Structure – Composition - Property Relations Of Fluoromolecular Fluids For 157 nm Immersion Lithography

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Effect of Fluid Index On Effective Wavelength

- Effective Lithography Wavelength
  - –Determined By Litho Wavelength
  - –& Immersion Fluid Index of Refrac.
    - **High Index 193i Fluids** ➔

$$\lambda_{eff} \approx \lambda_{litho} / n_{IF}$$

- **157i Immersion Fluids** ➔

Litho Wave-length	Fluid Index	Effective Wave length
193.4 nm	**1.436 (Water)**	**134.7 nm**
193.4 nm	1.53 (??)	**126.4 nm**
193.4 nm	1.60 (??)	**120.9 nm**
157.6 nm	1.316 (IF24)	**119.8 nm**
157.6 nm	1.326 (IF48)	**118.9 nm**
157.6 nm	1.329 (IF26)	**118.6 nm**
157.6 nm	1.366 (IF43)	**115.4 nm**
157.6 nm	1.436 (??)	**109.7 nm**
157.6 nm	1.53 (??)	**103 nm**
157.6 nm	1.60 (??)	**98.5 nm**

- **Immersion Fluid Property Goals**
- First Goal: Optical Absorbance < 0.4/cm = 1mm working distance
- Second Goal: High Refractive Index
- Other Critical Optical Variables
  - –$dn/dT < -1x10^{-4}/^oC$, $dn/d_\lambda < 0.002/nm$,
  - –Radiation Durable

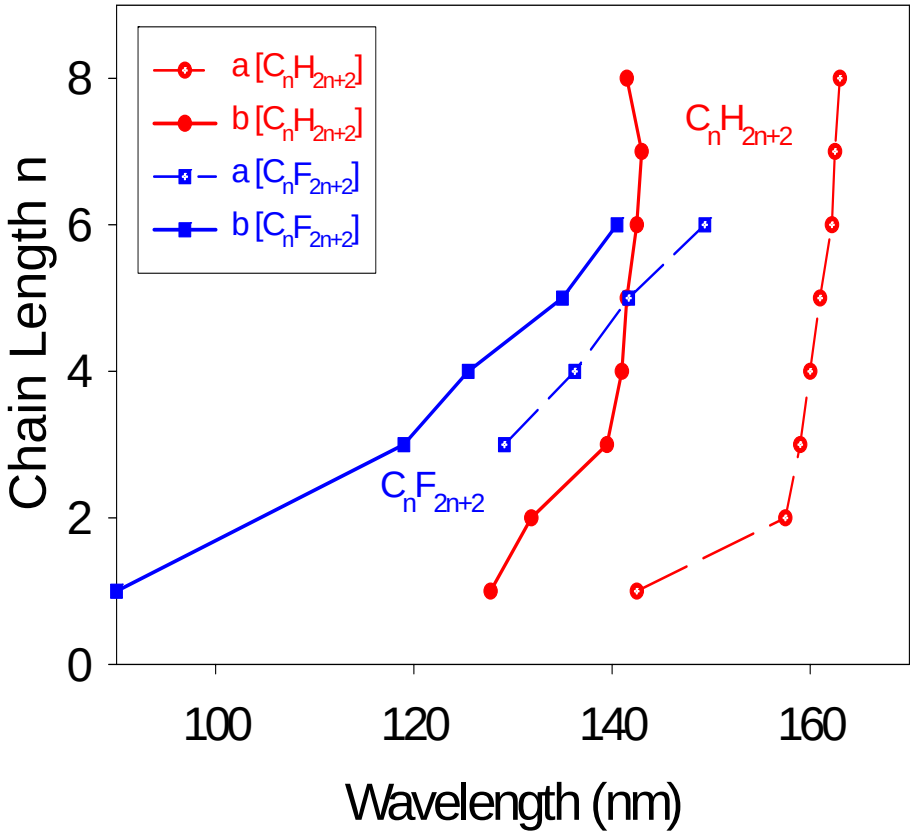
Outline

- Optical Absorbance:
  Structure Property Relations
- Index of Refraction:
  Of 157 nm Immersion Fluids
- Optical Perspectives:
  High Index & Low Absorbance
- Conclusions

