Infrared spectroscopy of III-V and II-VI core-shell nanoparticles

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Motivation and Objectives

- Need for good nanoparticle light emitters in visible/near IR for communications and bio-medical applications Þ **structure** and **dynamics** both important

- Recent progress in chemical fabrication of nanoparticles and core-shell nanoparticles with excellent emission properties

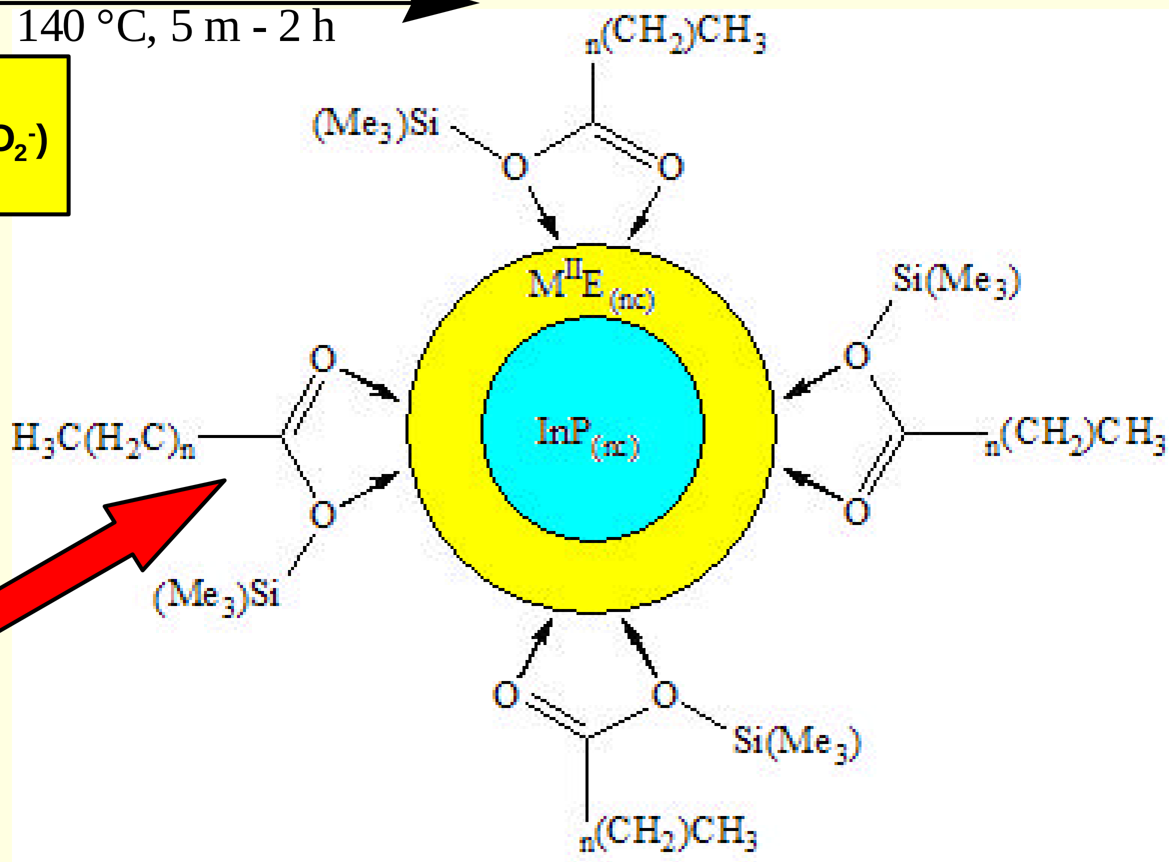
- **Vibronic properties important** Þ both **structure** and **dynamics** **(non-radiative recomb.)**
  - Optical phonons in InP nanoparticles and InP/II-VI core-shell nanoparticles -- IR and Raman spectroscopies
  - Dependence of vibronic properties on nanostructure dimensions (surface/interface) optical phonon modes

