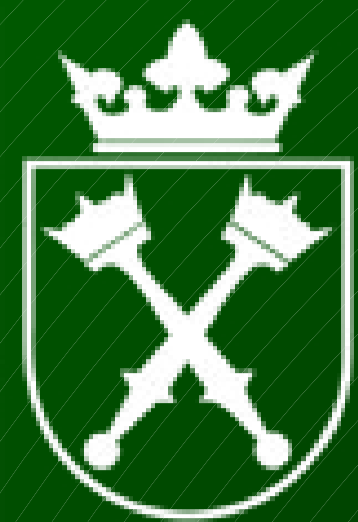


Vibronic contribution to the spectral shape of intense exciton absorption in oligothiophene crystals

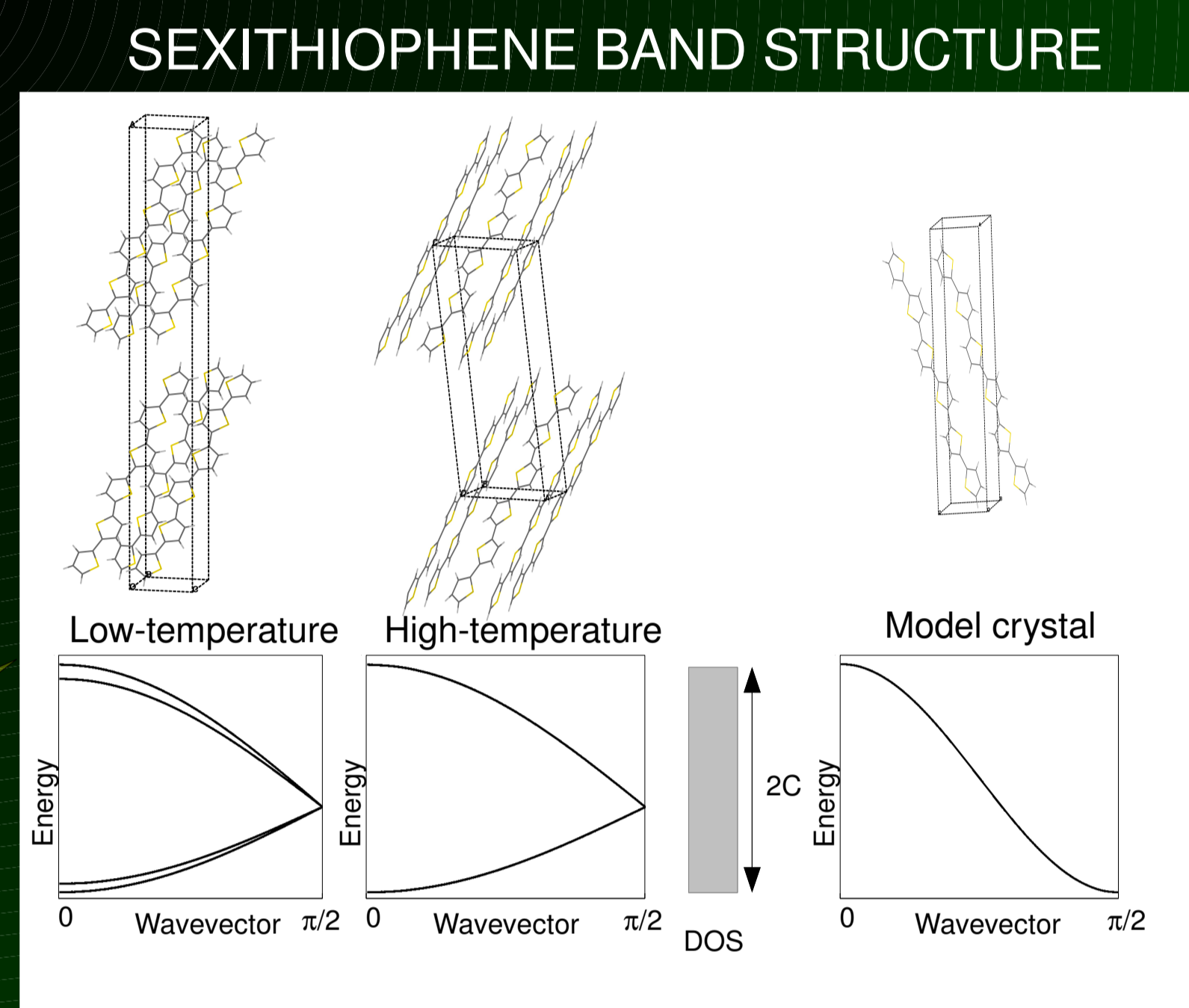
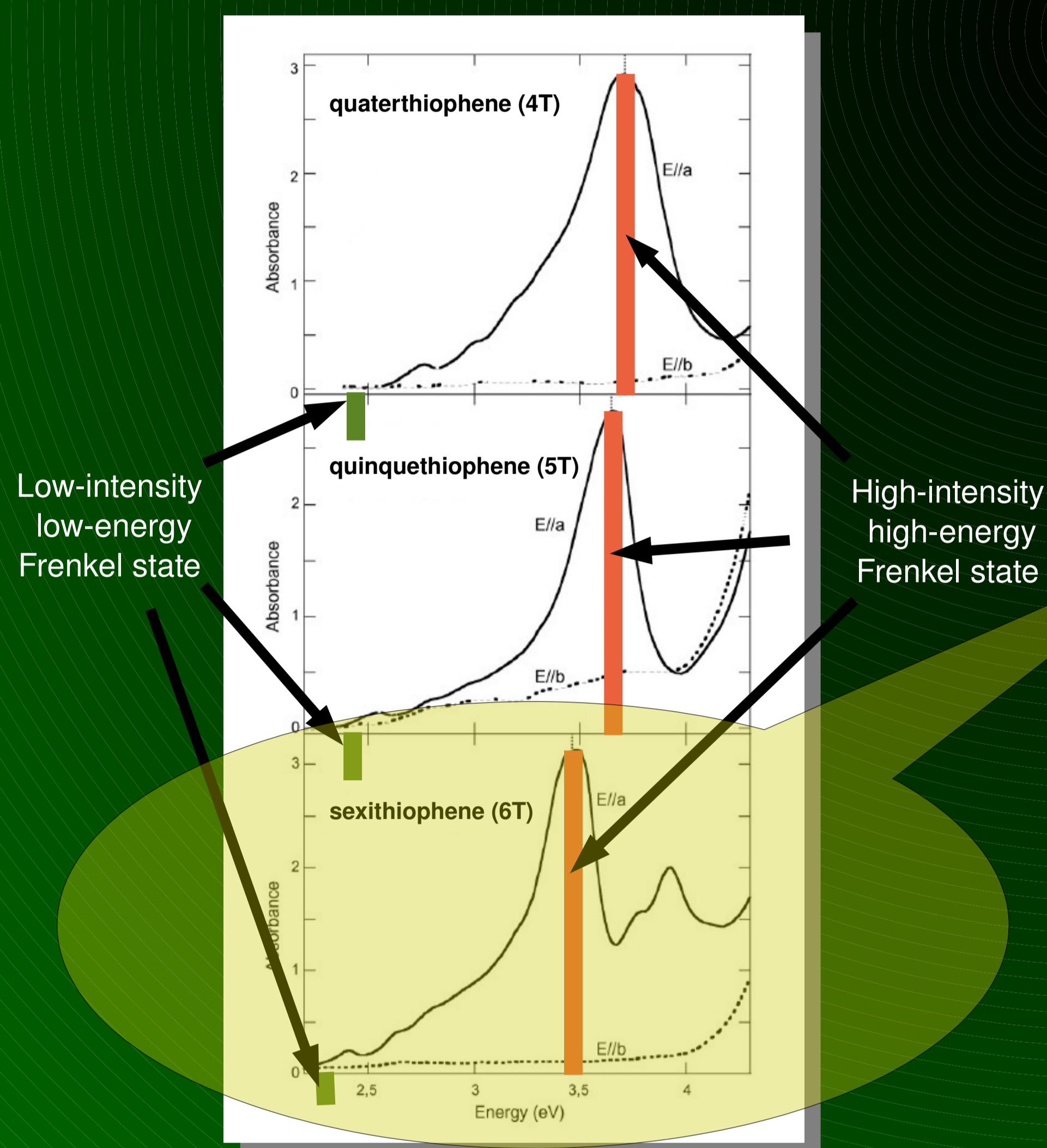


