

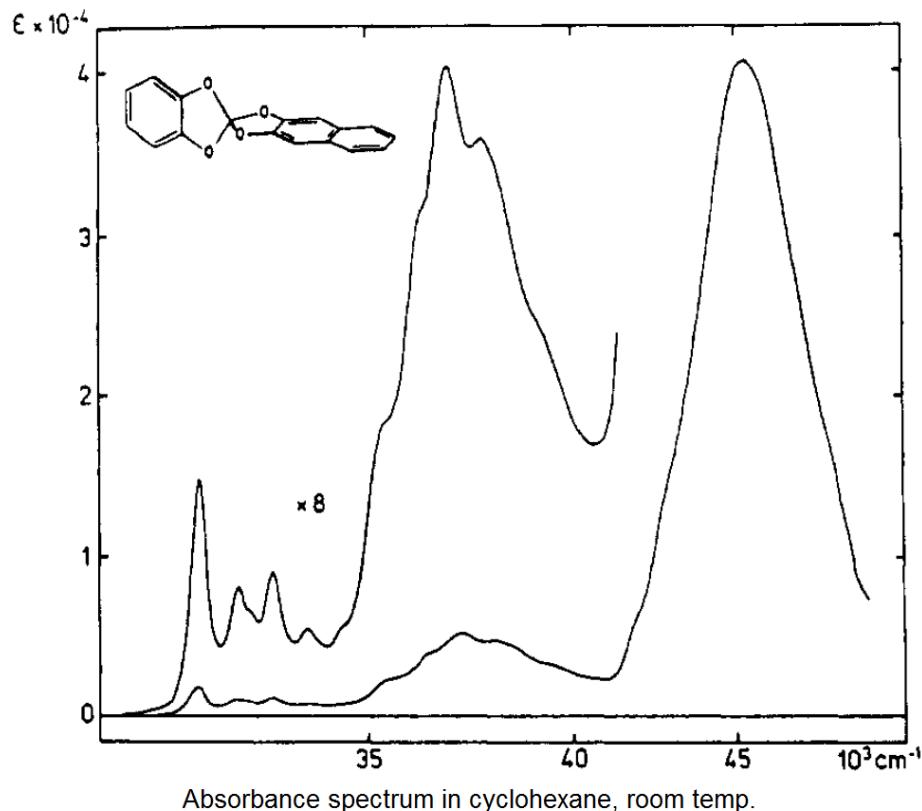


Molecular Applications of Linear Dichroism (LD) Spectroscopy

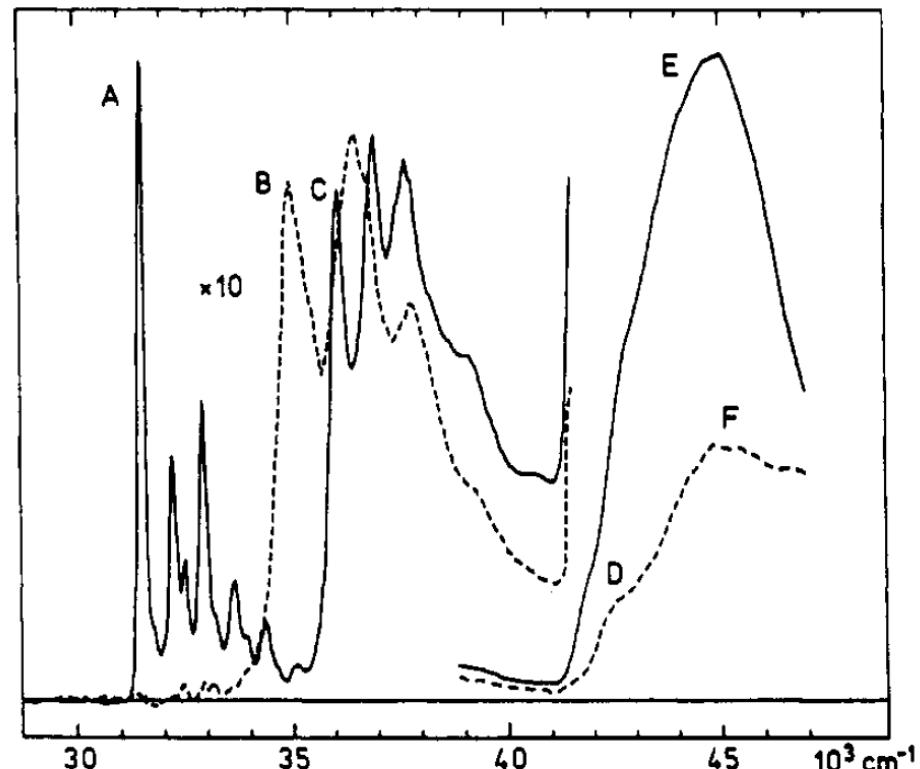
Bi-Ke Seminar
RUC, December 05, 2014

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Dept. of Science, Systems & Models
Roskilde University (RUC)

Optical absorbance spectroscopy:



Absorbance spectrum in cyclohexane, room temp.



Partial absorbance curves (stretched polyethylene, 77 K):
Full and dashed curves indicate long- and short-axis polarized
absorbance

Linear Dichroism (LD)

Programme:

**1) LD spectroscopy: Working equations
for uniaxial samples (quinizarin)**

Molecular structural applications:

2) IR: 1,6,6a λ^4 -Trithiapentalene (TTP)

3) IR & UV: Diphenyl-diacetylene (DPDA)

Main characteristica of optical absorption bands:

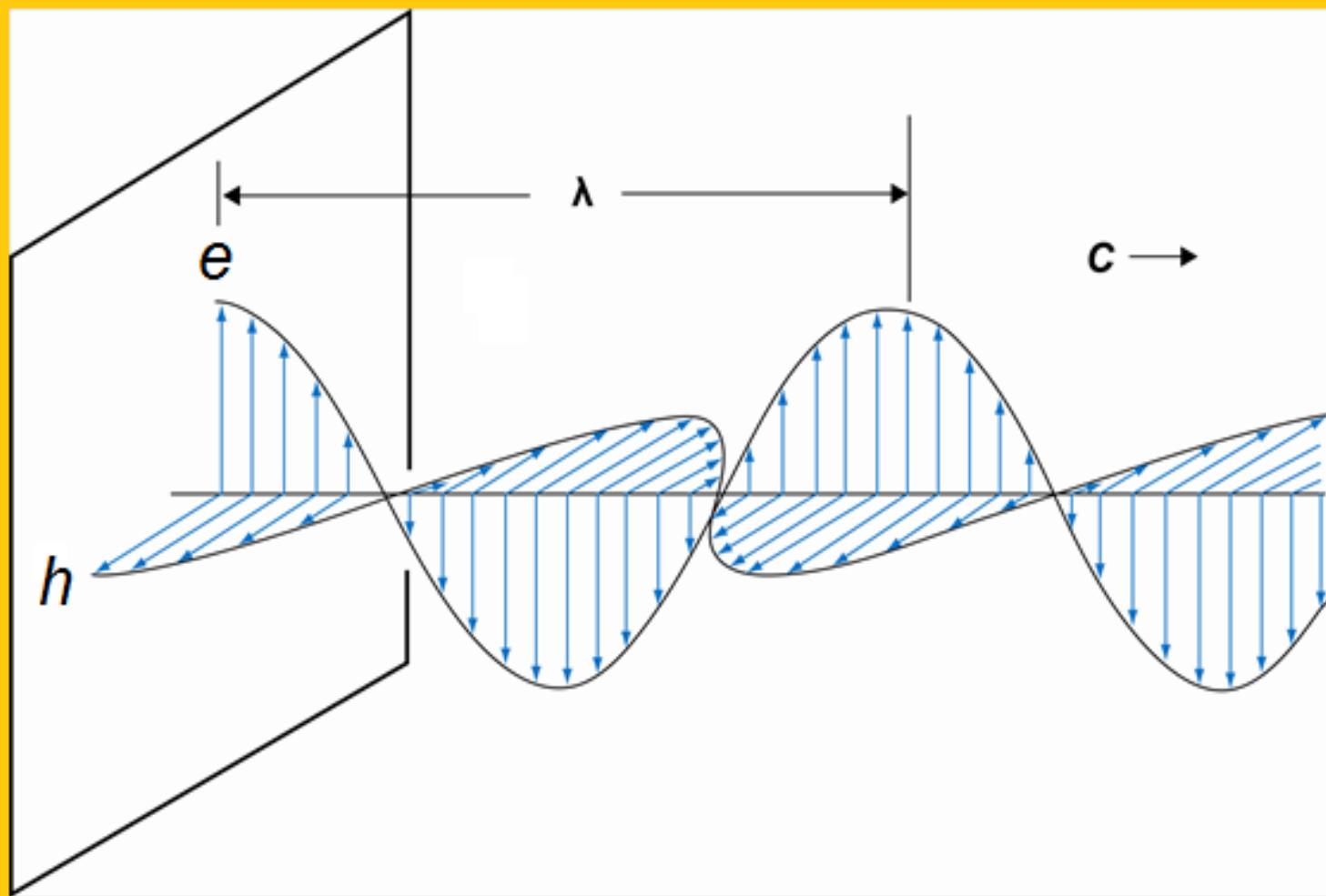
1) Transition energy

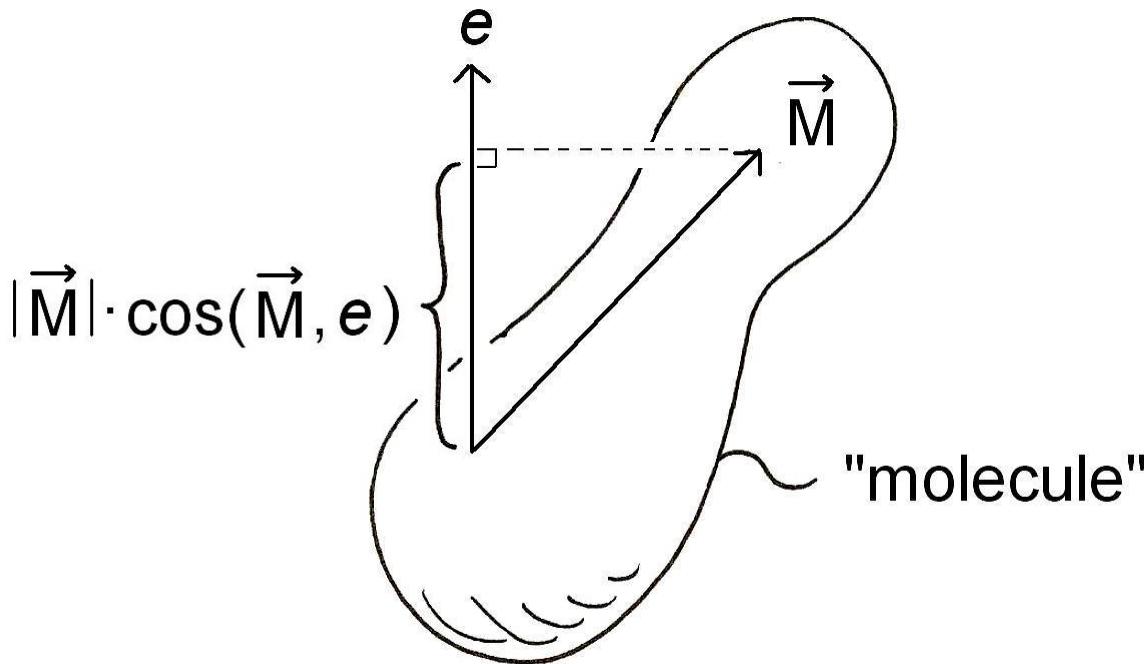
(frequency, wavenumber, wavelength)

