Identification of Molecules by Inelastic Electron Tunneling Spectroscopy (IETS)

- Broad spectra range (0 - 19000 cm⁻¹)
- High resolution (10 cm⁻¹) and sensitivity (~10⁻¹⁰ molecules)
- No selection rules (both infrared and Raman modes observed)

Characterization of Self-Assembling Tunnel Junctions (SATJ)

- Adjustable, oxide-free tunneling geometry
- Junctions formed and doped in-situ in low temperature environment

**SELF-ASSEMBLING TUNNEL JUNCTIONS (SATJ)**

Junction formed at contact point between two long, fine metallic wires
Tunnel barrier consists of inert gas film (Ar, He, Ne, ...)
Junction formed at contact point between two long, fine metallic wires

**ANALYSIS**

Data With Background and ZBF Removed

- Solid vertical lines: complete set of vibrational modes of CH₄ in the gas phase (both infrared and Raman active)
- Dashed vertical lines: consistent with vibrational modes of CH₄ chemisorbed on platinum (111) surface

**IETS DATA**

Ultra-Pure Neon - Platinum Junctions
- Single sweep of bias voltage (no signal averaging beyond the lock-in amplifier time constant (Fig 3a))
- Sensitivity for detecting a change in the integrated intensity of individual elastic peaks is ∆σ/σ ~0.02%
- Relatively smooth except for zero bias feature (ZBF) that represents a significant suppression of the junction conductance within 50 meV of zero bias

Ultra-Pure Neon - Platinum Junctions Doped With Acetylene
- Prominent peaks outside ZBF region corresponding to the vibrational modes of C₂H₂
- Theoretical function has three components:
  - Cubic function of bias voltage to model slowly varying background
  - Lorentzians convolved with modulation measurement function to fit inelastic peaks
  - Derivative of convolved Lorentzian centered about zero bias to model ZBF

**IETS INTENSITIES**

Gas-phase (infrared) intensity ratios (given by ratio of ∆σ/σ for two modes)

- IETS intensities should scale with infrared intensities if interaction is simple dipole scattering
- Experimental ratio of C-H stretching (91meV) to stretching (407meV) modes is 2.9 compared to theoretical ratio of ~12
- Chemisorbed-phase intensity ratios
  - Surface modes are compared with recent theoretical model since experimental surface-dipole matrix elements are unavailable
  - Experimental ratio of chemisorbed C-H bending (123meV) to stretching (368meV) modes is 0.12 compared to theoretical ratio that ranges from 1-5

Disparity between experiment and theory suggests electron-molecule interaction in this geometry cannot be modeled by simple dipole scattering and other mechanisms may better describe IETS intensities.

**REFERENCES**

4. A. Colidays and D. Currilla, to be published.