Optical Absorbance: Fluoromolecular Structure Property Relations

Structure: Role Of Bond Alternation On Absorbance

- Consider Short Chain Paraffin
  - –Perfluoroalkyl Chains

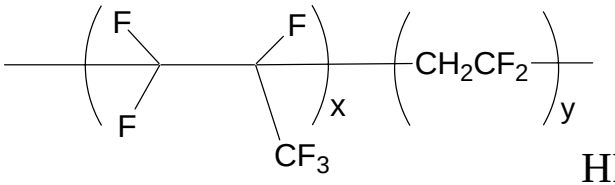


- Positions of Absorptions
  - –a = 1st Shoulder (dashed)
  - –b = 1st Maxima (solid)

- 1. Hydrocarbon Absorptions
  - –Occur At Longer Wavelengths
  - –Than Fluorocarbon Absorptions
- 2. Abs. Shifts To Long Wavelength
  - –With Increasing Chain Length
  - –$H(CH_2)_nH$ Absorbs for n > 1 to 2
  - –$F(CF_2)_nF$ Absorbs for n > 7 to 10
- To Achieve Transparency?
  - –Promote Bond Alternation
  - –To Break Up σ Bond Conjugation
- From Our Pellicle Polymer Work
  - –Vinylidene Fluoride Monomer

