Elipsometrija tankih slojeva organskih poluvodiča

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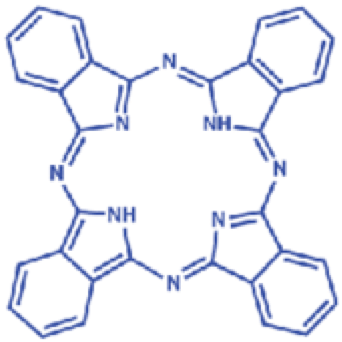
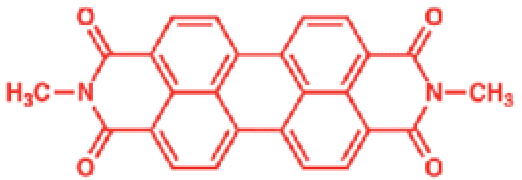
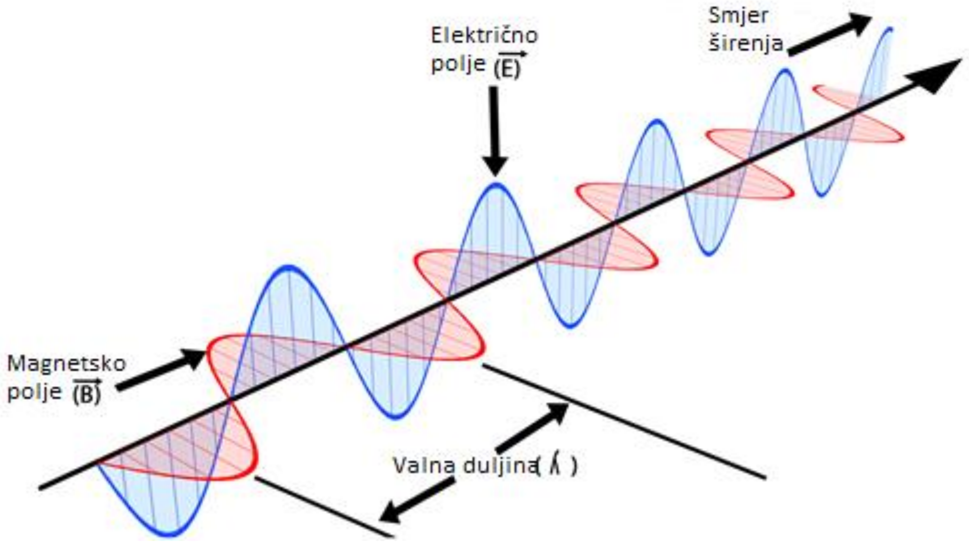
Ciljevi

- Određivanje opičkih svojstva H_2Pc-a i PTCDI-a
  - Dielektrična funkcija
- Utjecaj temperature; 20°C ili -160°C?
- Debljina?
- Hrapavost?
- Rad uređaja?

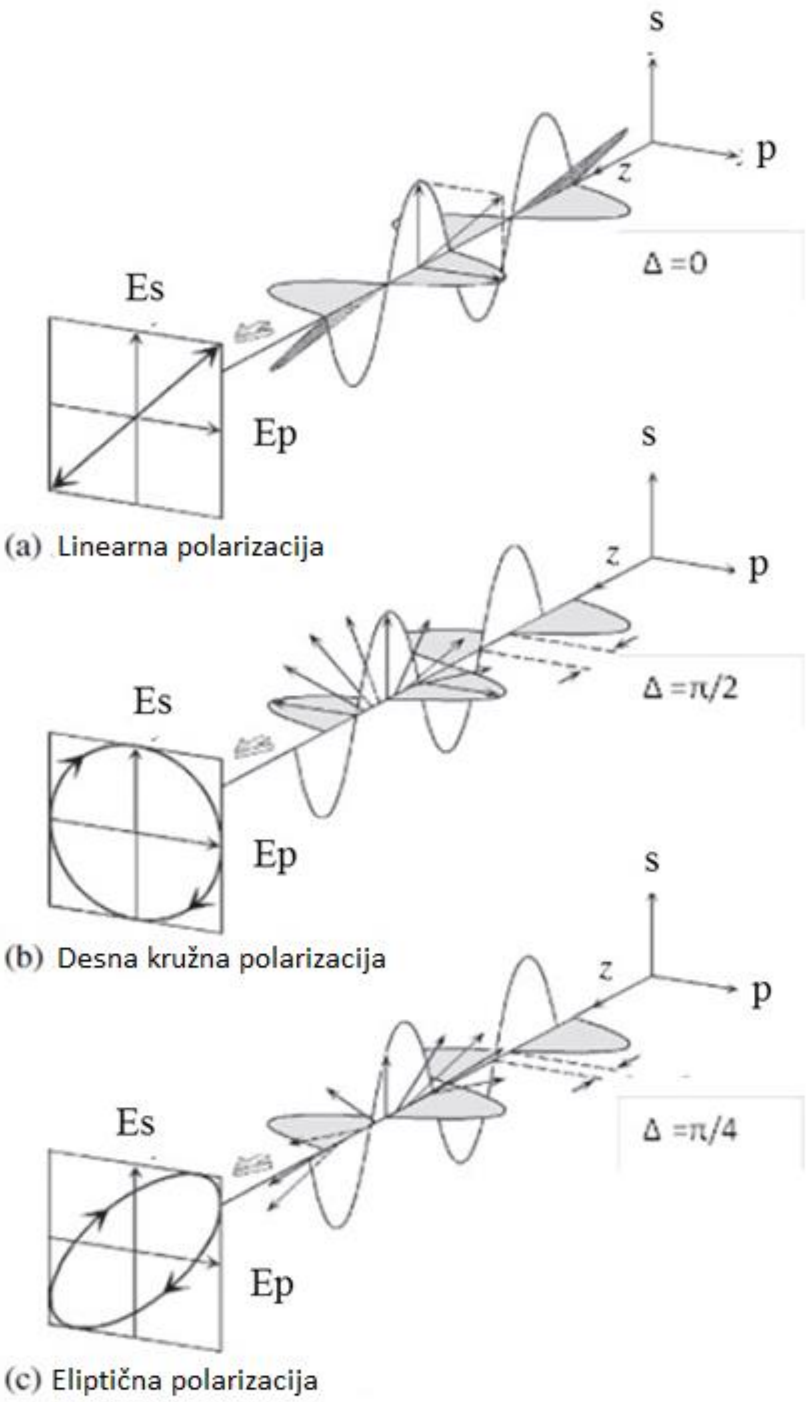




EM ravni val i polarizacija svjetlosti

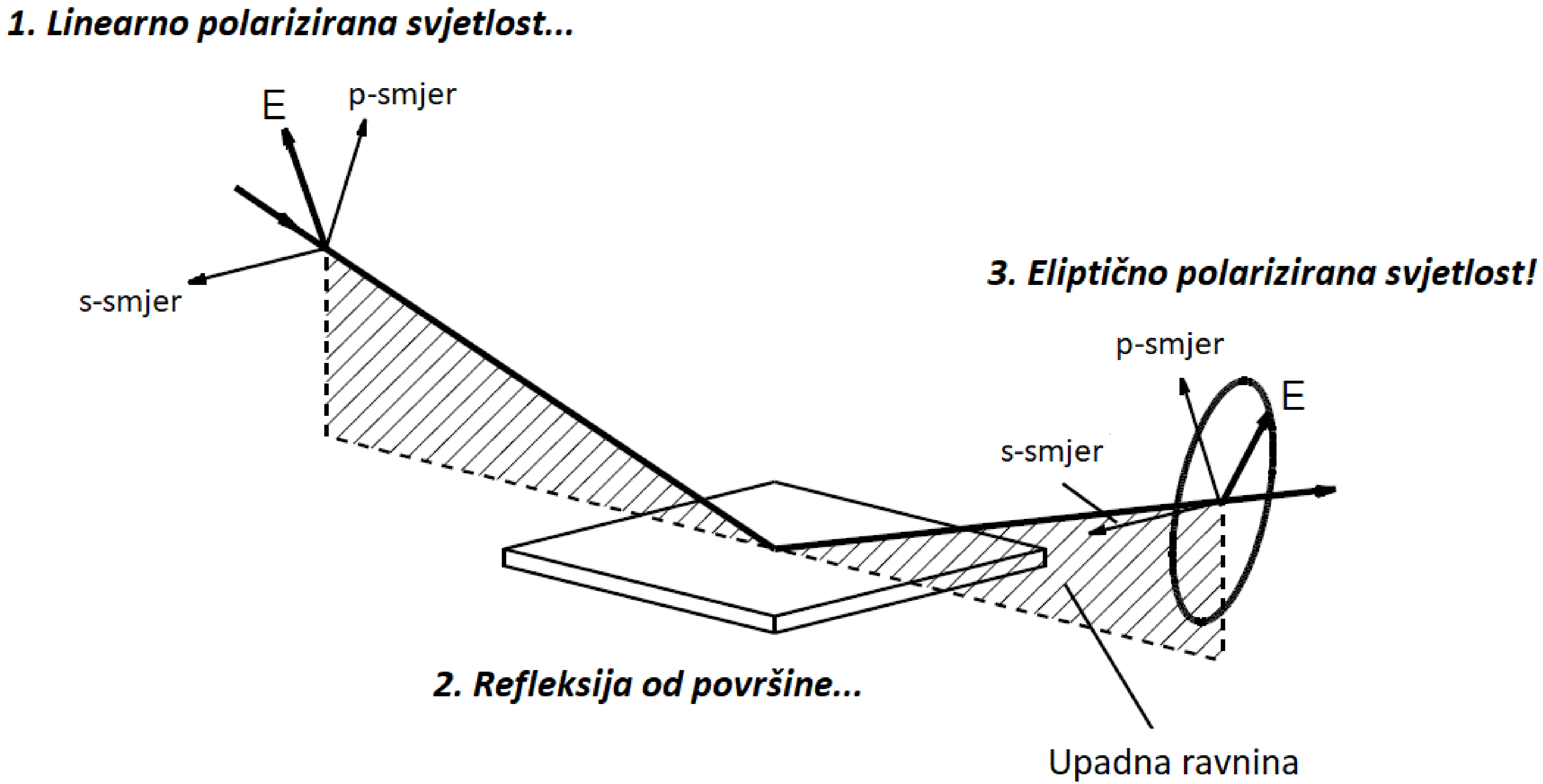


$\vec{E} =$



$$\vec{E}(\vec{r},t) = \vec{E}_0 \exp\left(\frac{i2\pi\tilde{n}}{\lambda}\vec{q}\cdot\vec{r}\right)\exp(-i\omega t)$$

Što je elipsometrija?



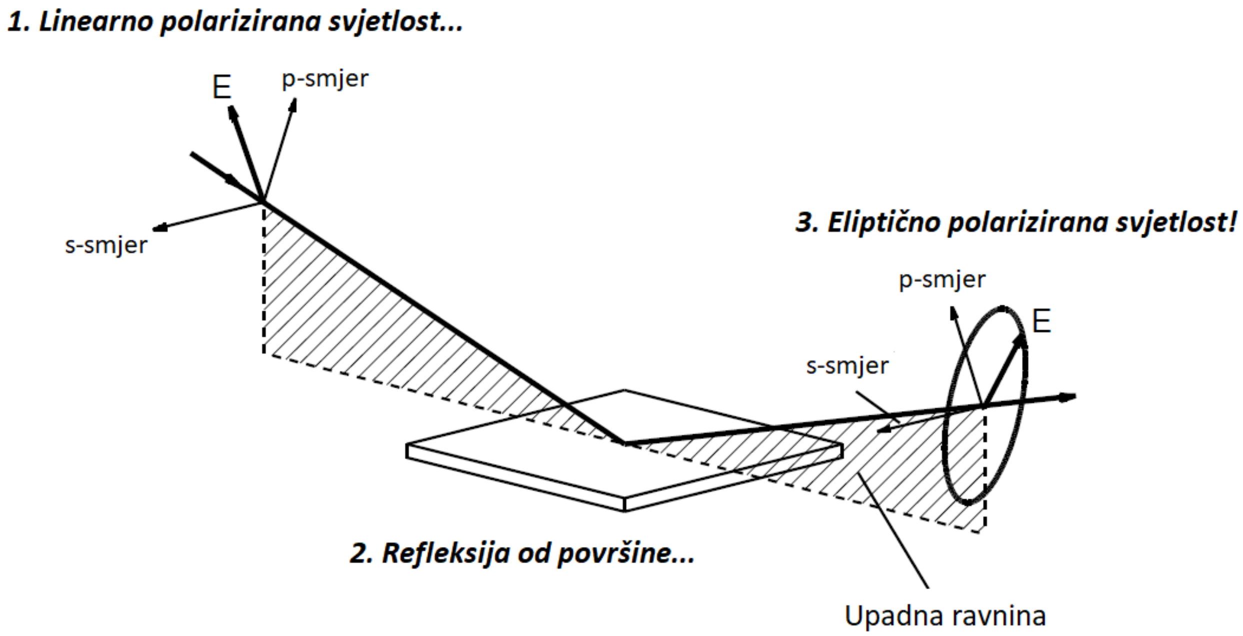
$$\vec{E} = \begin{bmatrix} \tilde{E}_p \\ \tilde{E}_s \end{bmatrix}$$

Što elipsometar mjeri?

- Promjena polarizacijskog stanja svjetlosti reflektirane s površine uzorka
- Mjerenje vrijednosti se izražavaju preko psi ψ i delta Δ varijabli

$$\tilde{\rho} = \frac{\tilde{R}_p}{\tilde{R}_s} = \tan\psi \, e^{i\Delta}$$

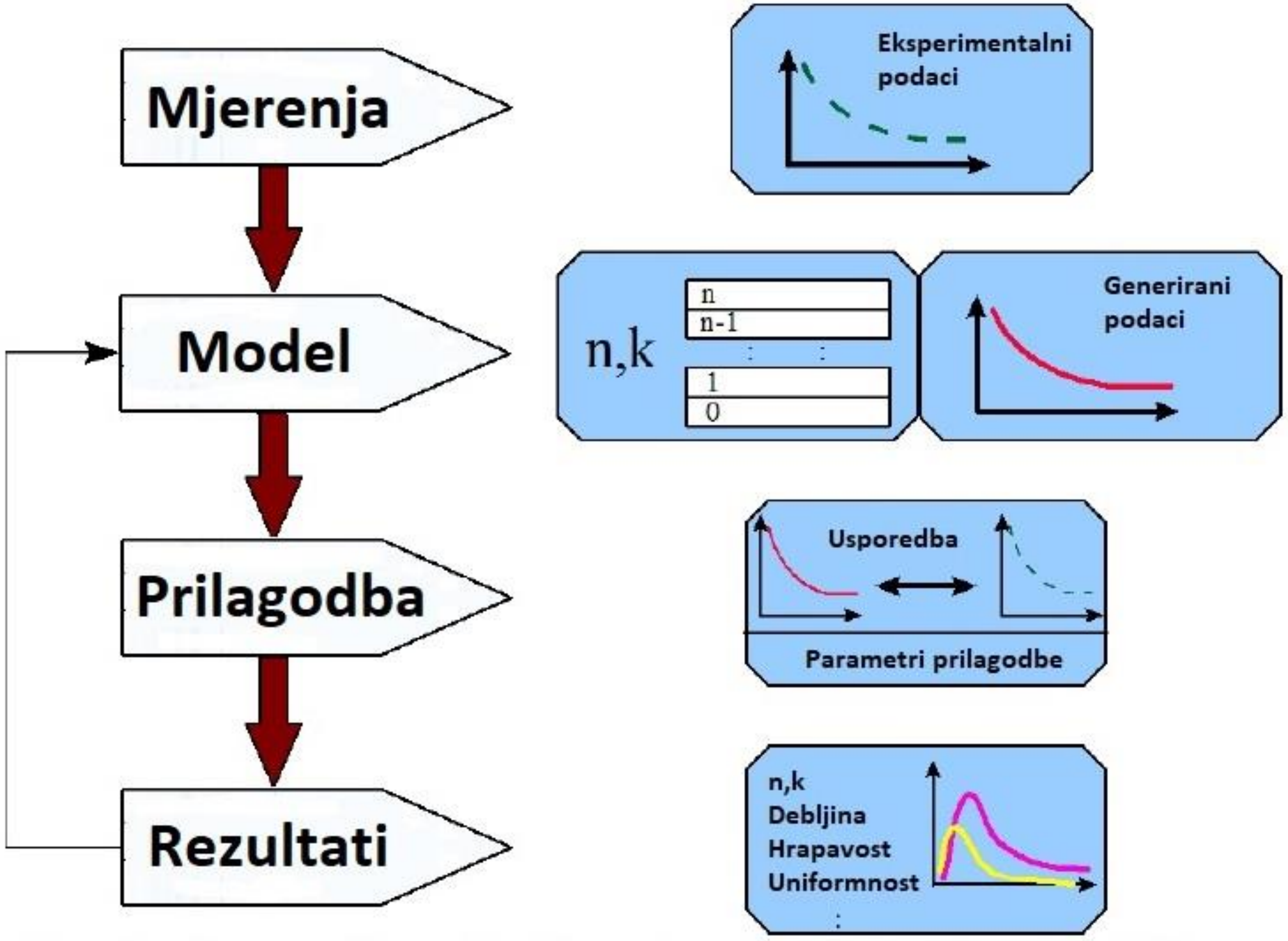
$$\vec{E} = \begin{bmatrix} \tilde{E}_p \\ \tilde{E}_s \end{bmatrix}$$