Sample Preparation

InP core $+ M^{II}X_2 + E \xrightarrow[\text{140 °C, 5 m - 2 h}]{\text{non-coordinating solvent}}$

M^{II} = Cd or Zn
X = Acetate ($CH_3CO_2^-$)
E = S or Se

- **Generation of core InP nanocrystals with *In-situ* surfactant**
- **Non-coordinating solvent– octadecene**
- **<u>Surfactant formed *"in-situ"* (none added)</u>**
- **Different precursor ratios and temperature sequences explored**



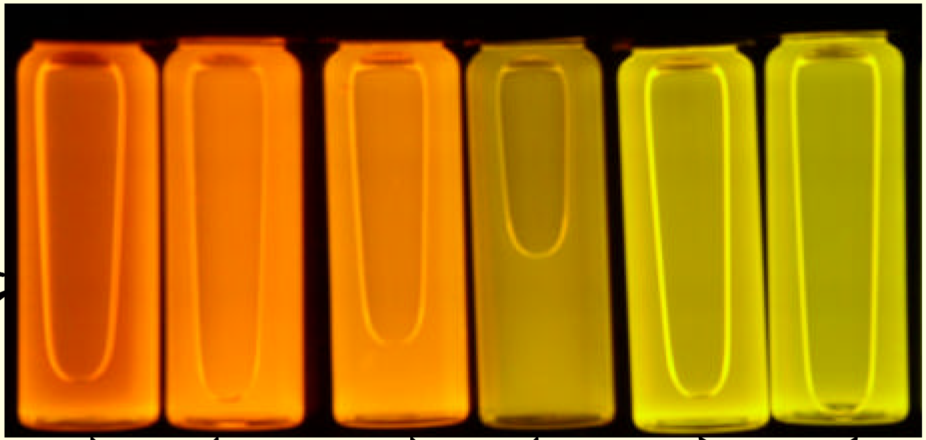
InP/II-VI core-shell nanocrystal

Advantages of present approach
(organic precursor)

- **Rapid fabrication and scalability of process**
- **Greater controllability (sizes and shapes of nanoparticles)**
- **Possibility of embedding nanoparticles in a wide range of matrices (liquids or solids)**

InP/II-VI nanocrystals in ambient light

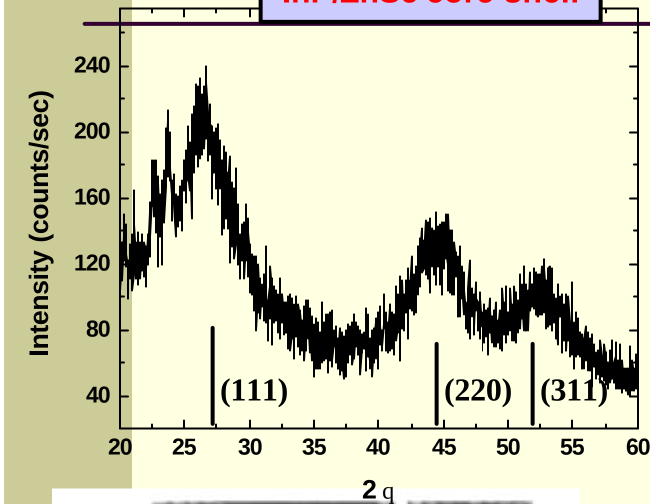
Shell thickness is tunable by varying amounts of shell precursors