$$CH_2{=}CF_2$$

  - –Yield Intrinsically Alternating Polymer

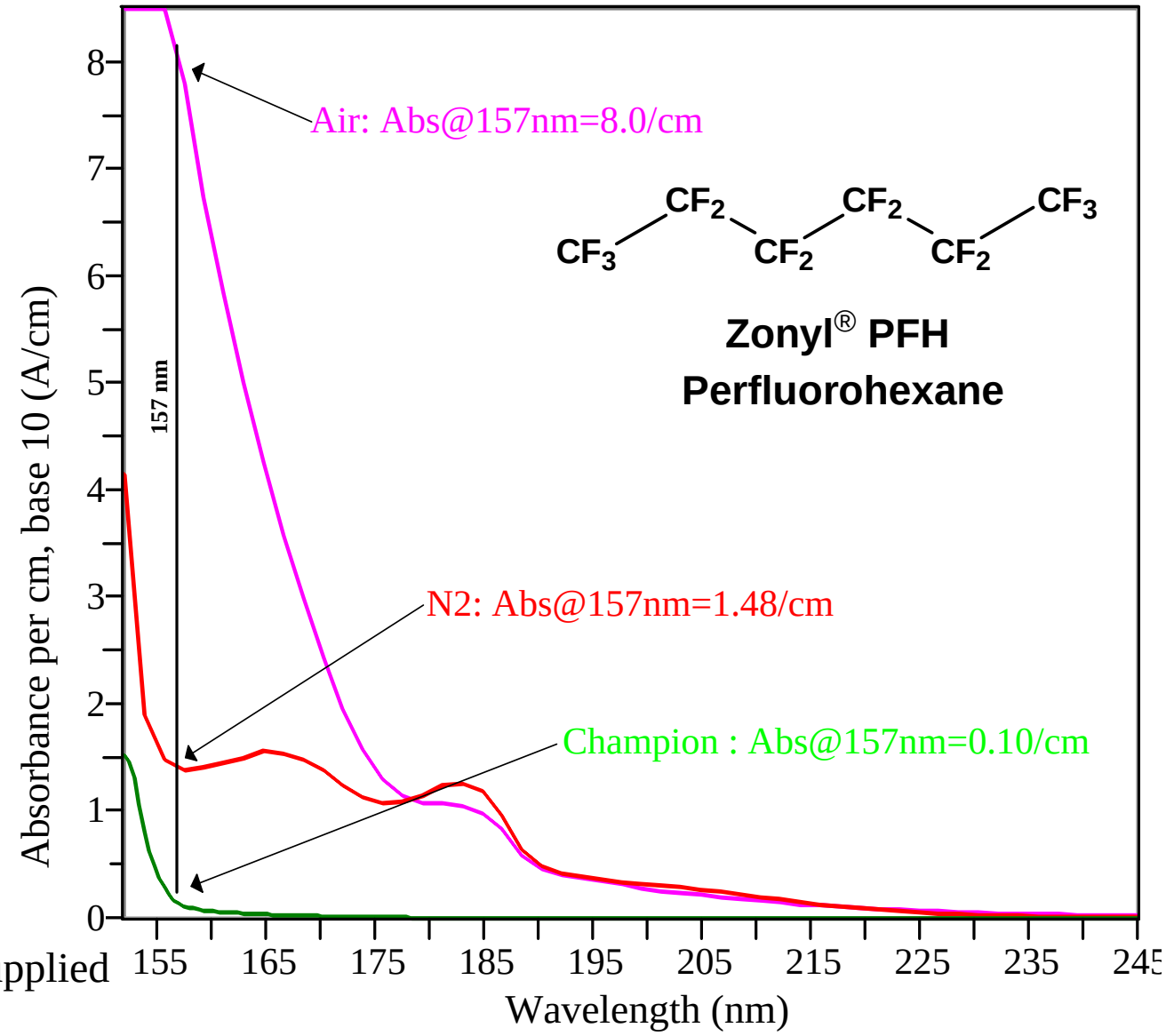


HFP/VF2

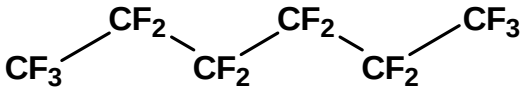
R. H. French et al., **Journal of Fluorine Chemistry**, **122**, 63-80, (2003).

Perfluorohexane Champion Result

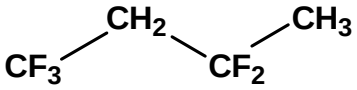
- A(157nm) = 0.10/cm
  - –0.10 to 0.18/cm
- Low Abs. Requires
  - –Oxygen Removal
  - –Water Removal
  - –Chemical Purification
- **Next: Rapid Screening**
  - –Measure Compounds as Supplied
  - –Force Interpretation
  - –Proof of Correlations By Success At Achieving Low Absorbance



