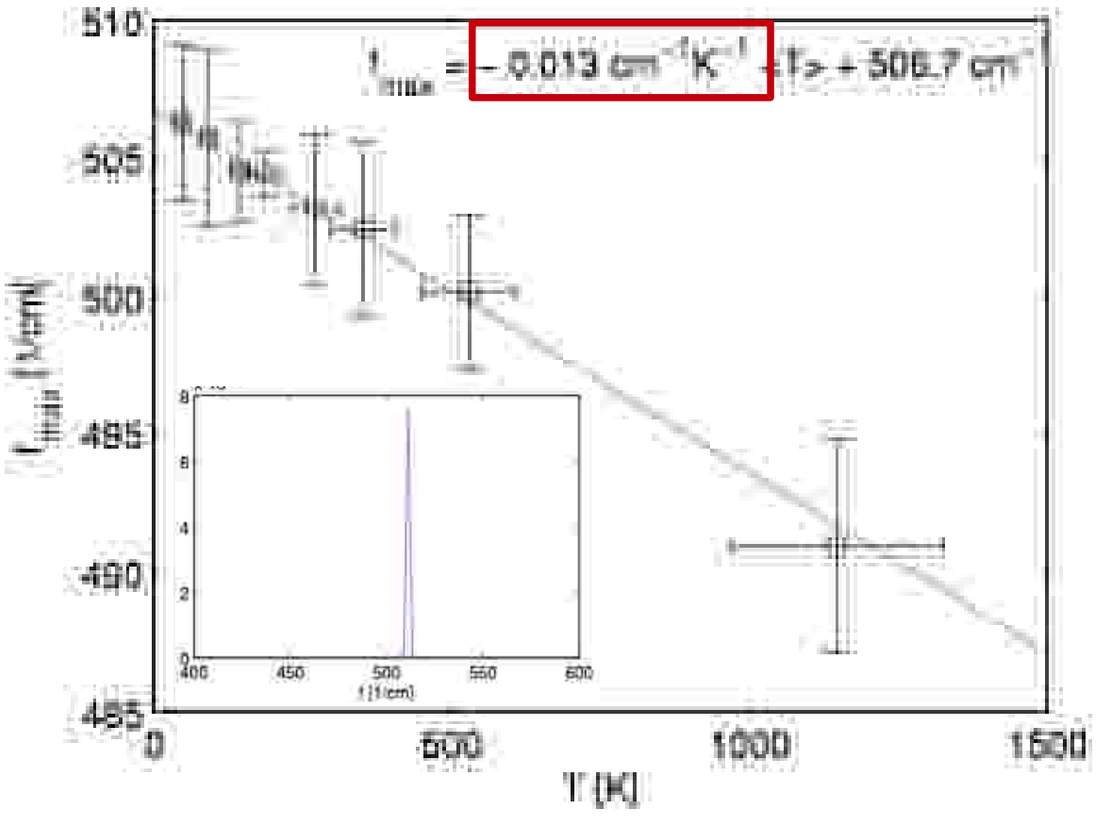
- Spectral function ~ Fourier transform of the Velocity Autocorrelation Function = power spectrum of the phonon velocities
- Use the subset of Raman/IR active phonon velocities

$$P_{Raman}(\omega) = \sum_{j}^{j_{Raman}} \left| \int v_j(t) \exp(-i\omega t) \right|^2$$

