Structural Applications of Polarization Spectroscopy on Aligned Molecular Assemblies

Methods in Soft Materials Science
RUC, January 29, 2015

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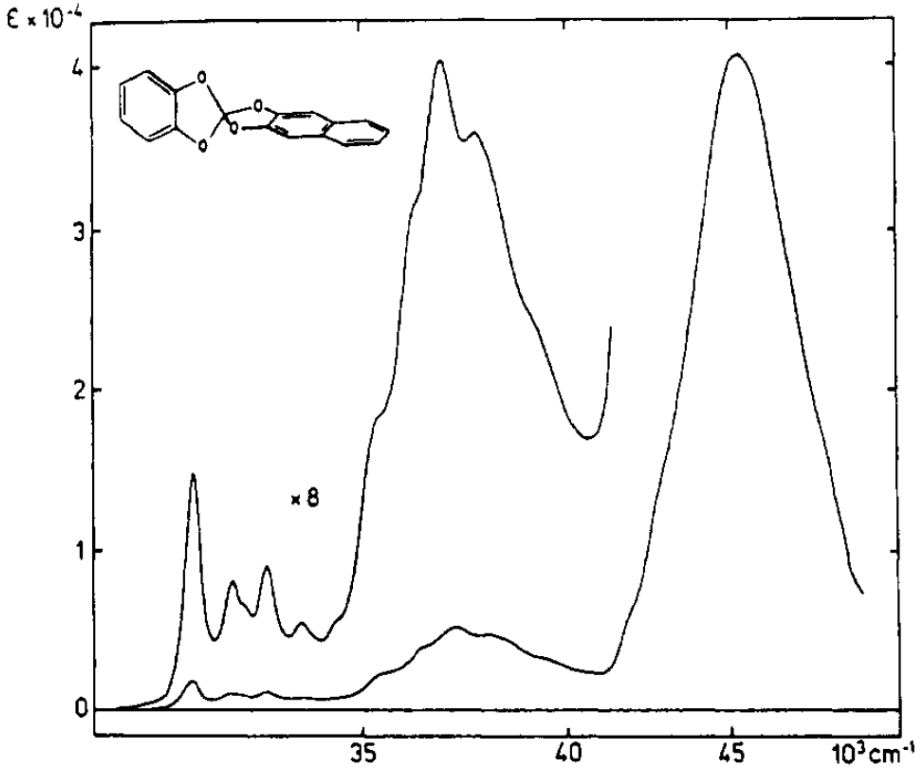
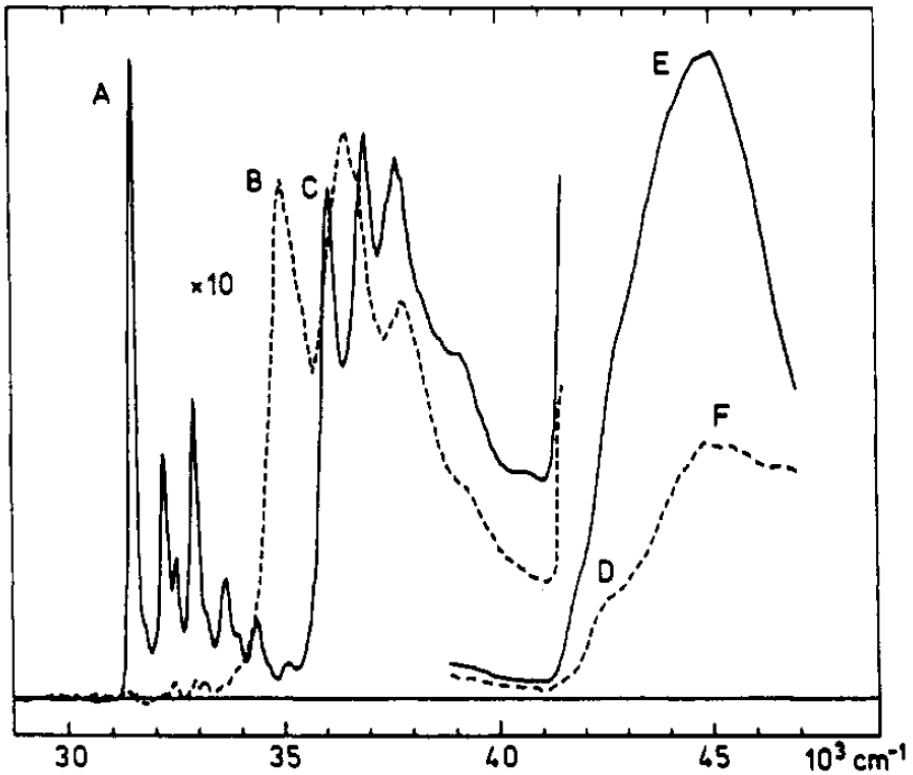
Optical absorbance spectroscopy:



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) **1,6,6aλ^4-Trithiapentalene**

3) **Diphenyl-diacetylene**

4) **Ellagic Acid + DNA (Flow LD)**

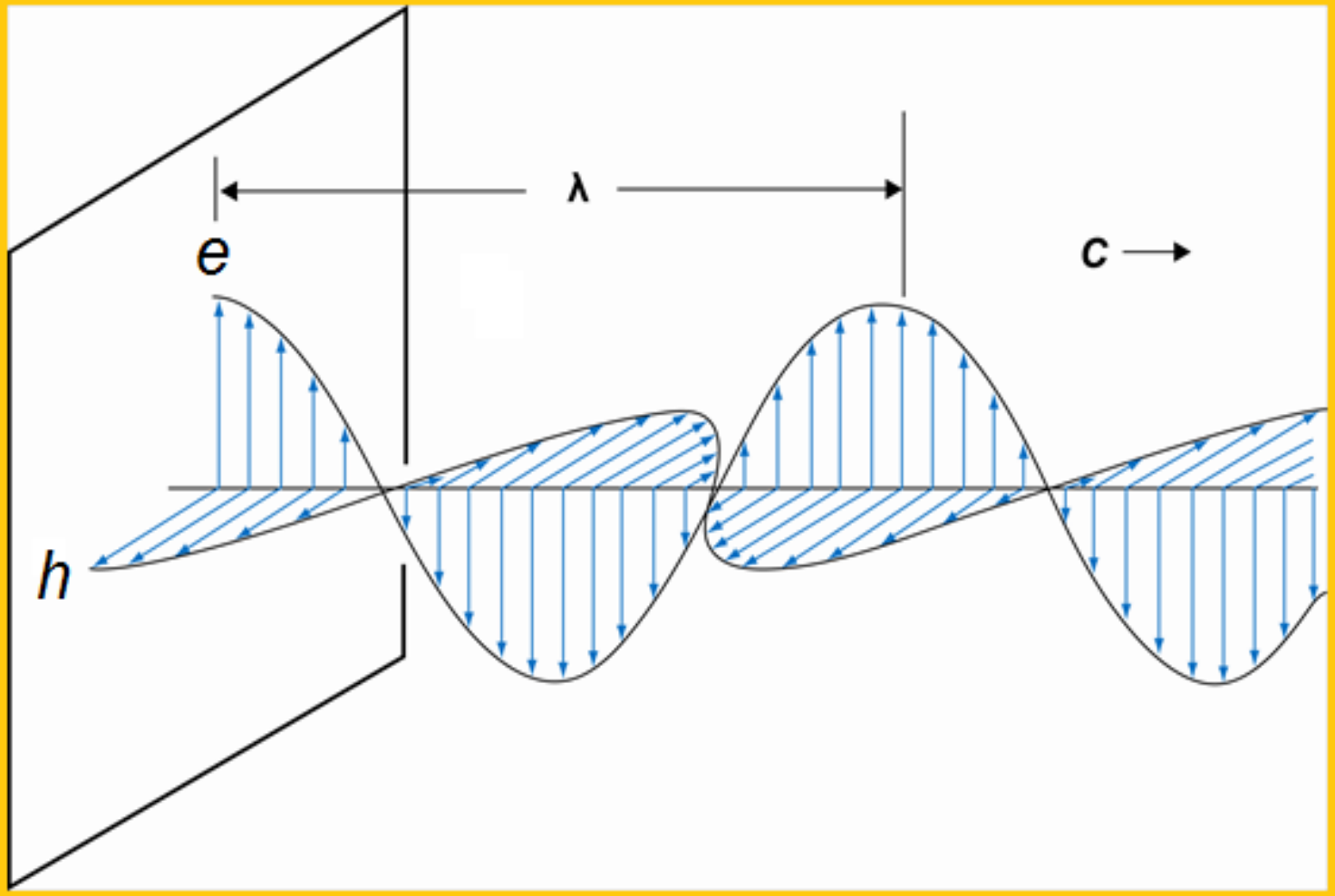
Main characteristica of optical absorption bands:

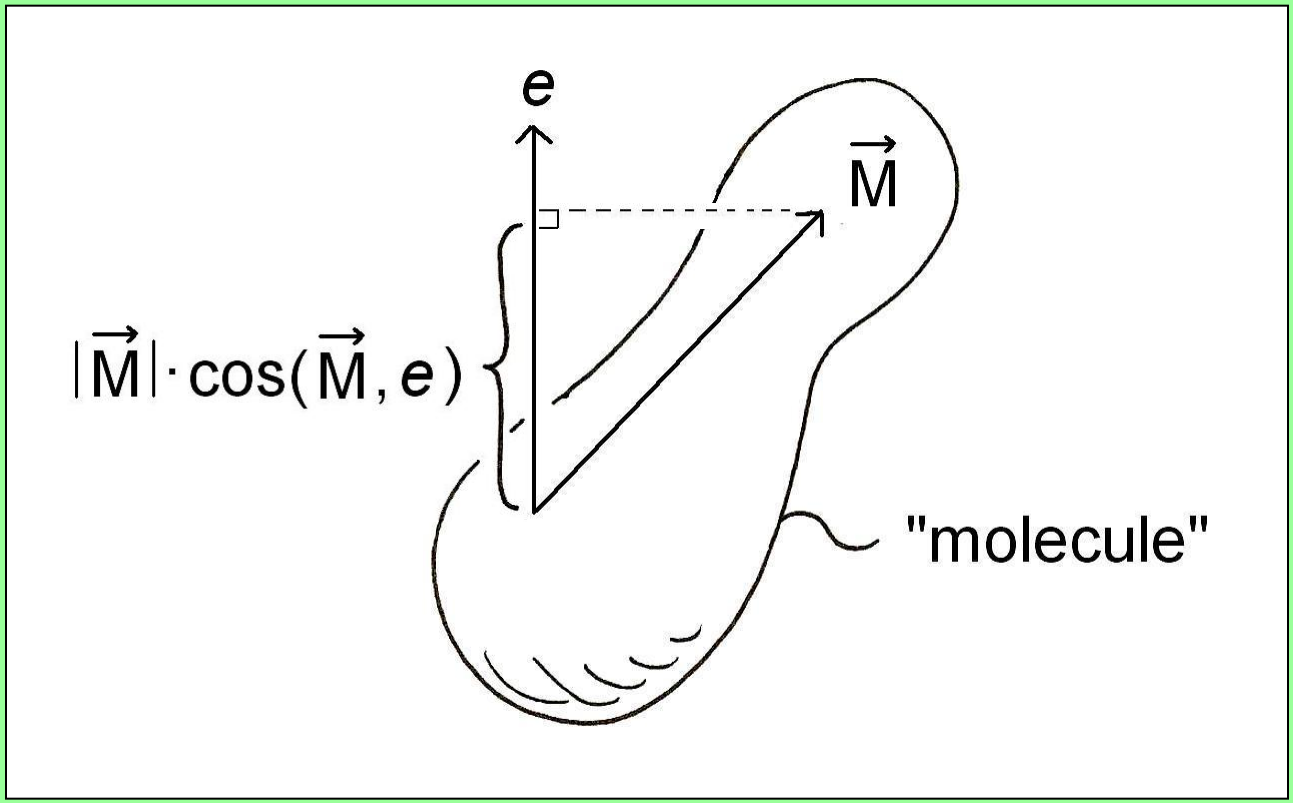
1) **Transition energy**
   (frequency, wavenumber, wavelength)

2) **Intensity** (absorbance, oscillator strength)

