

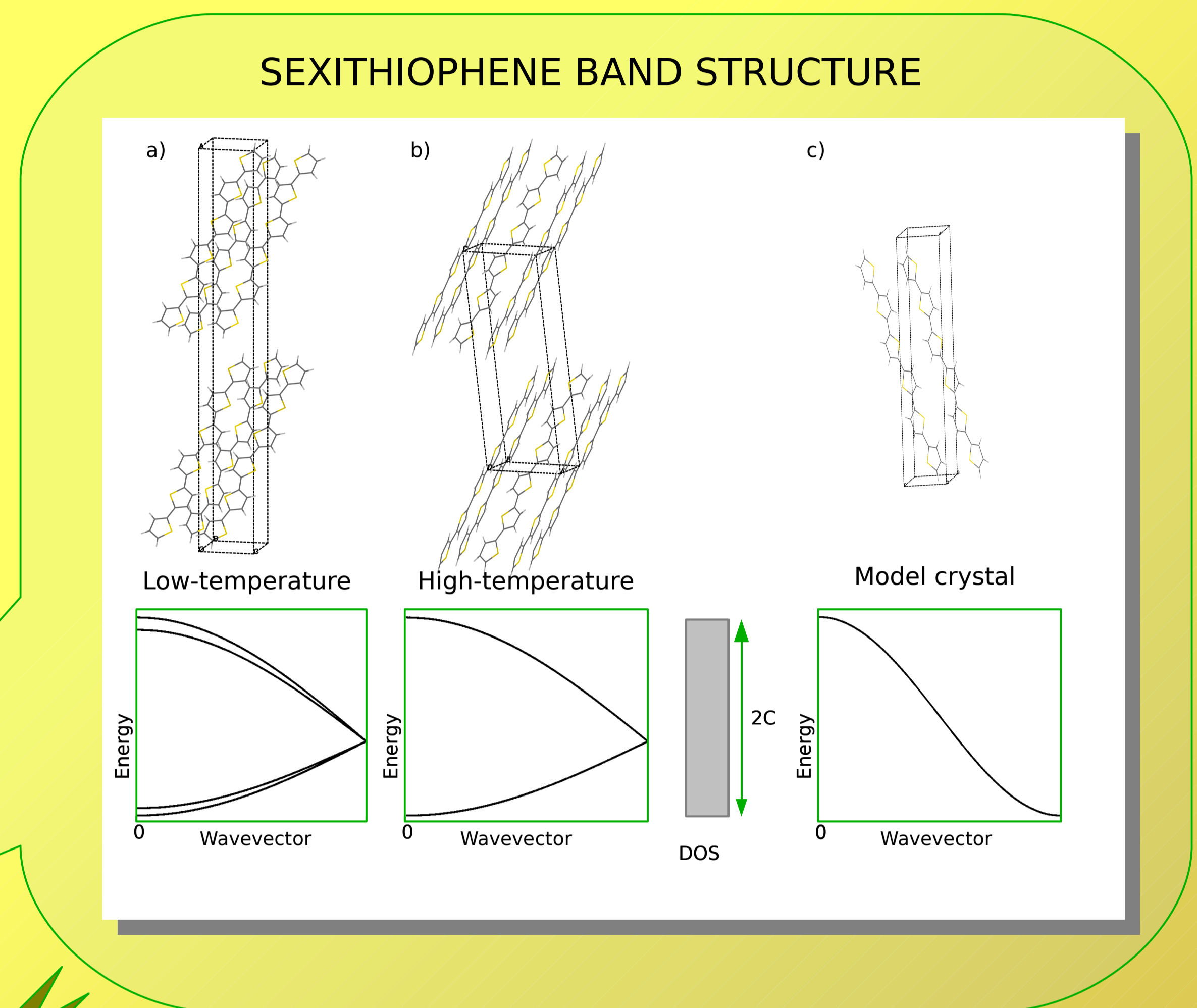
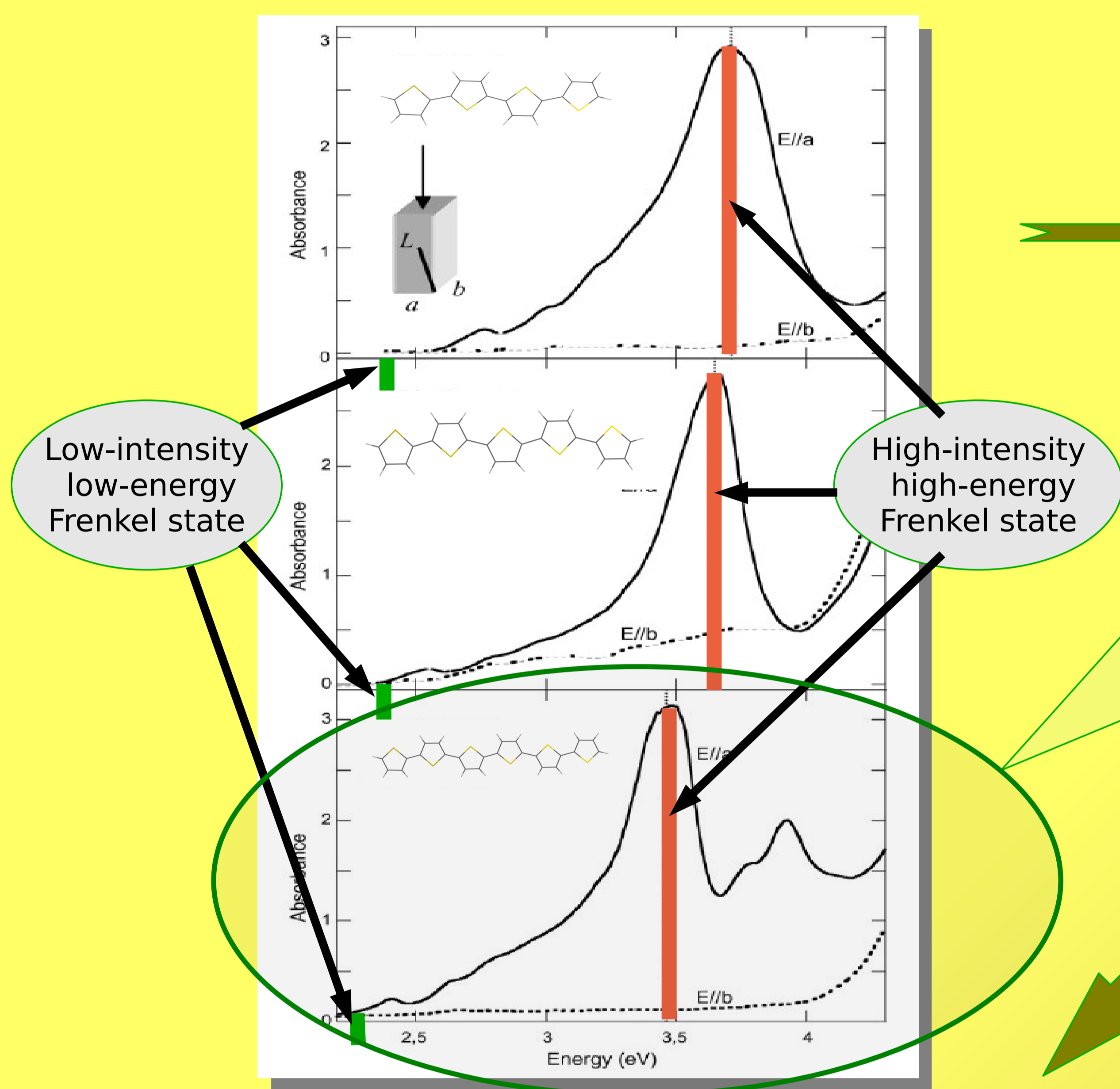
# Unbound exciton-phonon states in oligothiophene crystals – a model approach for spectroscopic purposes