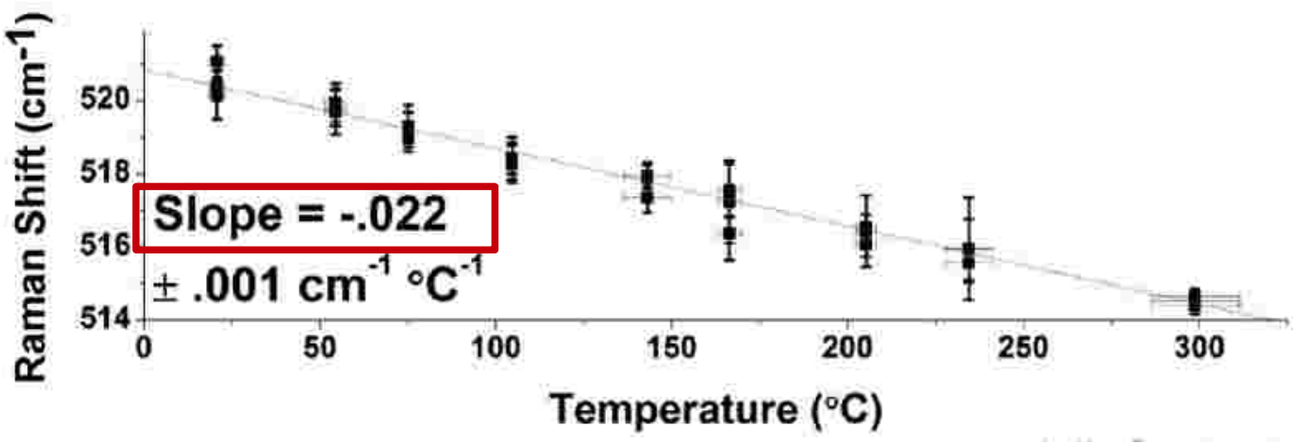
Results

Raman spectra of Bulk Silicon: Temperature dependence

simulation



experiment



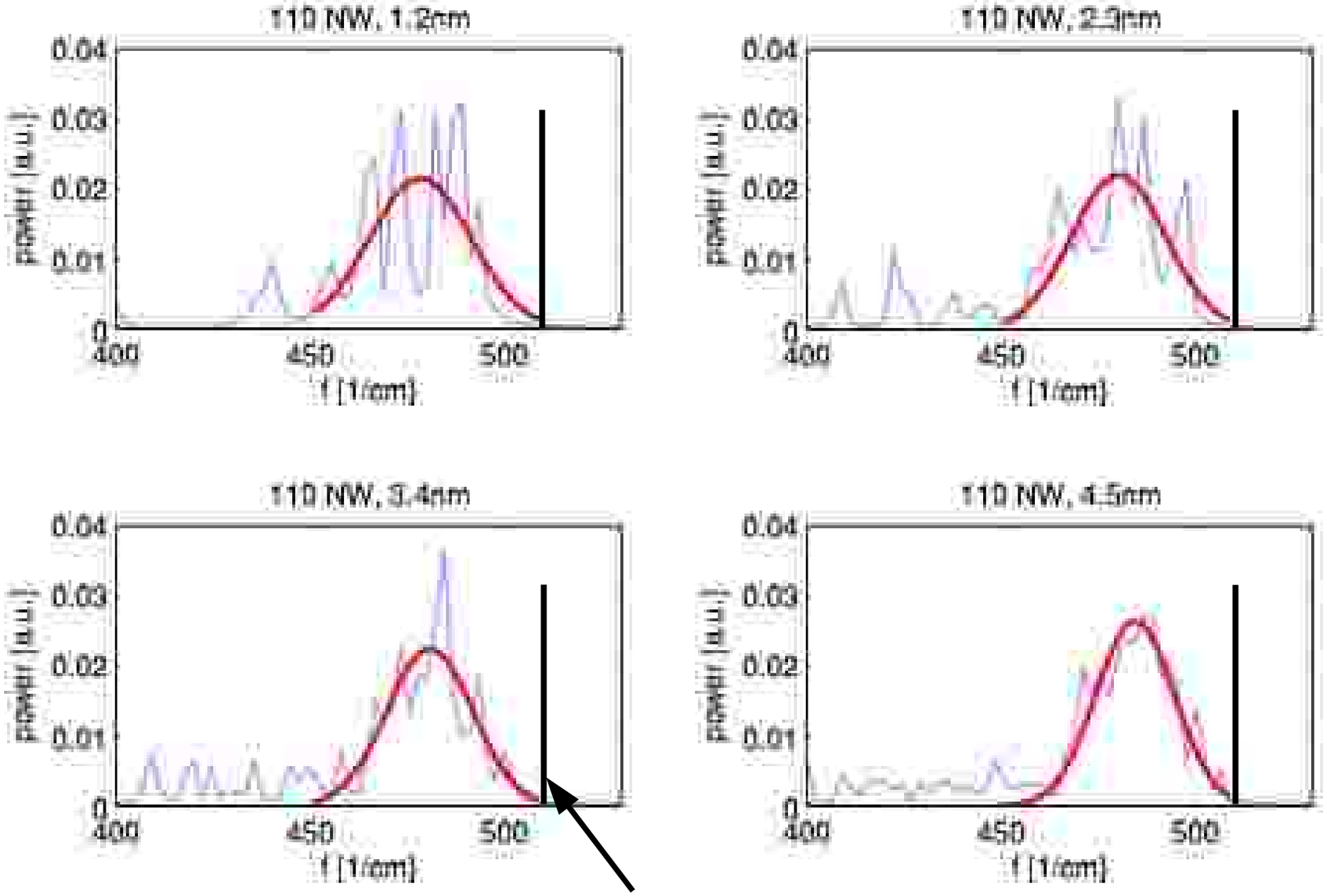
Doerk et al., Phys. Rev. B **80**, 073306 (2009)