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

Plane Polarized Radiation





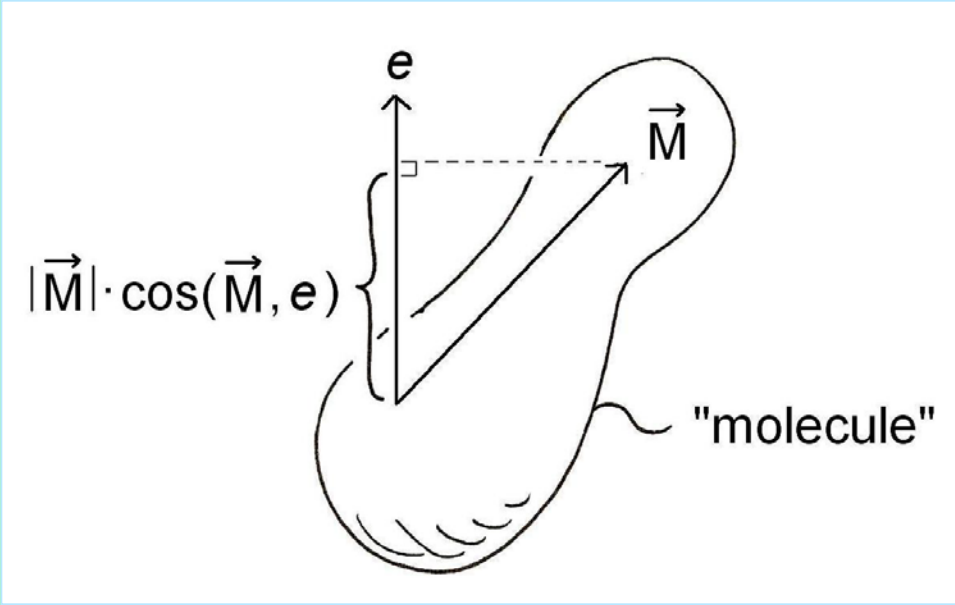
$\vec{M}$ = transition moment vector

e = electric field vector

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

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

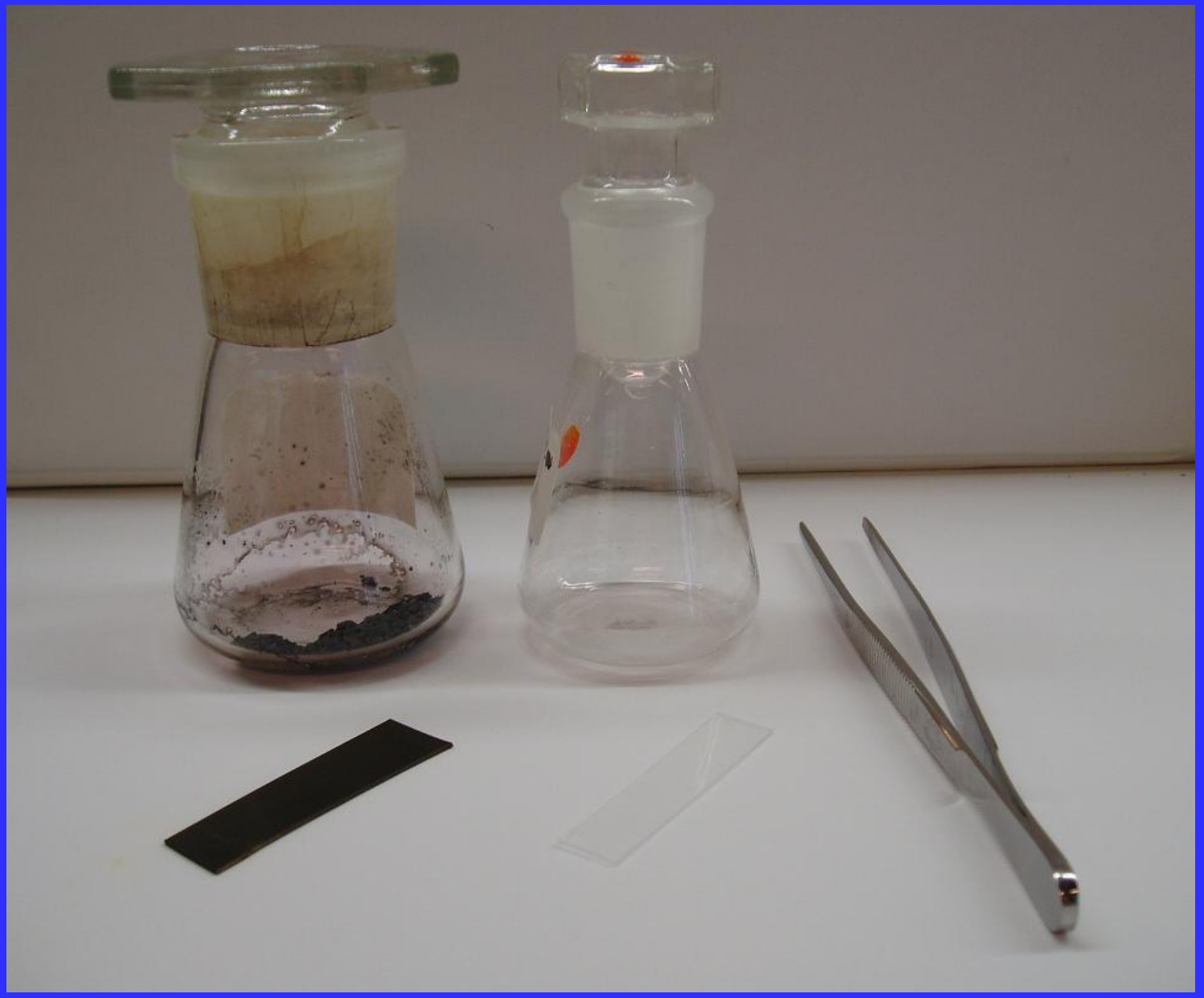
Absorbance Measurement

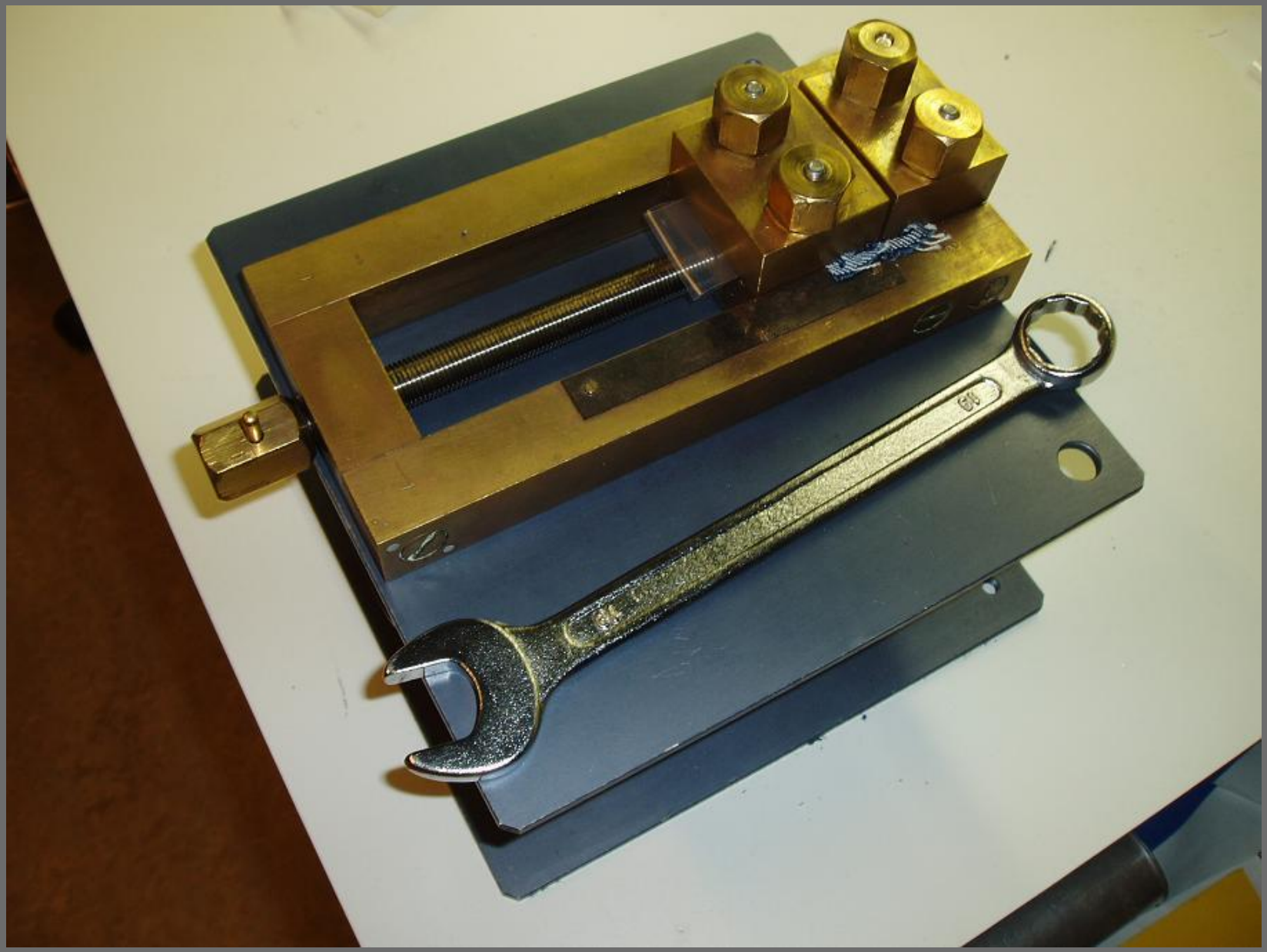


$$\text{Absorbance} = A(\tilde{\nu}) \cdot \left\langle \cos^2(\vec{M}, e) \right\rangle$$

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

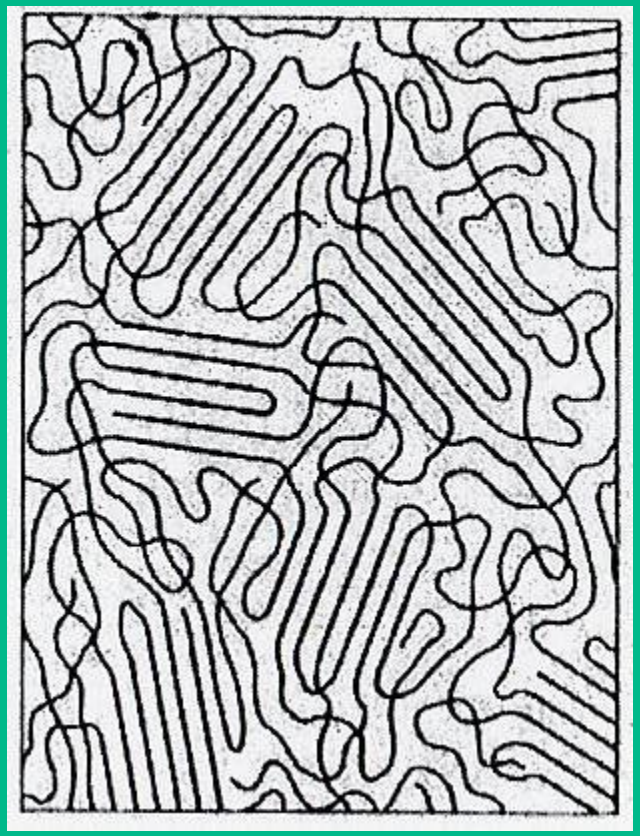
Stretched Polyethylene as an Anisotropic Solvent