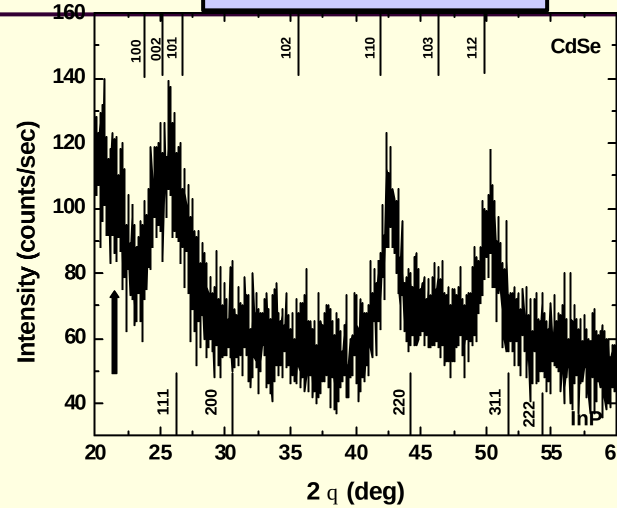
InP/CdS **InP/CdSe** **InP etched**

Characterization of samples by TEM and XRD

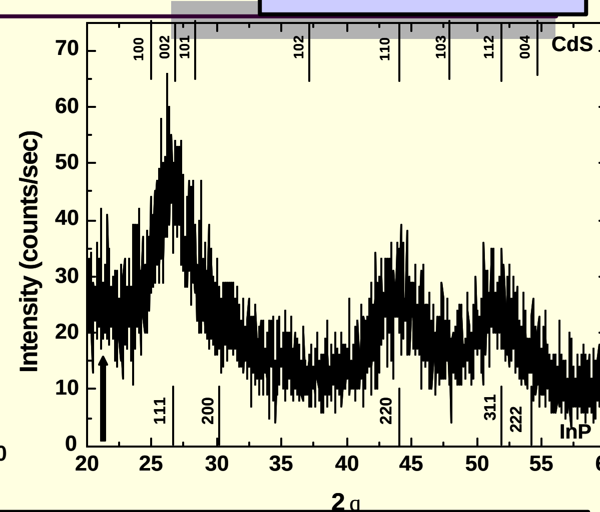
InP/ZnSe core-shell

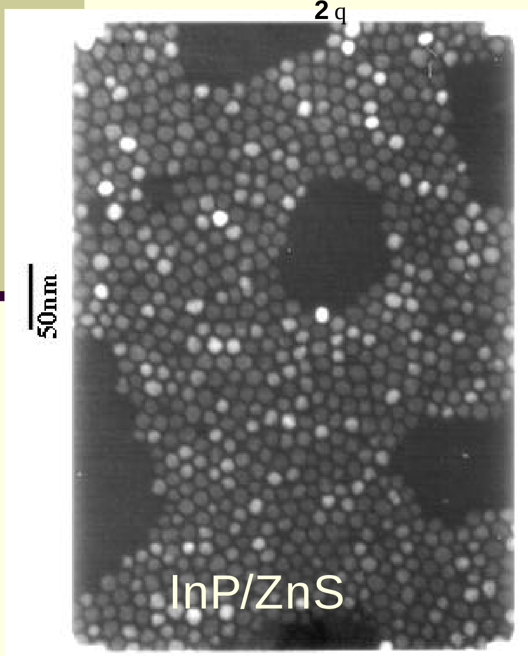


InP/CdSe core-shell



InP/CdS core-shell

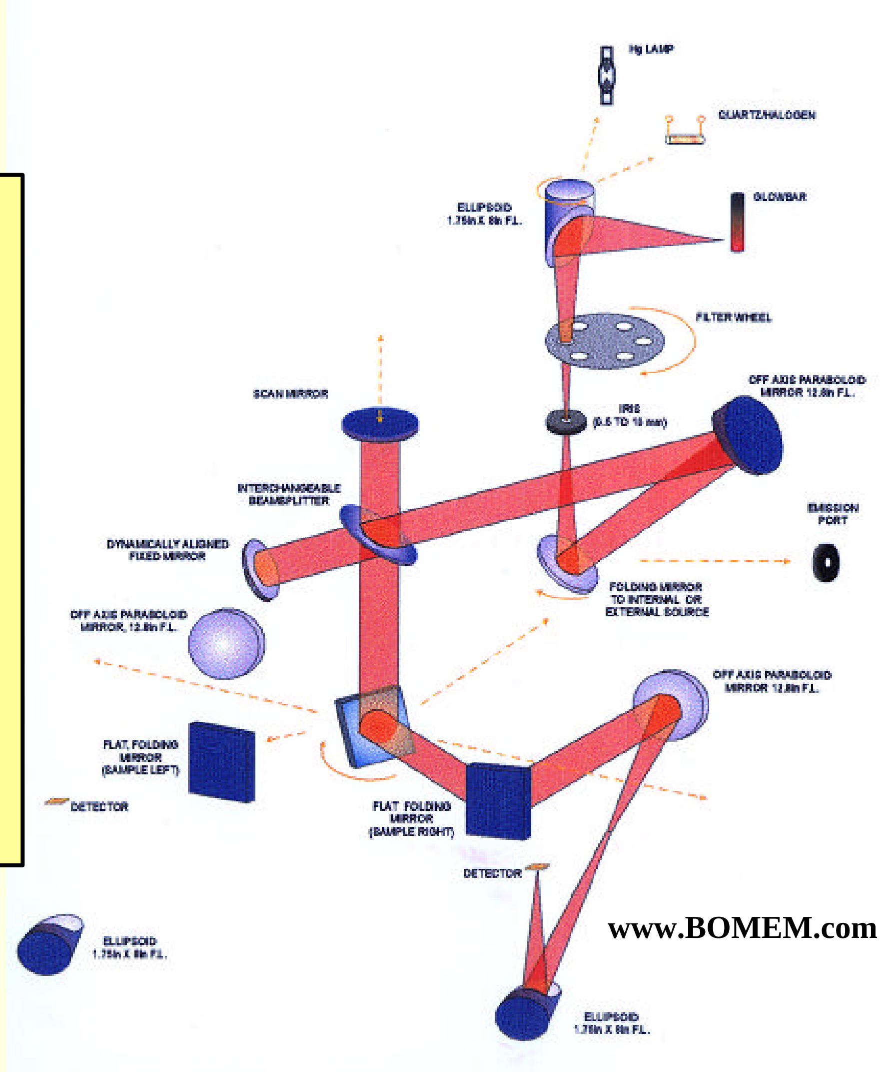




- X-ray diffraction
  - Þ peaks for (111), (220) and (311)
    - Þ CdS and CdSe samples appear to be wurtzite – ZnSe is zinc blende structure
- Transmission Electron Microscopy
  - Þ Nanoparticles are crystalline
  - Þ Sizes between 5 and 20 nm

Samples and IR Spectroscopy

- **Samples for IR Measurements**
  - **Nanoparticles in CsI matrix**
    - Þ **pellets**
- **Far IR transmission**
  - **BOMEM Fourier Transform IR Spectrometer**
  - **Si bolometer detector**
  - **6 µm Mylar beamsplitter (spectral range 20 - 370 cm^{-1})**