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**Observations:** General shape of crystal absorption spectrum is common to all oligothiophenes.



**WORKING HYPOTHESIS**  
This shape results from the interaction between the discrete upper Davydov component and the phonon quasi-continuum deriving from the forbidden lower component.

**MODEL**

- crystal with one molecule in the unit cell
- one exciton state per molecule
- one phonon mode per molecule
- linear vibronic coupling

$$\hat{H} = \sum_m E B_m^+ B_m + \sum_m \sum_n W(n) B_m^+ B_{m+n} + \sum_m a_m^+ a_m + \frac{b}{\sqrt{2}} \sum_m B_m^+ B_m (a_m^+ + a_m)$$

Labels: exciton diagonal energy, exciton propagation, phonon diagonal energy, coupling constant, linear exciton-phonon interaction.

**APPROACH**

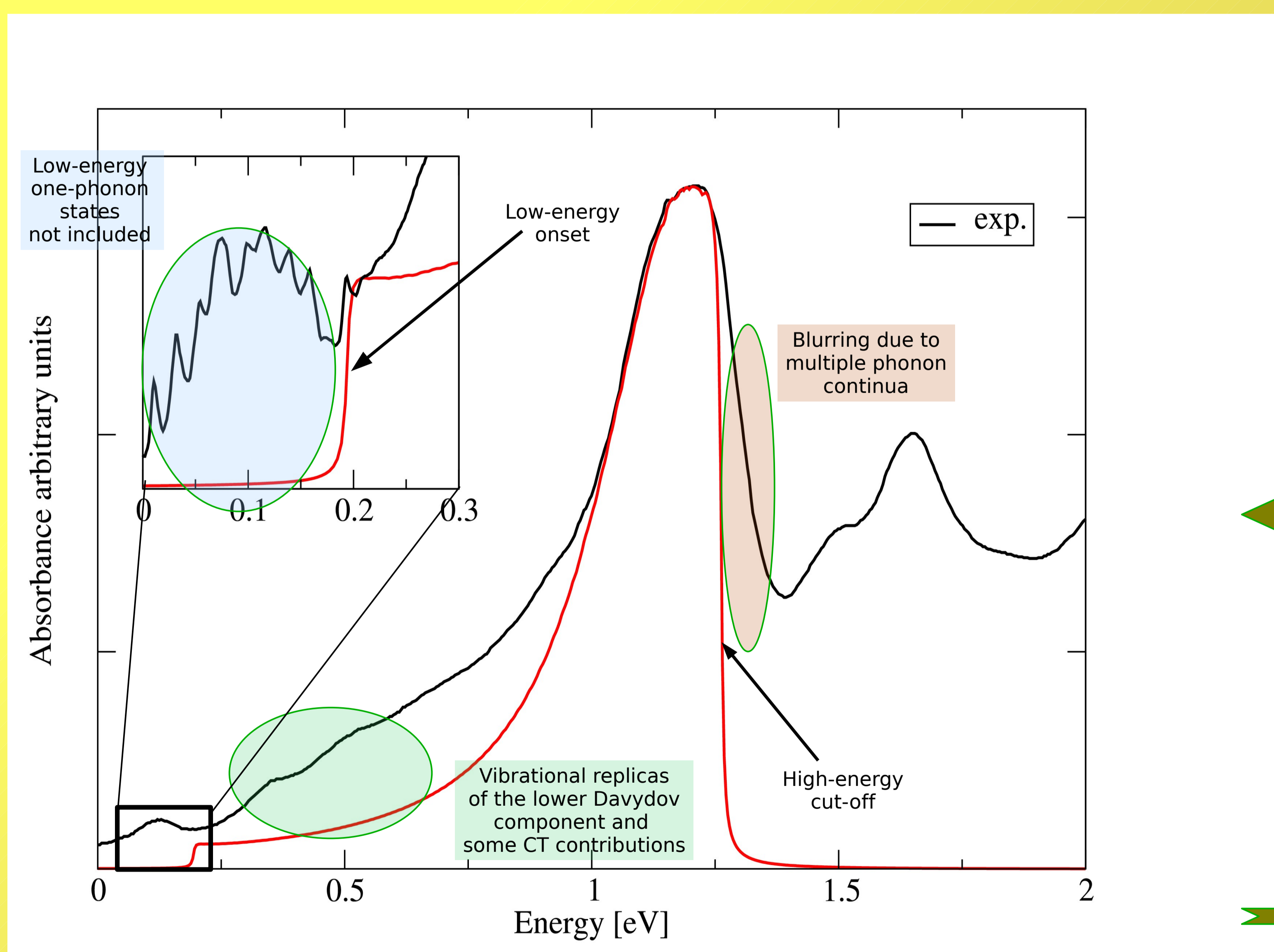
- weak vibronic coupling limit
- Fano configuration interaction formalism (uniform density of states)
- finite span of energy continuum

**RESULTS**

Absorption intensity

$$I(E) = \frac{N\mu^2 b^2}{4C} \times \frac{1}{\left(E - E_\phi - \frac{b^2}{4C} \ln \left| \frac{E - \alpha}{E - \beta} \right| \right)^2 + \frac{\pi^2 b^4}{16C^2}} \times \frac{1}{\frac{1}{\pi} \arctan \left( \frac{4C(\beta - E_\phi)}{\pi b^2} \right) - \frac{1}{\pi} \arctan \left( \frac{4C(\alpha - E_\phi)}{\pi b^2} \right)}$$

$\mu$  – transition dipole moment  
 $2C$  – energy span of the exciton band  
 $E_\phi$  – energy of the upper Frenkel component  
 $\alpha, \beta$  – bounds of the integration interval



**CONCLUSIONS**

- 1) Shape of the calculated curve defined only by two parameters (both from independent estimates).
- 2) Good agreement between experiment and the calculated profile lending credence to the applied simplistic approach.
- 3) Working hypothesis confirmed.

**Why are oligothiophenes so important???**

model systems → optoelectronic devices

relatively easy to study      light emitting diodes  
 high degree of crystallinity      field-effect transistors

The understanding of their electronic excitations (both the Frenkel and the charge transfer (CT) states) is of crucial relevance.

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