Acyclic Alkanes $C_nF_{2n+2-x}H_x$: H/F Ratio

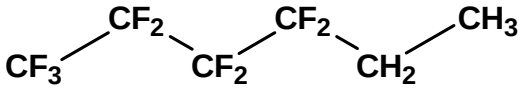


Perfluorohexane



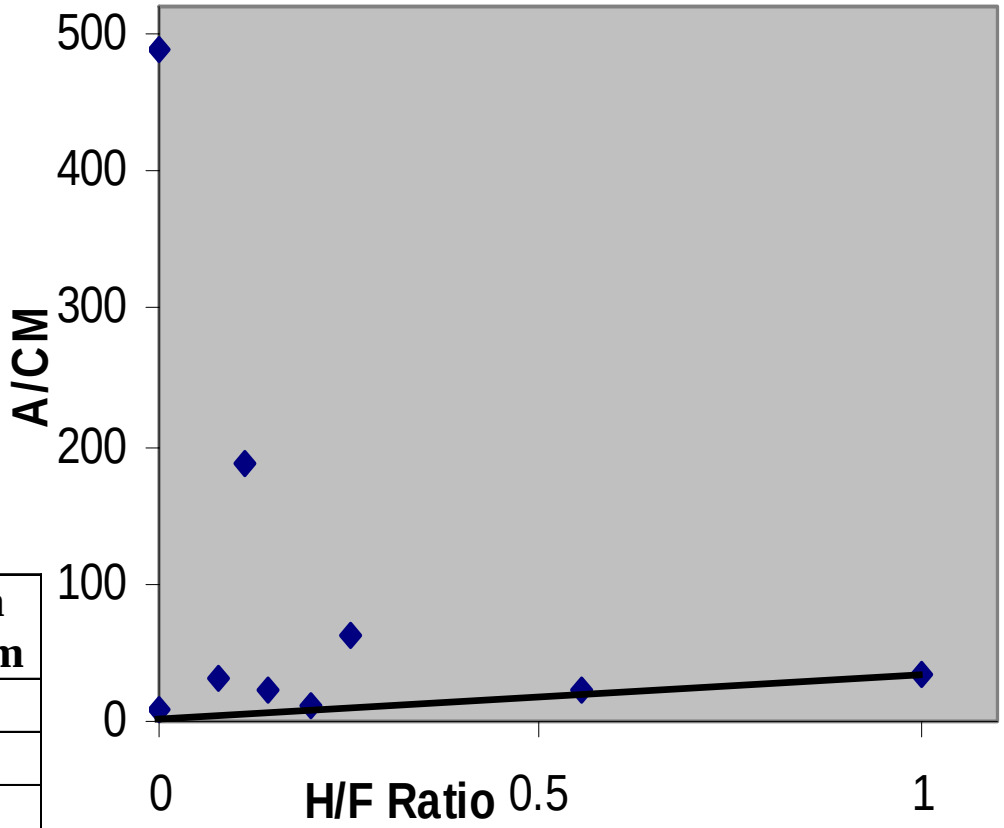
Solkane®

1,1,1,3,3-pentafluorobutane



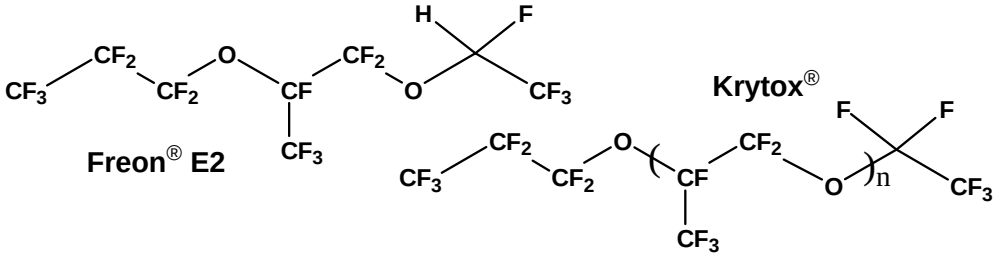
1,1,1,2,2,2,3,3,4,4-nonafluorohexane

#	Structure	A/cm 157 nm
	Acyclic Alkanes $C_nF_{2n+2-x}H_x$	
20	$F(CF_2)_6F$, perfluorohexane	9
21	C_8F_{18}, mixed perfluorooctanes	490
22	$\mathbf{H}(CF_2)_6F$, 1-H-perfluorohexane	32
23	$C_9F_{18}\mathbf{H_2}$, mixed di and trihydro	188
24	$CF_3CF_2\mathbf{CFHCFH}CF_2CF_2CF_3$	24
25	$CF_3\mathbf{CFHCFH}CF_2CF_3$	10
26	$\mathbf{H}(CF_2)_4\mathbf{H}$	63
27	$CF_3CF_2CF_2CF_2\mathbf{CH_2CH_3}$	22
28	$CF_3\mathbf{CH_2}CF_2\mathbf{CH_3}$, Solkane® 365 mfc	33