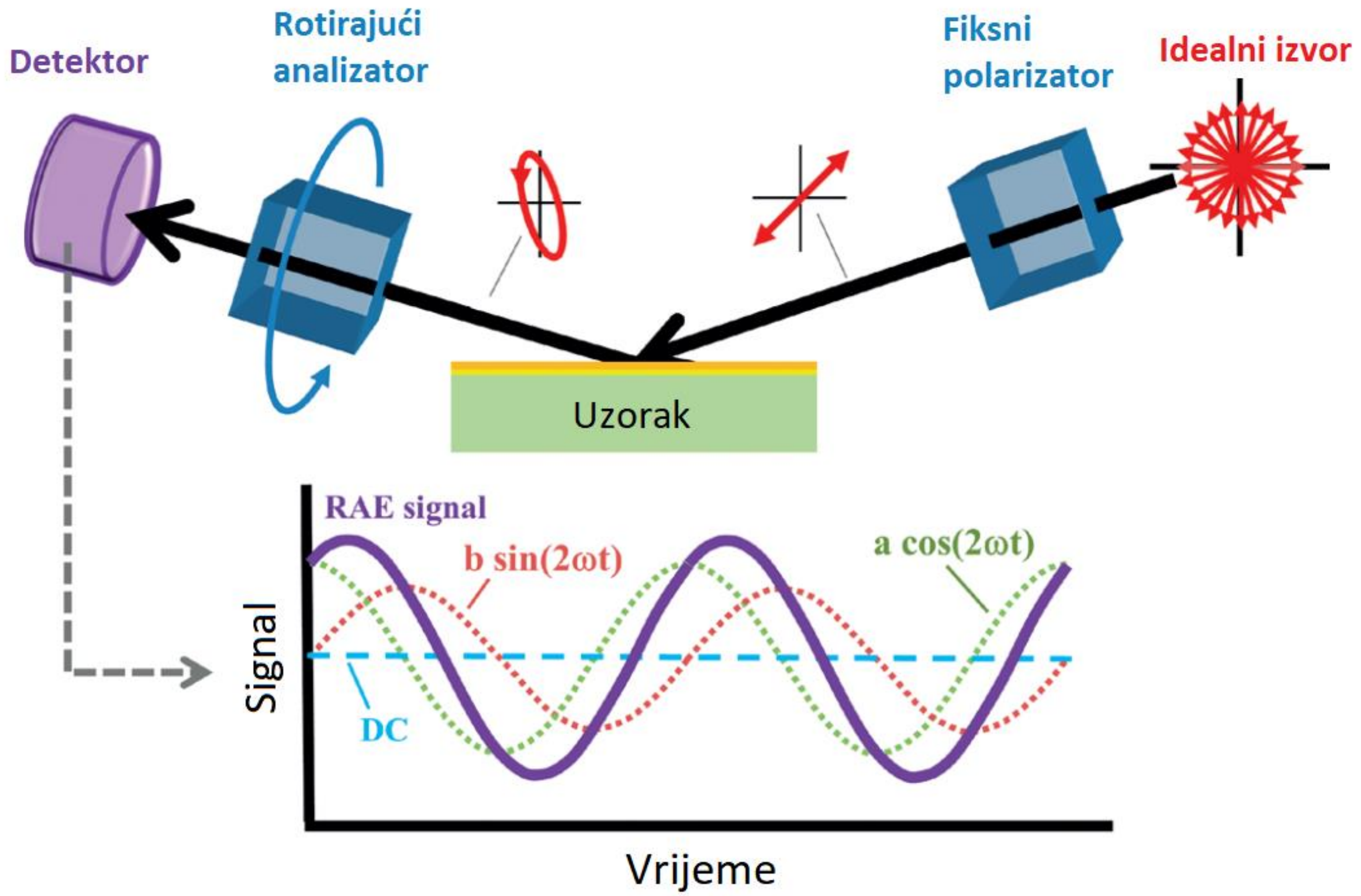
Koji se parametri mogu odrediti?

- Optičke konstante (n, k or ε_1, ε_2)
- Debljina tankog sloja
- Koncentracija dopiranja
- Površinska ili između slojeva hrapavost
- Optička anizotropija

Generalna procedura za optičke eksperimente

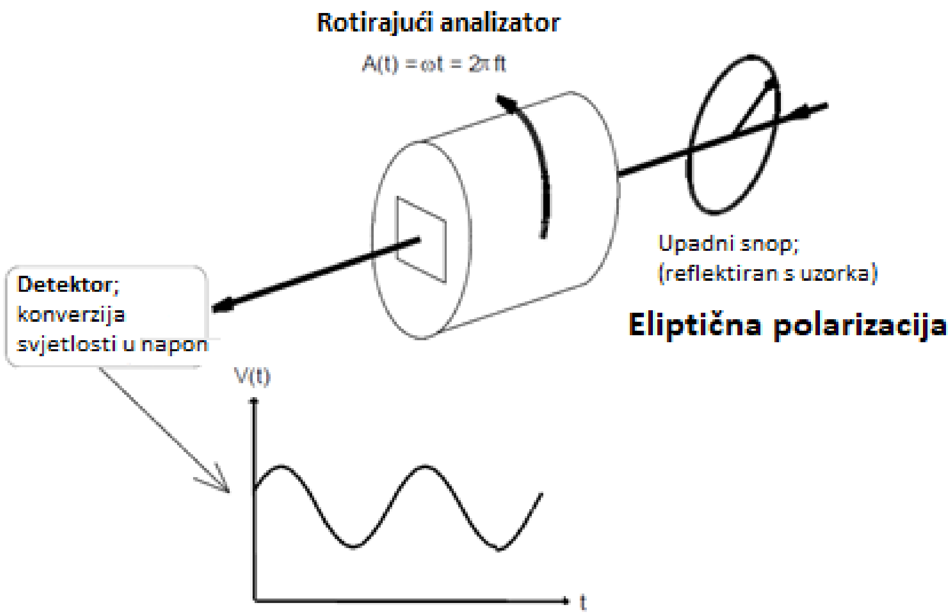


Elipsometar s rotirajućim analizatorom



$$\tilde{\rho} = \frac{\tilde{R}_p}{\tilde{R}_s} = \tan \psi \, e^{i\Delta}$$

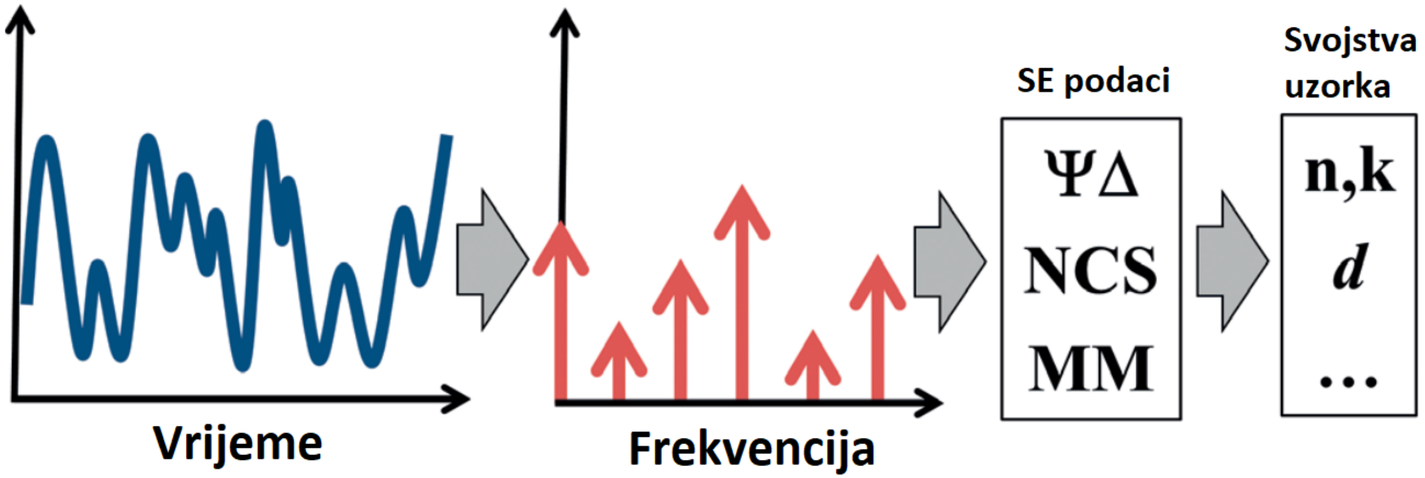
Mjerenja polarizacije



$$V(t) = DC + a \cdot \cos(2\omega t) + b \cdot \sin(2\omega t)$$

$$\alpha = \frac{a}{DC} = \frac{tan^2(\psi) - tan^2(P)}{tan^2(\psi) + tan^2(P)}$$

$$\beta = \frac{b}{DC} = \frac{2tan(\psi)\cos(\Delta)\,tan(P)}{tan^2(\psi) + tan^2(P)}$$



Još malo matematike...

$$\alpha = \frac{a}{DC} = \frac{tan^2(\psi) - tan^2(P)}{tan^2(\psi) + tan^2(P)}$$

$$\beta = \frac{b}{DC} = \frac{2tan(\psi)\cos(\Delta)\,tan(P)}{tan^2(\psi) + tan^2(P)}$$

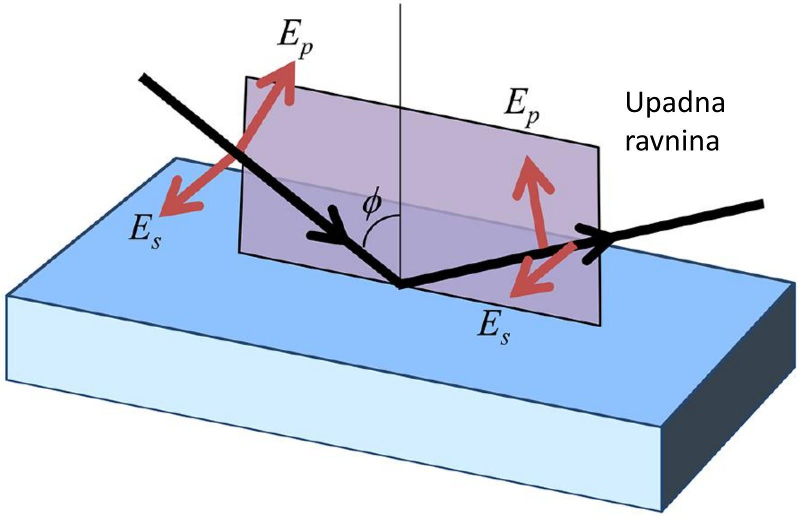
$$tan\psi = \sqrt{\frac{1+\alpha}{1-\alpha}}|tanP|$$

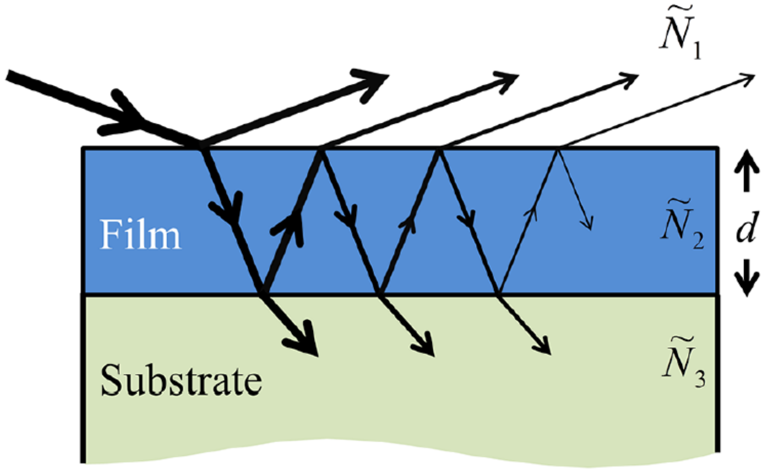
$$cos\Delta = \frac{\beta}{\sqrt{1-\alpha^2}} \cdot \frac{tanP}{|tanP|}$$

$$\tilde{\rho} = \frac{\tilde{R}_p}{\tilde{R}_s} = \tan\psi\, e^{i\Delta}$$

Fresnelovi koeficijenti → optička svojstva?

$$\tan\psi\, e^{i\Delta} = \frac{\tilde{R}_p}{\tilde{R}_s} \rightarrow n, k \text{ ili } \varepsilon_1,\ \varepsilon_1\,?$$





$$r_{p,12} = \frac{E_p^{refl}}{E_p^{inc}} = \frac{\tilde{n}_2\cos\Phi_1 - \tilde{n}_1\cos\Phi_2}{\tilde{n}_2\cos\Phi_1 + \tilde{n}_1\cos\Phi_2}$$

$$r_{s,12} = \frac{E_s^{refl}}{E_s^{inc}} = \frac{\tilde{n}_1\cos\Phi_1 - \tilde{n}_2\cos\Phi_2}{\tilde{n}_1\cos\Phi_1 + \tilde{n}_2\cos\Phi_2}$$

$$R_s = \frac{r_{s,12} + r_{s,23}e^{-i2\beta}}{1 + r_{s,12}r_{s,23}e^{-i2\beta}}$$

$$\beta = 2\pi\frac{d}{\lambda}\tilde{n}_2\cos\Phi_2$$

$$R_p = \frac{r_{p,12} + r_{p,23}e^{-i2\beta}}{1 + r_{p,12}r_{p,23}e^{-i2\beta}}$$

Regresijska analiza optičkih podataka

- Levenberg-Marquardt algoritam
- Maksimalan procijenitelj vjerovatnosti → srednja kvadratna pogreška, MSE

$$MSE = \sqrt{\frac{1}{2N - M} \sum_{i=1}^{N} \left[\left(\frac{\psi_i^{mod} - \psi_i^{exp}}{\sigma_{\psi,i}^{exp}} \right)^2 + \left(\frac{\Delta_i^{mod} - \Delta_i^{exp}}{\sigma_{\Delta,i}^{exp}} \right)^2 \right]}$$

N = number of (ψ,Δ) pairs
M = number of parameters in the model
σ = standard deviations on the experimental data points

Što su optičke konstante?