→ good agreement between experiment and theory:

- linear dependence + value for the slope

Results

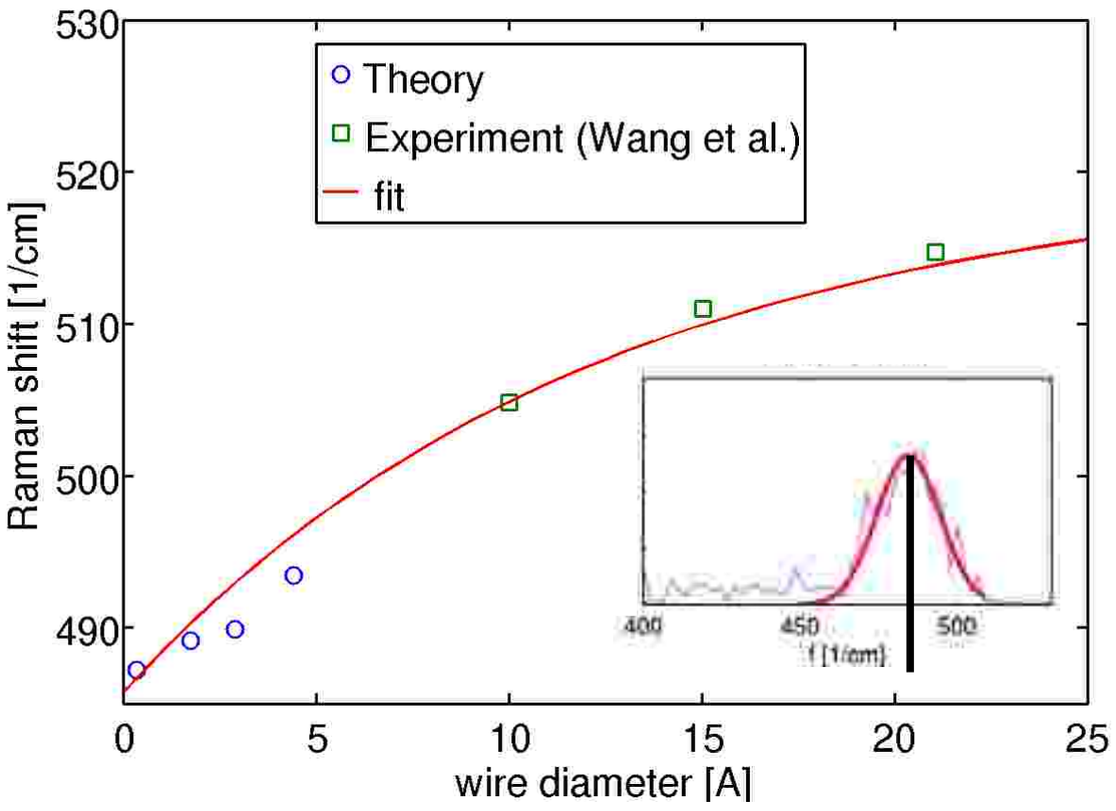
Raman spectra of Si-nanowires with different diameters