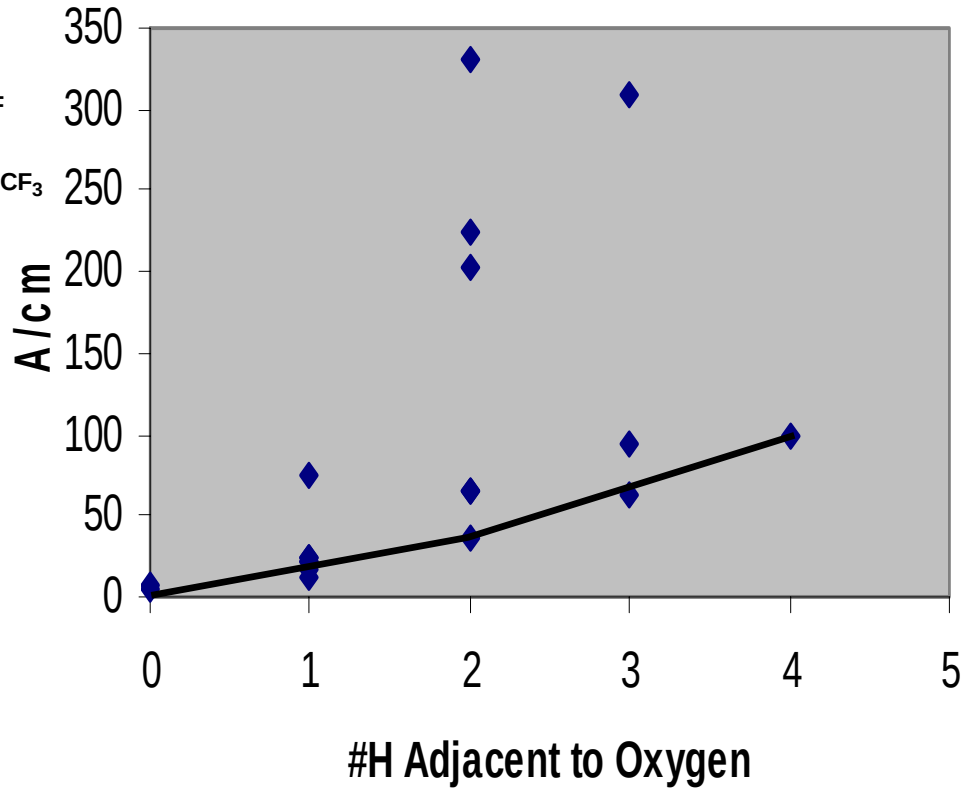


- Count Number of H and F Atoms
  - –Plot H/F Ratio vs. A/cm at 157 nm
- Increasing H/F Ratio Leads To Weak Increase in A/cm

Acyclic $C_nF_{2n+2-x}H_xO_y$ Ethers: α Hydrogens



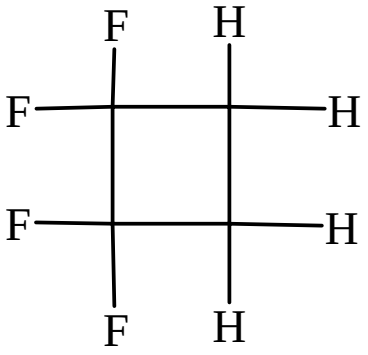
#	Structure		A/cm 157 nm
	Acyclic $C_nF_{2n+2-x}H_xO_y$ Ethers, ≤ 1 -OCH-		
1	$F[CF(CF_3)CF_2\mathbf{O}]_1\mathbf{CFH}CF_3$	Freon® E1	76
2	$F[CF(CF_3)CF_2\mathbf{O}]_2\mathbf{CFH}CF_3$	Freon® E2	20
3	$F[CF(CF_3)CF_2\mathbf{O}]_3\mathbf{CFH}CF_3$	Freon® E3	24
4	$F[CF(CF_3)CF_2\mathbf{O}]_4\mathbf{CFH}CF_3$	Freon® E4	22
5	$F[CF(CF_3)CF_2\mathbf{O}]_5\mathbf{CFH}CF_3$	Freon® E5	22
6	$F[CF(CF_3)CF_2\mathbf{O}]_9\mathbf{CFH}CF_3$	Freon® E9	12
7	$\mathbf{HCF_2}(OCF2)_m(OCF2CF2)_n\mathbf{CF_2H}$	H-Galden®	37
8	$F[CF(CF_3)CF_2O]_nCF_2CF_3$, dried	Krytox®	7
	Acyclic $C_nF_{2n+2-x}H_xO_y$ Ethers, ≥ 2 -OCH-		
9	$CF_3\mathbf{CH_2O}CF_2CHF_2$		64
10	$CF_3\mathbf{CH_2O}CF_2CFHCF_3$		202
11	$HCF_2CF_2\mathbf{CH_2O}CF_2CF_2H$		80
12	$HCF_2CF_2\mathbf{CH_2O}CF_2CF_2CF_3$		330
13	$CF_3CF_2CF_2O\mathbf{CFH}CF_2\mathbf{OCH_2}CF_3$		310
14	HCF2CF2**OCH2CH2O**CF2CF$_2$H		100
15	$HCF_2CF(CF_2CF_3)\mathbf{OCH_2}CF_3$		430
16	$CF_3CF(CF_3)CF(\mathbf{OCH_2}CH_3)CF_2CF_2CF_3$		>1800
17	$HCF_2C(\mathbf{OCH_2}CF_3)(CFHCF_3)_2$		5600
18	$(CF_3)_2CFCF_2\mathbf{OCH_3}$ + $\mathbf{CH_3O}(CF_2)_3CF_3$		62
19	$\mathbf{CH_3O}CF_2CFHCF_3$		94



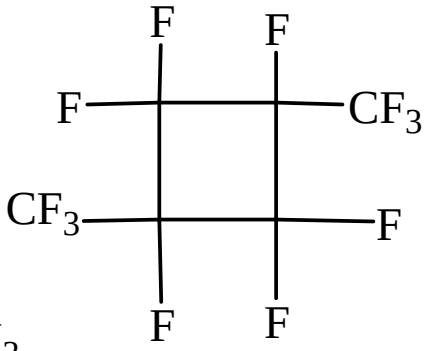
- Count Number of Hydrogens α to Ether Oxygen
  - –Plot versus A/cm at 157 nm
- A/cm at 157 nm Increases With Number of α Hydrogens