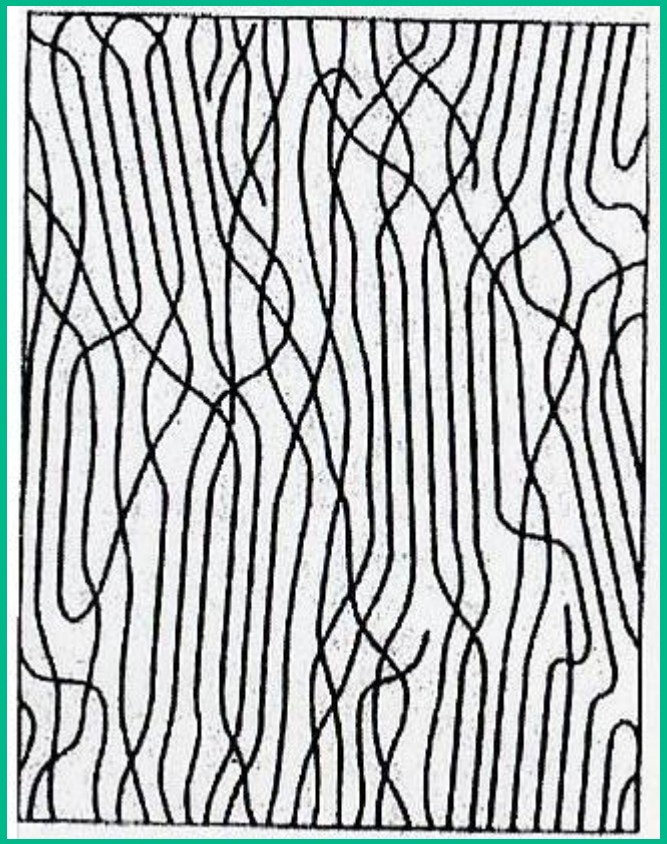


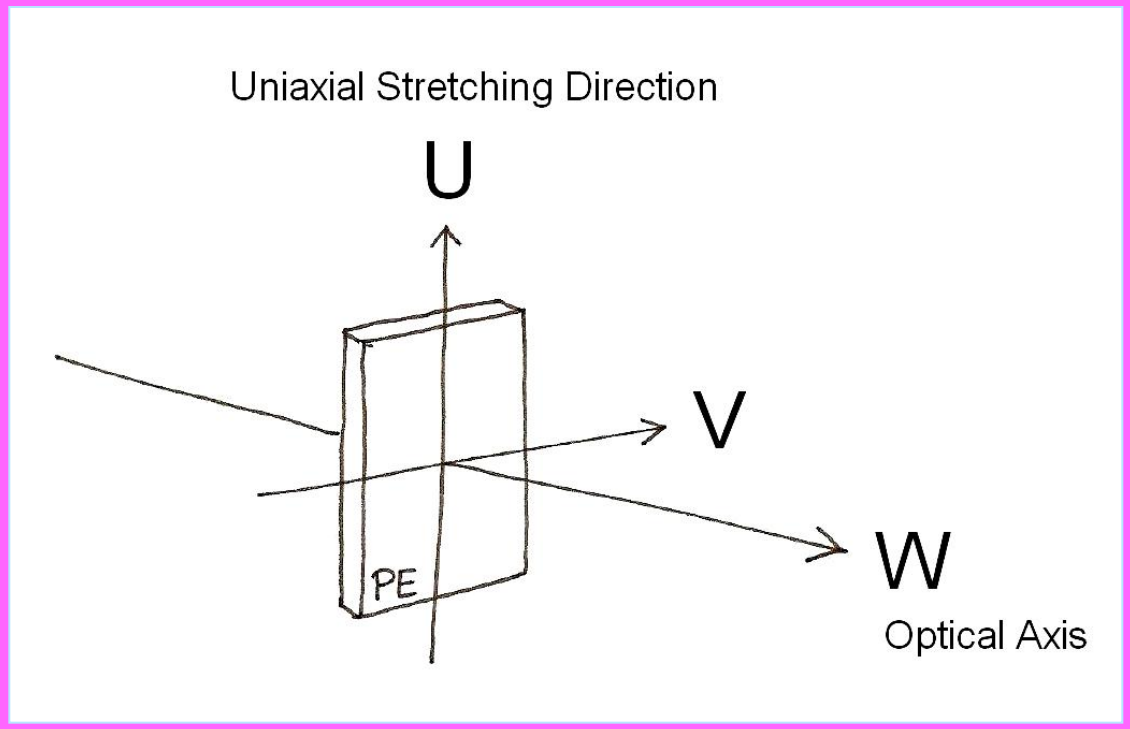
L. R. G. Treloar: *Introduction to Polymer Science*, Wykeham Publ. 1970

Simplified model of polyethylene (PE)



Corresponding model of stretched polyethylene (PE)





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

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

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

Uniaxial Sample

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

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

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

We define the Orientation Factor *K*:

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

Thulstrup, Eggers, Michl 1970

Uniaxial Sample

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

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

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

Dichroic Ratio, *d*:

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

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

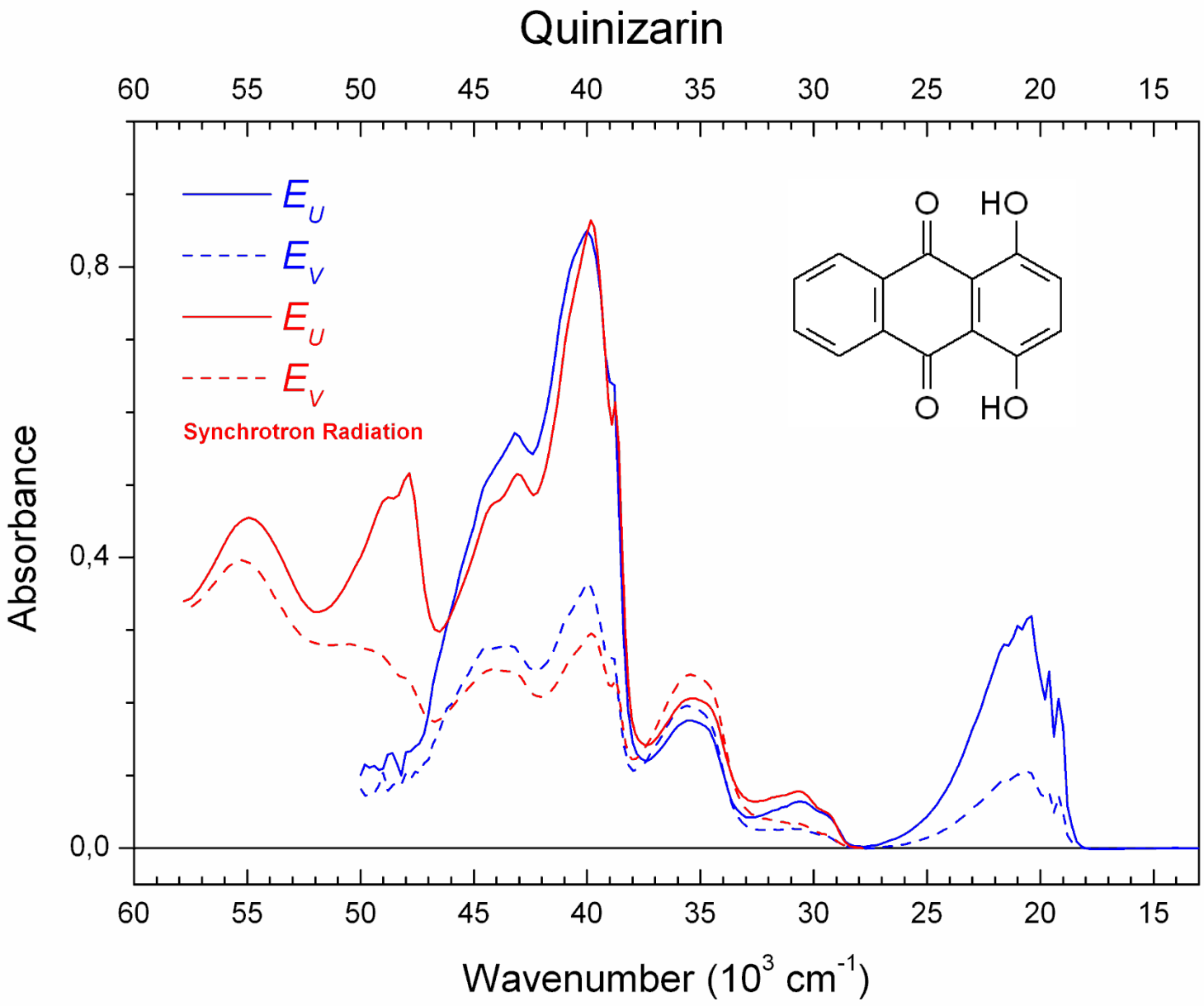
$$E_U(\tilde{\nu}) = \sum_i A_i(\tilde{\nu}) \cdot K_i$$

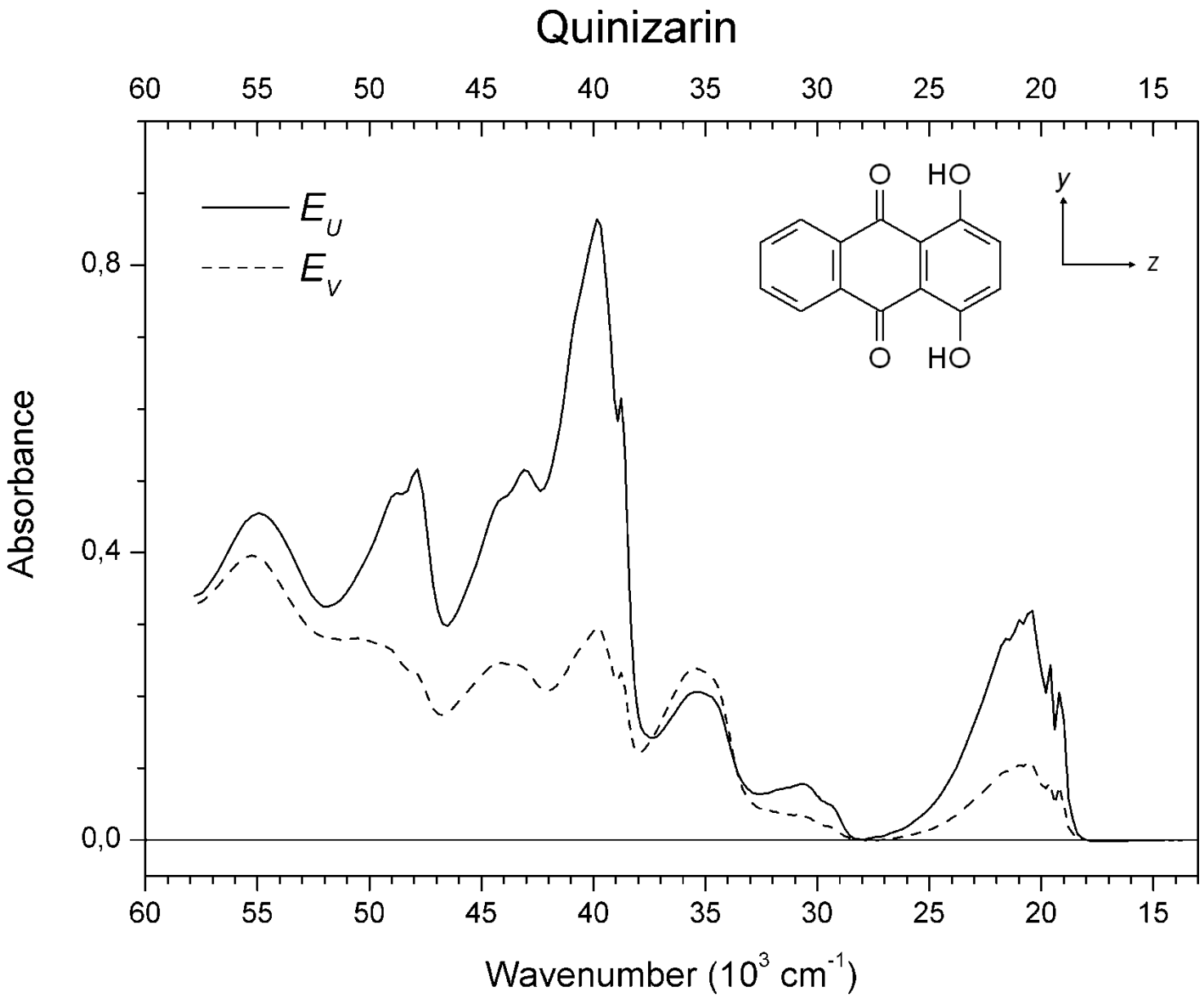
$$E_V(\tilde{\nu}) = \sum_i A_i(\tilde{\nu}) \cdot \frac{1}{2}(1 - K_i)$$

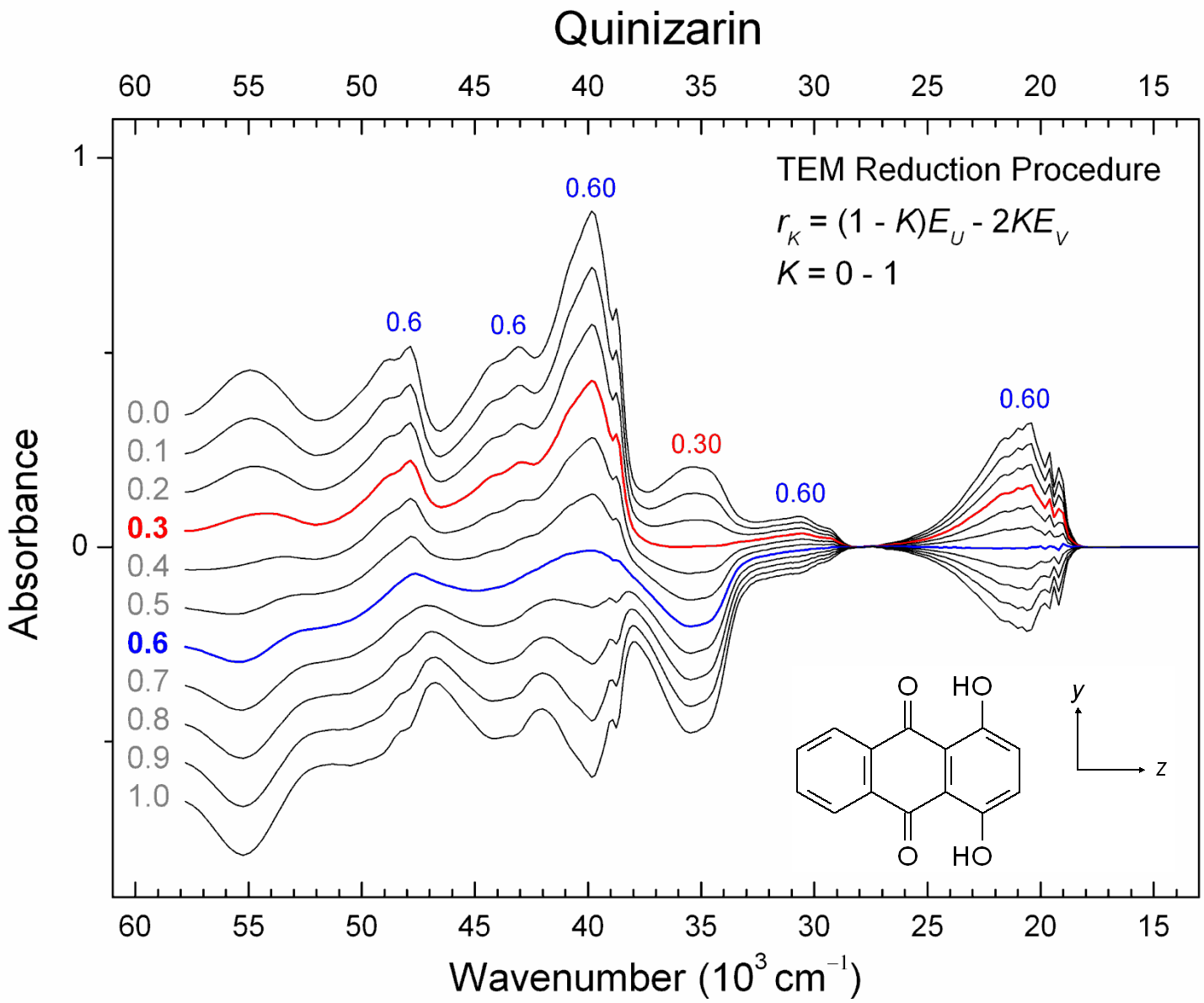
TEM procedure for overlapping transitions:

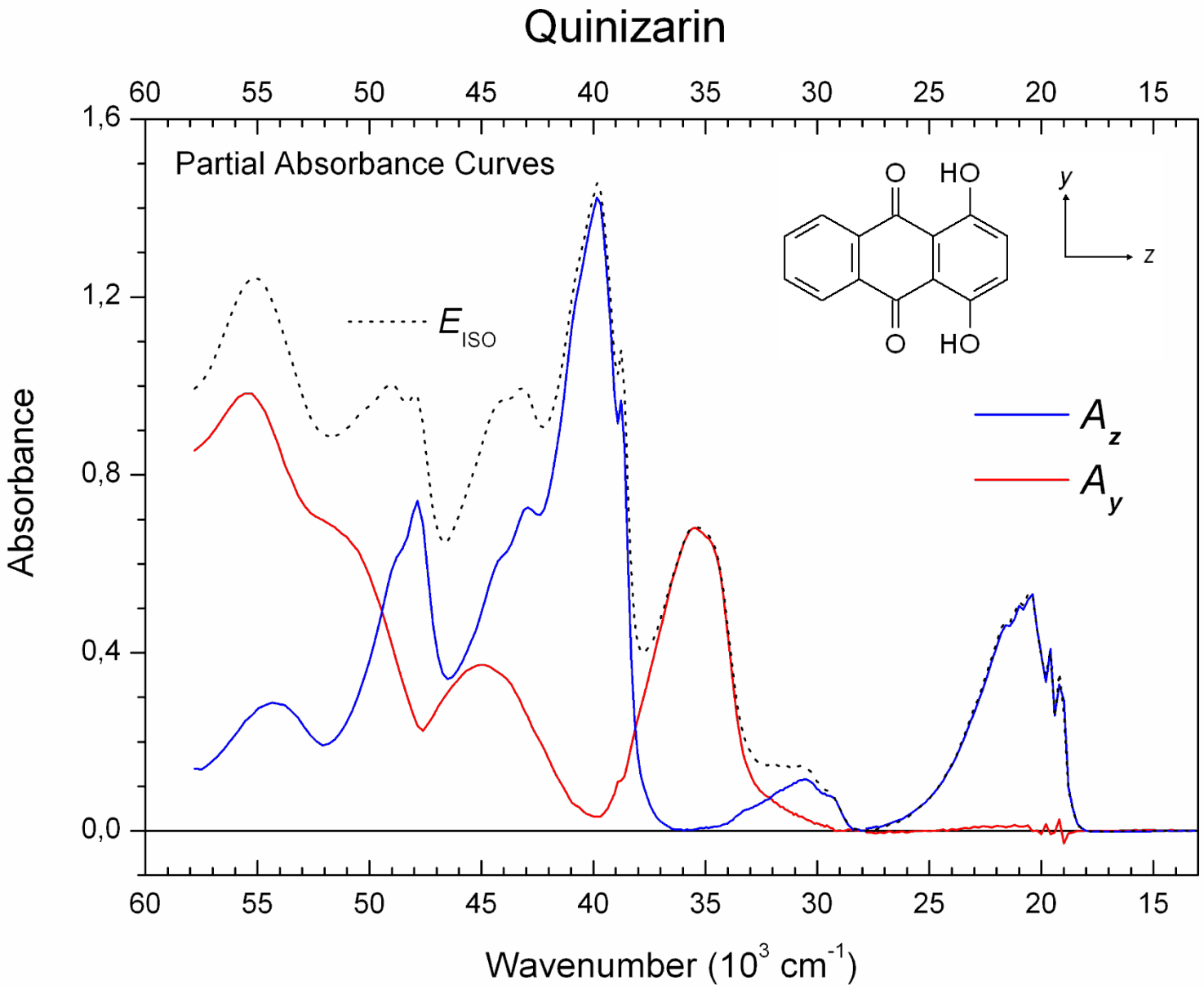
$$r_K = (1 - K) \cdot E_U(\tilde{\nu}) - 2K \cdot E_V(\tilde{\nu})$$

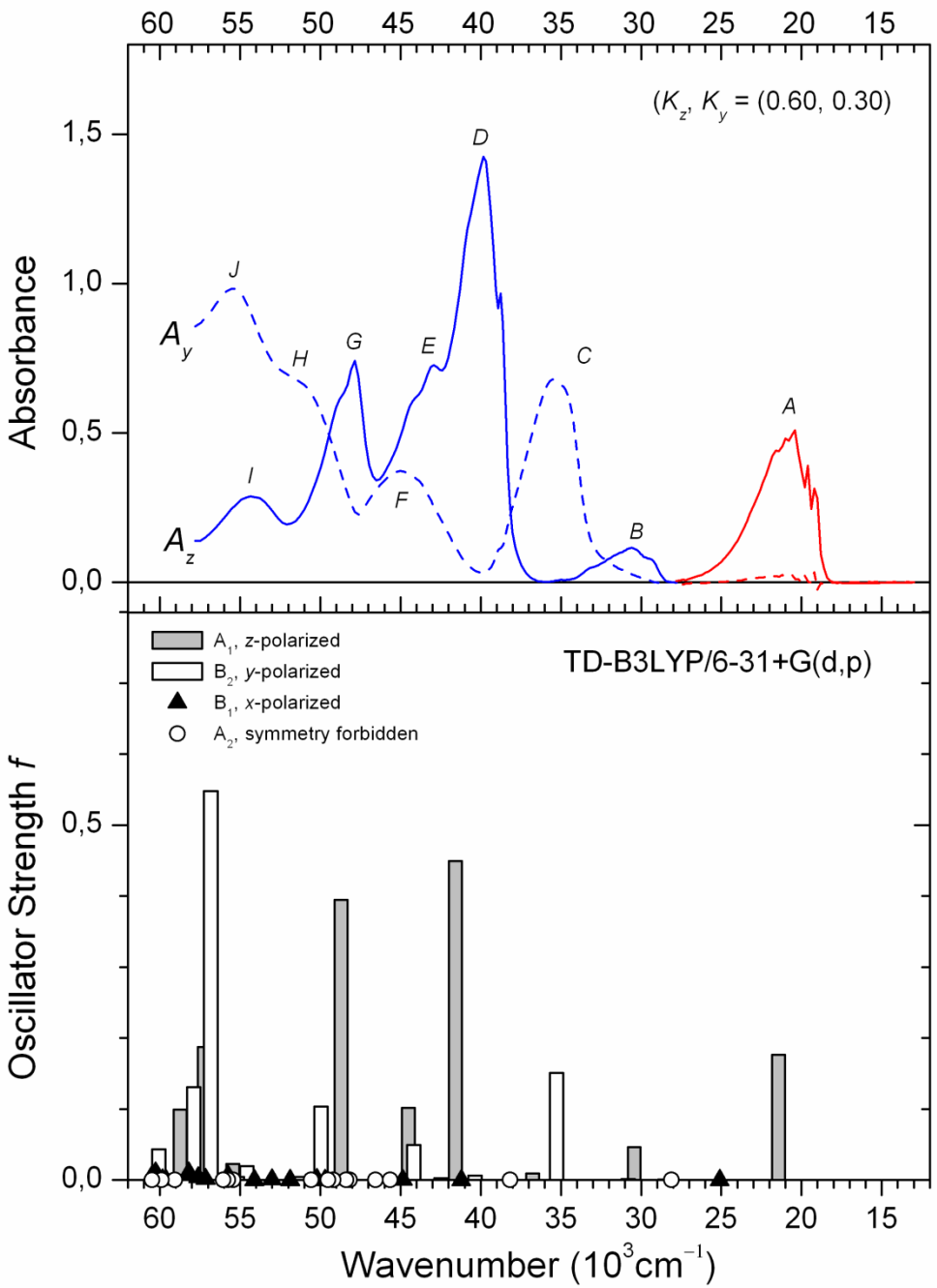
A spectral feature (peak or shoulder) due to transition *i* vanishes from r_K when $K = K_i$. The K_i value can thus be determined by visual inspection.

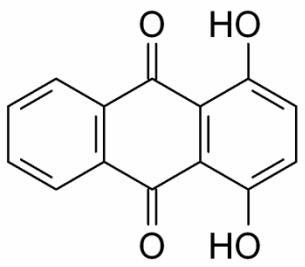

Quinizarin
60
55
50
45
40
35
30
25
20
15
0,8
0,4
0,0
Absorbance
E_U
E_V
E_U
E_V
Synchrotron Radiation
O
HO
O
HO
Wavenumber (10^3 cm^{-1})


Quinizarin
60
55
50
45
40
35
30
25
20
15
0,8
0,4
0,0
Absorbance
E_U
E_V
O
HO
O
HO
y
z
Wavenumber (10^3 cm^{-1})

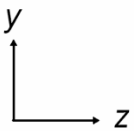

Quinizarin
TEM Reduction Procedure
$r_K = (1 - K)E_U - 2KE_V$
$K = 0 - 1$
0.60
0.6
0.6
0.30
0.60
0.60
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Absorbance
1
0
60 55 50 45 40 35 30 25 20 15
Wavenumber (10^3 cm^{-1})
O HO
O HO
y
z


Quinizarin
Partial Absorbance Curves
E_{ISO}
A_z
A_y
O
HO
O
HO
y
z
Absorbance
1,6
1,2
0,8
0,4
0,0
60
55
50
45
40
35
30
25
20
15
Wavenumber (10^3 cm^{-1})