- Parametri koji karakteriziraju ponašanje materijala u prisutnosti vanjskoj EM vala

$$\vec{P} = \widetilde{\chi_e}\varepsilon_0\vec{E}$$

$$\vec{D} = (1 + \widetilde{\chi_e})\varepsilon_0\vec{E} = \tilde{\varepsilon}\vec{E}$$

→ Koliko je materijal polarizabilan

$$\tilde{\varepsilon} \equiv (1 + \widetilde{\chi_e})\varepsilon_0 = \tilde{\varepsilon}_r\varepsilon_0$$

$$\vec{E}(\vec{r}, t) = \vec{E}_0 \exp\left(\frac{i2\pi\tilde{n}}{\lambda}\vec{q}\cdot\vec{r}\right)\exp(-i\omega t)$$

$$\tilde{n} = n - ik$$

$$\tilde{\varepsilon} = \varepsilon_1 - i\varepsilon_2$$

$$\tilde{\varepsilon} = \tilde{n}^2$$

Prijelazi elekrona iz osnovnog u pobuđeno stanje određuju imaginarni dio dielektrične funkcije!

Kramers-Kronig relacija

$$\varepsilon_1(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E' \varepsilon_2(E')}{E'^2 - E^2} dE'$$

$$\varepsilon_2(\omega) = \frac{\sigma(\omega)}{\omega} \qquad \sigma(\omega) = e\mu n$$

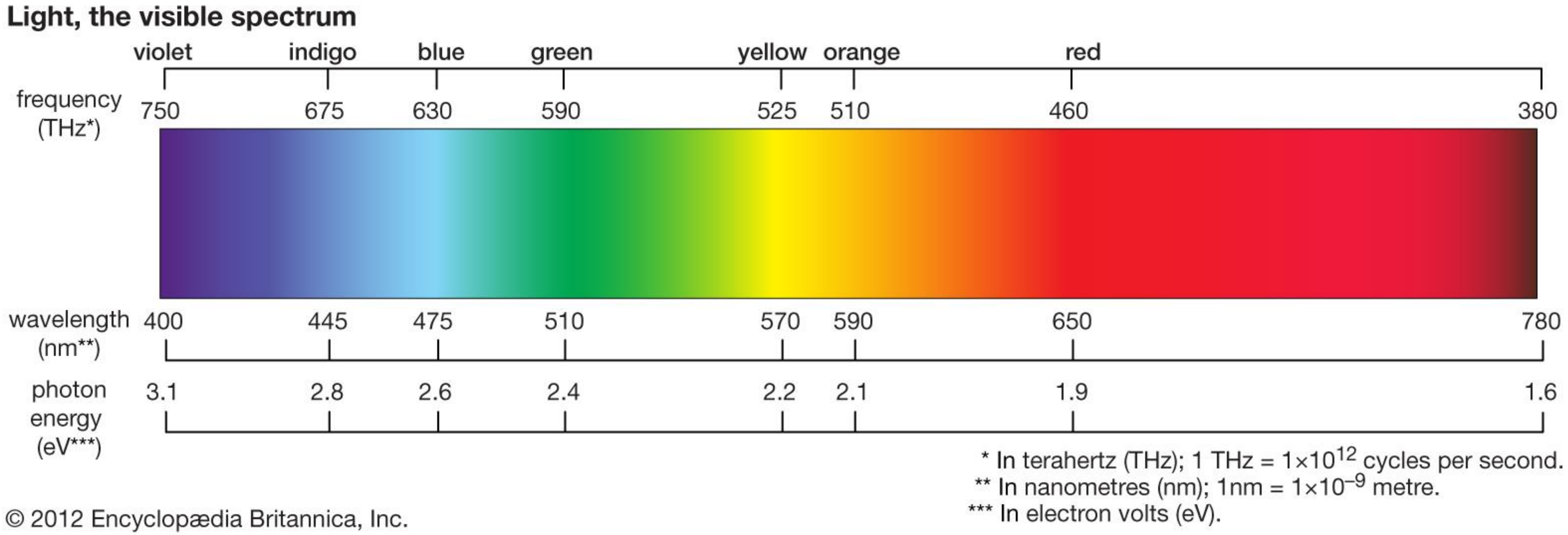
$$\varepsilon_2 \propto n$$

Optička svojstva svih materijala određena su u potpunosti tipom i jakošću optičke apsorpcije koja se dogodi u materijalu

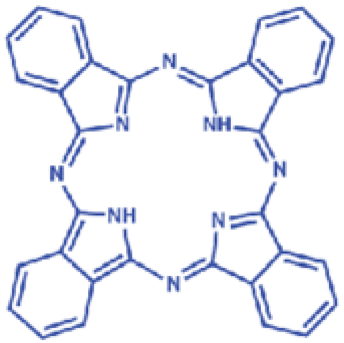
Osnovni mehanizmi kojima se energija svjetlosnog snopa apsorbira u materijalu:

- Intervrpčana apsorpcija
- Intravrpčana apsorpcija
- Apsorpcija slobodnih nosioca naboja

Vidljivi dio spektra



H_2Pc – bezmetalni pftalocijanin



- 2 kristalne faze; α i β
- Dvije apsorpcijske vrpce mogu se zapaziti, vrpca blizu 2 eV (620 nm; Q vrpca) I jedna blizu 3.5 eV (350 nm; B ili Soret vrpca)
- Obje vrpce pridjeljene su π-π* pobuđenjima makrocikličkog π sistema sastavljenog od C i N atoma

170 A. T. Davidson: Absorption spectra of phthalocyanine

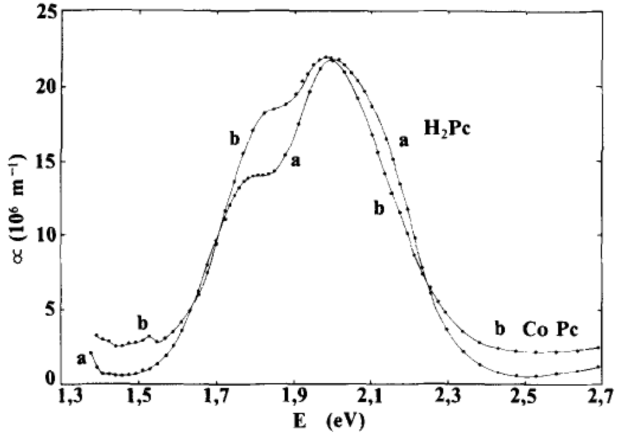


FIG. 3. The visible absorption spectra of (a) H_2Pc (x = 175 nm) and (b) CoPc (x = 100 nm) films.

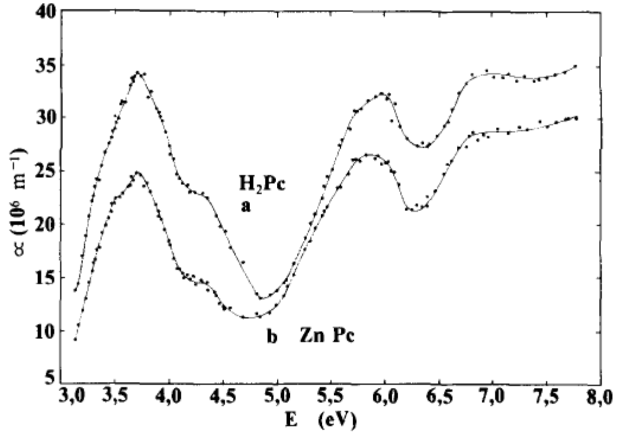


FIG. 5. The absorption spectra between 3.1 and 7.8 eV for (a) H_2Pc (x = 25 nm) and (b) ZnPc (x = 40 nm) films.

J. Chem. Phys. 77, 168 (1982); doi: 10.1063/1.443636

TABLE I. Maxima (in eV) seen in the absorption spectra of phthalocyanine films. The main peak in each band is underlined. nr means not resolved.

Compound	Visible (Q)	Soret (B)	Variable (N)	(C)	Far UV band
H_2Pc	1.79 2.00	3.33 3.53 3.74	4.29	5.66 5.93	6.94 nr

PTCDI – N,N’-dimetilperilen-3,4:9,10-tetrakarboksilni diimid

- PTCDI ima područje apsorpcije centrirano pri 494 nm (2.5 eV) i pri 580 nm (2.14 eV).
- Q vrpca: jedno rame pri 2.5 eV (π-π∗ pobuđenje), jedan maksimum pri 2.14 eV (vrh ekscitona)
- B vrpca : pri 3.35 eV ; π-π∗ pobuđenje
- N vrpca: Slaba apsorpcija pri 4~4.75 eV (izmjena naboja (CT) iz sp_z mješane orbitale u elektronski sistam makroskopskog prstena PTCDI-a)
- C vrpca: pri 5.6 eV ; π-π∗ pobuđenje

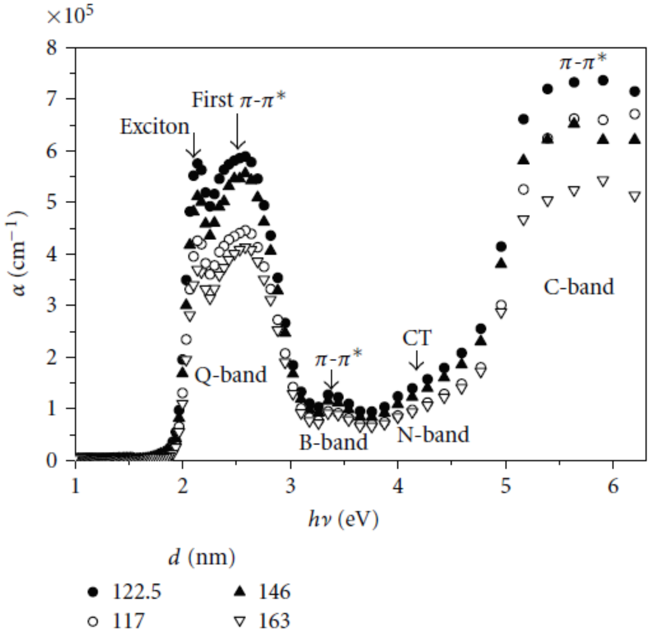
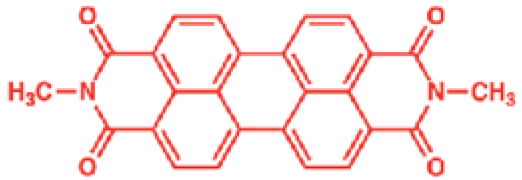


FIGURE 8: Optical absorption spectra of PTCDI thin films.

M. M. El-Nahhas, H. Abdel-Khalek, E. Salem, "Structural and Optical Properties of Nanocrystalline 3,4,9,10-Perylene-Tetracarboxylic-Diimide Thin Film„ https://doi.org/10.1155/2012/698934



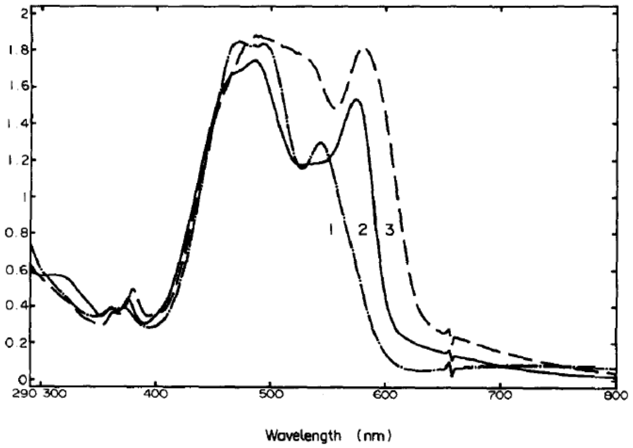
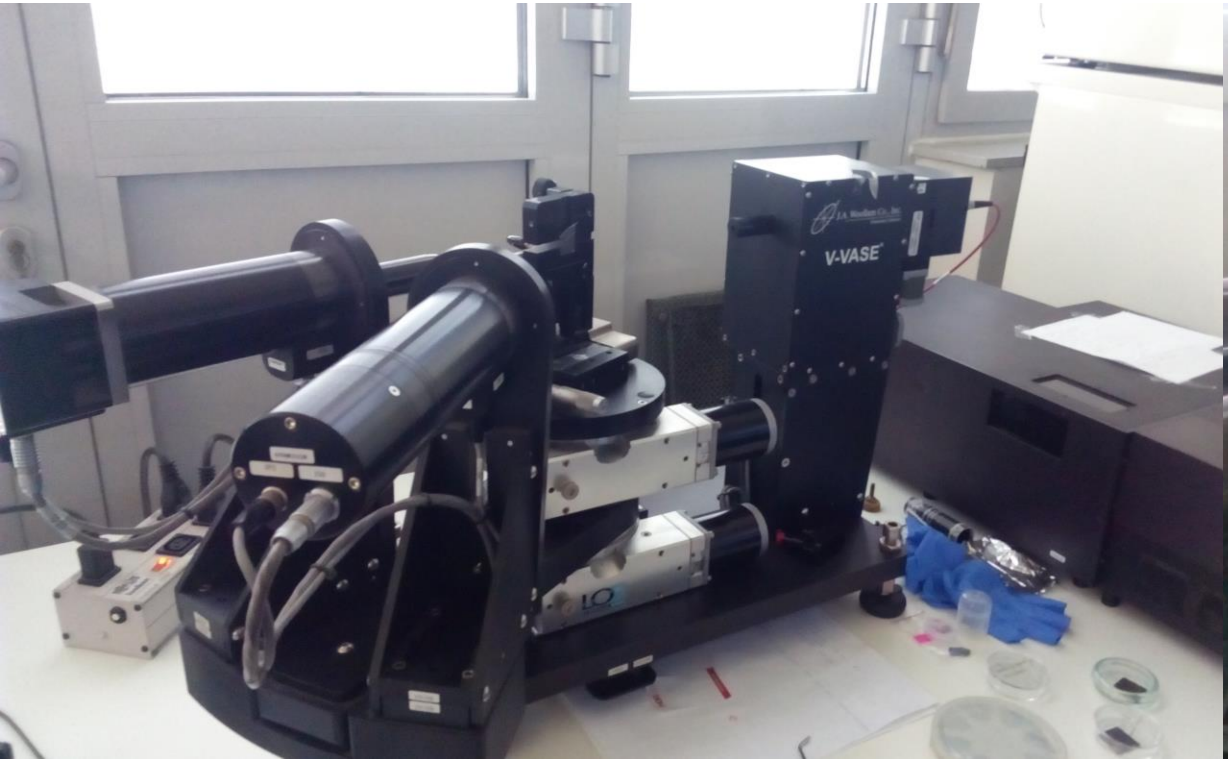
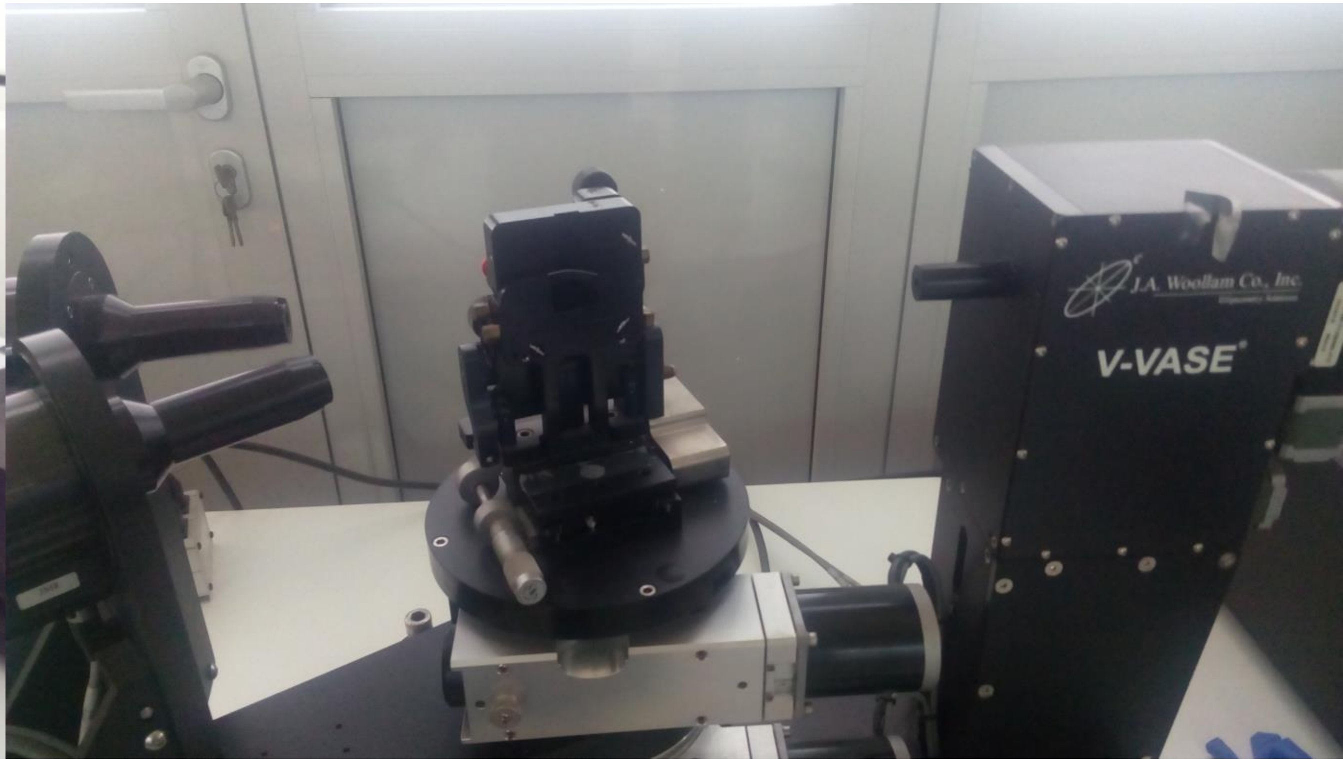


Fig. 1. Absorption spectra of PTCDPh (1), PTCDMe (2) and PTCDI (3).