Cyclic Fluorocarbons: Absorb Strongly at 157 nm

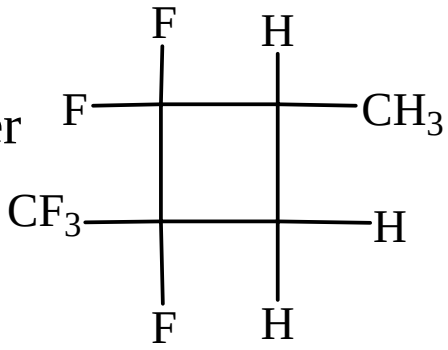
- Cyclobutanes



TFE/E Cyclic Dimer
A/cm > 2000



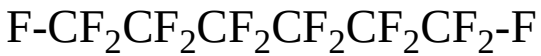
HFP Cyclic Dimer
A/cm = 1000



HFP/P Cyclic Dimer
A/cm > 2000

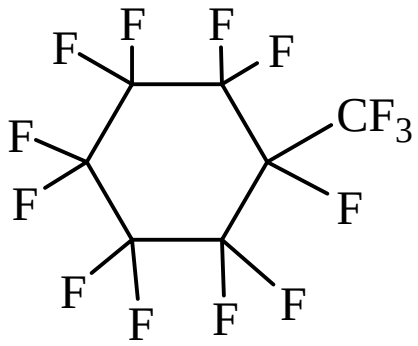
- Four Membered Rings
  20 to 5000X More Absorbing
  Than Acyclic Analogs