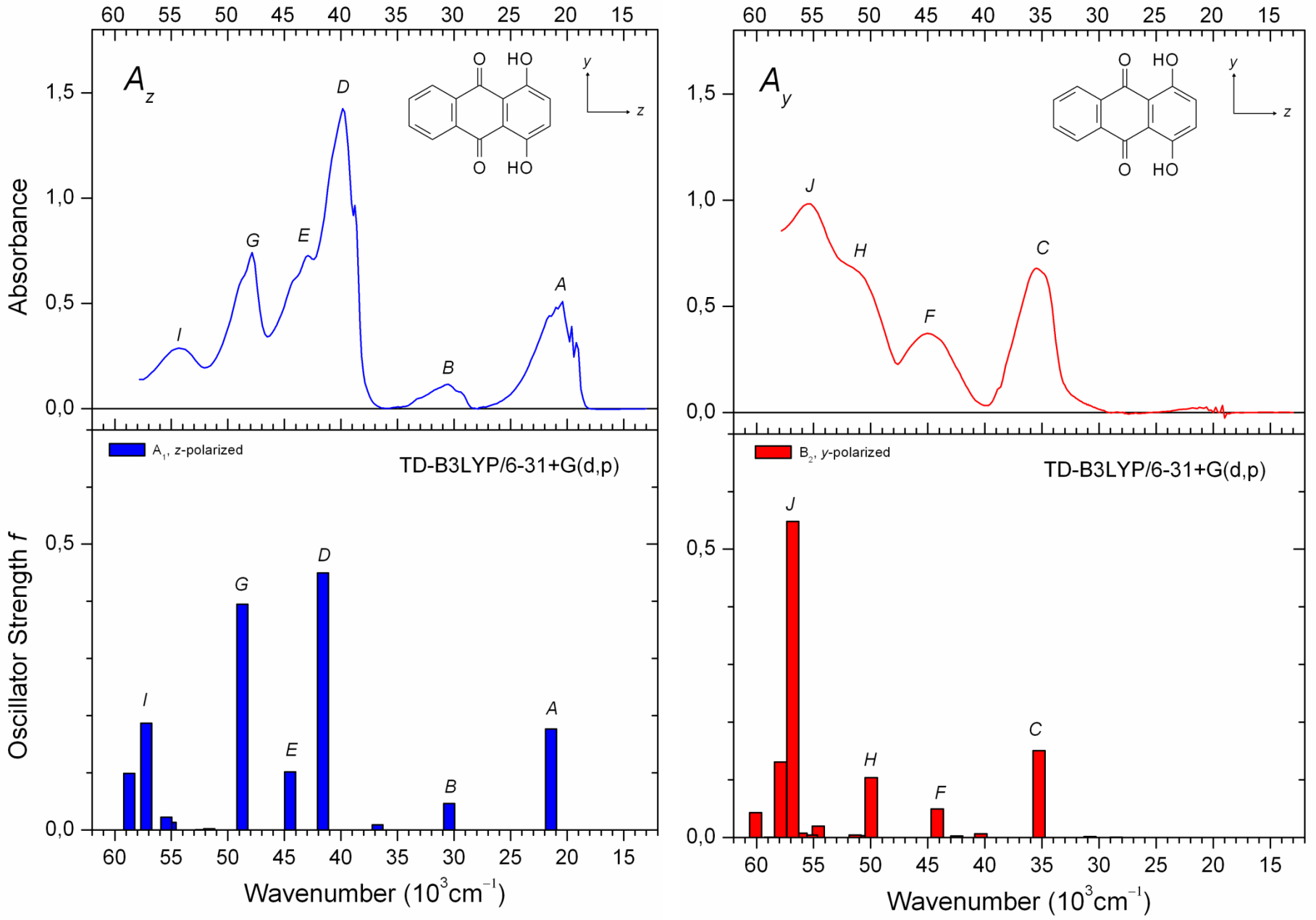




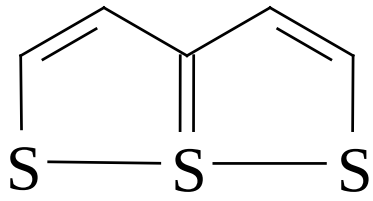
Quinizarin



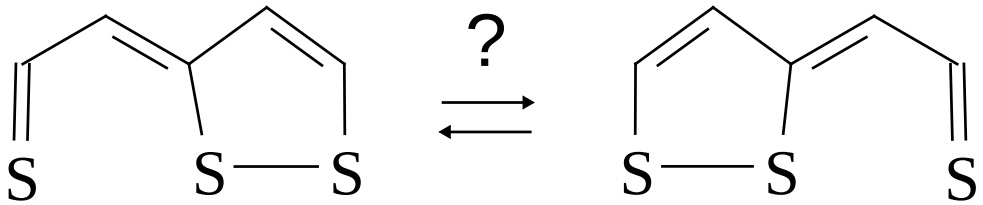
D.D. Nguyen, N.C. Jones, S.V. Hoffmann, J. Spanget-Larsen, *Spectrochim. Acta A* **77**, 279-286 (2010).


A_z
A_y
Absorbance
Oscillator Strength f
Wavenumber (10^3 cm^-1)
A1, z-polarized
B2, y-polarized
TD-B3LYP/6-31+G(d,p)
TD-B3LYP/6-31+G(d,p)
A
B
C
D
E
F
G
H
I
J
O
HO
y
z

1,6,6aλ^4-Trithiapentalene



C_{2v}



C_s C_s

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:

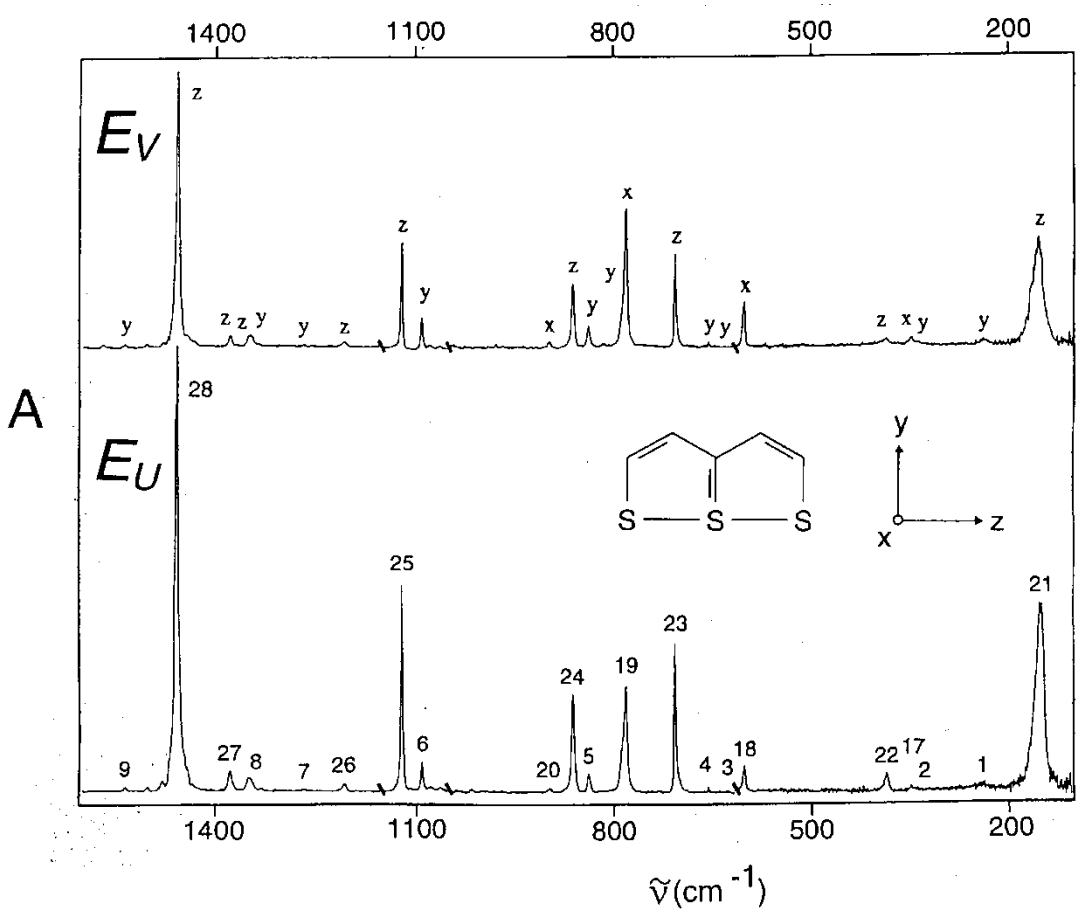
$$K_x + K_y + K_z = 1$$

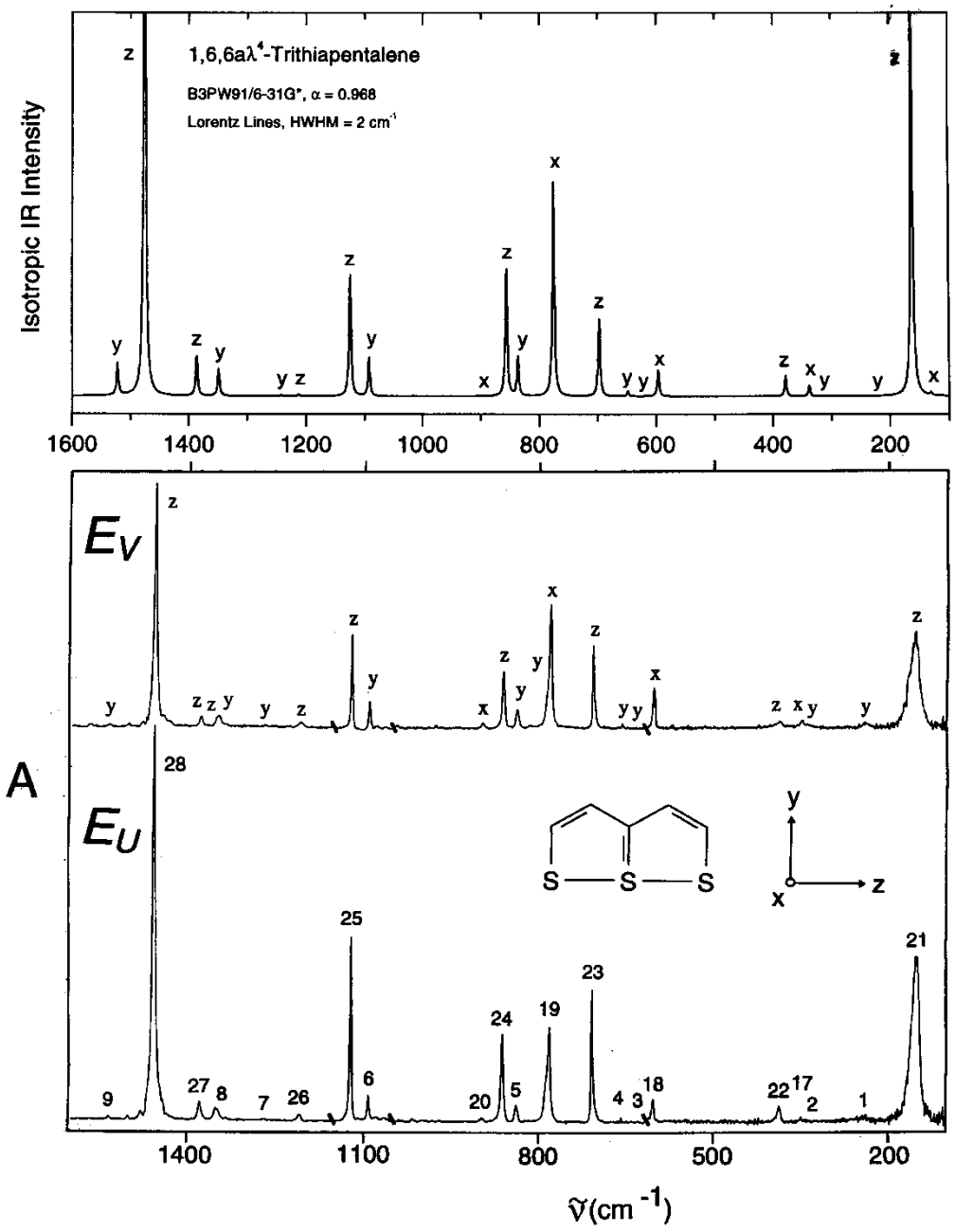
(1) If more than three significantly different *K* values are observed, the molecular symmetry must be different from D_{2h}, D_2, and C_{2v}.

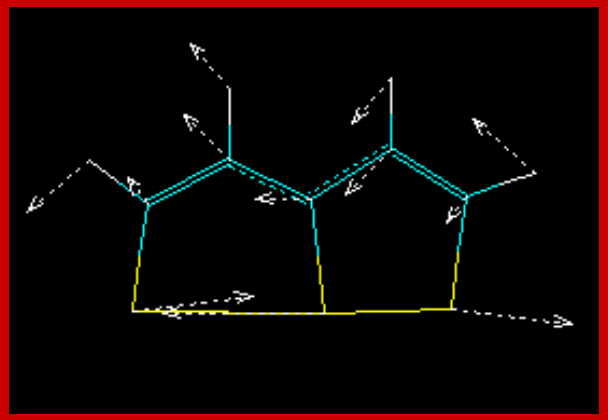
(2) If the observed *K* values for a large number of transitions fall in three distinct groups, with the three characteristic values adding up to unity, this is strong evidence for the presence of molecular symmetry elements, consistent with D_{2h}, D_2, or C_{2v}.