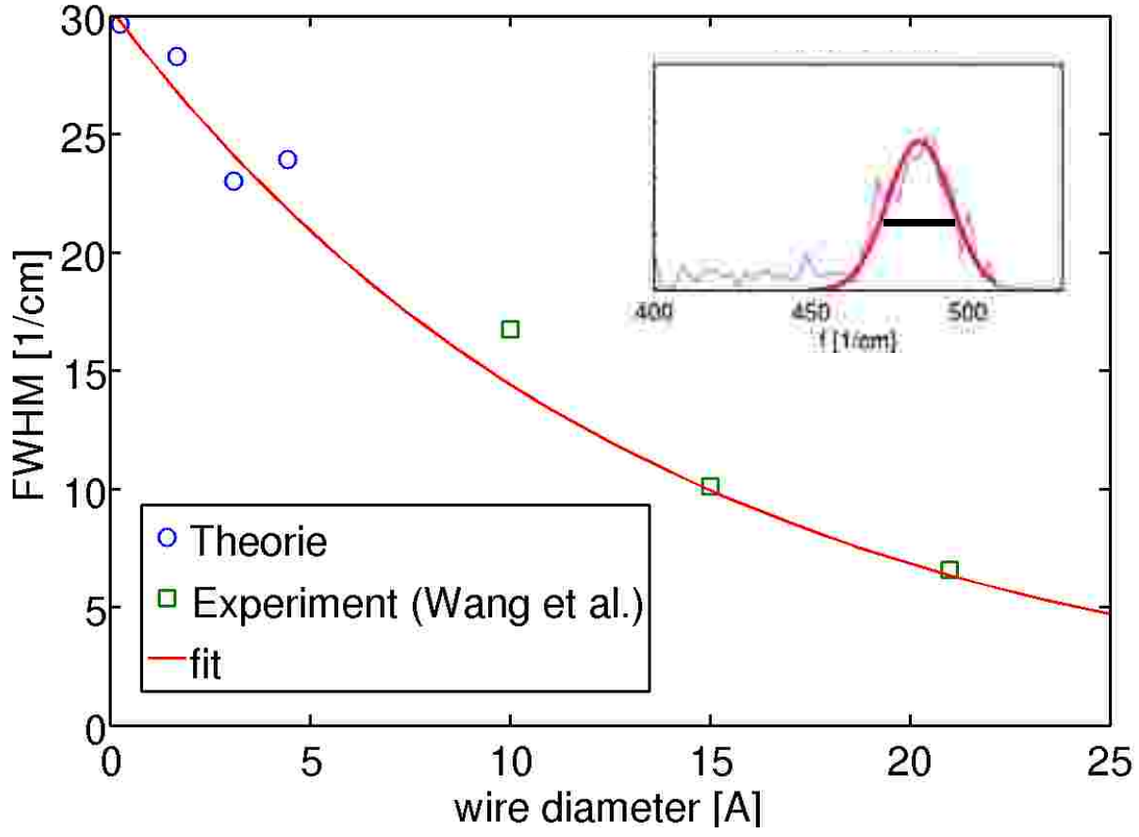


- redshift of bulk peak
- frequency band with Gaussian shape at about 480 cm^{-1}

Results

Raman spectra of Si-nanowires with different diameters





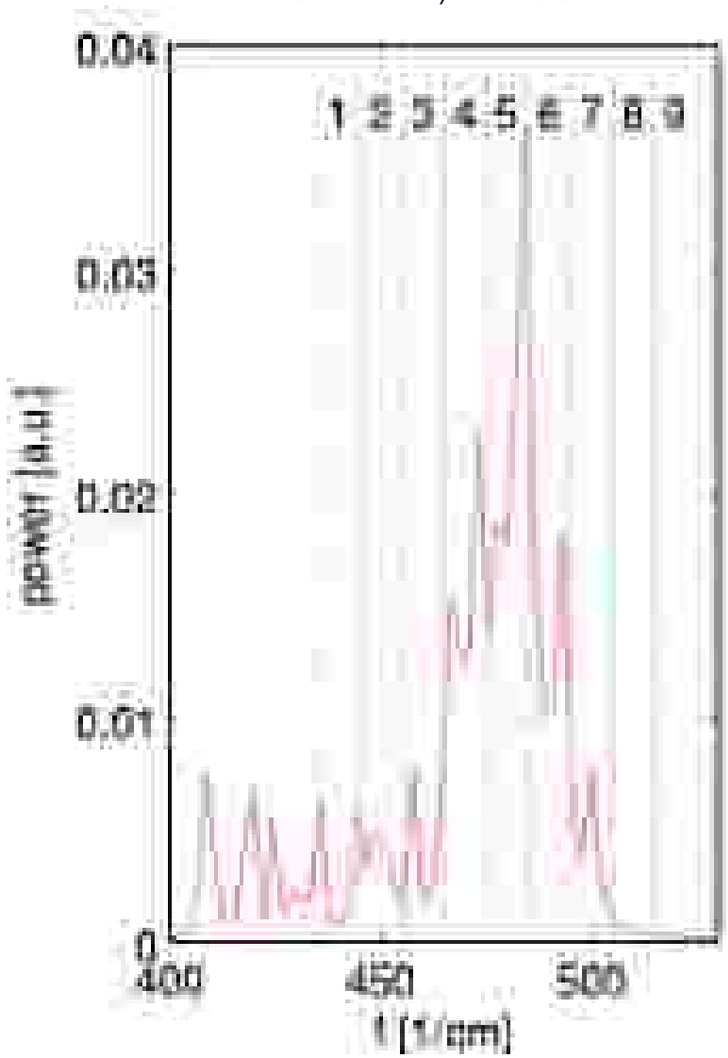
Wang et al., Phys. Rev. B **61**, 16827 (2000)