Poly(PPVE/Ethylene)
A/cm $\leq$ ~100



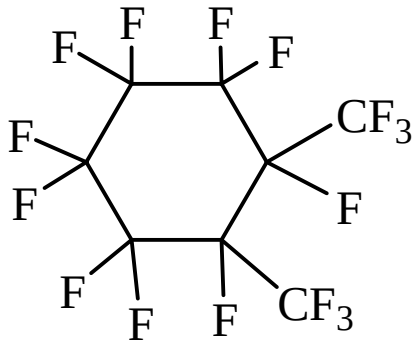
Perfluorohexane
A/cm = 0.2

6 Membered Rings Also Absorb Strongly



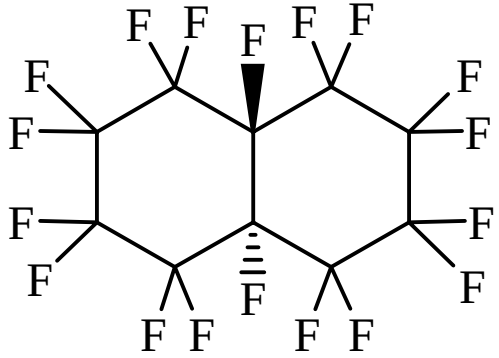
Perfluoromethylcyclohexane

A/cm = 634



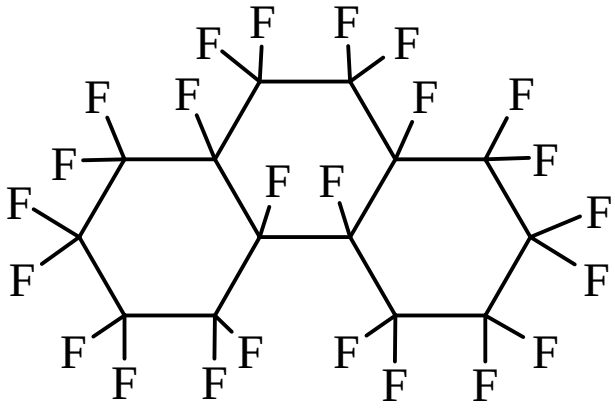
Perfluoro-1,2-dimethylcyclohexane

A/cm = 317



Perfluorodecalin

A/cm > 2000



Perfluorotetradecahydrophenanthrene

A/cm > 2000

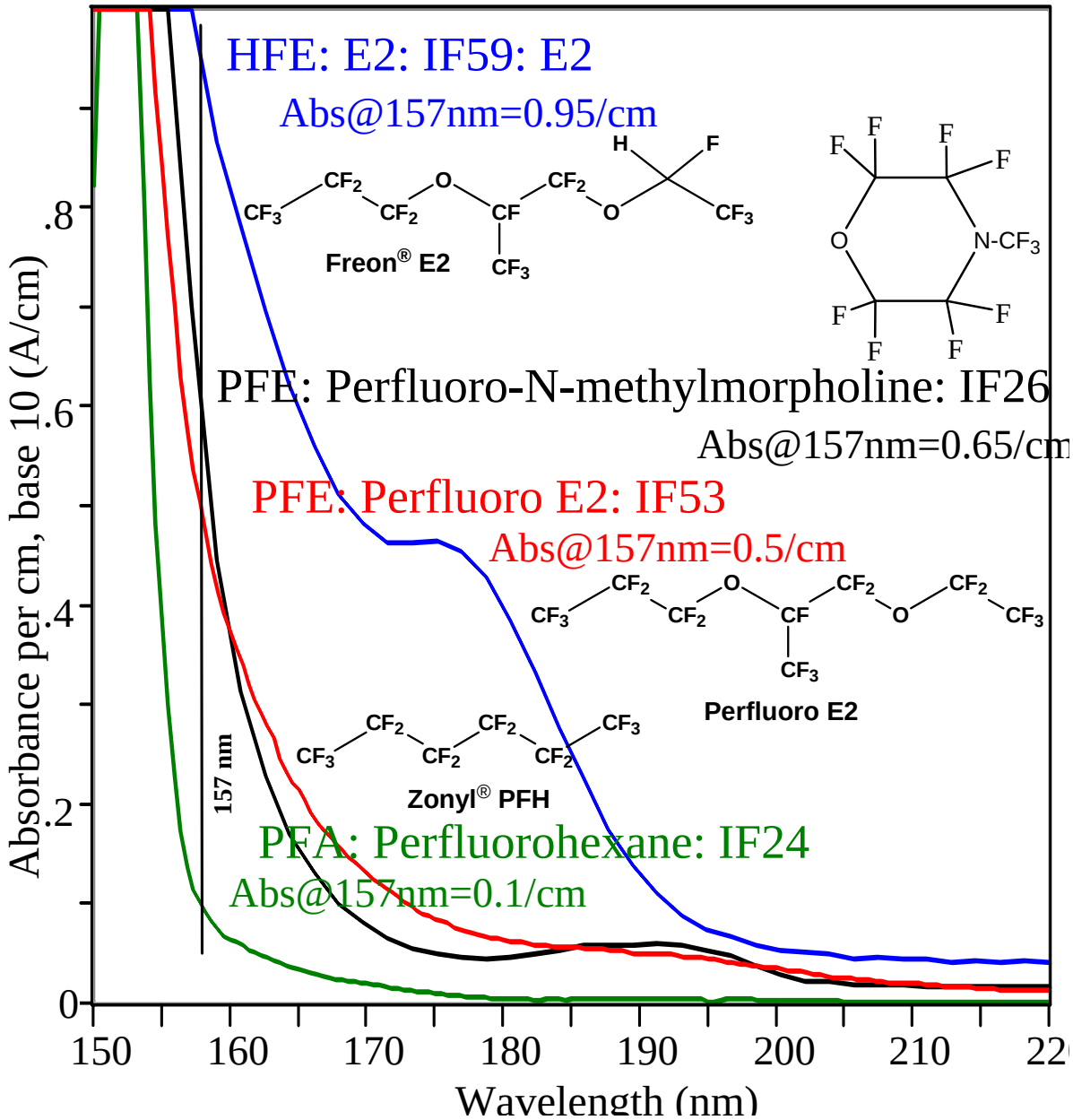
- 6 Membered Rings Also Absorb Strongly at 157 nm

Structure-Property Relations For Absorbance

- "Intrinsic" Absorbance At 157 nm Is Masked By
  - –Dissolved Gases And Water
  - –Undesirable Organic Contaminants
- Results From Initial Rapid Screening:
- Good for Transparency
  - –Bond Alternation to Break Up Conjugation
    - »e.g. CF_2/CH_2 or CF_2/O
  - –Acyclic Fluoroalkanes
  - –Acyclic Fluoroethers
- Bad for Transparency
  - –Rings in Fluorocarbons (4 and 6 Member Rings)
  - –High Hydrogen Content
  - –Hydrogen Alpha to Ether Oxygen