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

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







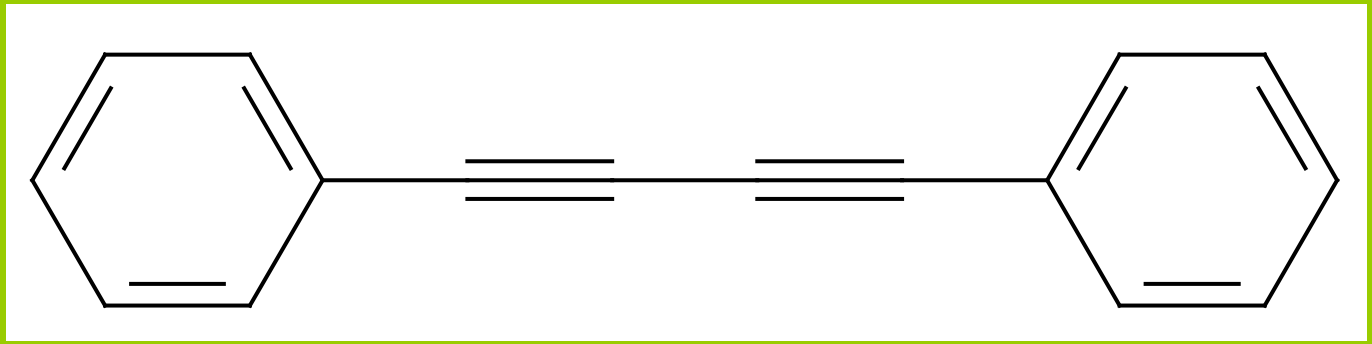
”Bell-Clapper” mode
(153 cm^{-1})

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

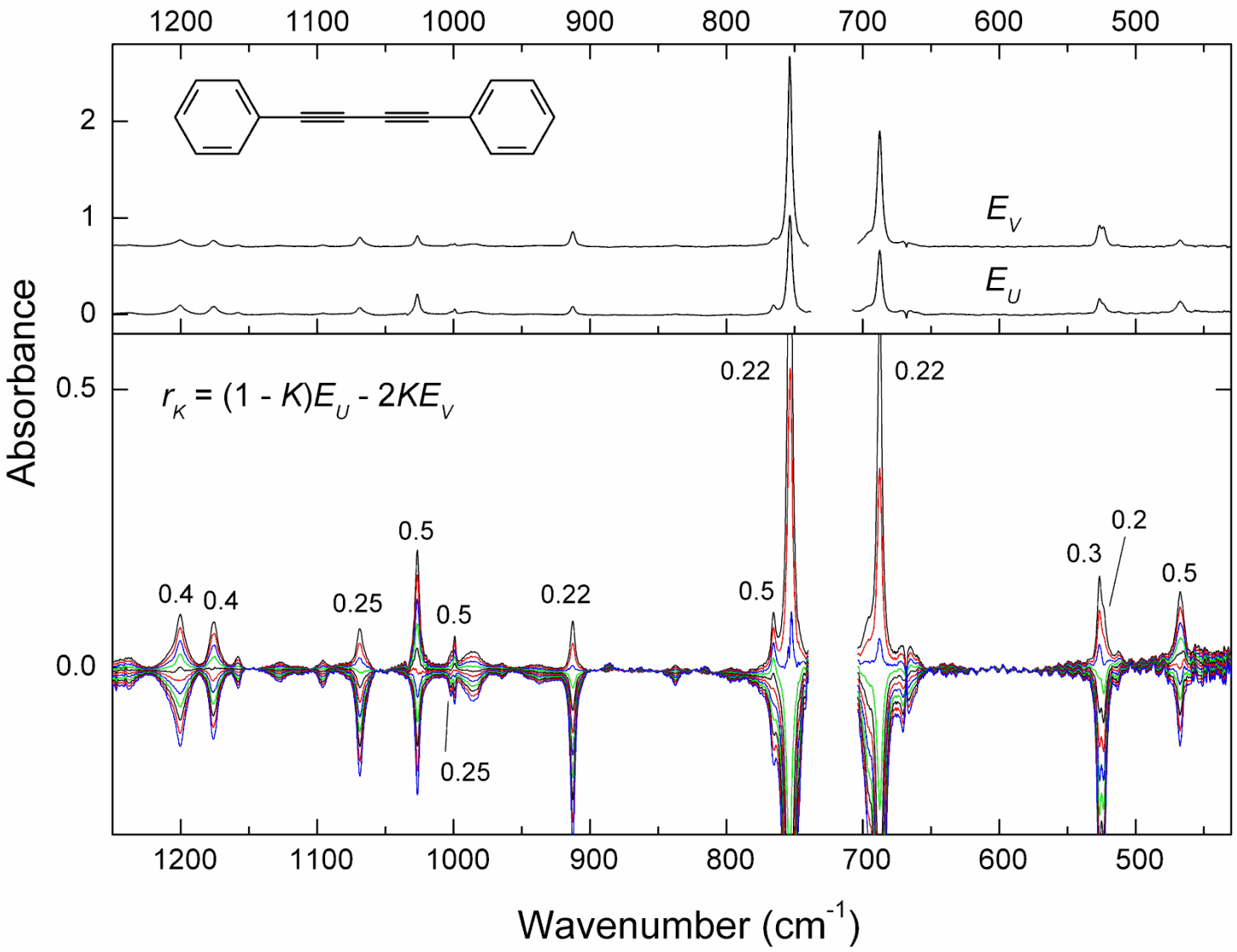
Experimental observation of the ”Bell-Clapper” transition confirms it

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

Diphenyldiacetylene (DPDA)



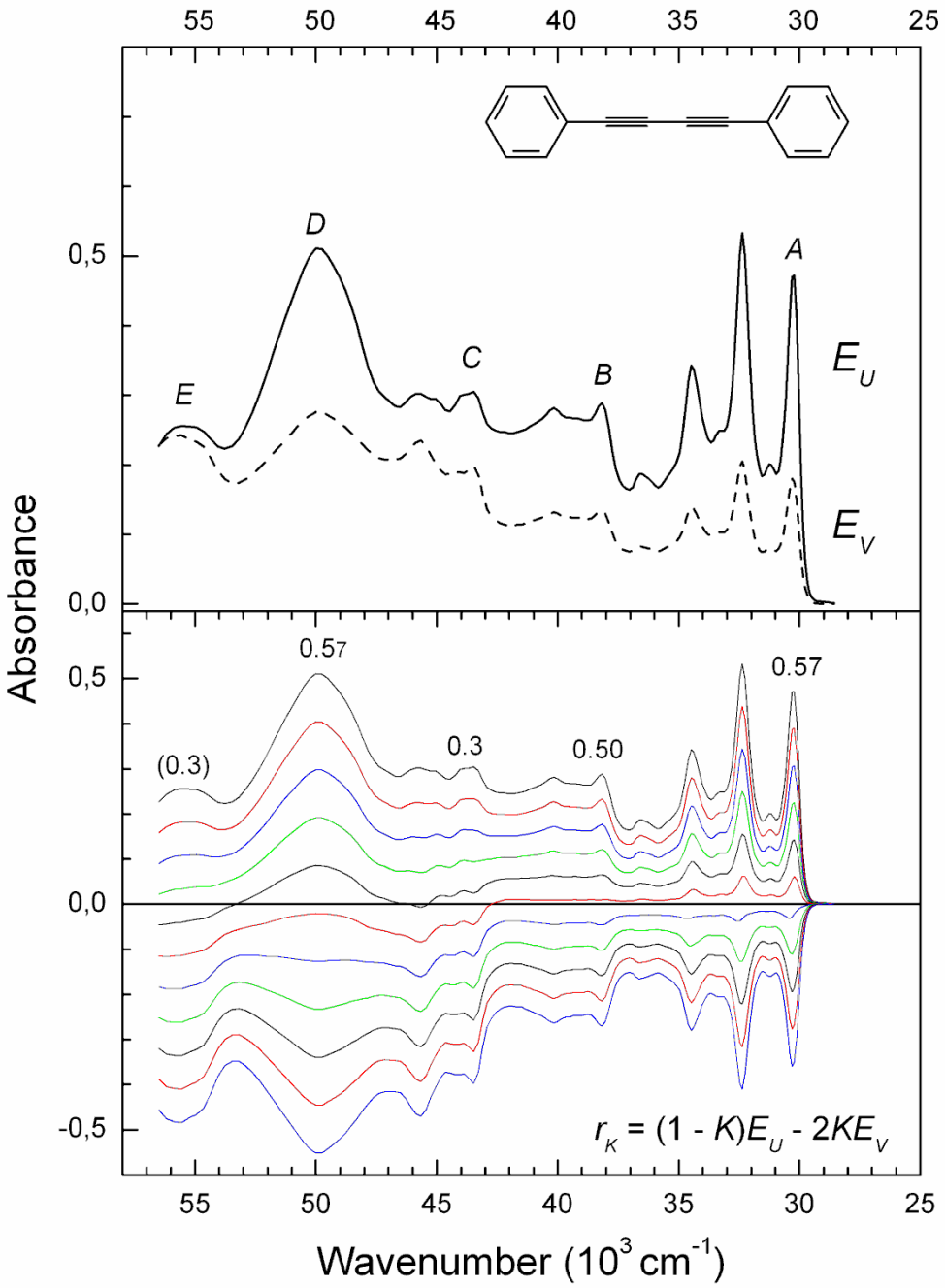
FTIR-LD of DPDA aligned in stretched LDPE



UV-SRLD of DPDA aligned in LDPE

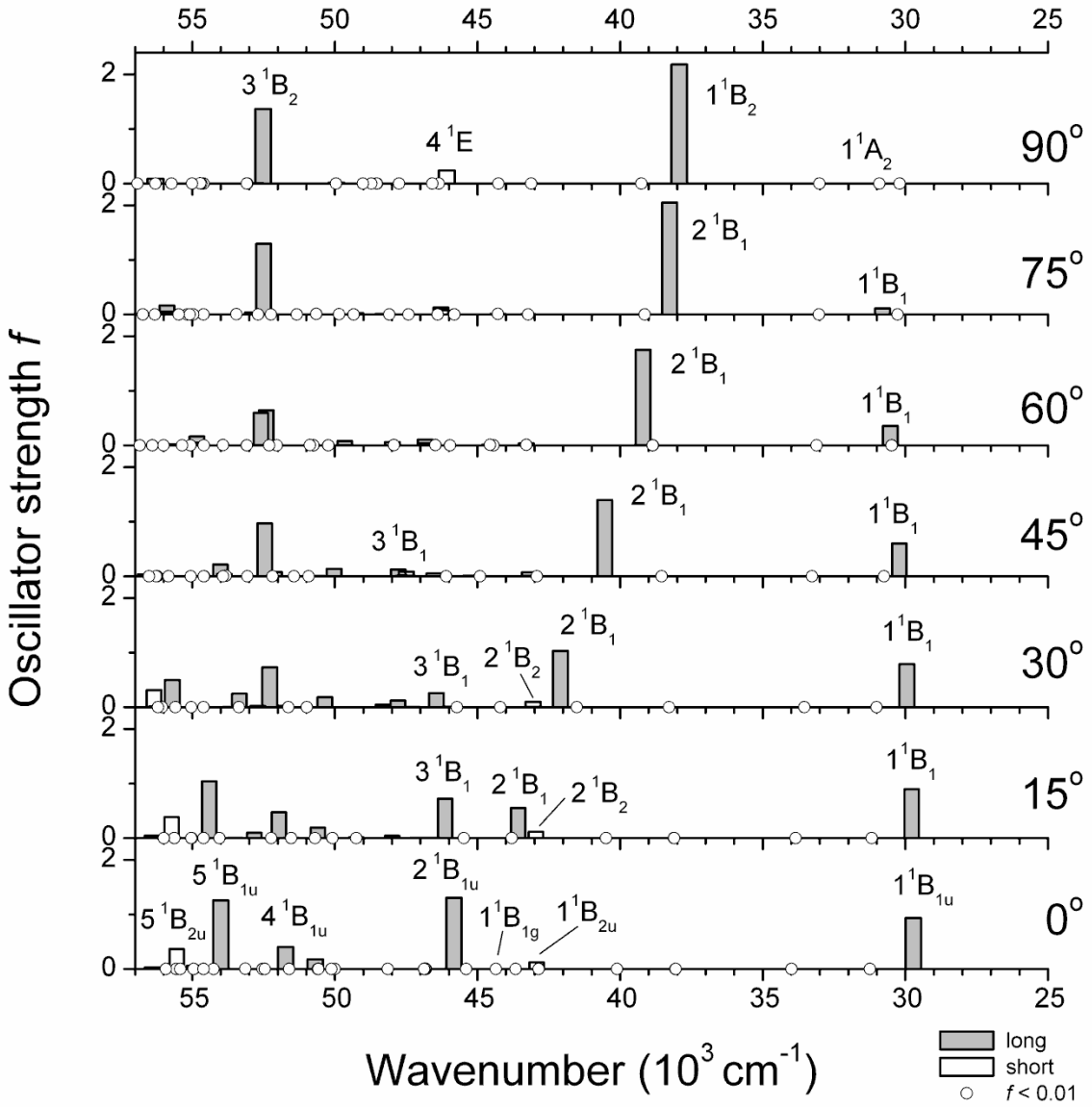
The observed orientation factors are inconsistent with the presence of a single, symmetric species.

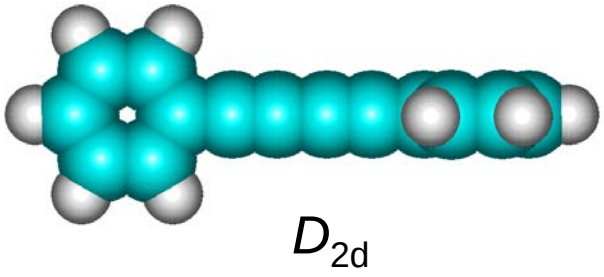
Do we observe overlapping contributions from different rotamers?