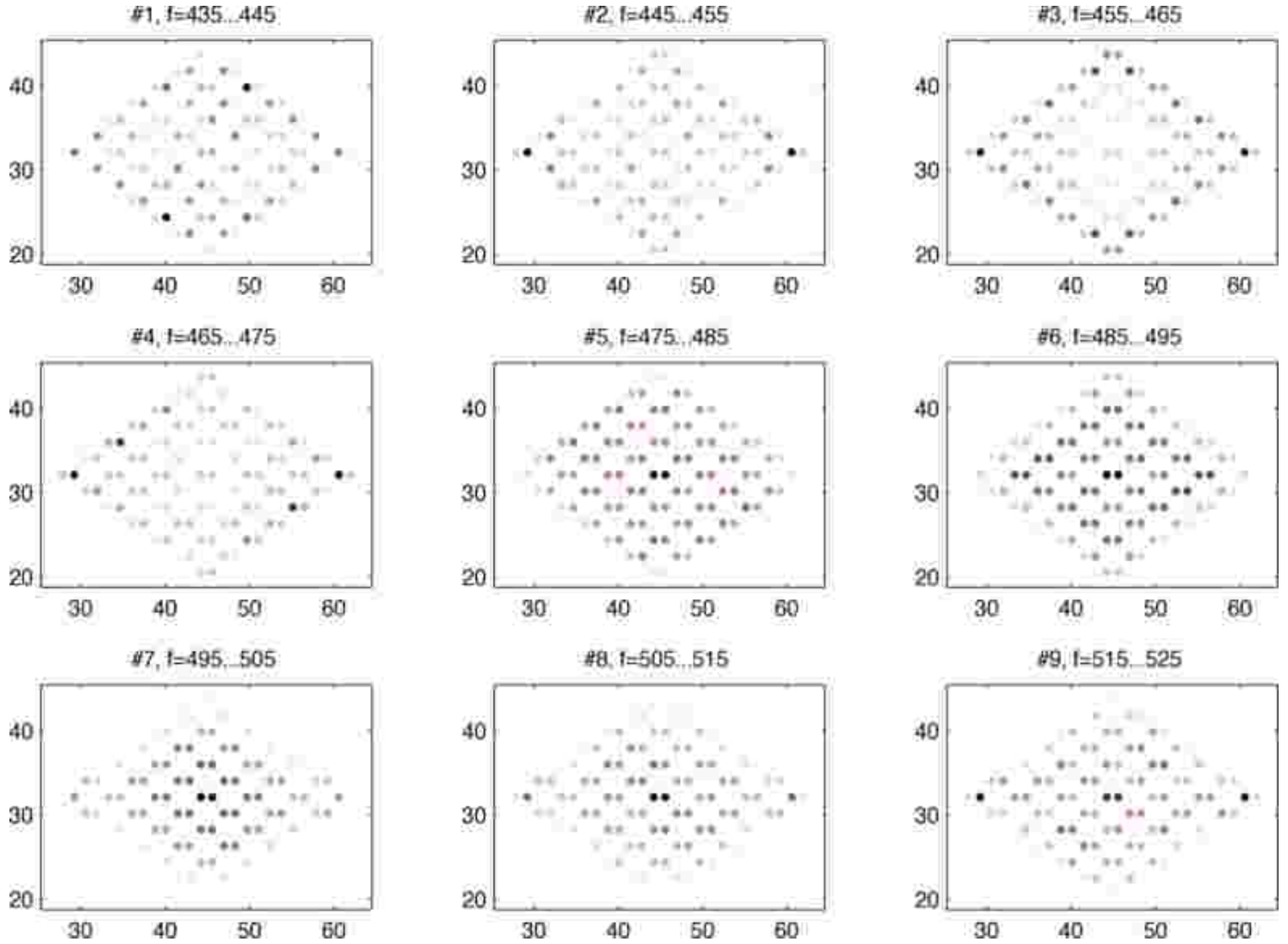
→ good agreement between experiment and theory