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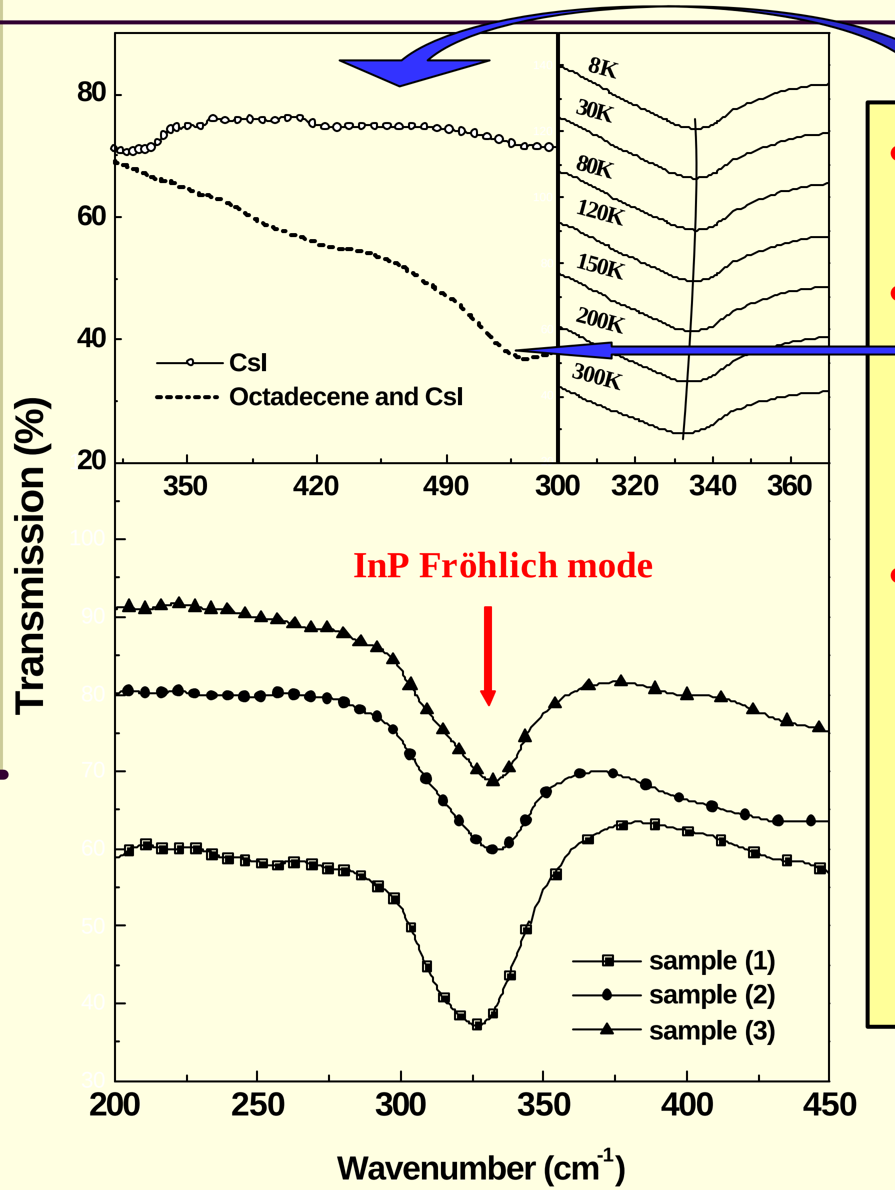
Results (InP nanoparticles



- **CsI transparent in region of interest**
- **Solvent (octadecene) transmission spectrum does not interfere with characteristic bands of InP**
- **Fröhlich mode**
  - Common feature in transmittance spectra of InP nanoparticles embedded in CsI matrix
  - Same temperature dependence as TO mode

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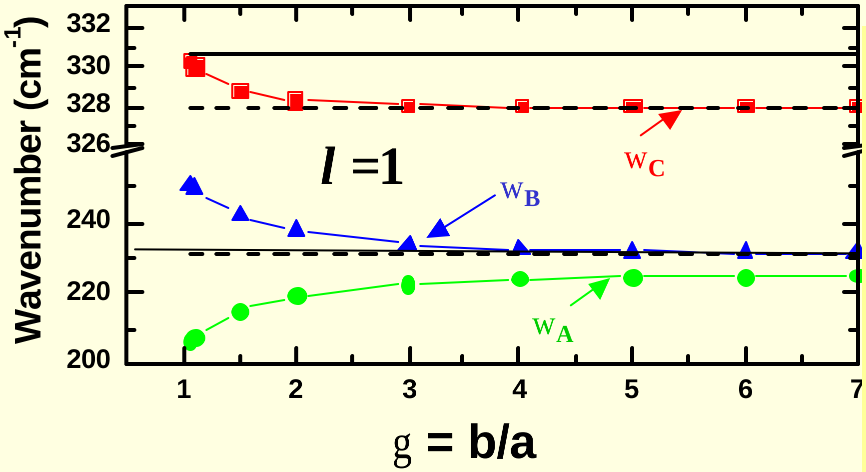
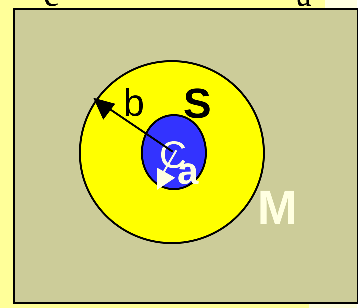
InP/ZnSe core-shell