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Observations: General shape of crystal absorption spectrum is common to all oligothiophenes [1,2].



MODEL

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

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

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

APPROACH

- weak vibronic coupling limit
- Fano configuration interaction formalism (uniform density of states) [3]
- finite span of energy continuum

RESULTS

Absorption intensity [4]

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

μ - transition dipole moment
 $2C$ - energy span of the exciton band
 E_+ - energy of the upper Frenkel component
 α, β - bounds of the integration interval

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.

PARAMETERS

Compound	$2C$ ¹⁾	b^{*2} ²⁾	b^{eff}
4T	0.94	1.41	1.9
5T	1.06	1.35	1.8
6T	1.08	1.27	1.7

¹⁾ experimental Davydov splitting
²⁾ calculated (DFT/TDDFT, B3LYP, TZVP) [5]

COUPLING CONSTANT

In case of more than one phonon mode per molecule [3]:

$$b^* = \sqrt{\sum_i b_i^2 \frac{\omega_i}{\omega}}$$

After taking into account polariton effects [6]:

$$b^{eff} = b^* + \delta$$

CONCLUSIONS

1) For a given crystal, the shape of the calculated absorption profile is governed by two parameters only: the effective coupling constant and the Davydov splitting at $k = 0$ (both obtained from independent estimates).

2) The agreement between the experimental and the calculated shape of the absorption curve is very good, lending credence to the applied simplistic model.

3) The main qualitative features of the bands, common to all oligothiophenes (specifically, the long low-energy onset of the main peak and its steep high-energy cutoff) are very well reproduced.

The working hypothesis is tentatively confirmed.

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