Results

Atom resolved Raman spectrum of a Si-nanowire

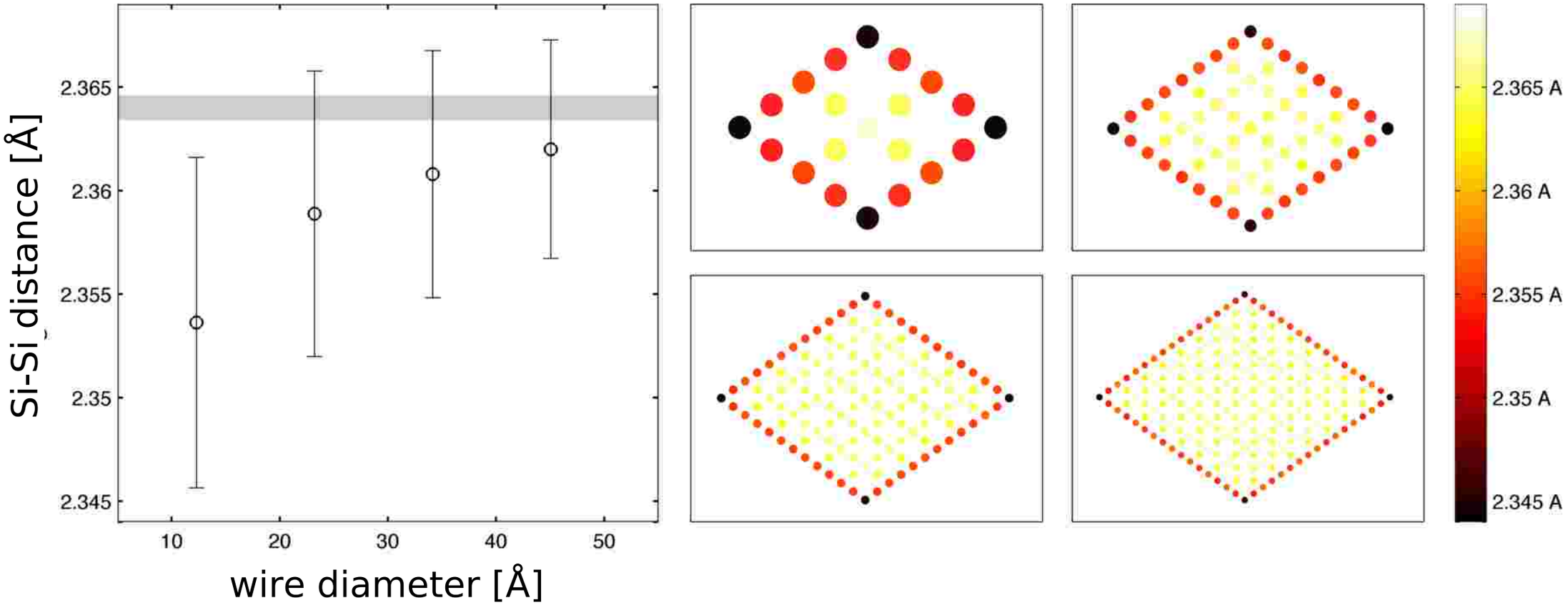
<110> NW, D=3.4 nm





Results

Structural analysis of Si-nanowires



- surface layer has reduced bond lengths → surface strain
- from the second layer on the system is like bulk silicon

Summary

- Method to calculate Raman/IR spectra of nanostructures was developed
- Good agreement with experiment for
  - Temperature dependence of the Raman peak of bulk Si
  - Diameter dependence of the peak position/FWHM for the main Raman frequency band of Si nanowires
- Able to interpret the spectrum in terms of atomic displacements / phonon modes

THANK YOU FOR YOUR ATTENTION

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