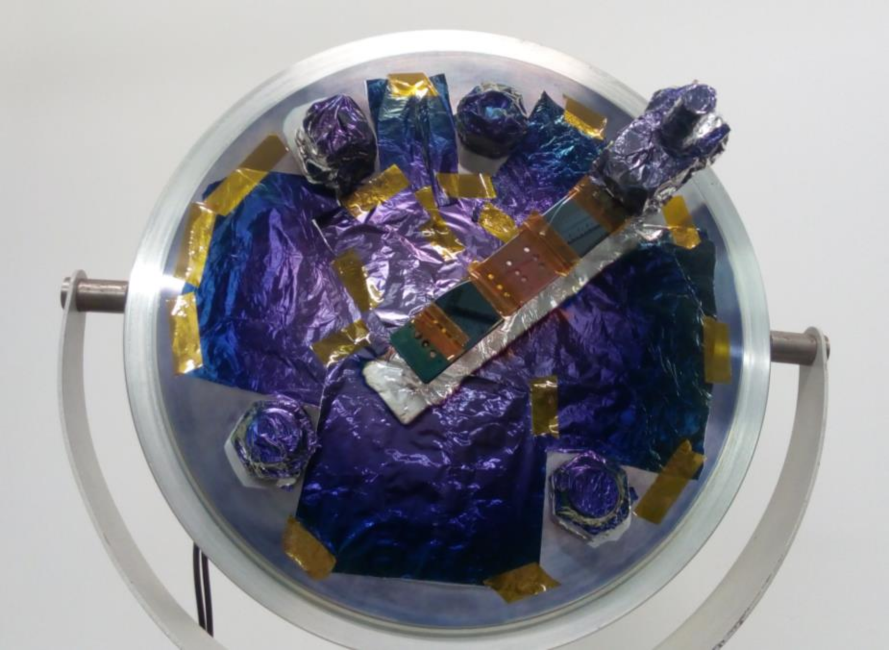
Kelly. Akers, Ricardo. Aroca, Ah Mee. Hor, and Rafik O. Loutfy The Journal of Physical Chemistry 1987 91 (11), 2954-2959 DOI: 10.1021/j100295a061

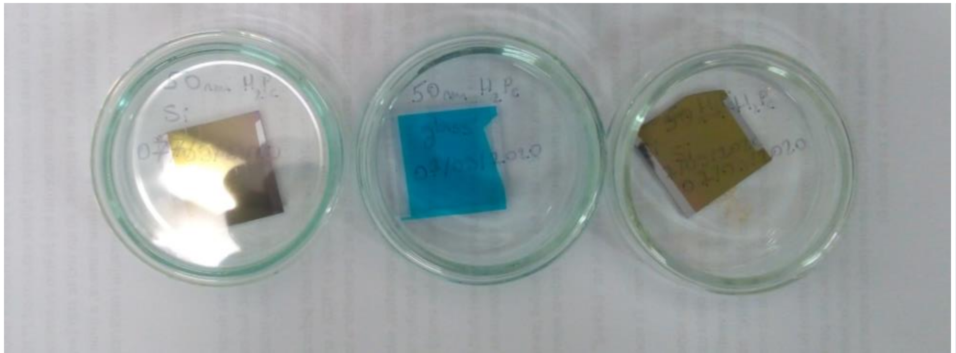
W-VASE elipsometar

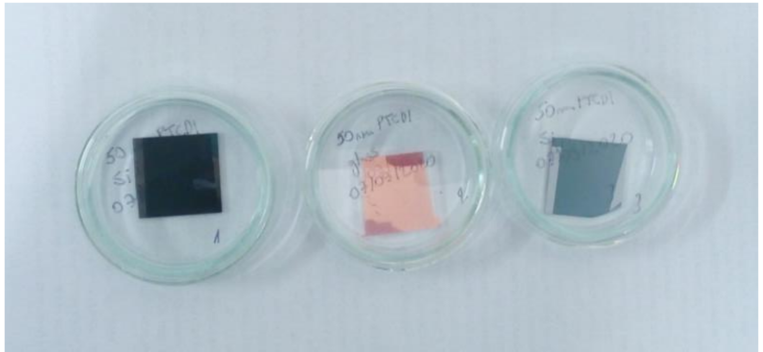




Termalna evaporacija

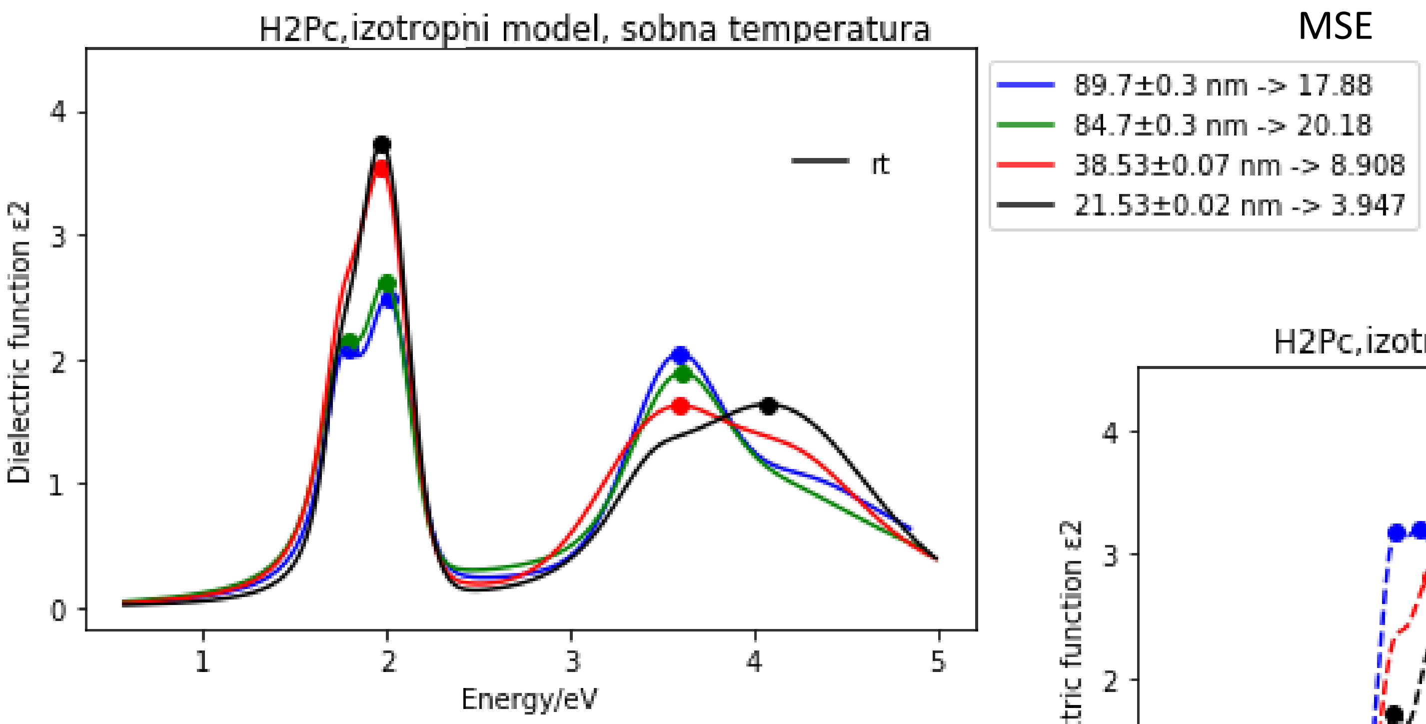


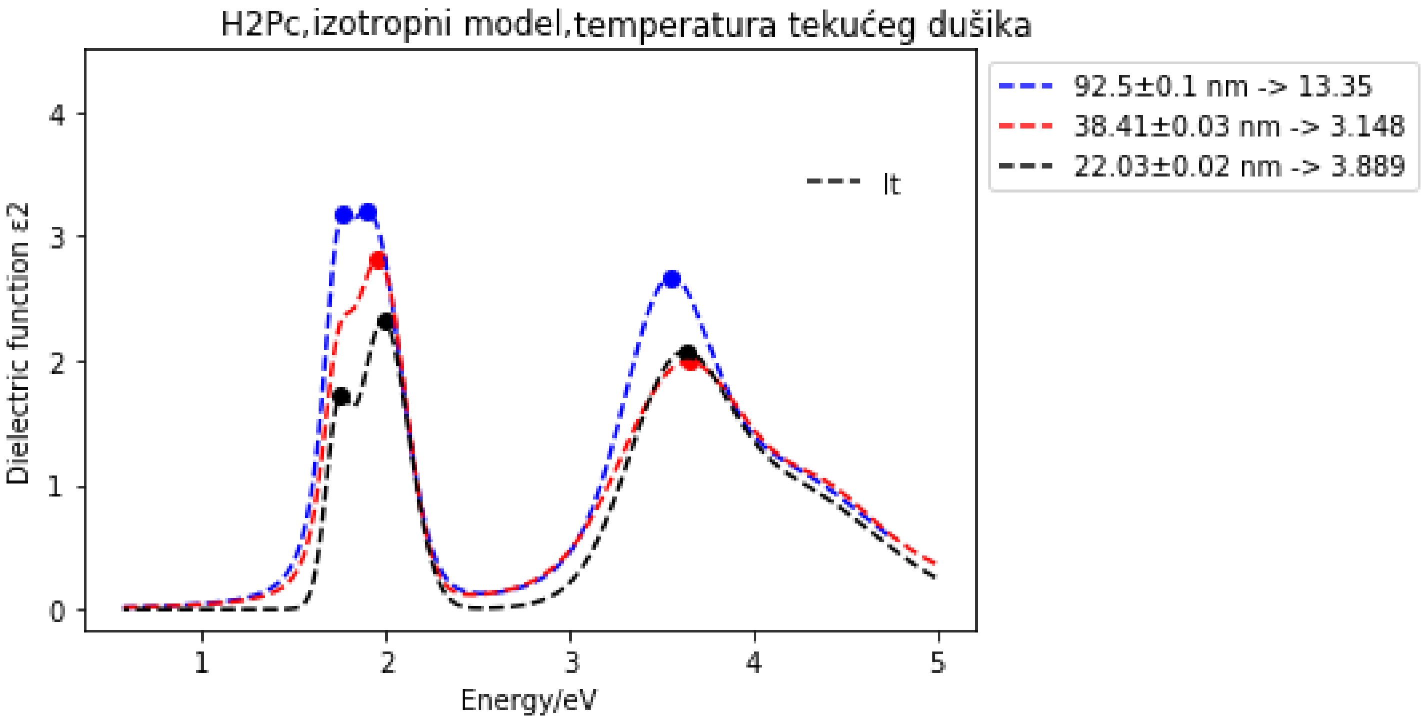




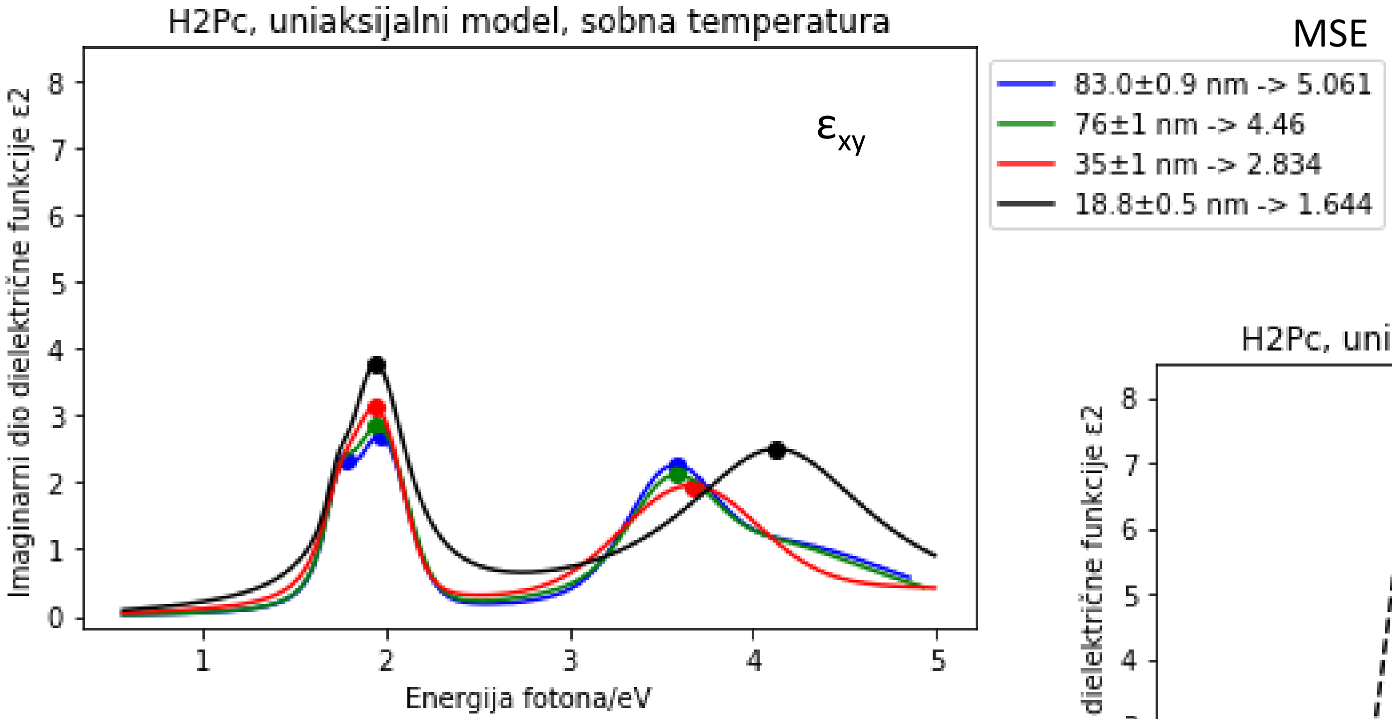
Rezultati mjerenja (modeliranja)