SO phonon modes from continuum dielectric model

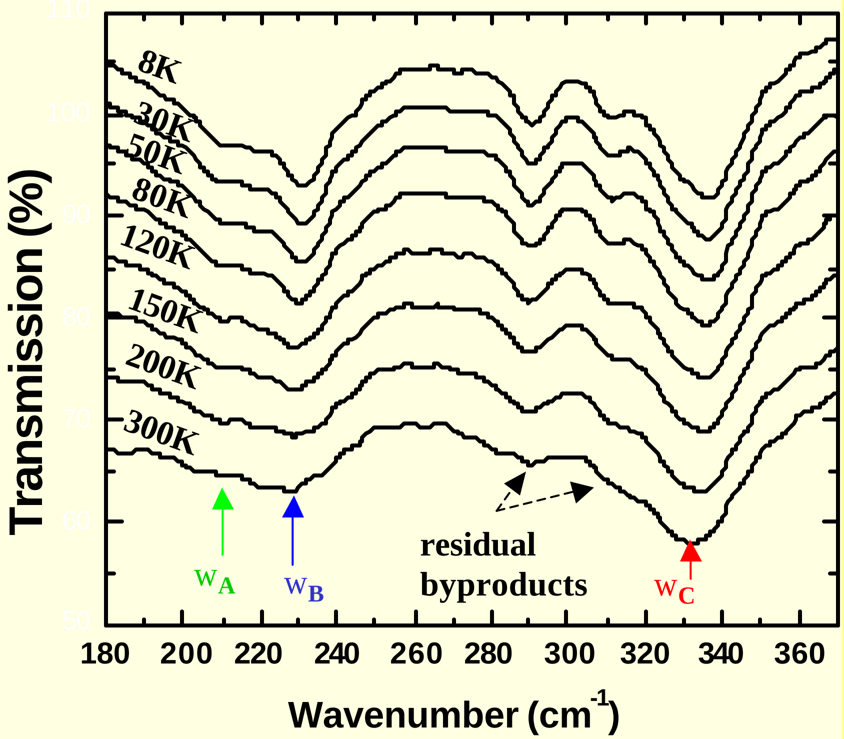


$$\frac{\varepsilon^{S}(\omega)}{\varepsilon^{M}(\omega)} = -\frac{\varepsilon^{C}(\omega)\left[\gamma^{2l+1}-1\right]+\varepsilon^{S}(\omega)\left[1+\frac{l+1}{l}\gamma^{2l+1}\right]}{\varepsilon^{S}(\omega)\left[\gamma^{2l+1}-1\right]+\varepsilon^{C}(\omega)\left[1+\frac{l}{l+1}\gamma^{2l+1}\right]}$$



γ = ratio of radius of shell (b) to core (a)