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

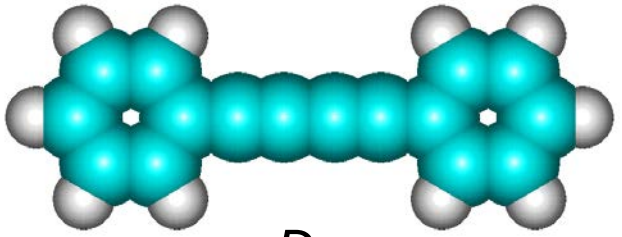
TD-PBE1PBE/6-31+G*//6-31G*



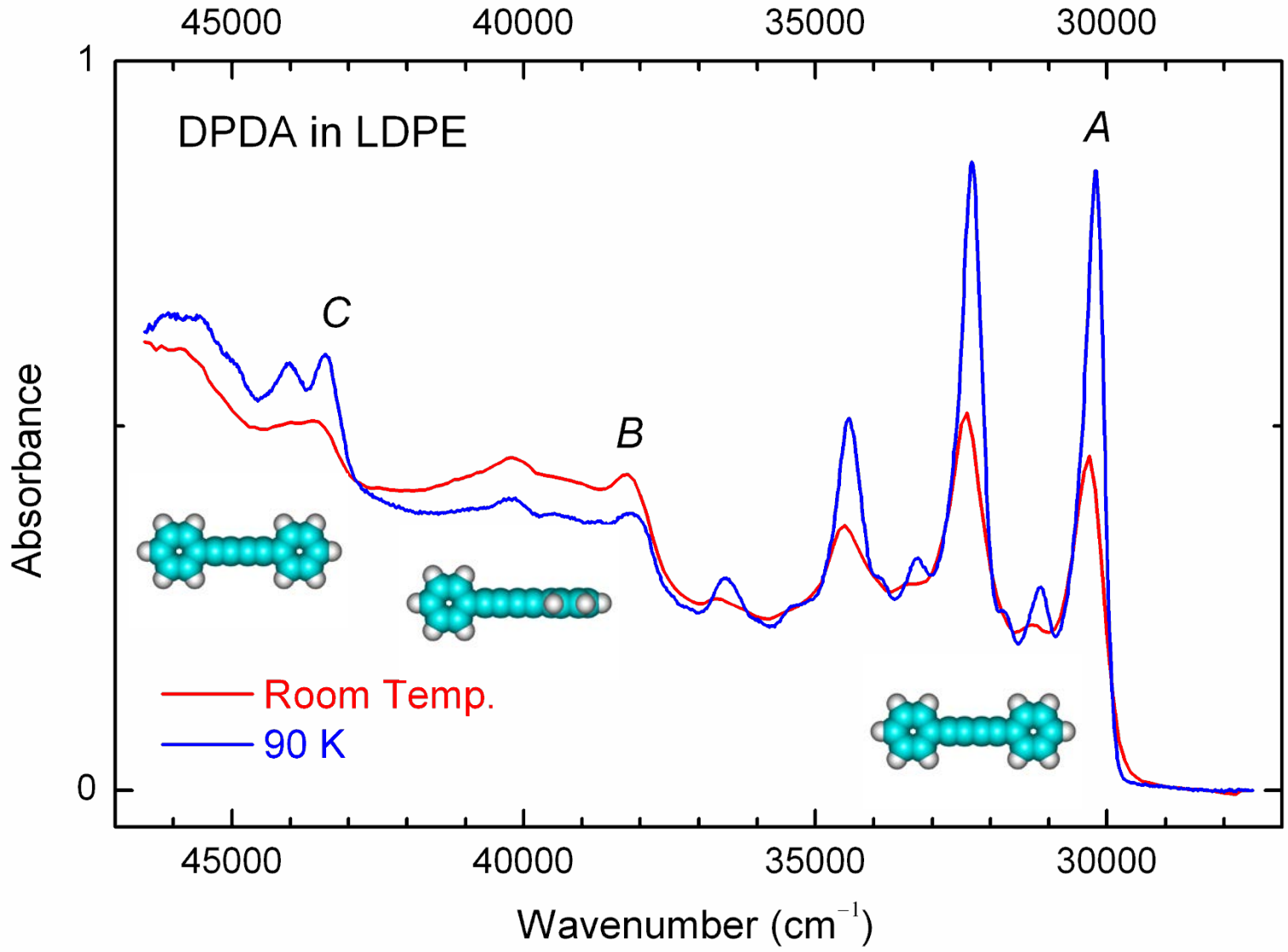


D_{2d}

ΔE = ~0.3 kcal/mol

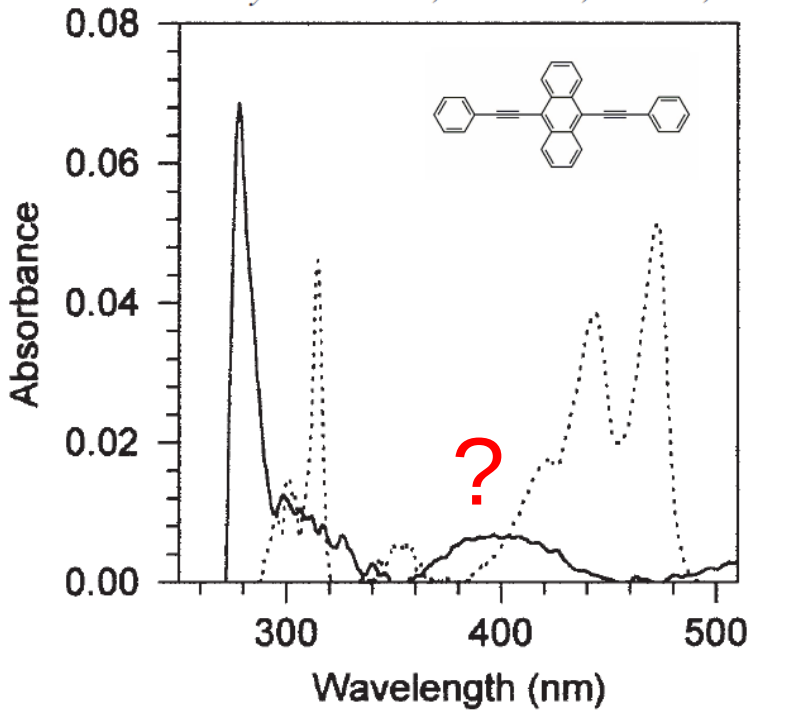


D_{2h}


45000
40000
35000
30000
1
0
DPDA in LDPE
A
B
C
Absorbance
Room Temp.
90 K
45000
40000
35000
30000
Wavenumber (cm^{-1})

BPEA

Levitus and Garcia-Garibay
J. Phys. Chem. A, Vol. 104, No. 38, 2000



P.W. Thulstrup, N.C. Jones, S.V. Hoffmann, J. Spanget-Larsen,
Chem.Phys.Lett. **559**, 35-40 (2013)

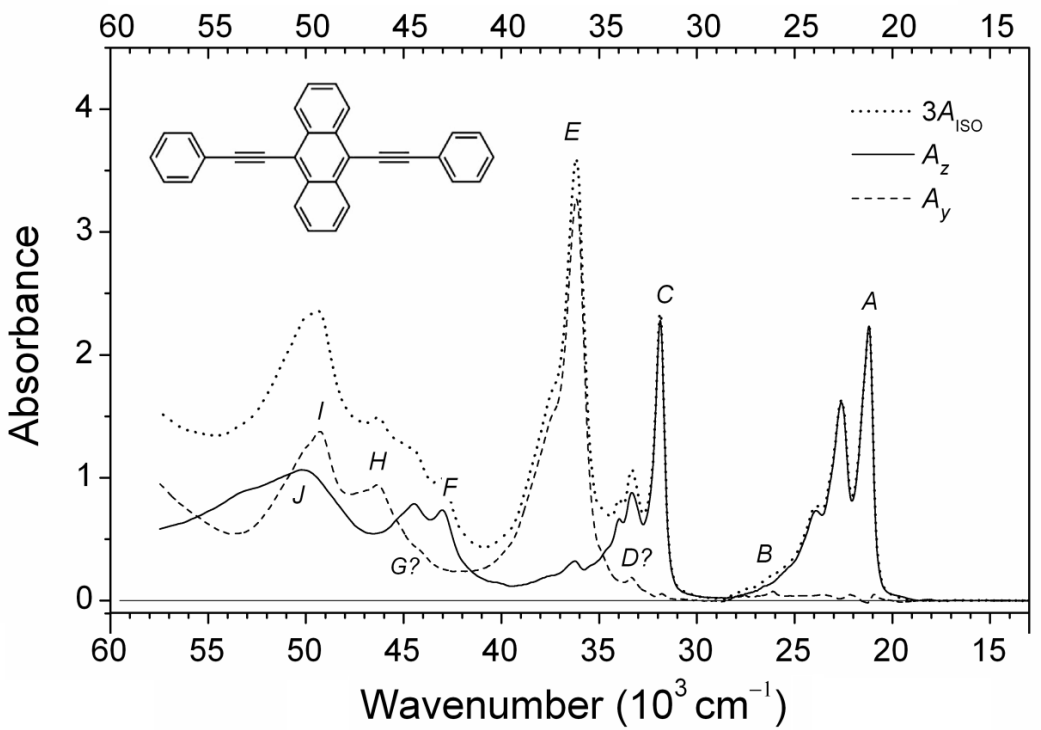
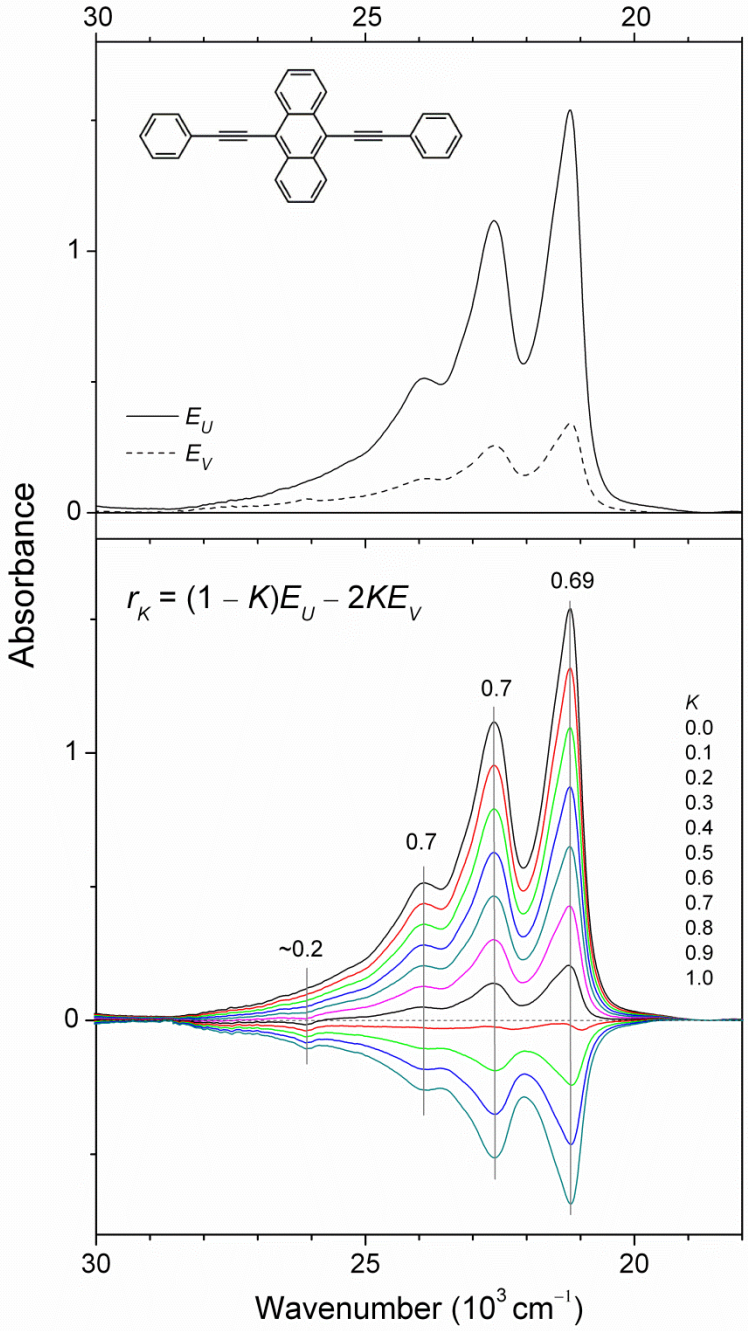


Figure 4. Purely polarized spectra obtained from the stepwise reduction procedure discussed in the text. Solid line: A_y, spectrum polarized along the *y*-axis. Dotted line: A_z, spectrum polarized along the *z*-axis.