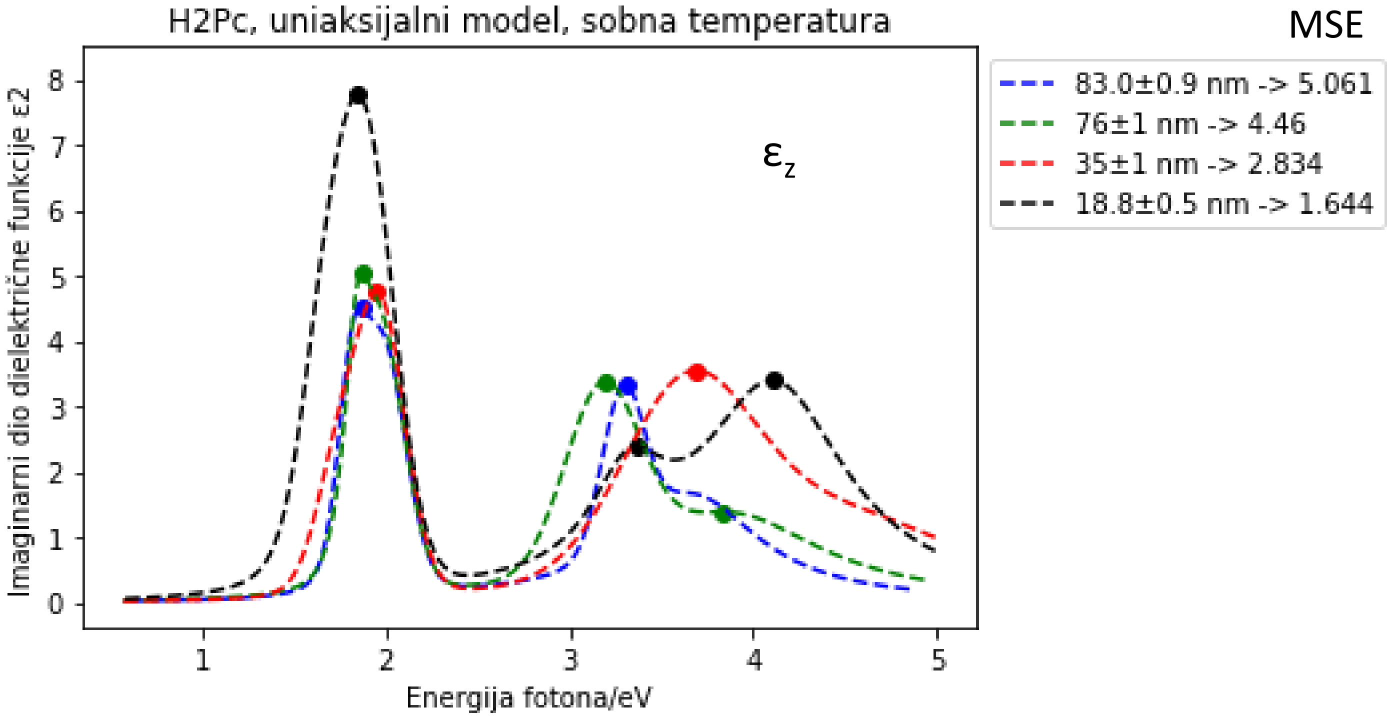
H_2Pc, izotropni model



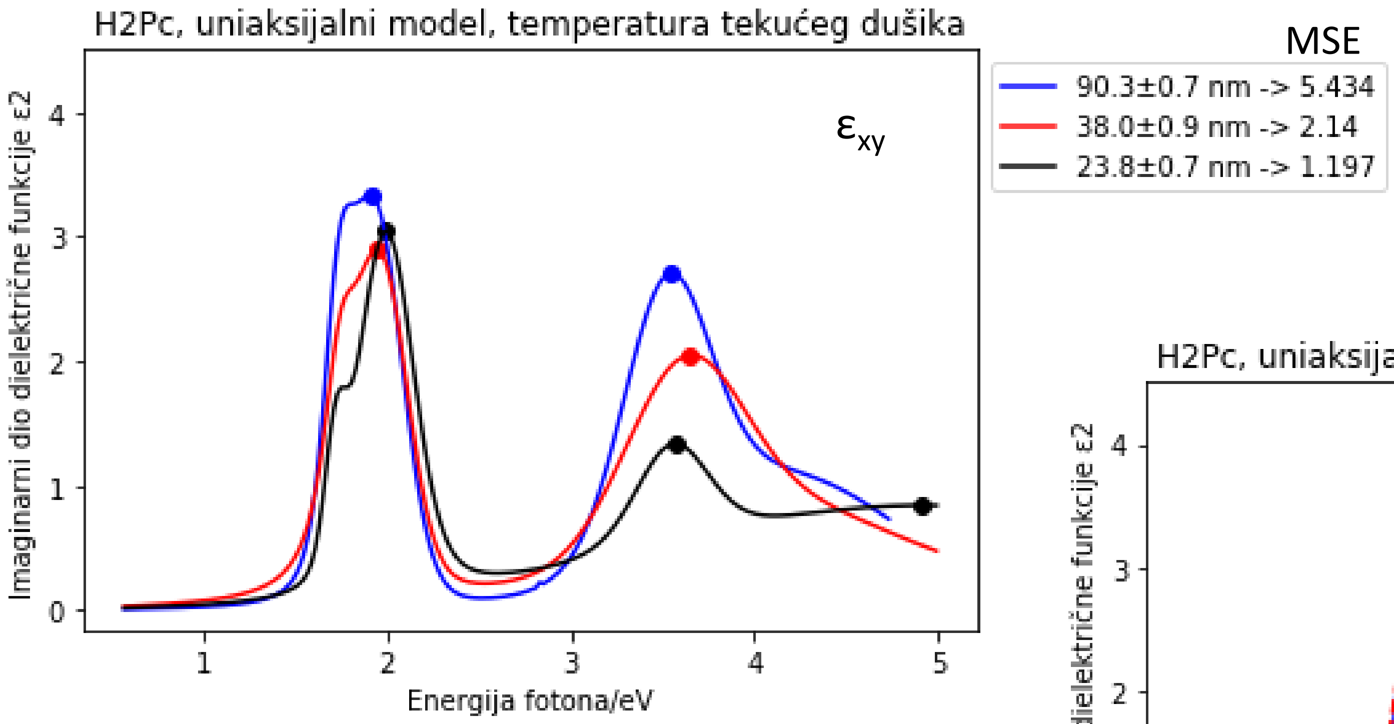


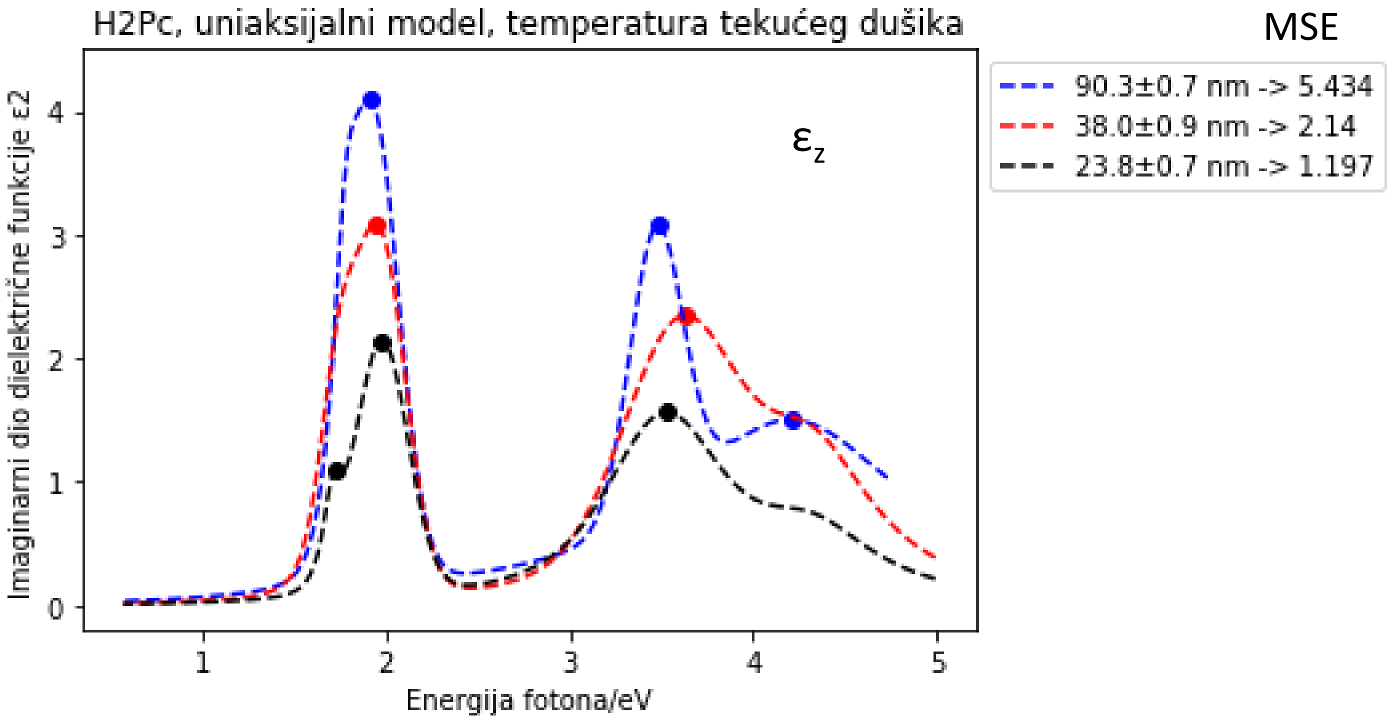
H_2Pc, uniaksijani model: 20°C



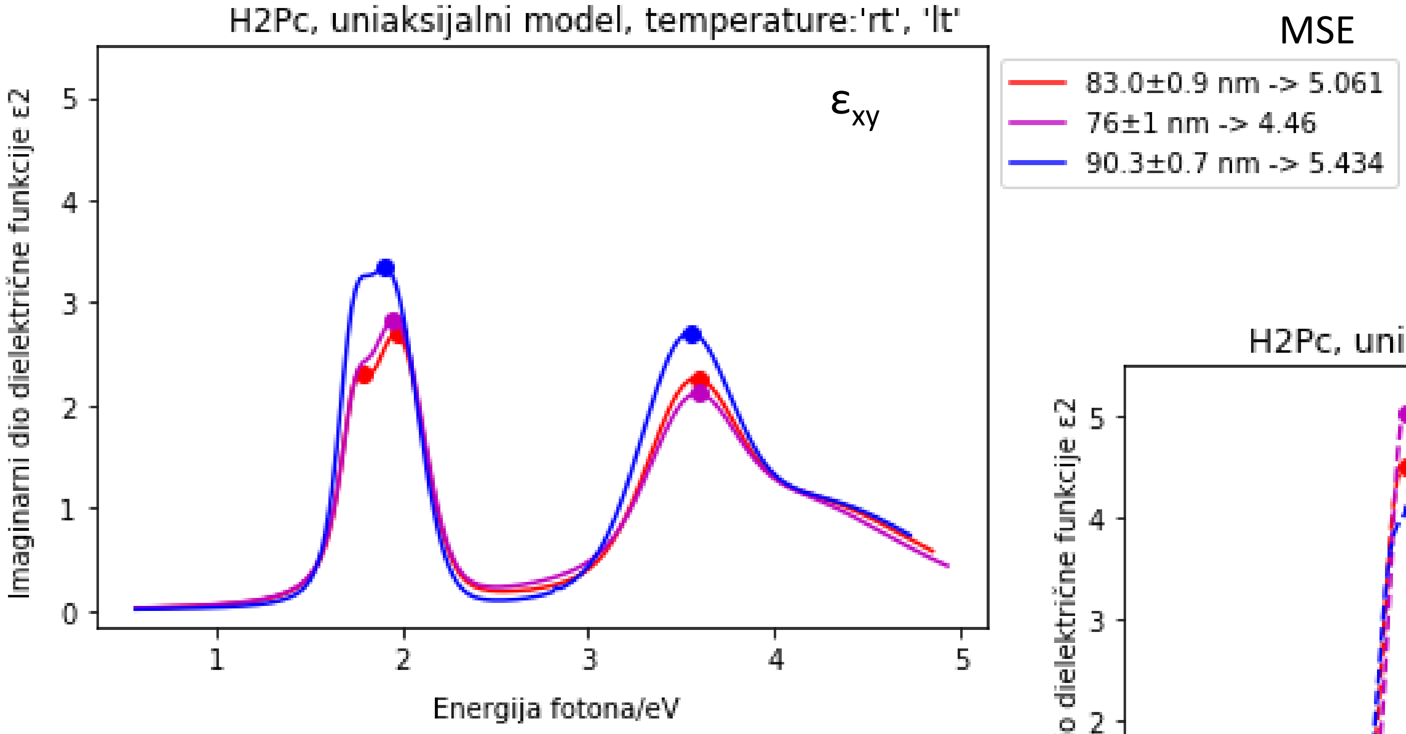


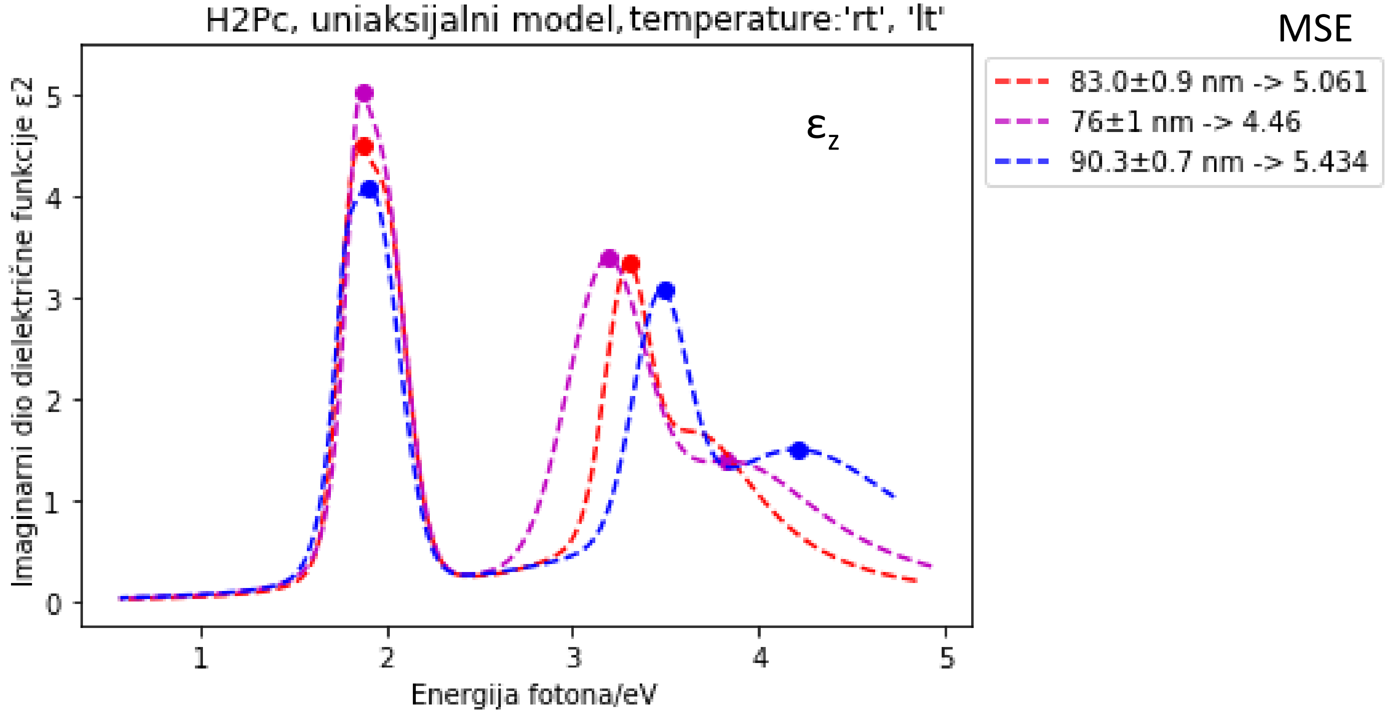