***l* = angular mom./spherical harmonic Quantum number**

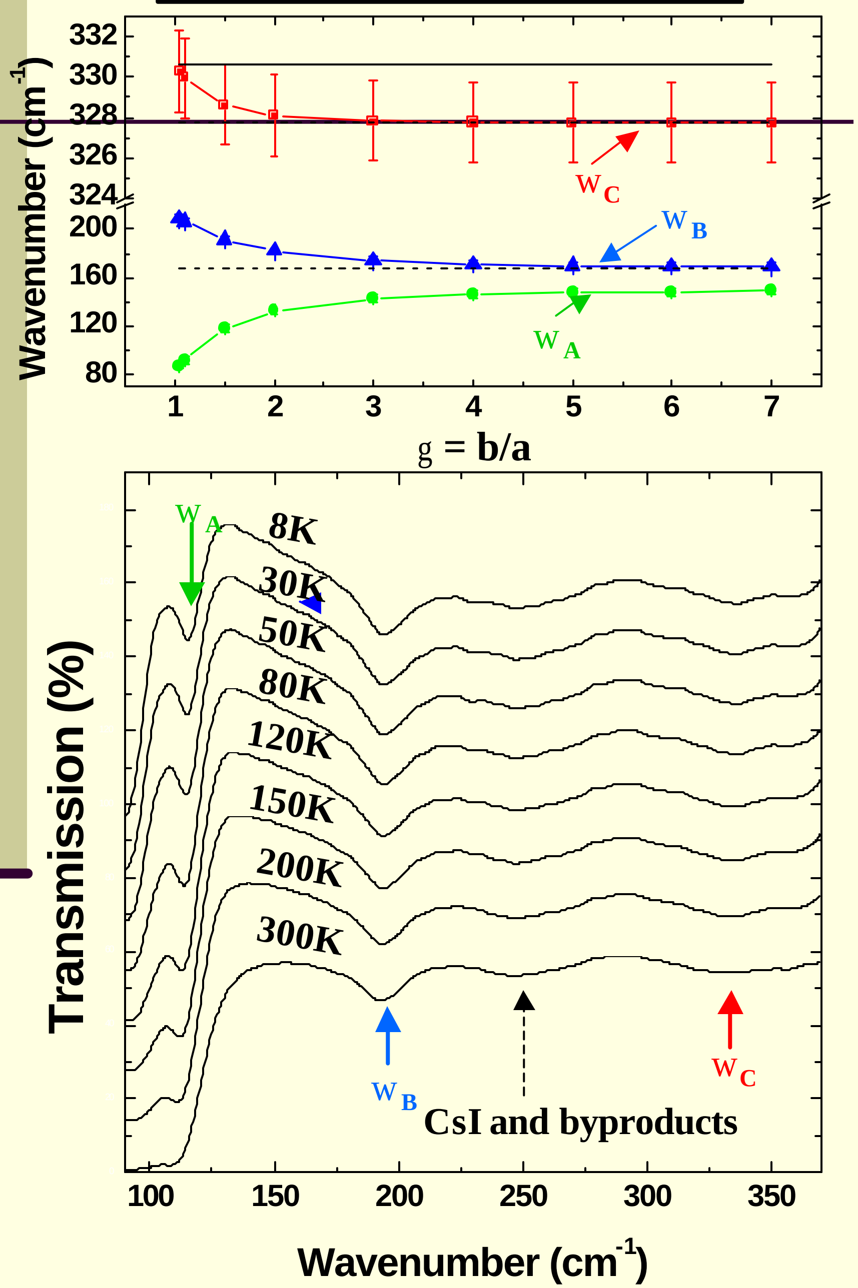


ω_C = **core (InP) vibrational mode frequency (Fröhlich mode)**

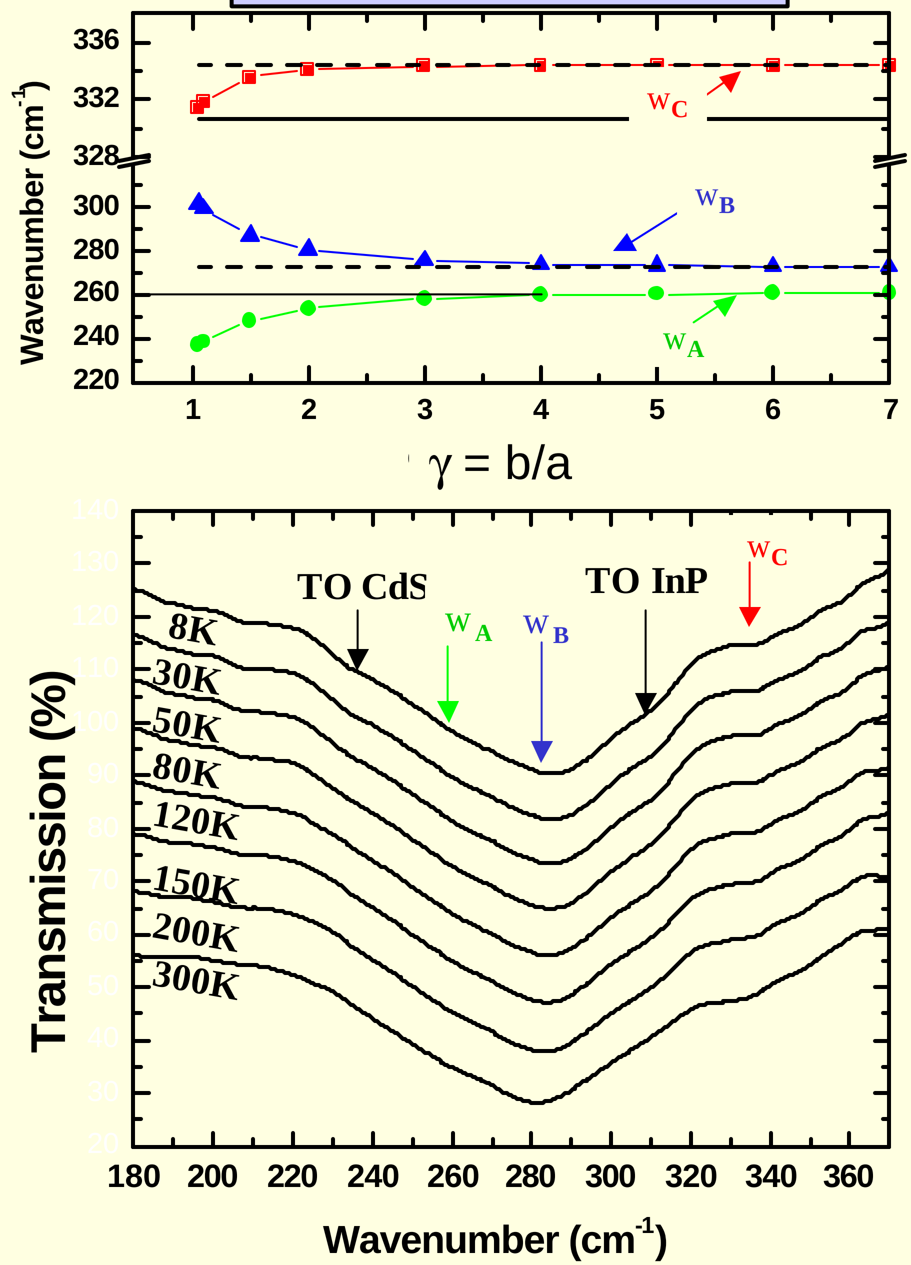
ω_B = **surface vibrational mode frequency at interface between shell and matrix**

ω_A = **vibrational mode frequency of shell**

InP/CdSe core-shell
w/zinc blende phonons



InP/CdS core-shell
w/zinc blende phonons



Summary and Conclusions

- **Comparison between theory and experiment**
  - **InP/ZnSe g ~ 1.4 to 2.5**
  - **InP/CdSe g ~ 1.2 to 1.6**
  - **InP/CdS g ~ 1.5 to 3**
- **For thin shell (*eg.* InP/ZnSe, InP/CdSe) three vibrational modes, w_C, w_B, and w_A , are resolved**

- **InP nanoparticles**
  - IR transmission spectra of InP nanoparticles exhibit common feature ⇒ Fröhlich mode
- **InP/II-VI core-shell nanoparticles**
  - Good agreement between theoretical and IR experimental results
  - IR spectroscopy can provide detailed characterization of their structure

IR absorption spectroscopy good probe of quality of core-shell nanoparticles – shell thickness