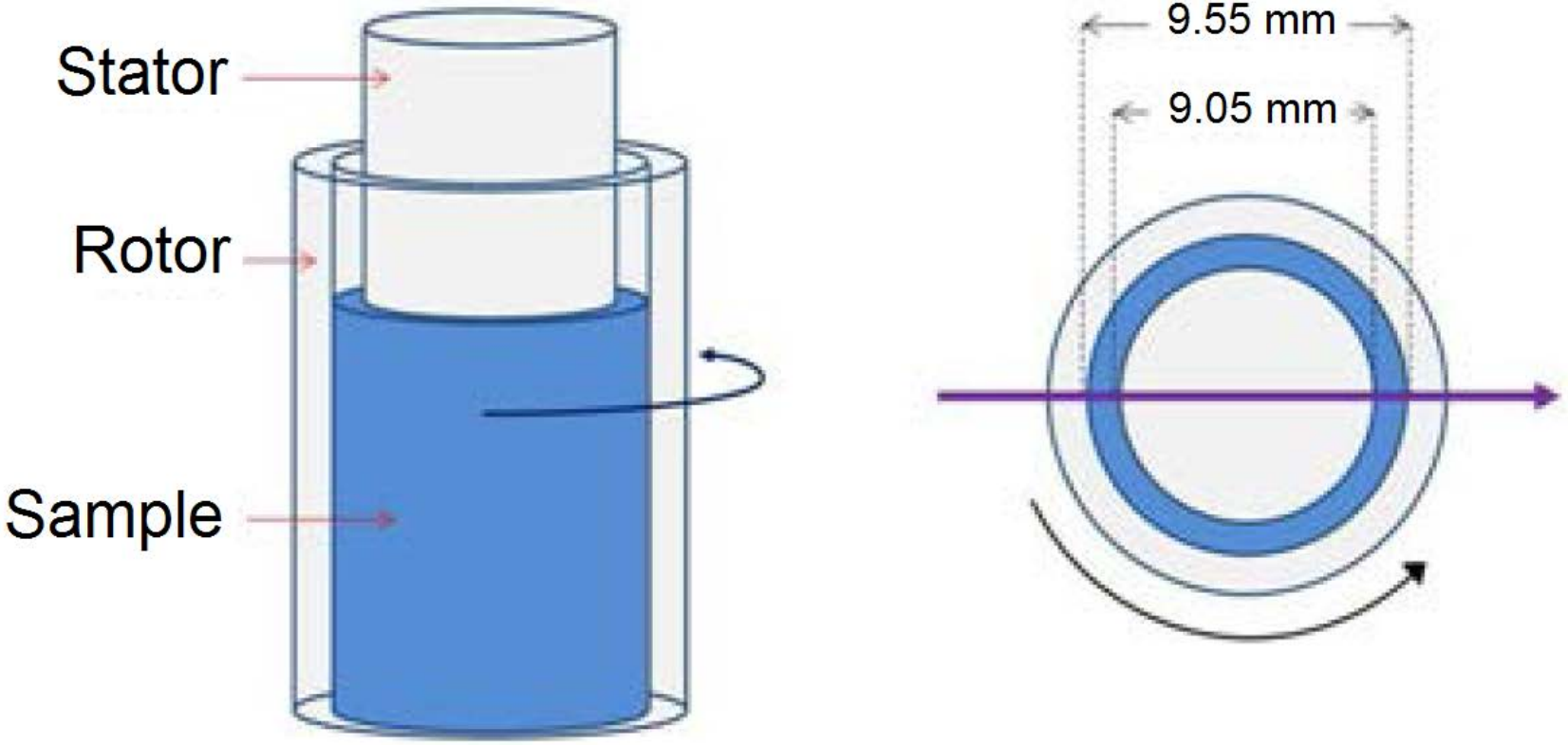

30
25
20
1
0
E_U
E_V
Absorbance
$r_K = (1 - K)E_U - 2KE_V$
0.69
0.7
0.7
~0.2
K
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1
0
30
25
20
Wavenumber (10^3 cm^{-1})

Flow LD Experiments

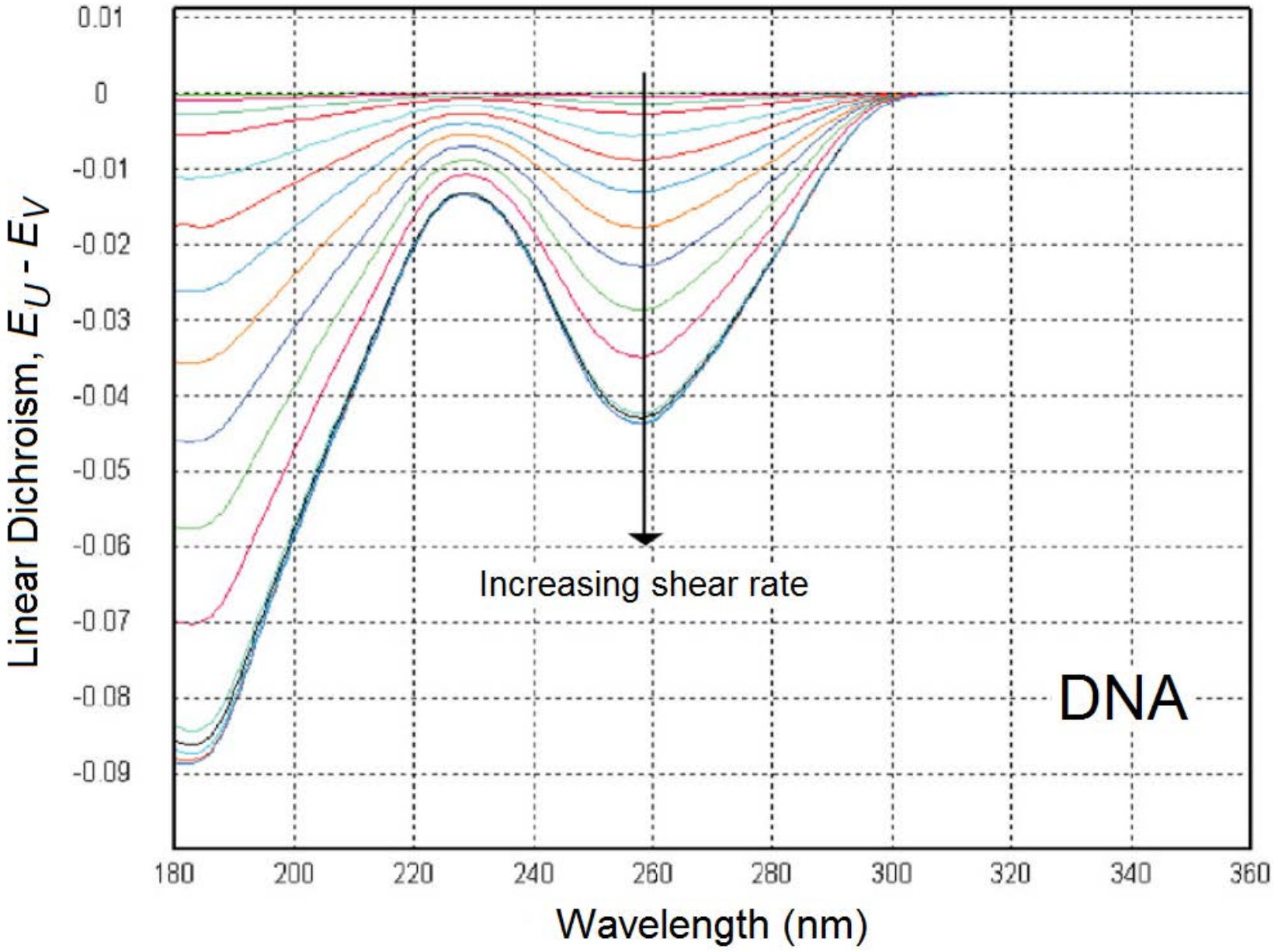
Biological Polymers

One way to obtain an aligned sample of a biological polymer is by application of a flow gradient. For example, macromolecular DNA is oriented in a flow gradient, whereas small molecules are not.

Hence, Flow LD experiments can be applied in investigations of the interaction between small molecules and DNA.



Schematics of the Couette Cell

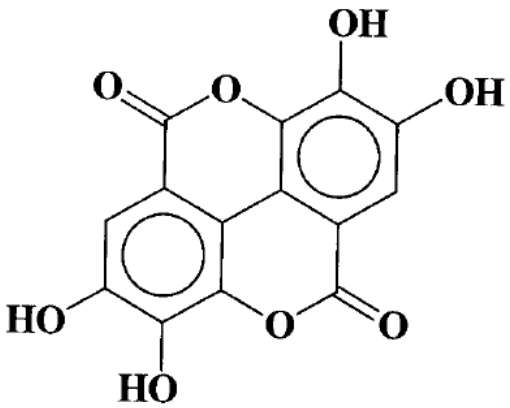


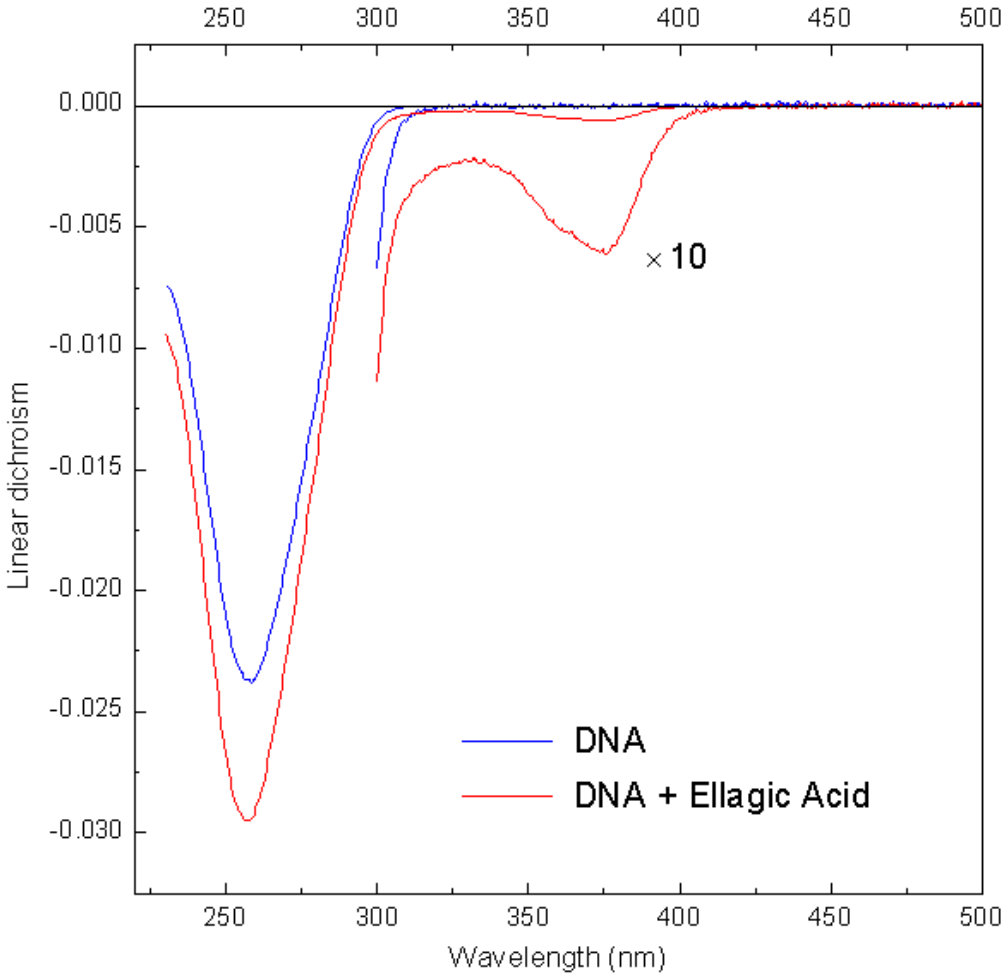
LD spectra of DNA down to 180nm and shear rates from 10 to 10,200 s^{-1}

Biochemical and Biophysical Research Communications **265**, 416–421 (1999)

Interaction between Ellagic Acid and Calf Thymus DNA Studied with Flow Linear Dichroism UV–VIS Spectroscopy[1]

Peter W. Thulstrup,[2,3] Thorsten Thormann,[2,3] Jens Spanget-Larsen, and Hanne Cathrine Bisgaard
Department of Life Sciences and Chemistry, Roskilde University, Universitetsvej 1, DK-4000 Roskilde, Denmark





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Eva M. Karlsen

ISA:
Søren Vrønning Hoffmann
Nykola C. Jones

KU Life:
Peter Waaben Thulstrup


UNIVERSITAS ROSKILDENSIS
IN TRANQUILLO MORS
IN FLUCTU VITA