2) Intensity (absorbance, oscillator strength)

3) Polarization, *i.e.*, transition moment direction

Plane Polarized Radiation





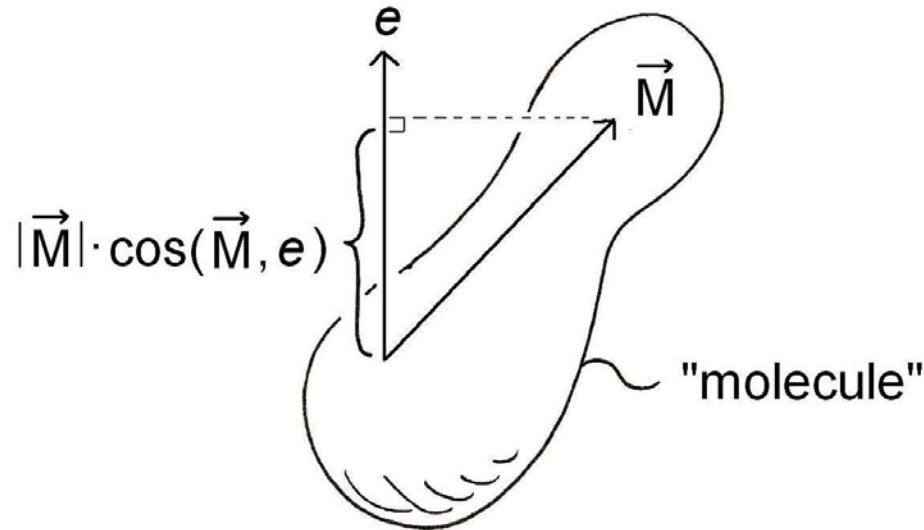
\vec{M} = transition moment vector

e = electric field vector

(\vec{M}, e) = angle between \vec{M} and e

$$\text{Transition Probability} \propto |\vec{M}|^2 \cos^2(\vec{M}, e)$$

Absorbance Measurement



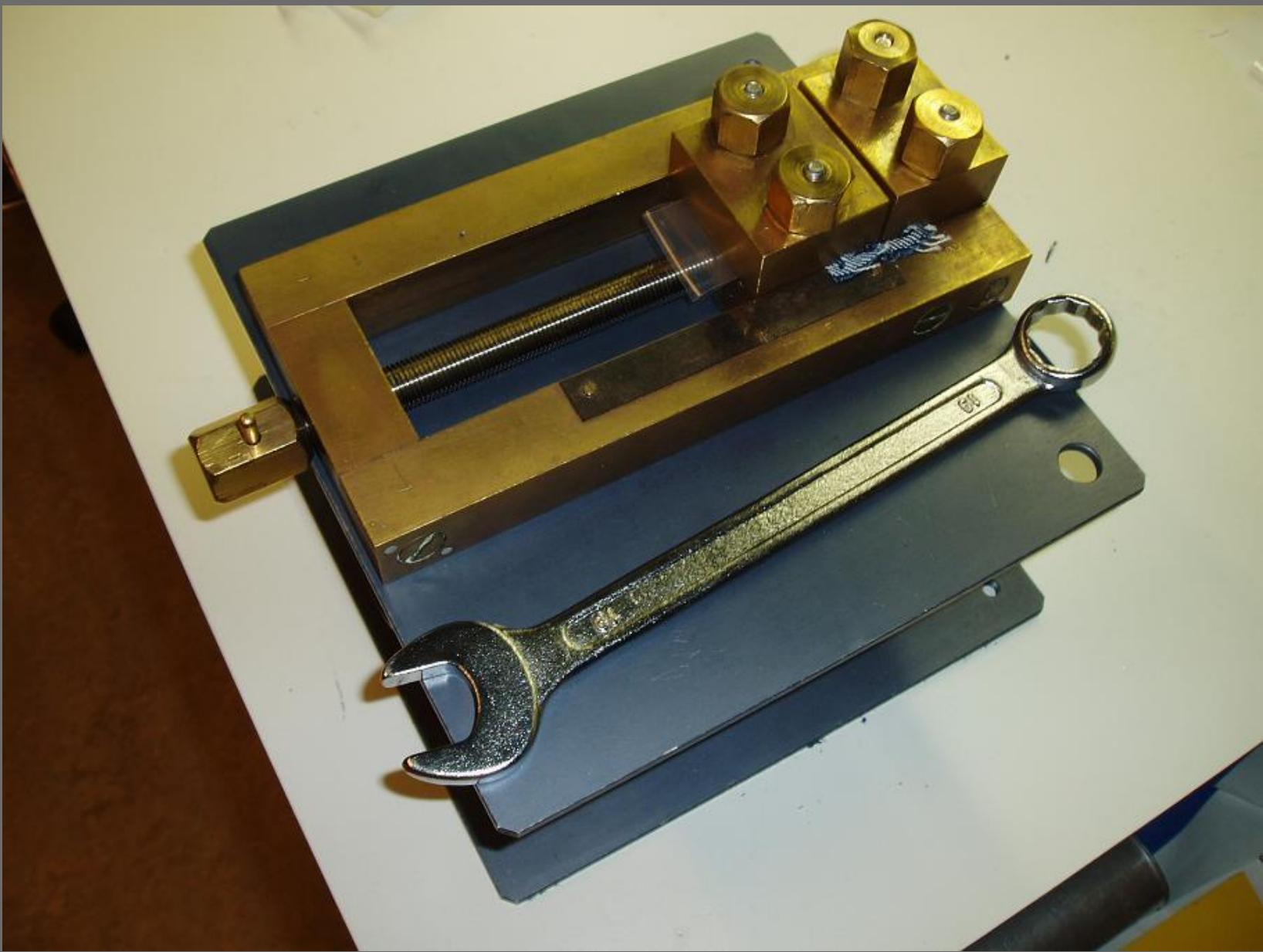
$$\text{Absorbance} = A(\tilde{\nu}) \cdot \langle \cos^2(\vec{M}, e) \rangle$$

where $A(\tilde{\nu})$ is the absorbance measured for $(\vec{M}, e) = 0$

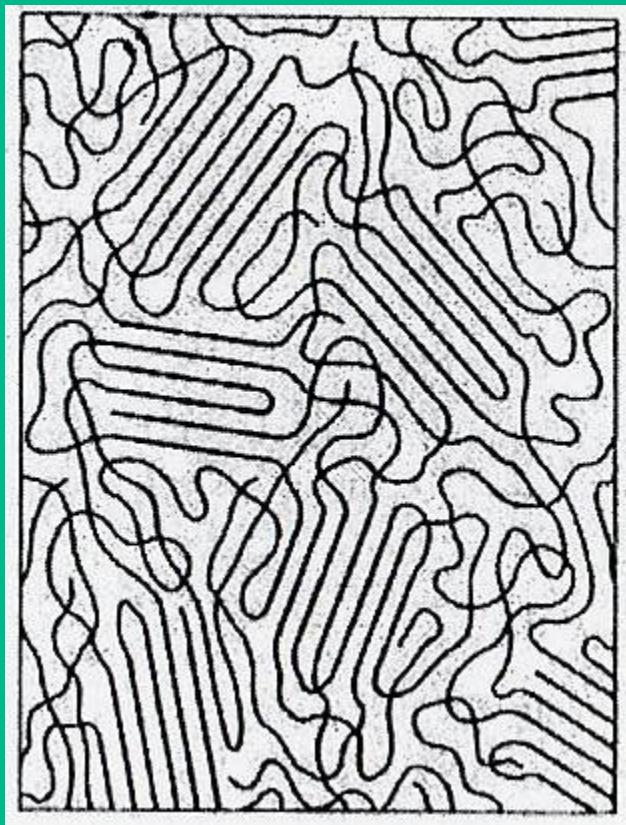
Stretched Polyethylene as an Anisotropic Solvent