H_2Pc, uniaksijani model: -160°C



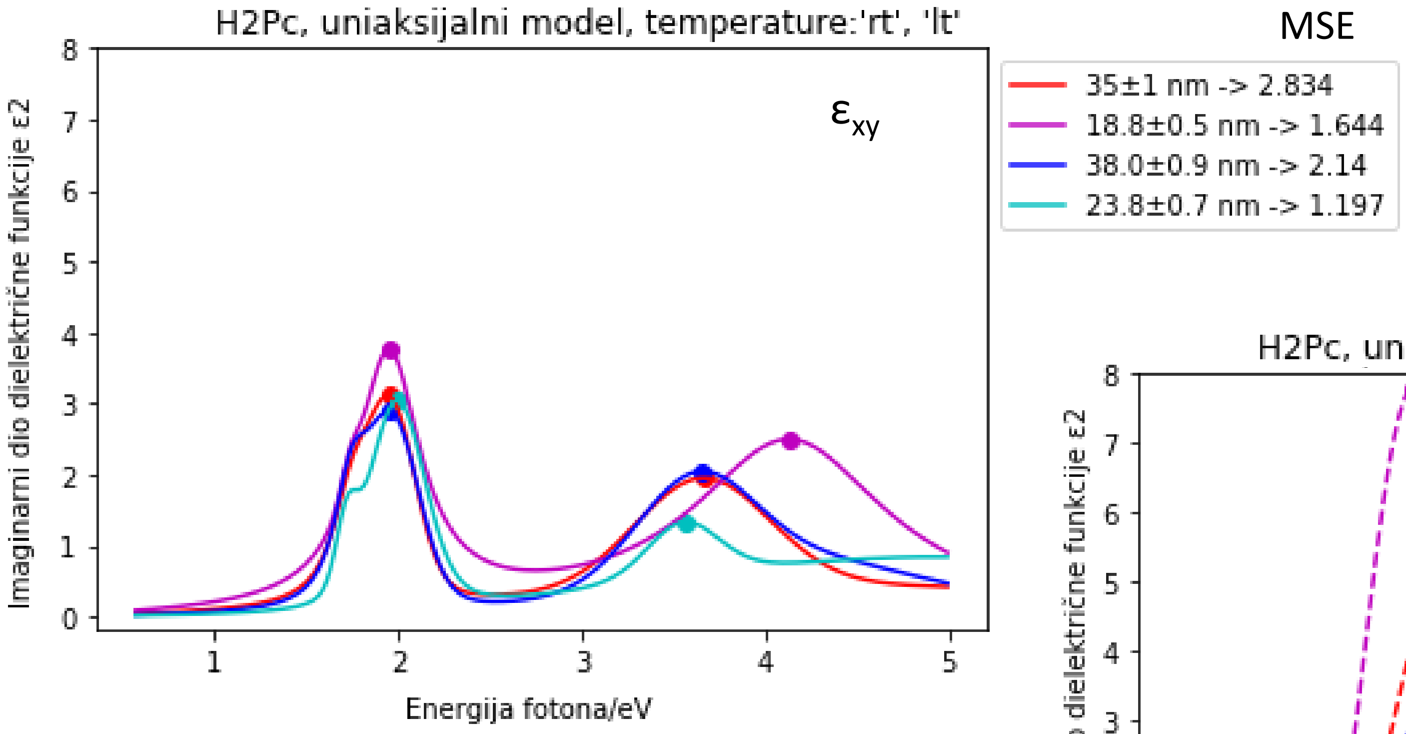


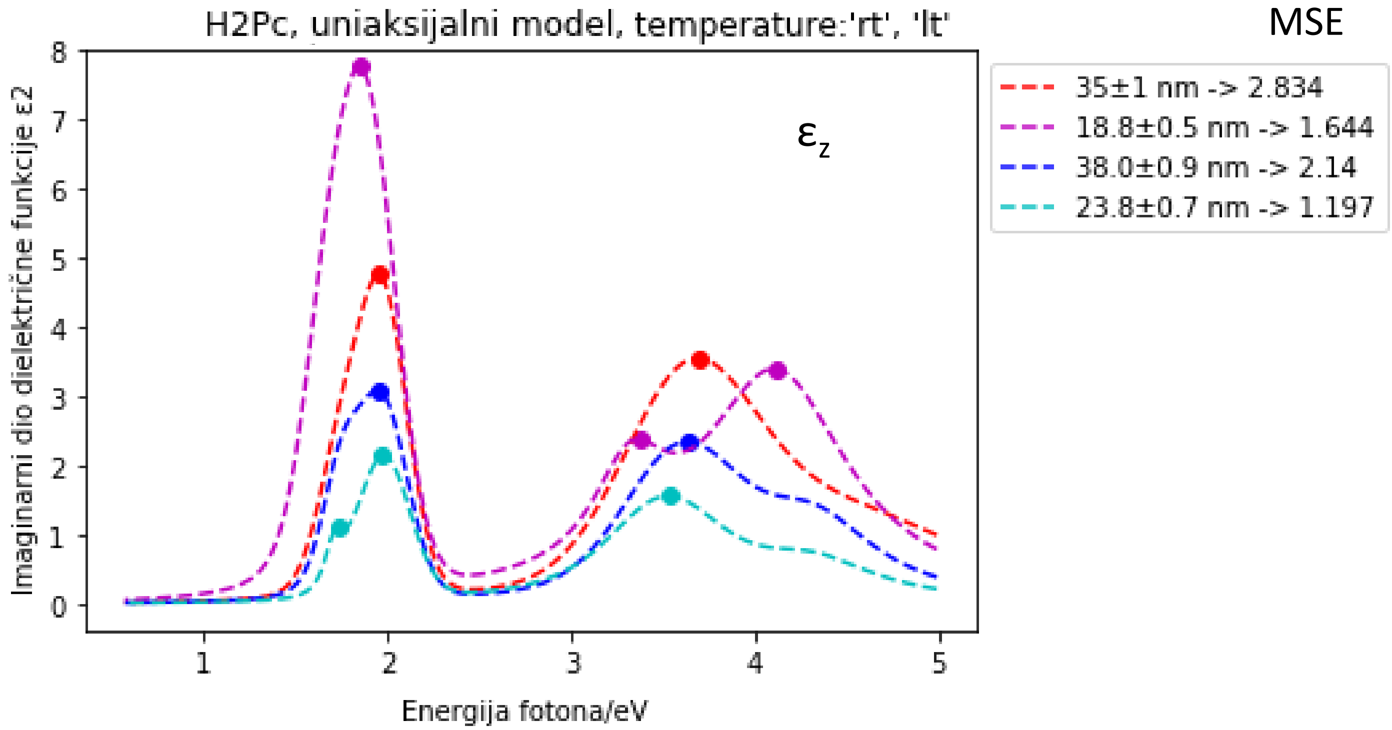
H_2Pc, uniaksijani model: Deblji slojevi



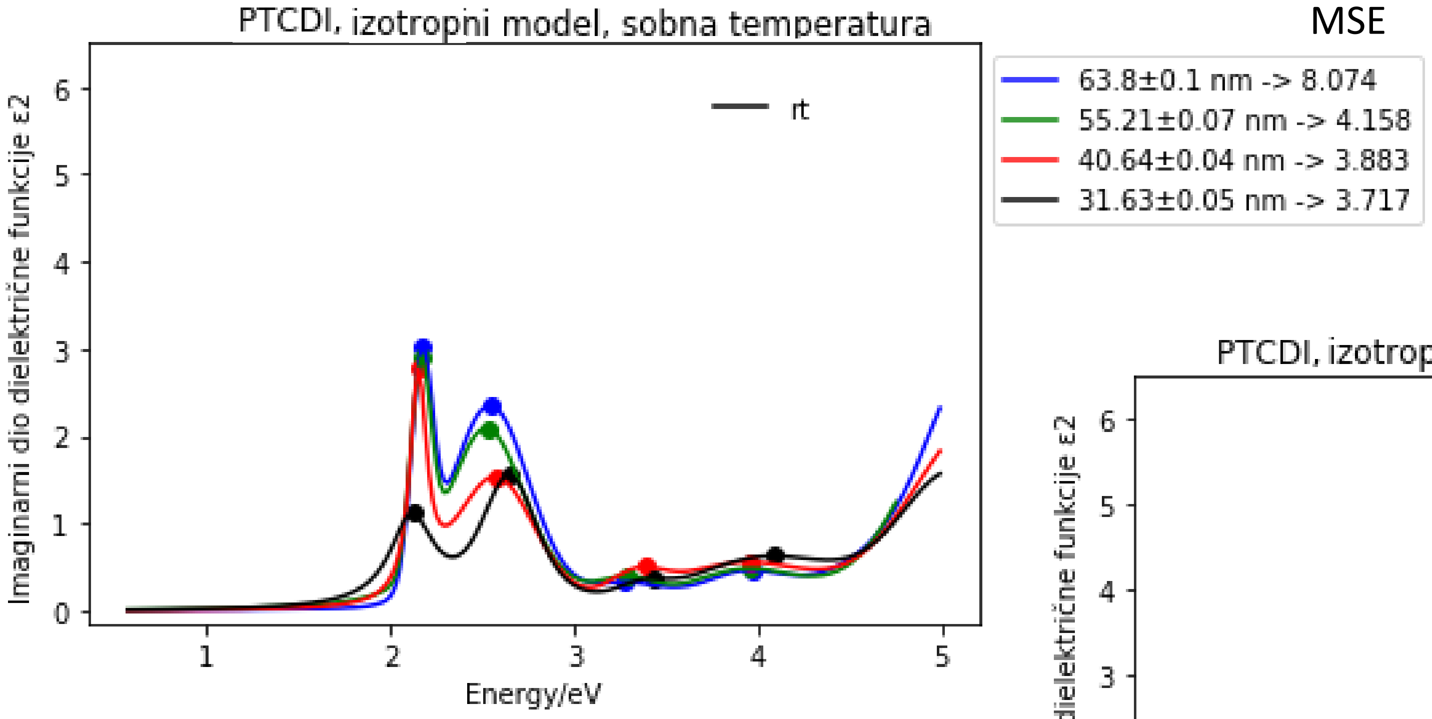


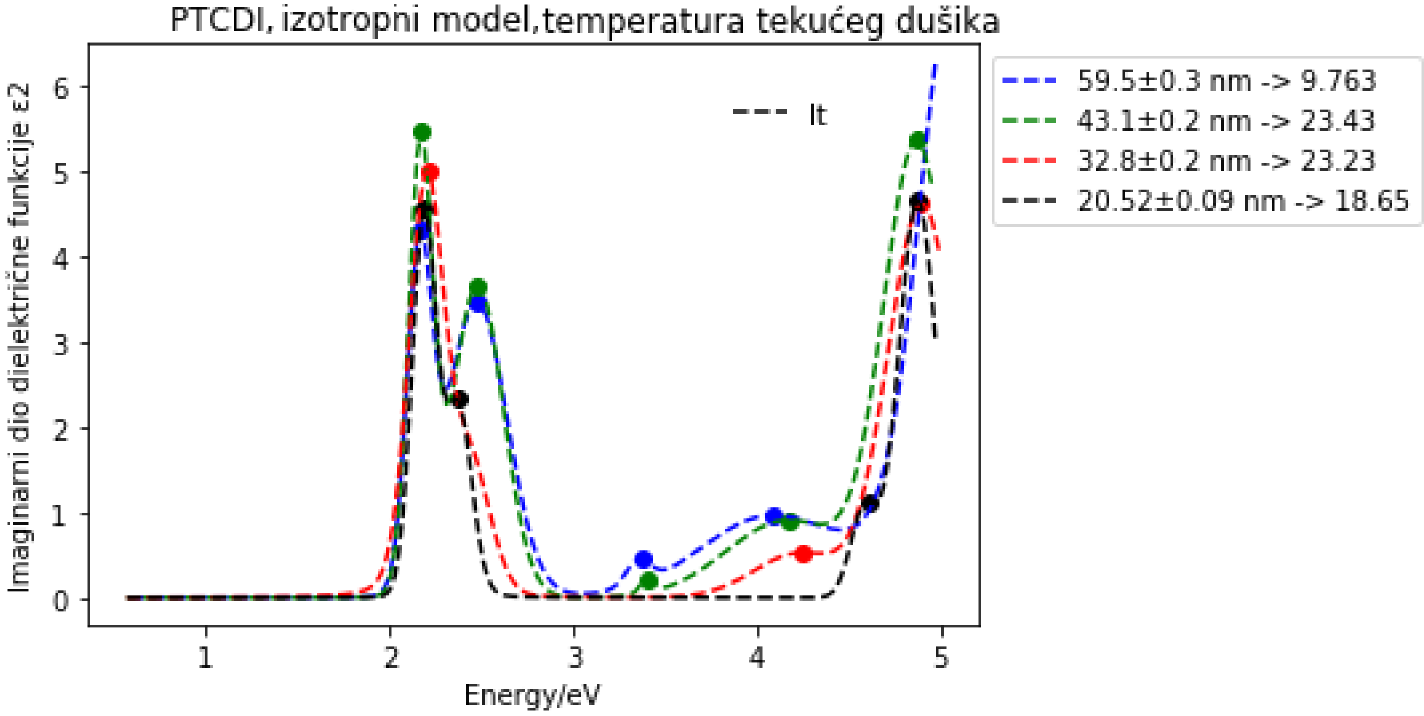
H_2Pc, uniaksijalni model: Deblji slojevi