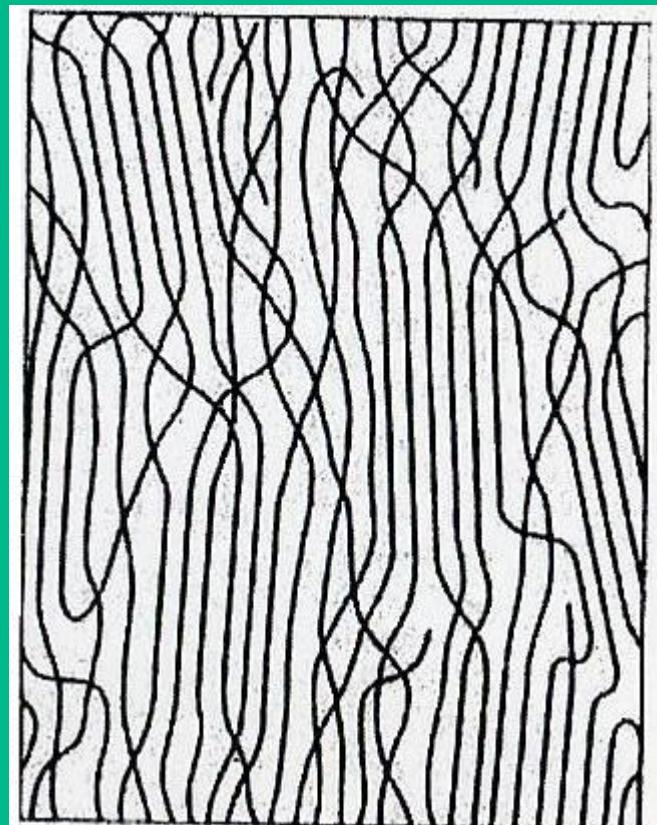




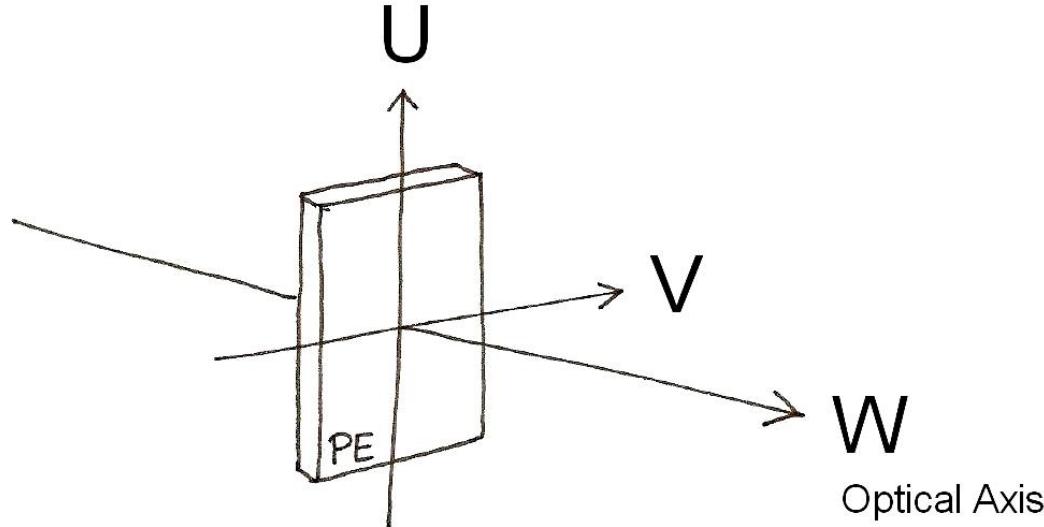
Simplified model
of polyethylene (PE)



Corresponding model of
stretched polyethylene (PE)



Uniaxial Stretching Direction



$$E_U(\tilde{\nu}) = A(\tilde{\nu}) \cdot \langle \cos^2(\vec{M}, U) \rangle$$

$$E_V(\tilde{\nu}) = A(\tilde{\nu}) \cdot \langle \cos^2(\vec{M}, V) \rangle$$

~~$$E_W(\tilde{\nu}) = A(\tilde{\nu}) \cdot \langle \cos^2(\vec{M}, W) \rangle$$~~

Uniaxial Sample

$$\langle \cos^2(\vec{M}, V) \rangle = \langle \cos^2(\vec{M}, W) \rangle$$

$$\langle \cos^2(\vec{M}, U) \rangle + \langle \cos^2(\vec{M}, V) \rangle + \langle \cos^2(\vec{M}, W) \rangle = 1$$

$$\Rightarrow \langle \cos^2(\vec{M}, V) \rangle = \frac{1}{2} \left(1 - \langle \cos^2(\vec{M}, U) \rangle \right)$$

We define the Orientation Factor K :

$$K \equiv \langle \cos^2(\vec{M}, U) \rangle$$

Uniaxial Sample

$$K \equiv \langle \cos^2(\vec{M}, U) \rangle$$

$$E_U(\tilde{\nu}) = A(\tilde{\nu}) \cdot \langle \cos^2(\vec{M}, U) \rangle = A(\tilde{\nu}) \cdot K$$

$$E_V(\tilde{\nu}) = A(\tilde{\nu}) \cdot \langle \cos^2(\vec{M}, V) \rangle = A(\tilde{\nu}) \cdot \frac{1}{2}(1 - K)$$

Dichroic Ratio, d :

$$d \equiv \frac{E_U(\tilde{\nu})}{E_V(\tilde{\nu})} = \frac{2K}{1 - K} \Rightarrow K = \frac{d}{2 + d}$$

In general, several transitions "i" contribute to the observed dichroic absorption curves:

$$E_U(\tilde{\nu}) = \sum_i A_i(\tilde{\nu}) \cdot K_i$$

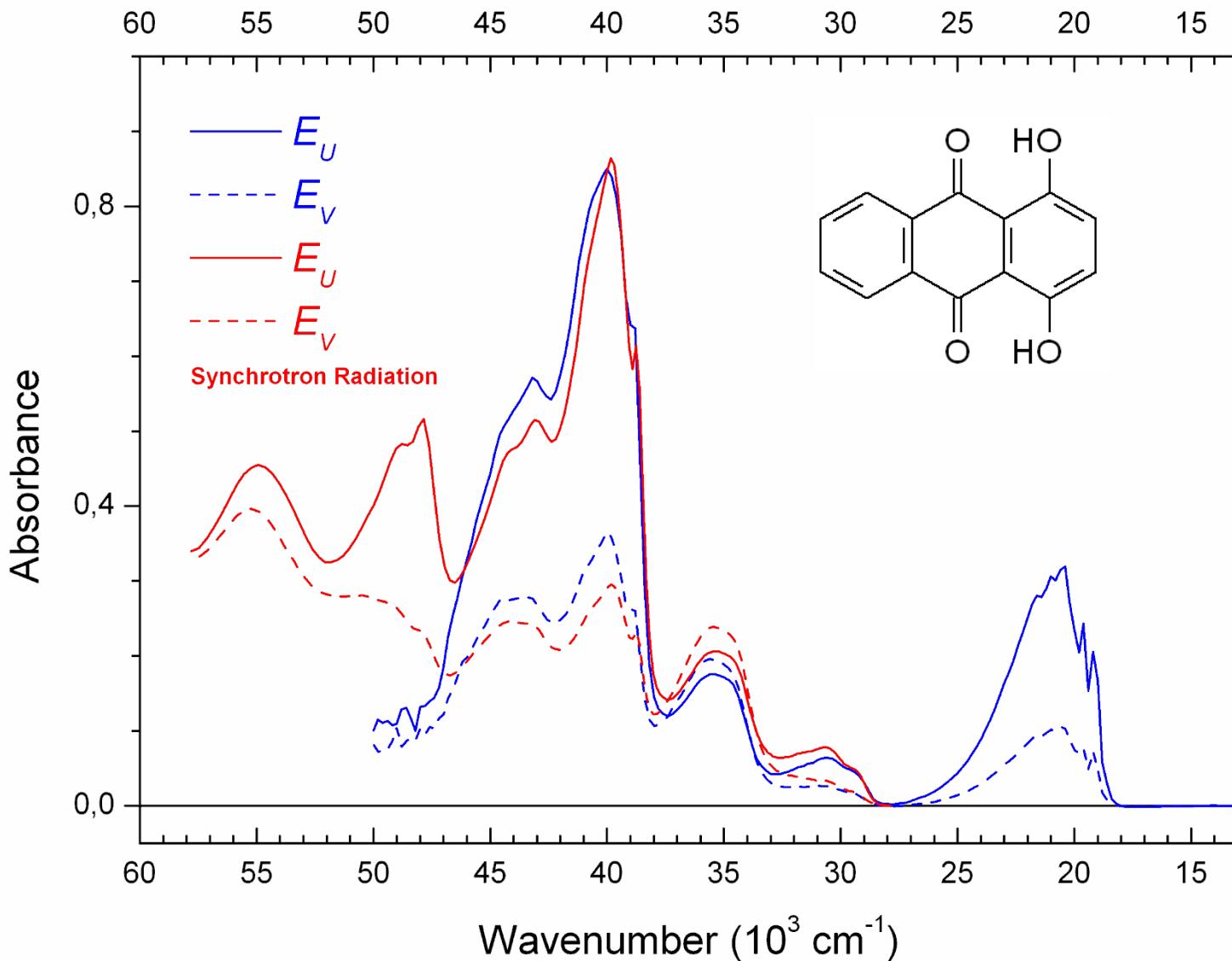
$$E_V(\tilde{\nu}) = \sum_i A_i(\tilde{\nu}) \cdot \frac{1}{2}(1 - K_i)$$

TEM procedure for overlapping transitions:

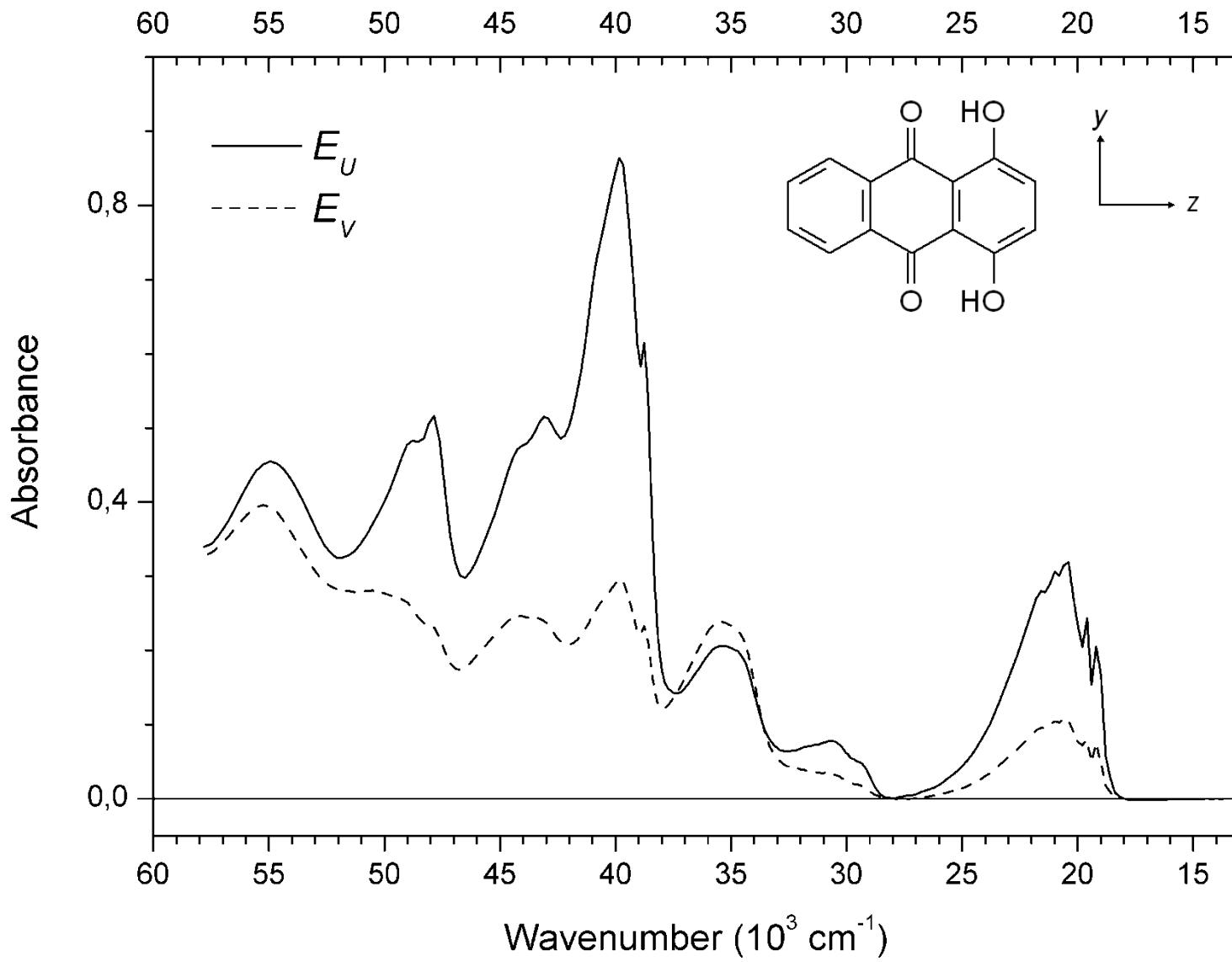
$$r_K = (1 - K) \cdot E_U(\tilde{\nu}) - 2K \cdot E_V(\tilde{\nu})$$

A spectral feature (peak or shoulder) due to transition *i* vanishes from r_K when $K = K_i$. The K_i value can thus be determined by visual inspection.

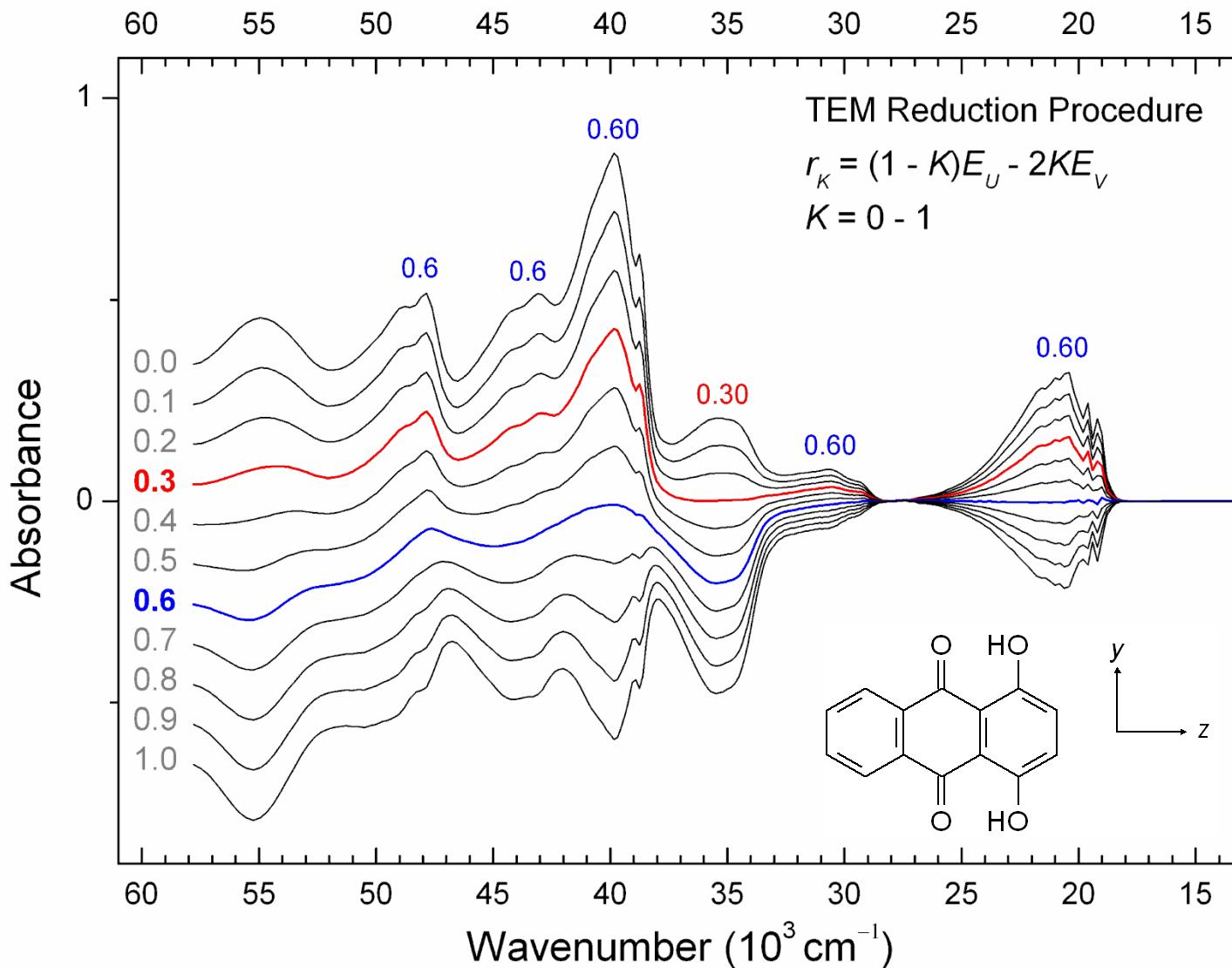
Quinizarin



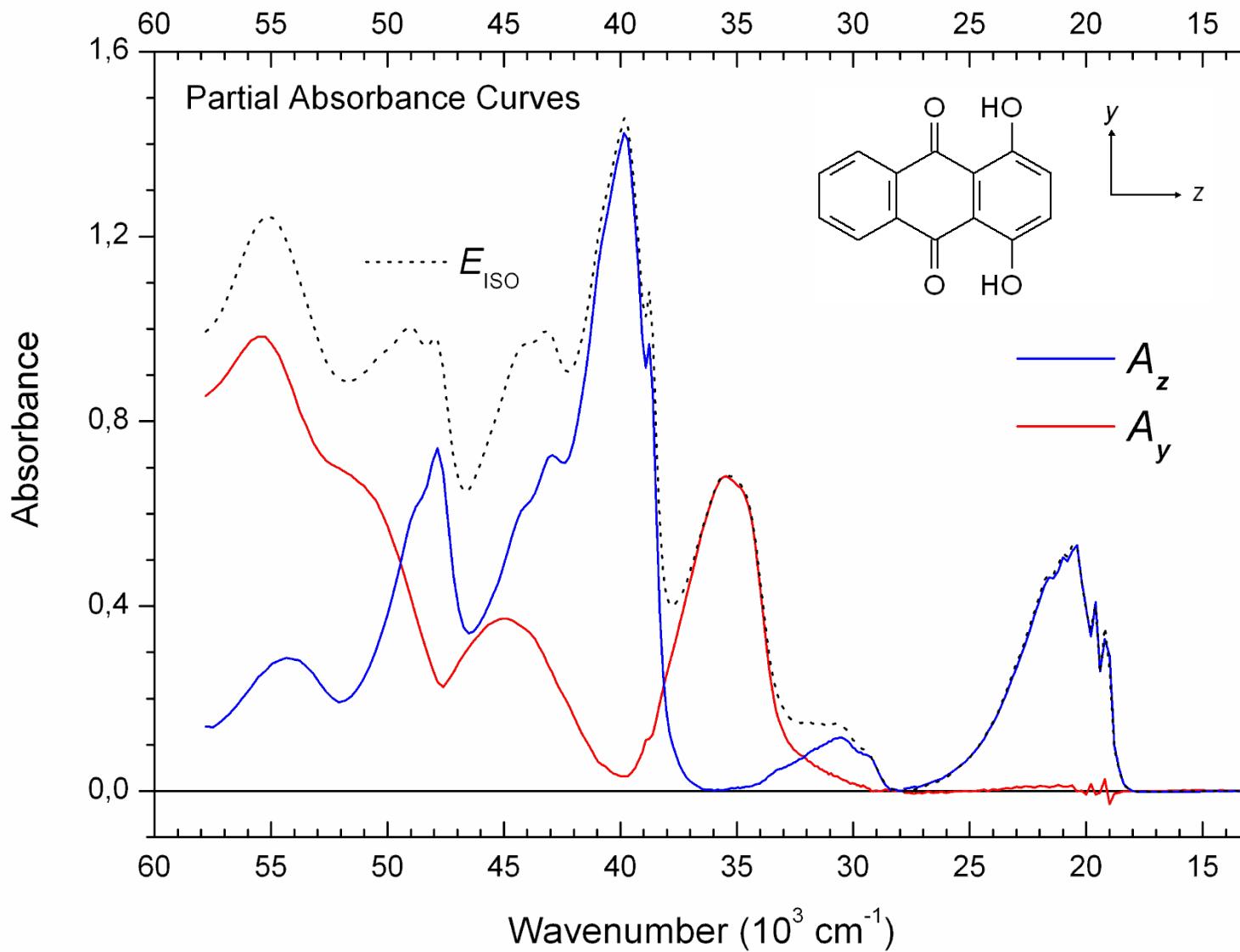
Quinizarin

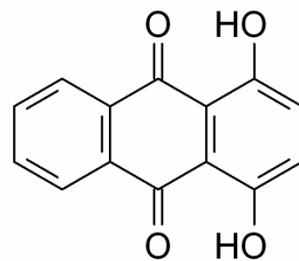
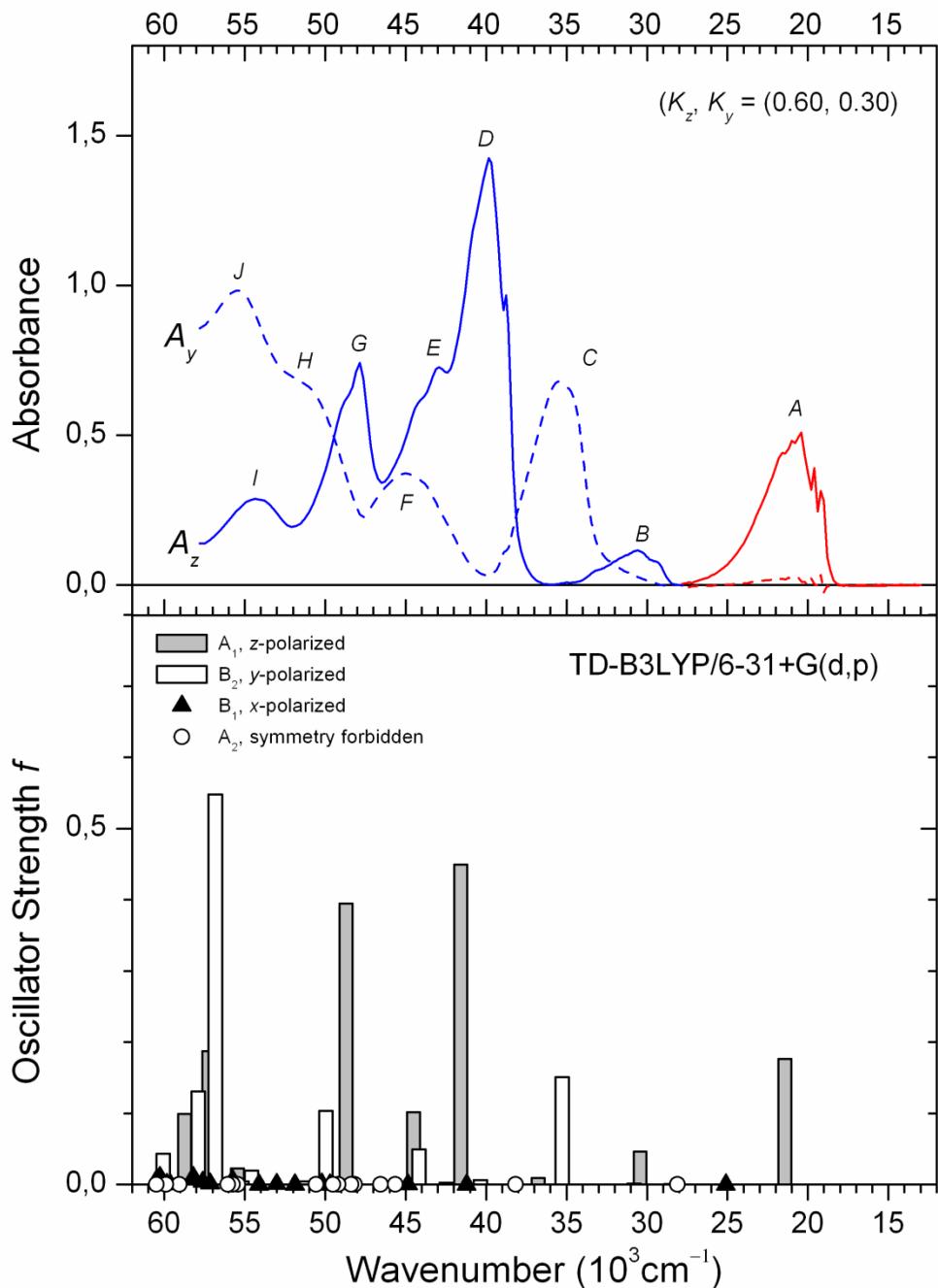


Quinizarin



Quinizarin

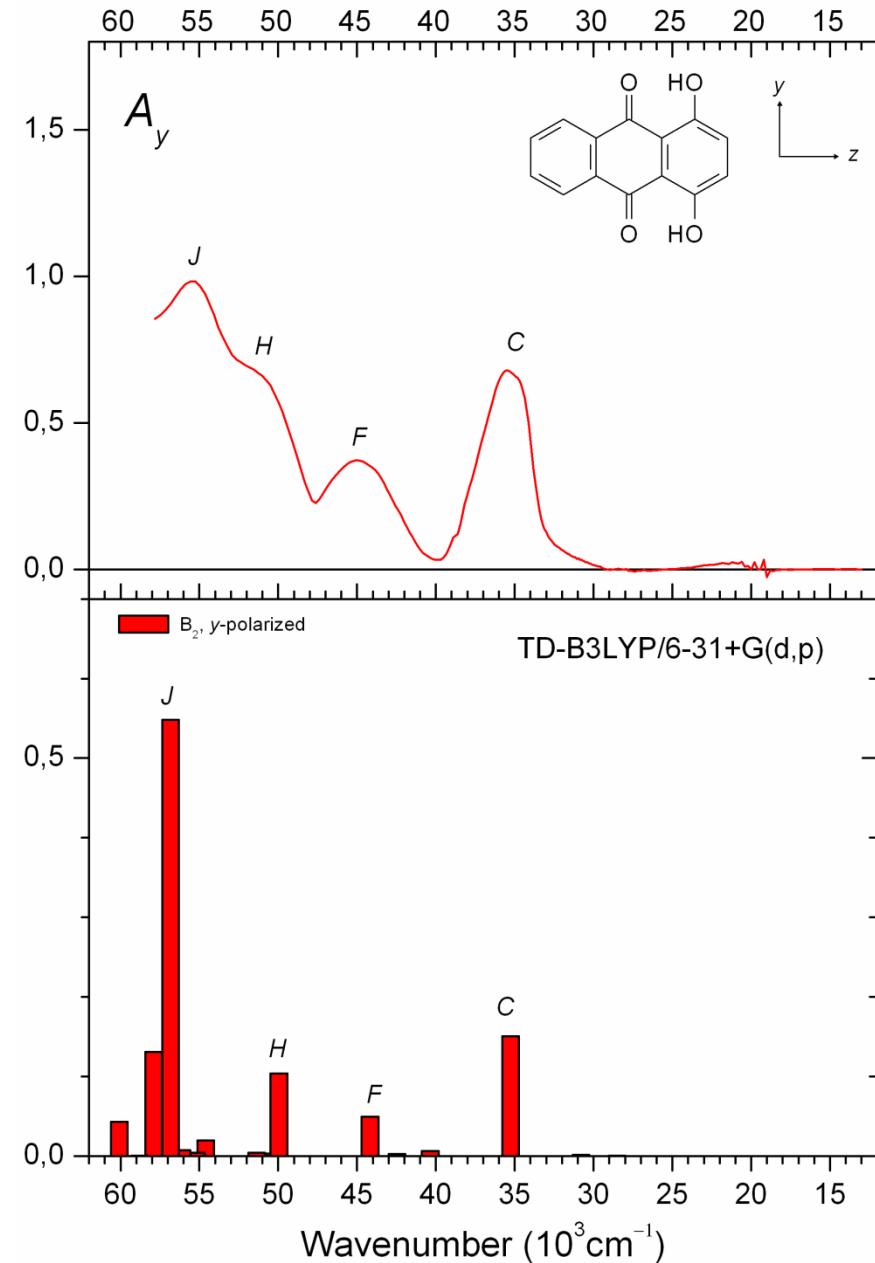
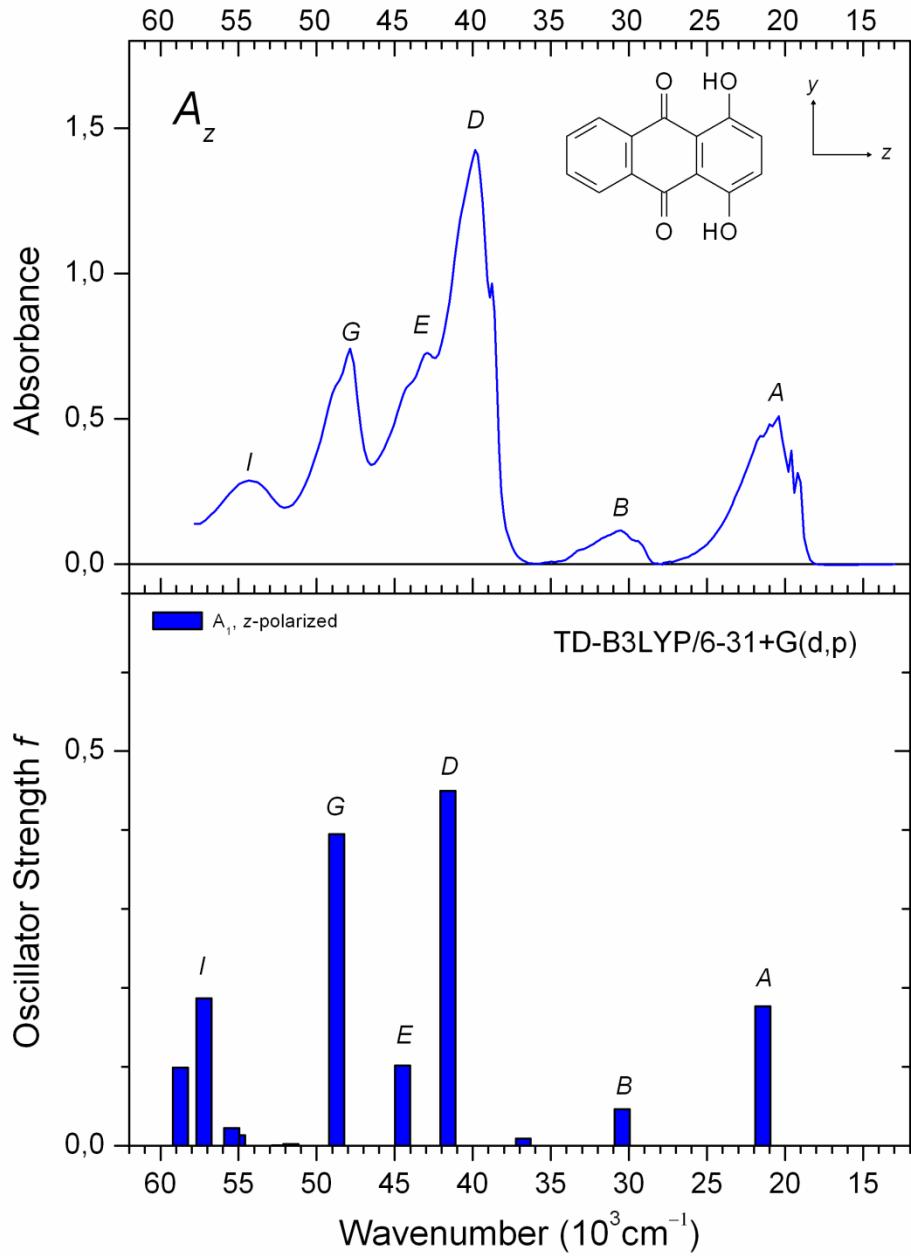