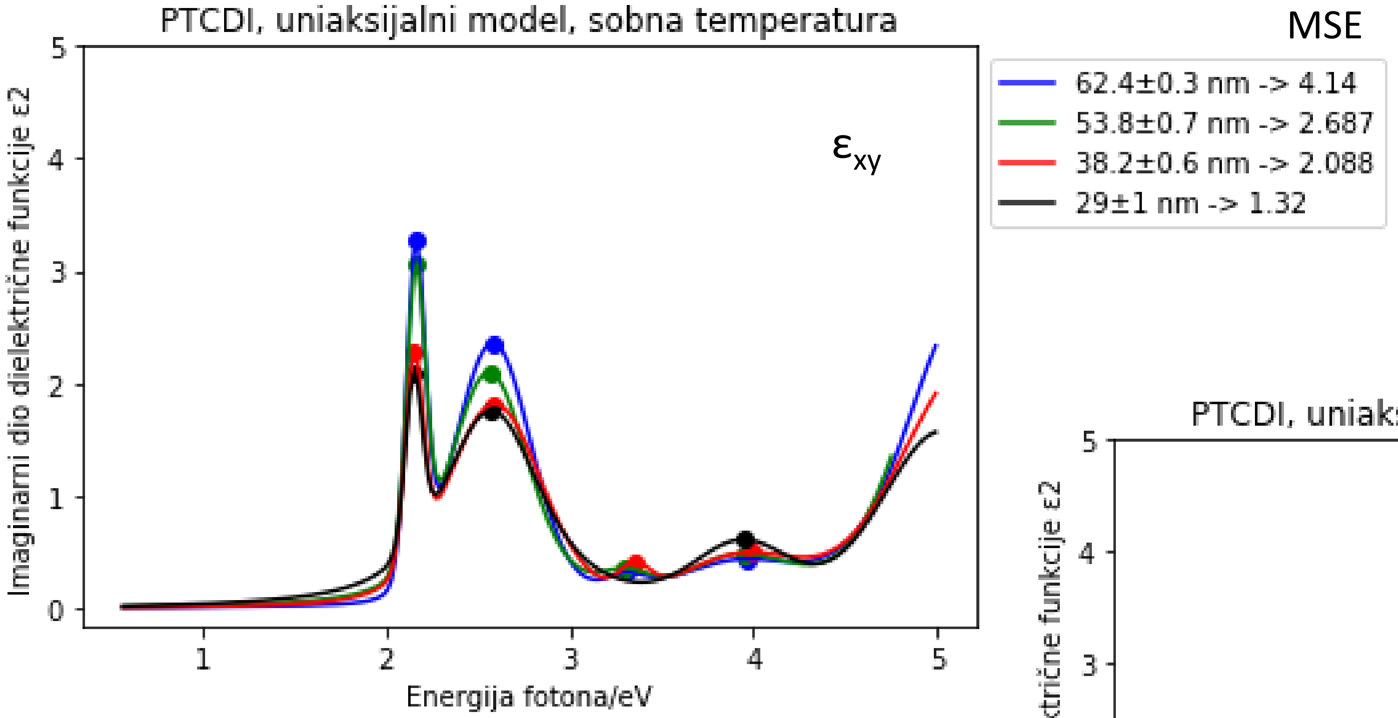


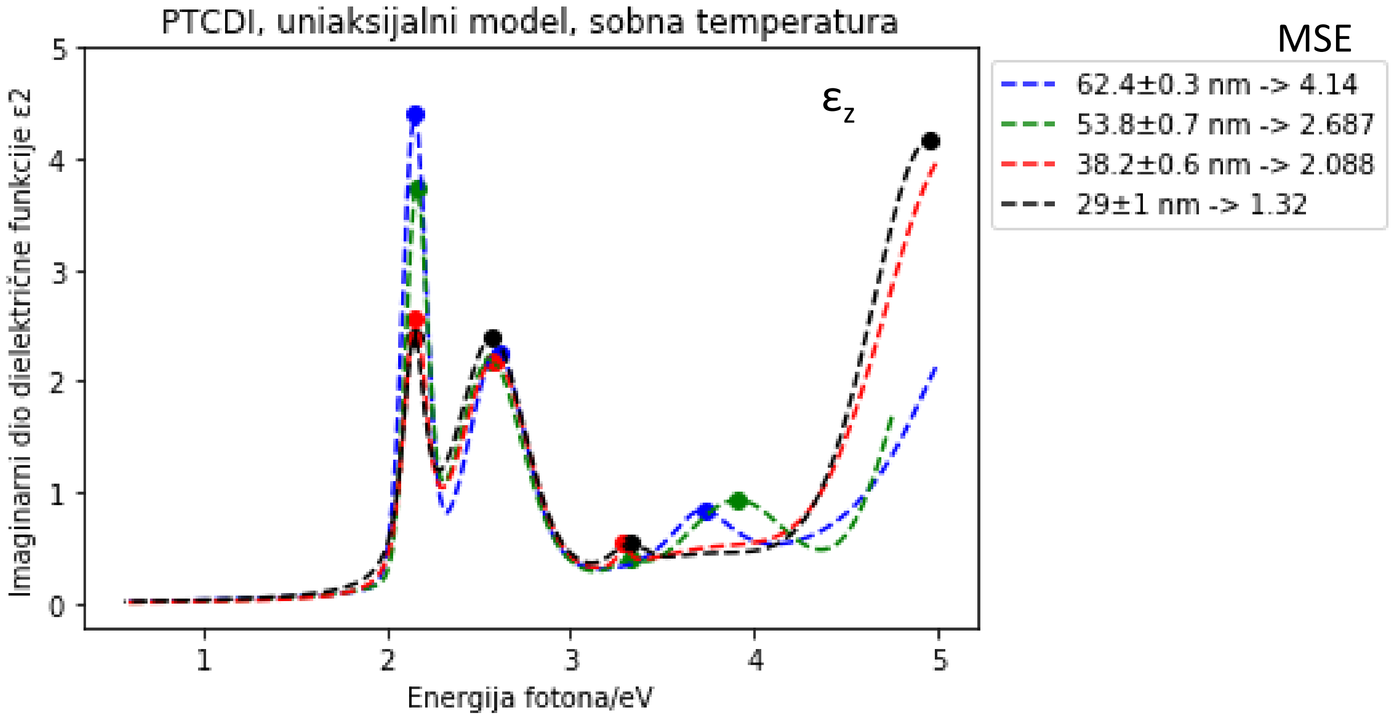
PTCDI, izotropni model



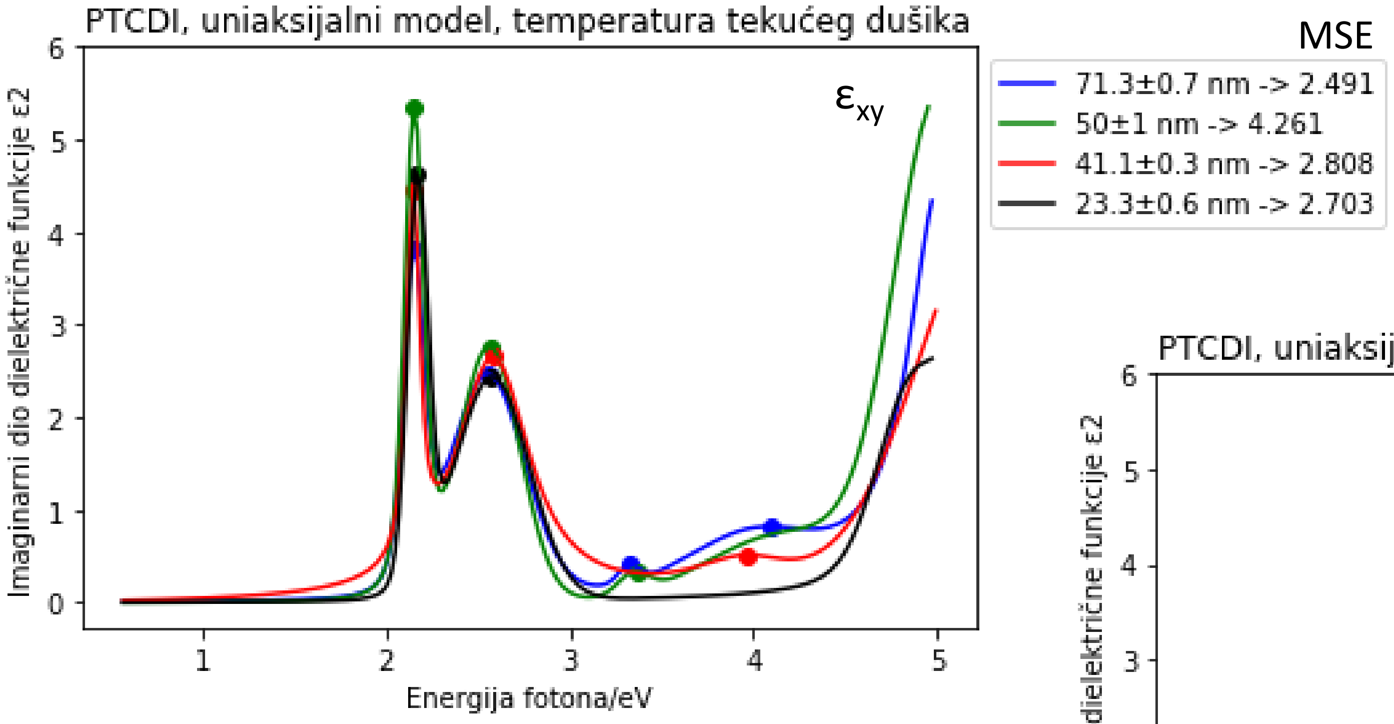


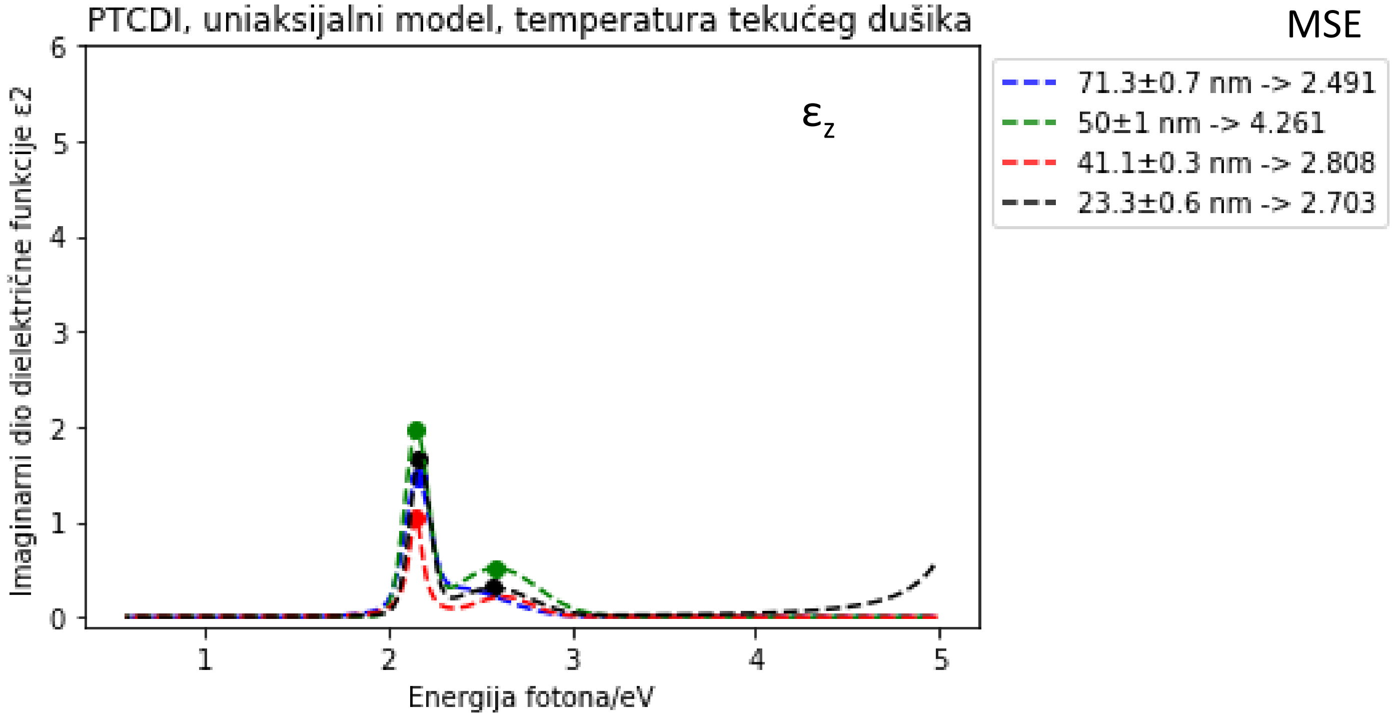
PTCDI, uniaksijalni model: 20°C



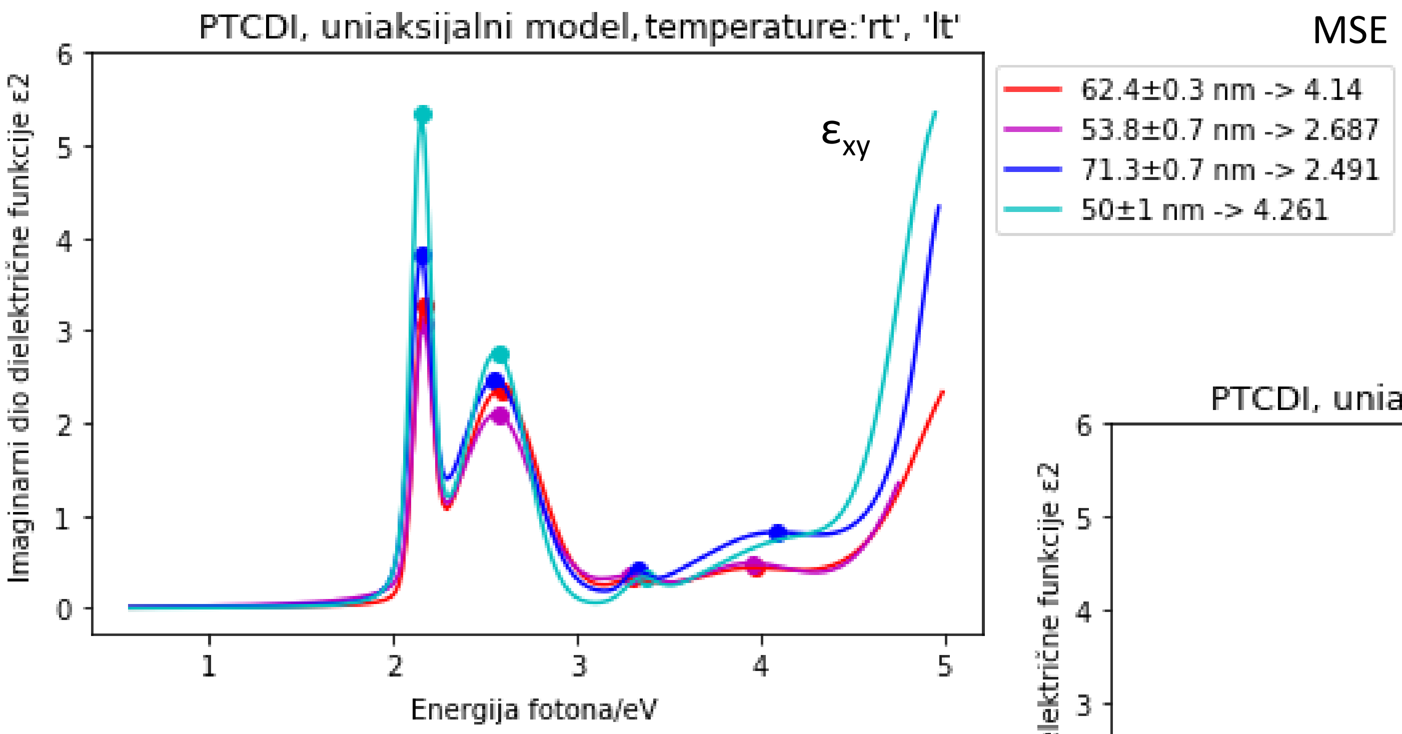


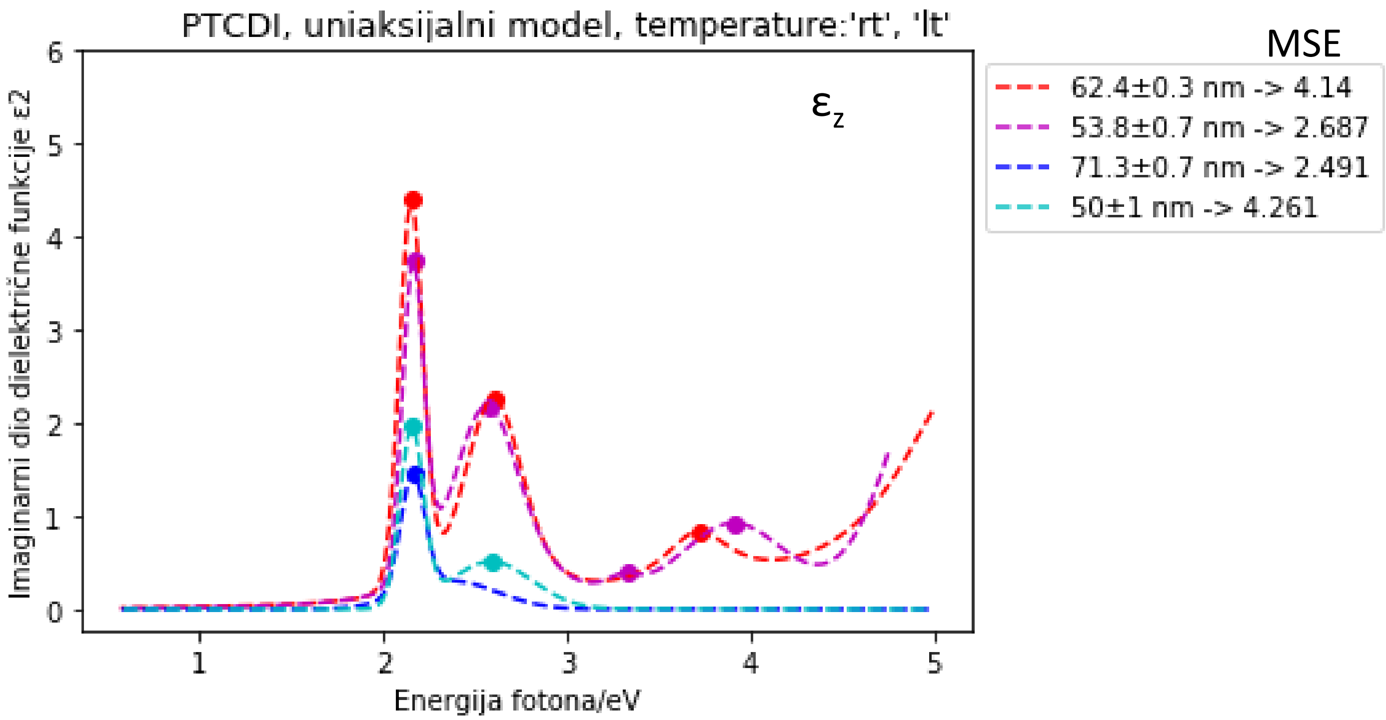
PTCDI, uniaksijani model: -160°C



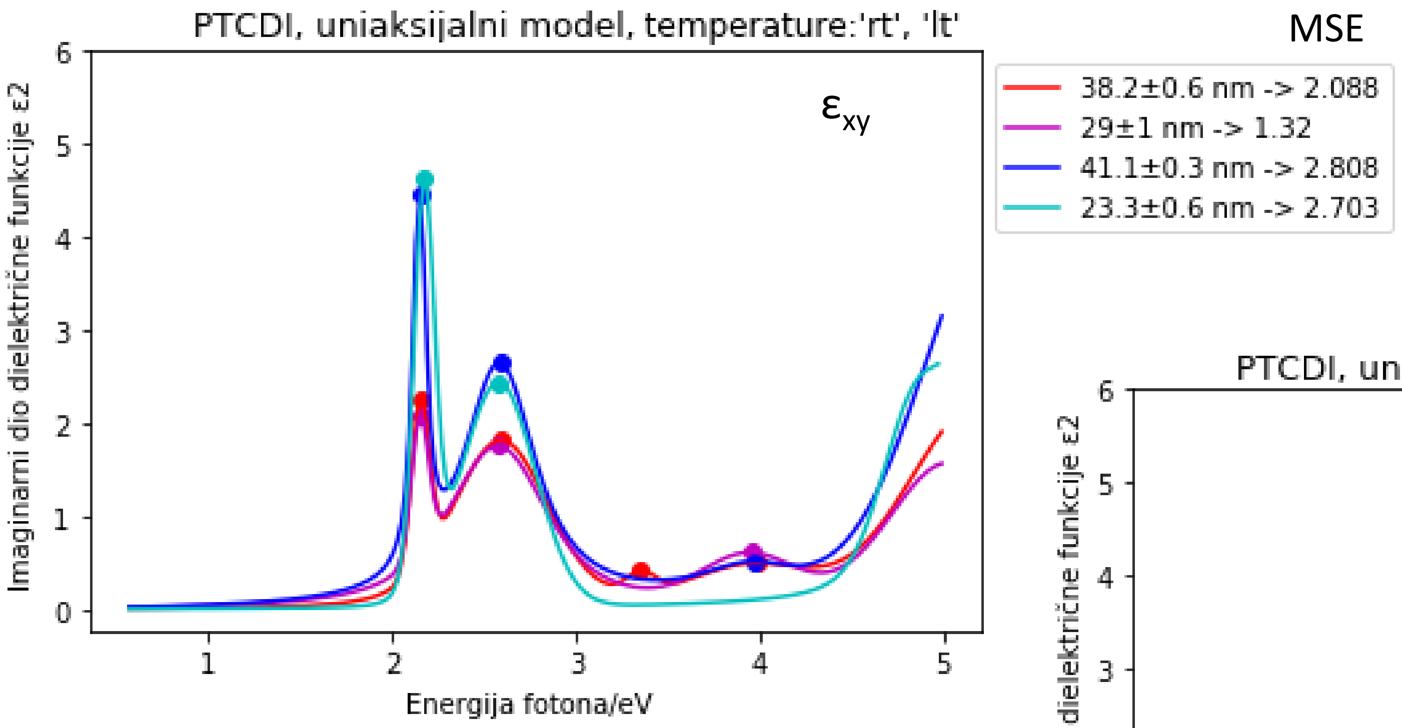


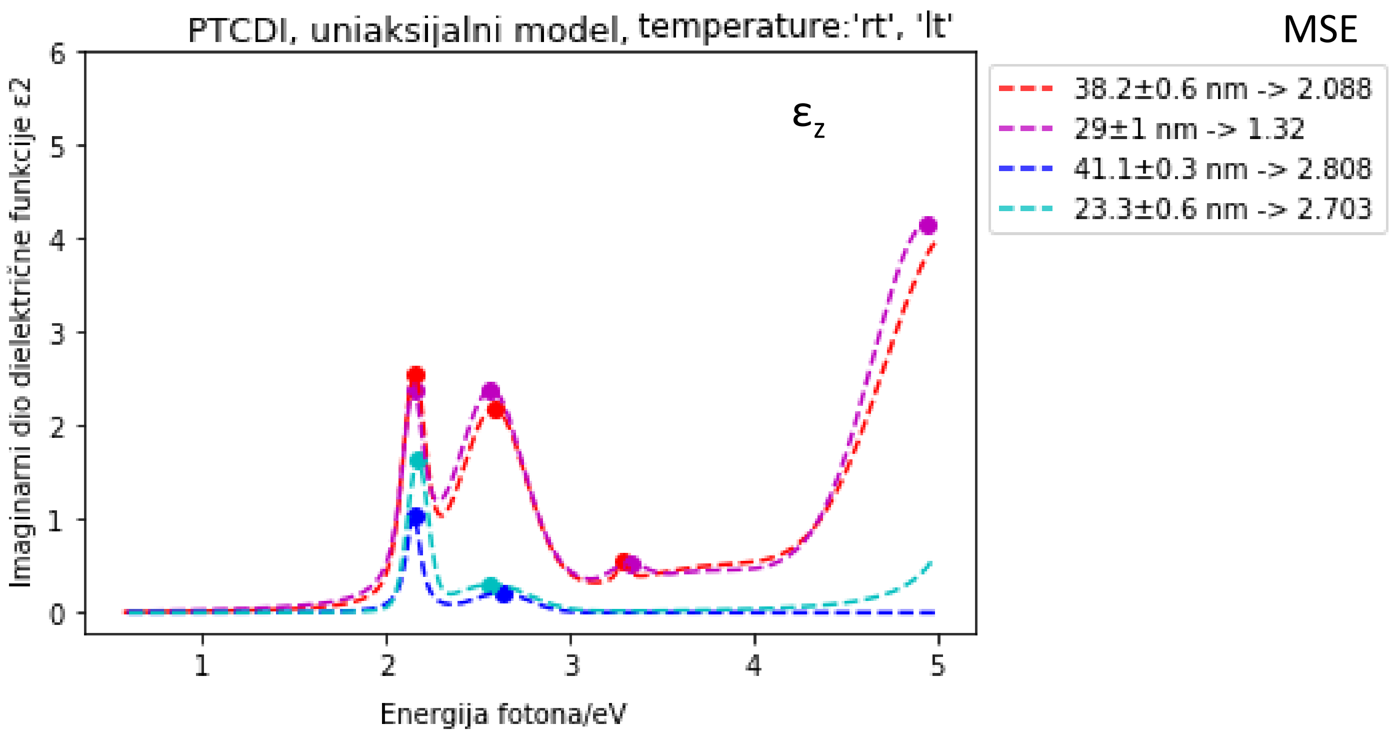
PTCDI, uniaksijani model: Deblji slojevi





PTCDI, uniaksijani model: Tanji slojevi





Zaključak

	H_2Pc				PTCDI			
	Debljina ↑				Debljina ↑			
	ε_{xy}		ε_z		ε_{xy}		ε_z	
	E	Amp	E	Amp	E	Amp	E	Amp
RT	* B vrpca; ↓	↓	B vrpca; ↓	* ↓	.	↑	.	↑
LT	.	↑	.	↑	.	↑	.	↑

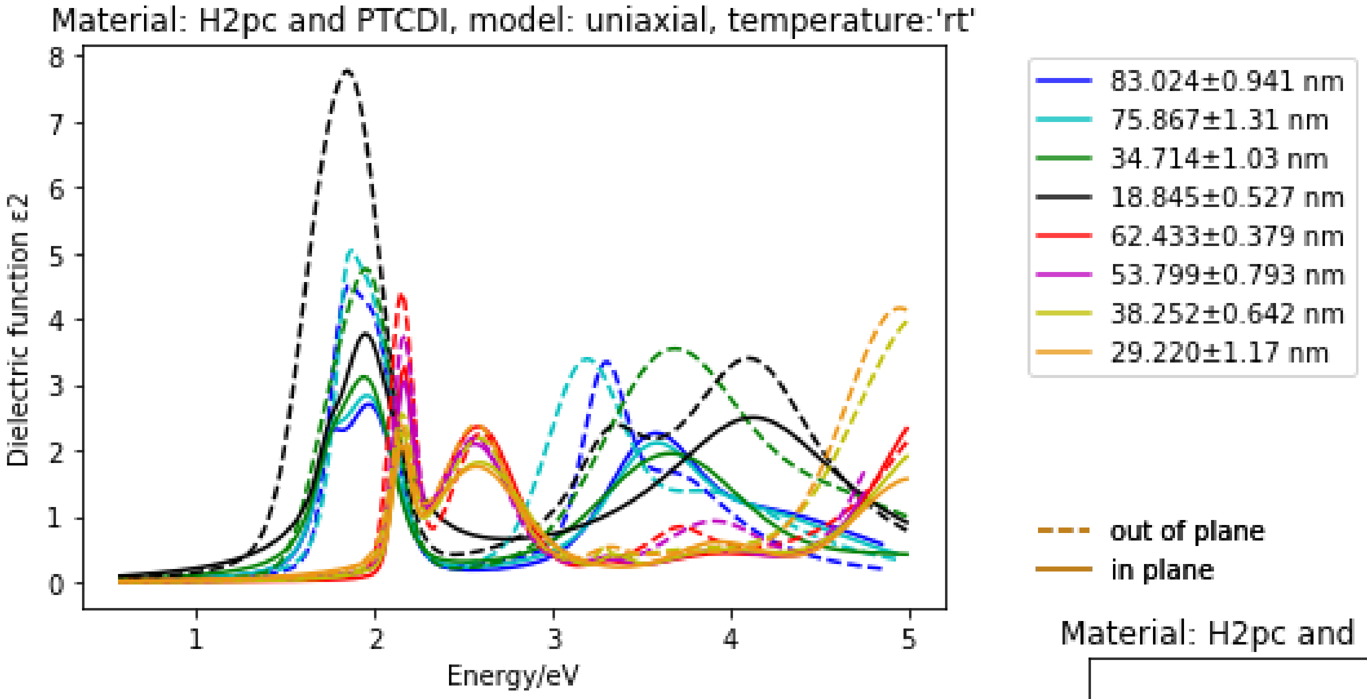
	H_2Pc				PTCDI			
	ε_{xy}		ε_z		ε_{xy}		ε_z	
	E	Amp	E	Amp	E	Amp	E	Amp
Temp ↑	N	↓	N	↑	.	↓	C vrpca!	↑

	H_2Pc				PTCDI			
	RT		LT		RT		LT	
	E	Amp	E	Amp	E	Amp	E	Amp
||→⊥	.	↑	.	N	.	↑	C vrpca ?	↓