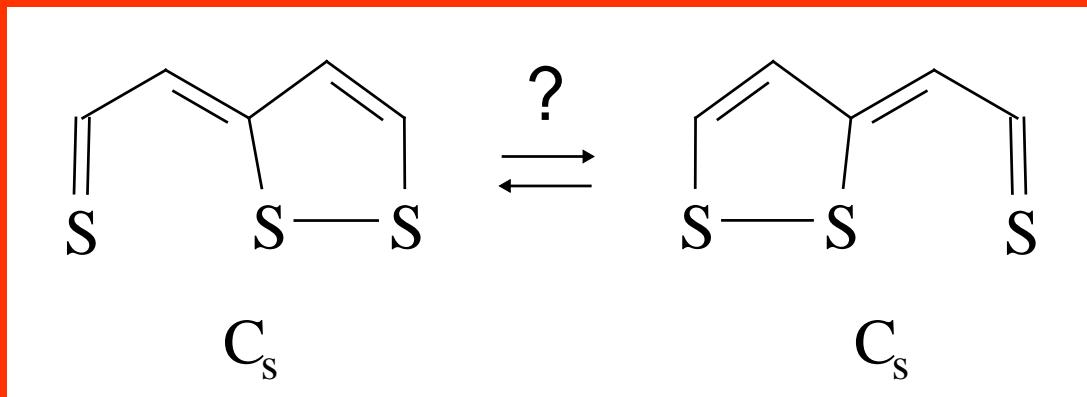
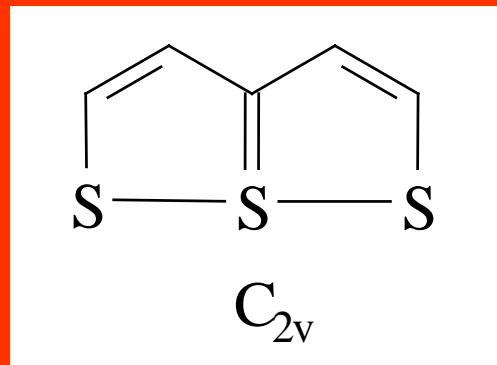
y
 z

Quinizarin

D.D. Nguyen, N.C. Jones, S.V. Hoffmann,
J. Spanget-Larsen, *Spectrochim. Acta A* **77**,
279-286 (2010).



$1,6,6a\lambda^4$ -Trithiapentalene



If a molecule has D_{2h} , D_2 , or C_{2v} point group symmetry, optically allowed transitions must be polarized along one of the three mutually perpendicular molecular symmetry axes x , y , and z .

The observed K values should thus adopt only three distinct values, corresponding to the orientation factors K_x , K_y , and K_z for the three symmetry axes, and the three values should add up to unity:

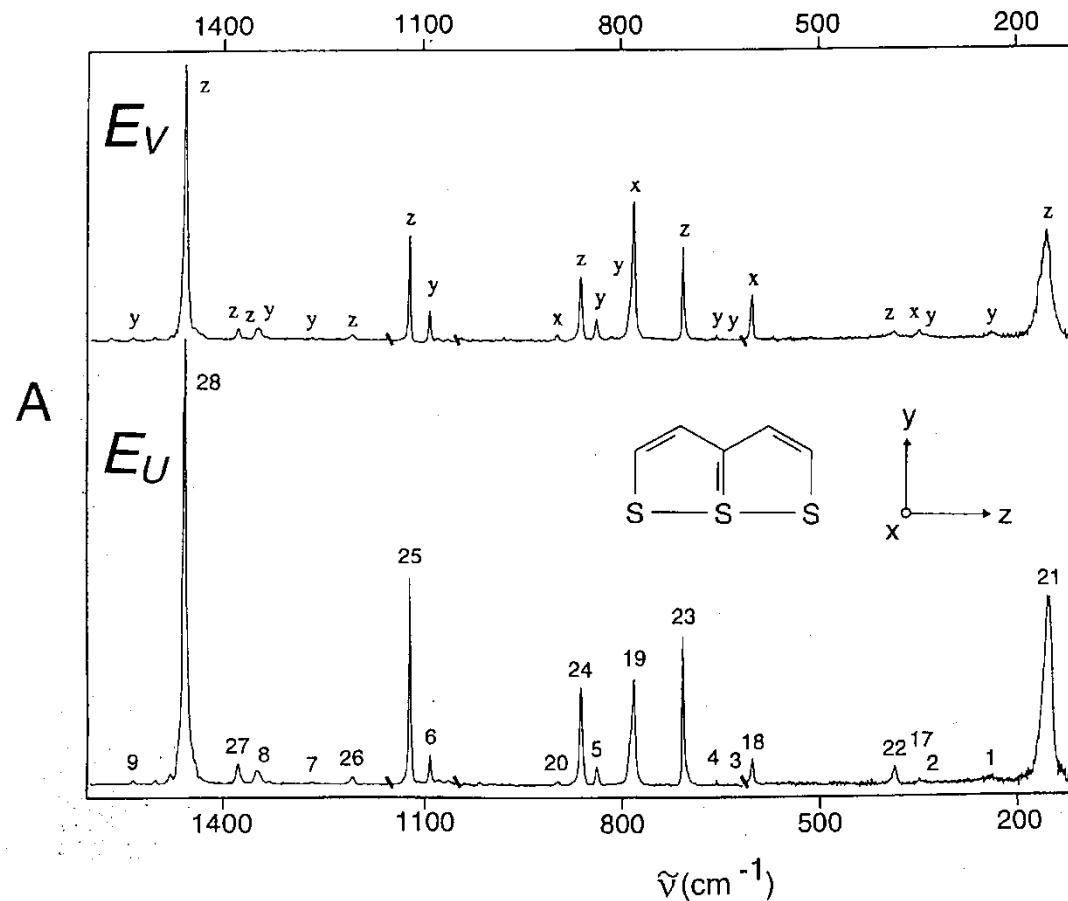
$$K_x + K_y + K_z = 1$$

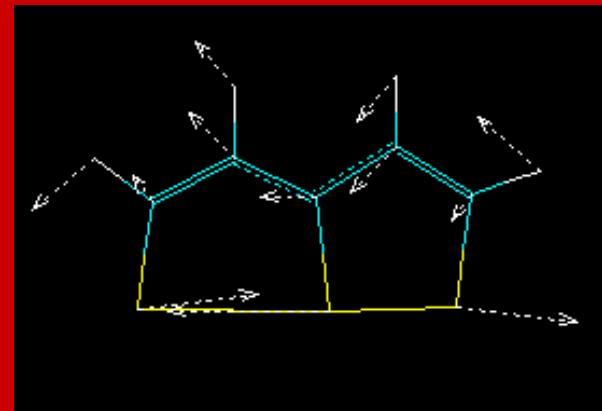
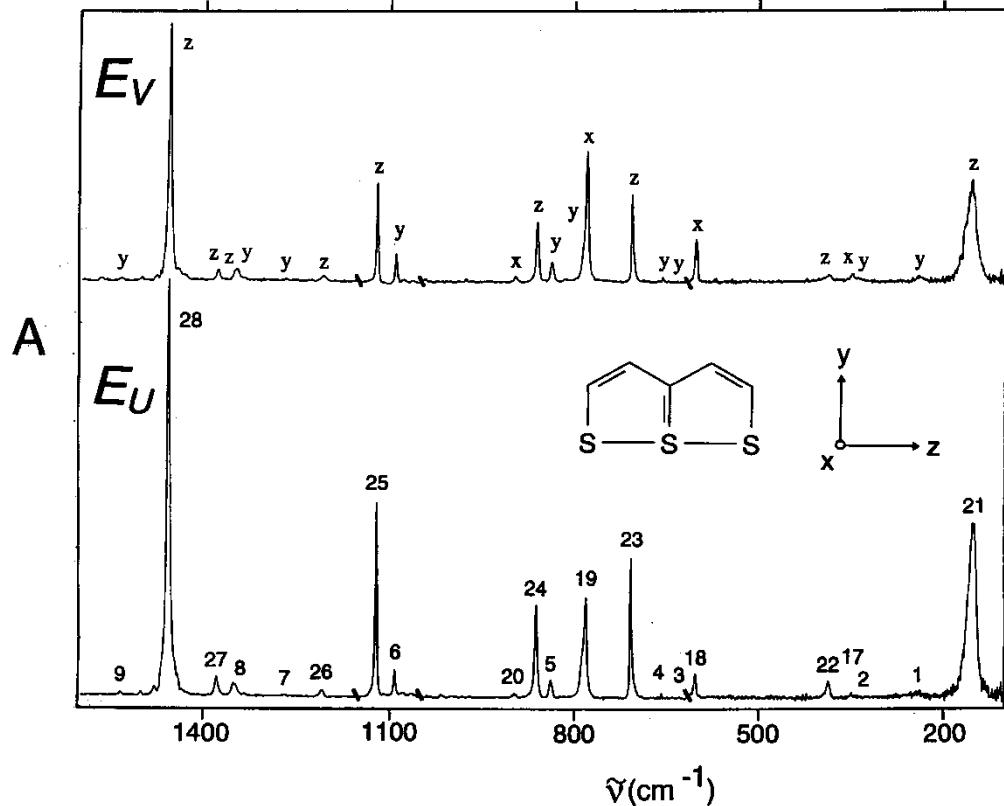
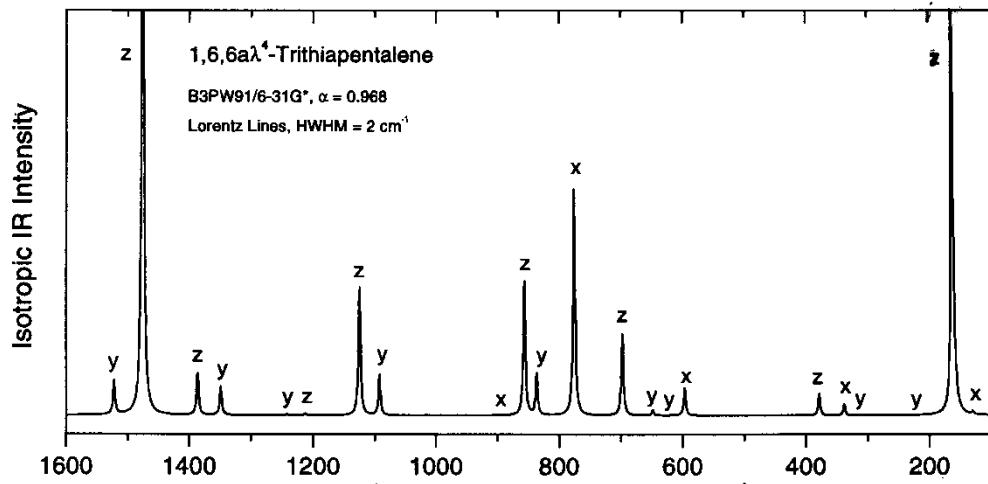
(1) If more than three significantly different K values are observed, the molecular symmetry must be different from D_{2h} , D_2 , and C_{2v} .