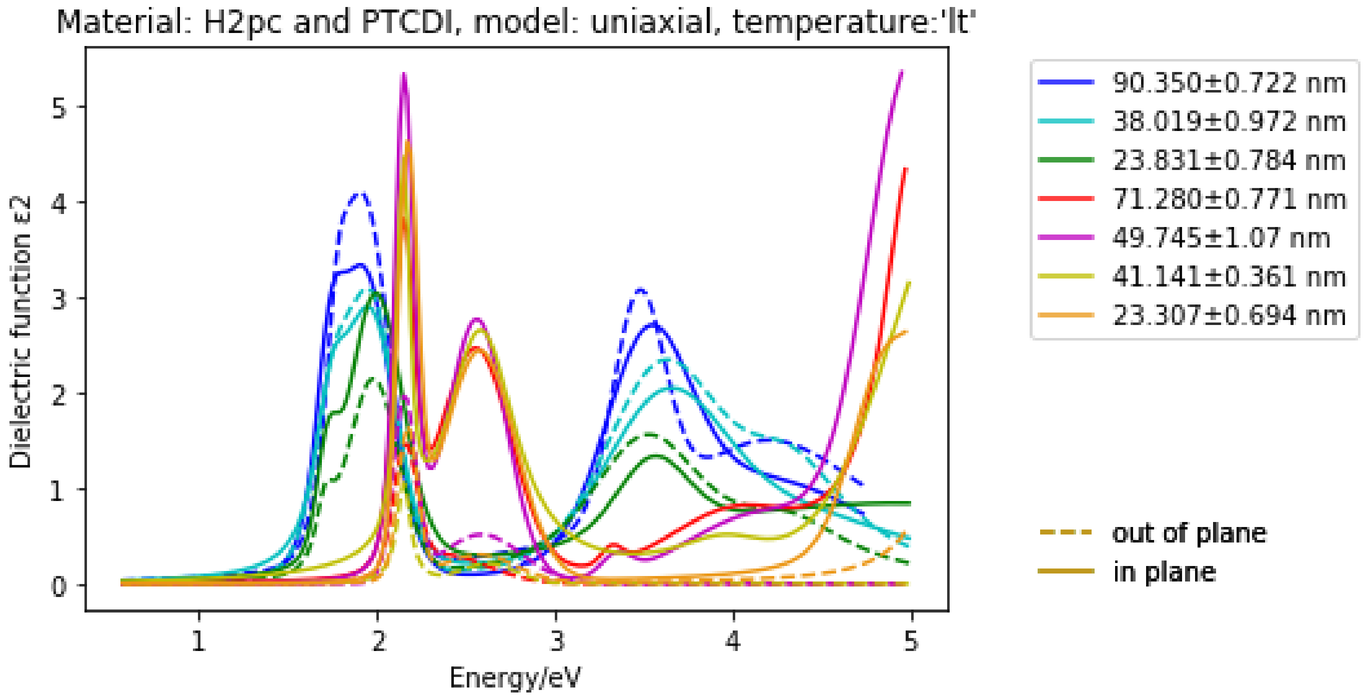
Zaključak

- Elipsometrija = moćna metoda za optičku karakterizaciju materijala
- Izotropni model nedovoljan za modeliranje H_2Pc i PTCDI tankih slojeva
- Nužno koristiti anikasijani model
- Zamiješćena ovisnost ε_{xy} i ε_z o debljini i temperaturi za oba materijala
- Veliki utjecaj temperature depozicije na komponentu ε_z uzorka PTCDI-a
- Hrapavost u modelu?
- Potvrda modela?

Hvala na pažnji!



Material: H2pc and PTCDI, model: uniaxial, temperature:'rt'
Dielectric function ε2
Energy/eV
83.024±0.941 nm
75.867±1.31 nm
34.714±1.03 nm
18.845±0.527 nm
62.433±0.379 nm
53.799±0.793 nm
38.252±0.642 nm
29.220±1.17 nm
out of plane
in plane



Material: H2pc and PTCDI, model: uniaxial, temperature:'lt'
Dielectric function ε2
Energy/eV
90.350±0.722 nm
38.019±0.972 nm
23.831±0.784 nm
71.280±0.771 nm
49.745±1.07 nm
41.141±0.361 nm
23.307±0.694 nm
out of plane
in plane