(2) If the observed K values for a large number of transitions fall in three distinct groups, with the three characteristic values adding up to unity, this is strong evidence for the presence of molecular symmetry elements, consistent with D_{2h} , D_2 , or C_{2v} .

$$K_i \equiv \langle \cos^2(\vec{M}_i, U) \rangle$$

$$(K_x, K_y, K_z) = (0.240 \pm 0.01, 0.306 \pm 0.01, 0.462 \pm 0.02)$$





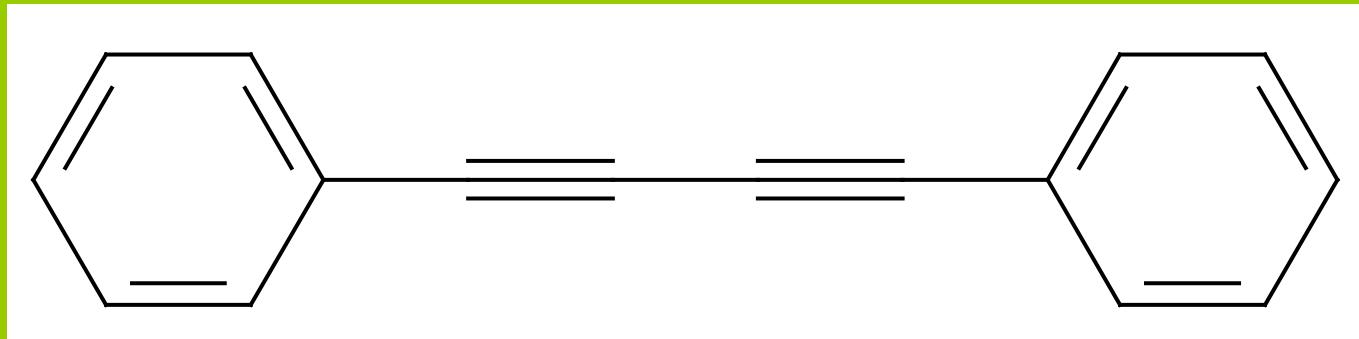
"Bell-Clapper" mode (153 cm^{-1})

The observed orientation factors indicate that the molecule has a rigid, symmetrical structure (C_{2v})

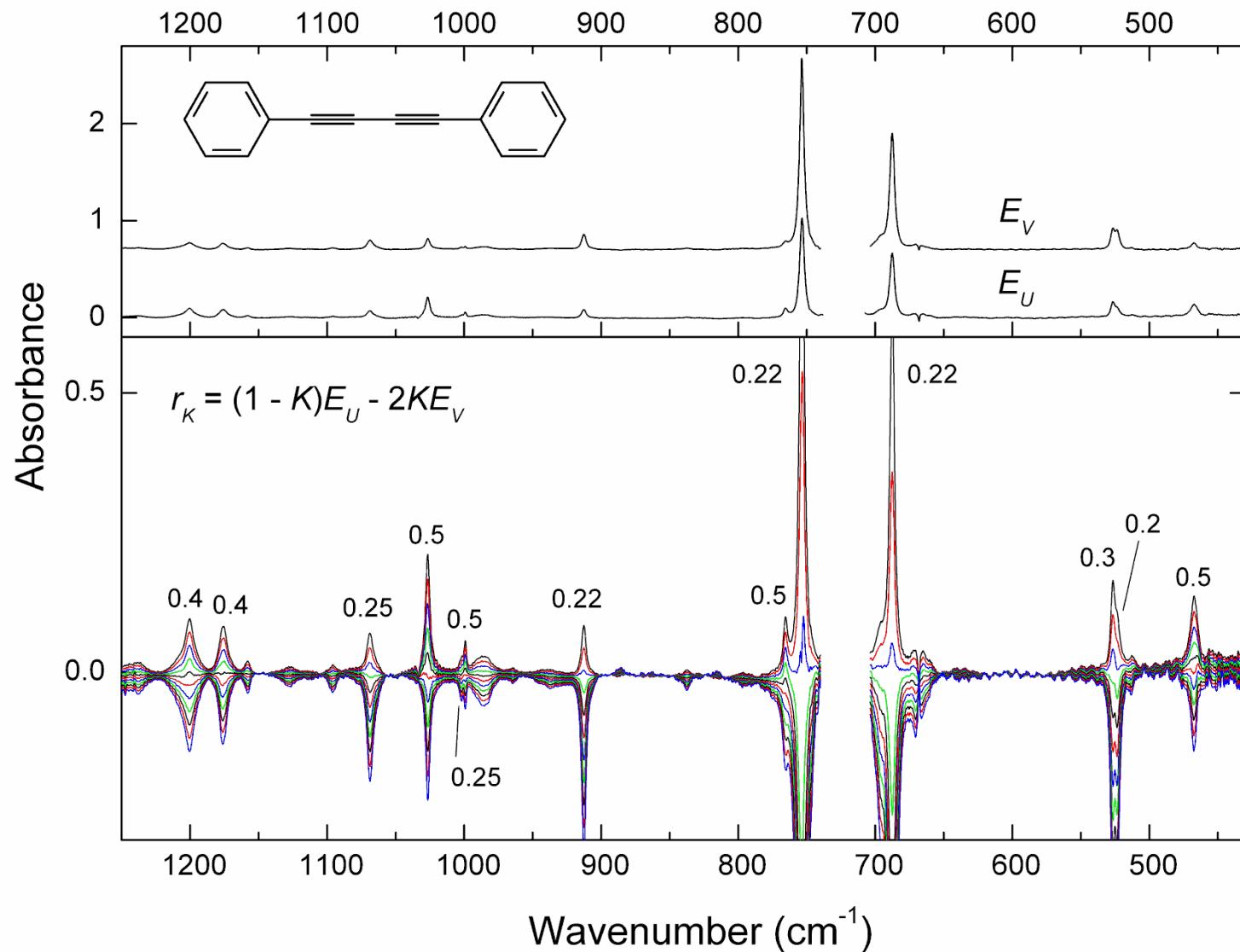
Experimental observation of the "Bell-Clapper" transition confirms it

K.B. Andersen, J. Abildgaard, J.G. Radziszewski, J. Spanget-Larsen:
J. Phys. Chem. A **101**, 4475 (1997)

Diphenyldiacetylene (DPDA)



FTIR-LD of DPDA aligned in stretched LDPE

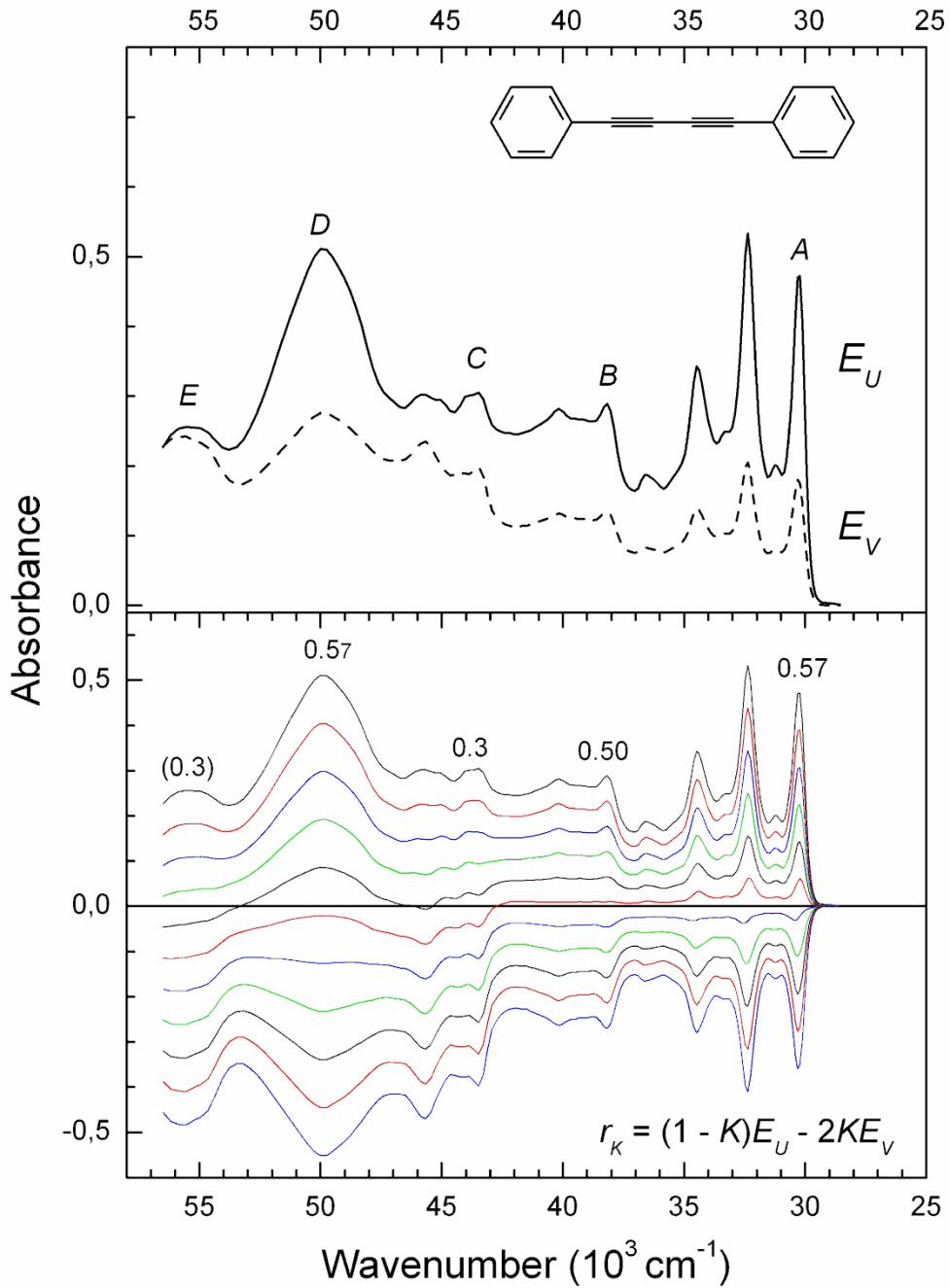


UV-SRLD of DPDA aligned in LDPE

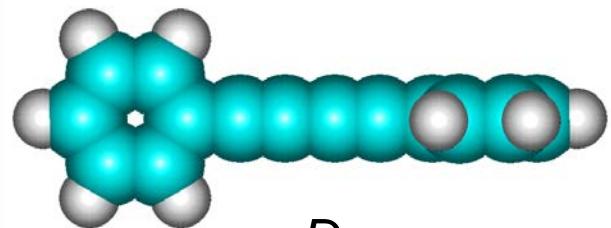
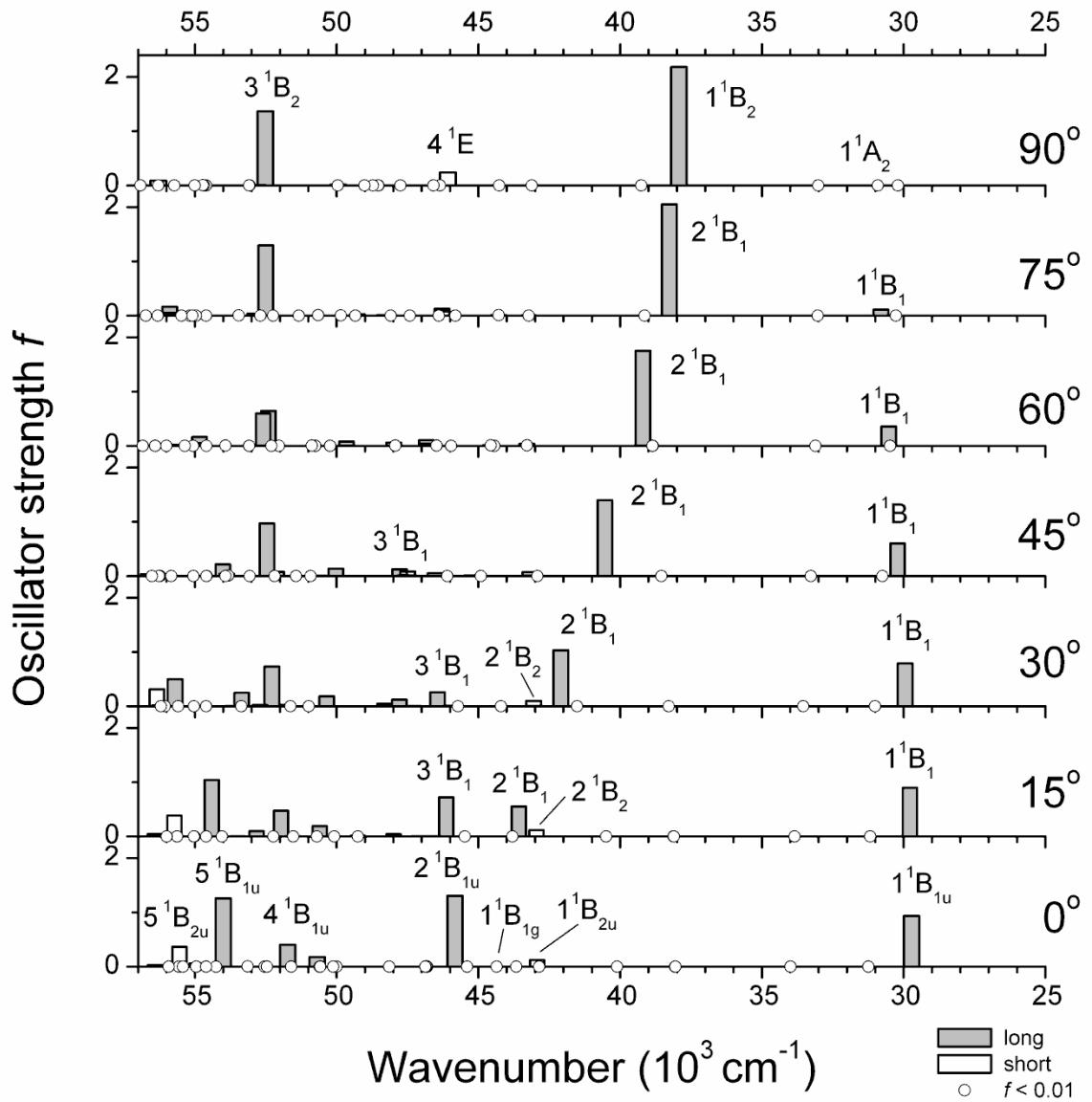
The observed orientation factors are inconsistent with the presence of a single, symmetric species.

Do we observe overlapping contributions from different rotamers?

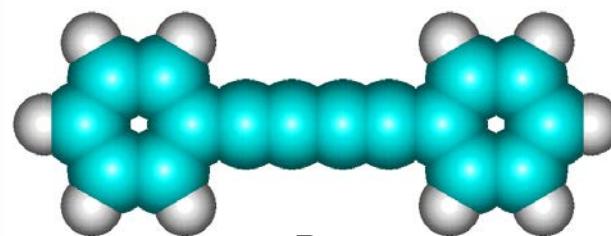
P.W. Thulstrup, S.V. Hoffmann,
B.K.V. Hansen, J. Spanget-Larsen,
PCCP **13**, 16168-16174 (2011)

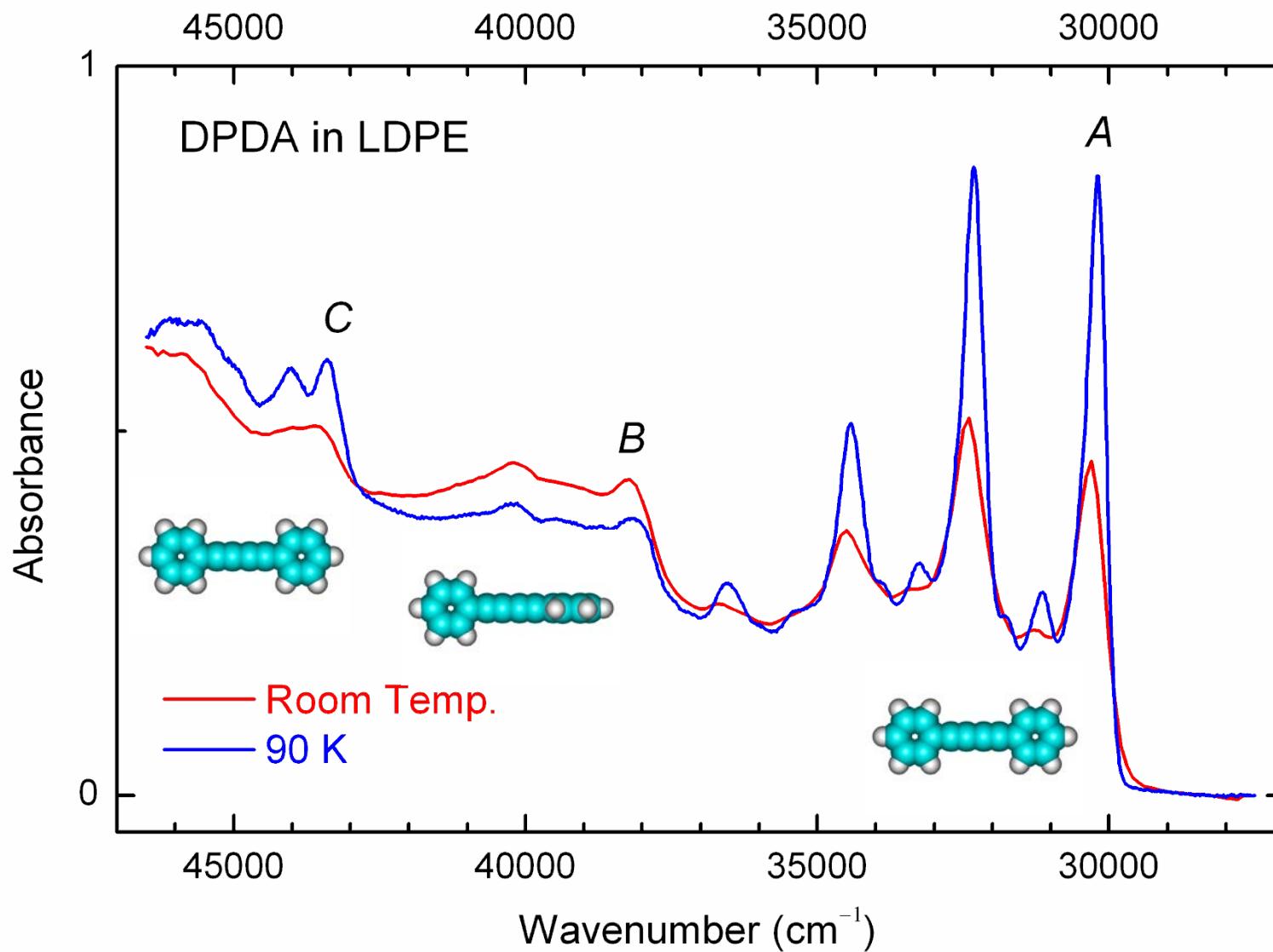


TD-PBE1PBE/6-31+G*//6-31G*



$\Delta E = \sim 0.3 \text{ kcal/mol}$





Acknowledgements

RUC:

Nguyen Duc Duy

Bjarke K. V. Hansen

Eva M. Karlsen

ISA:

Søren Vrønning Hoffmann

Nykola C. Jones

KU Life:

Peter Waaben Thulstrup