Examples Of The Immersion Fluid Classes

- **Perfluoroalkane**
  - –Perfluorohexane:
    A=0.1/cm
- **Perfluoroethers**
  - –Perfluoro-N-methylmorpholine:
    A=0.65/cm
  - –Perfluoro E2:
    A=0.5/cm
- **Hydrofluoroethers**
  - –E2:
    A=0.95/cm
- Essential Requirements
  - –Oxygen Removal
  - –Water Removal
  - –Chemical Purification



Index of Refraction
Of 157 nm Immersion Fluids

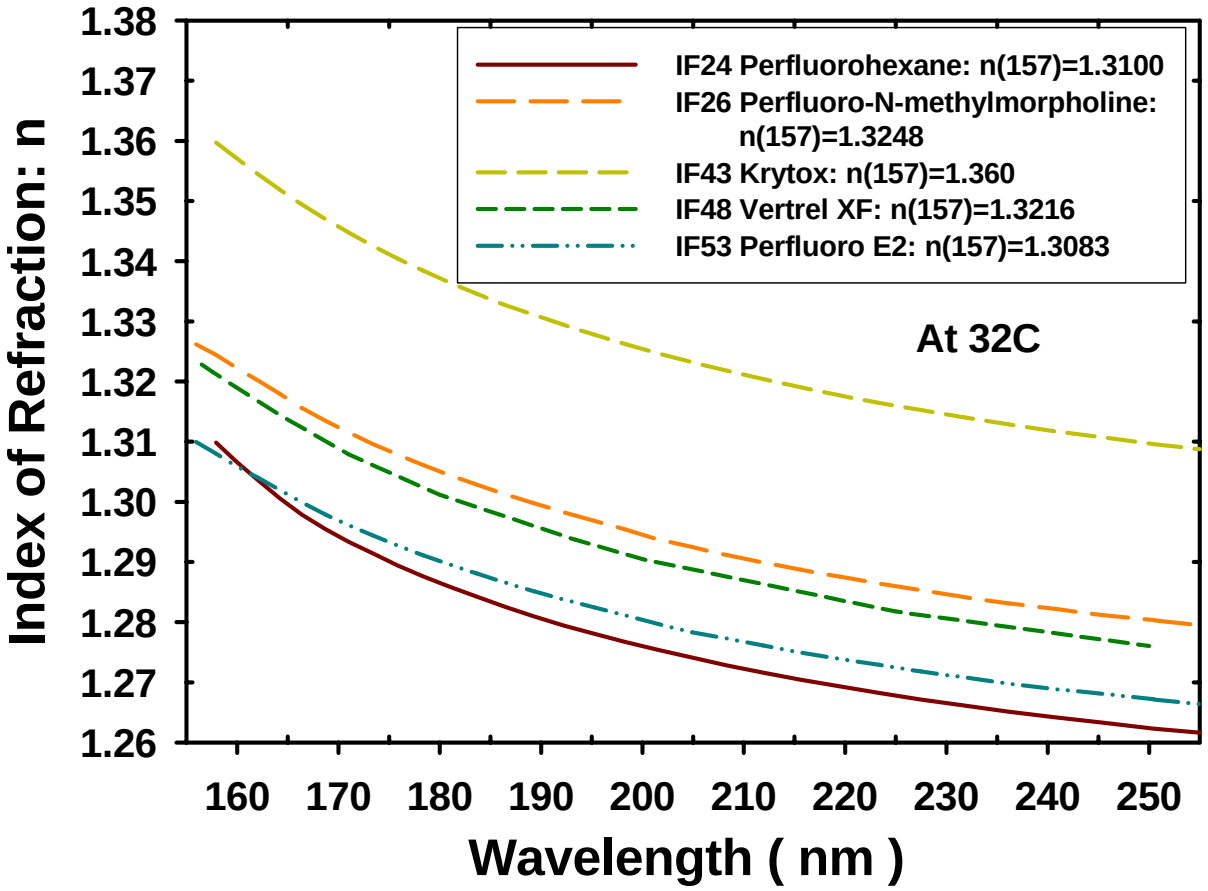
Refractive Indices of 4 Candidate Fluids

- Index By Two Methods
  - –Minimum Deviation Prism
  - –Hilger-Chance Refractometer
- Also Determined dn/dT

- Lower Index Values
  - –Compared To Water(193nm)
- Higher Temp. Dep. Of Index

- Krytox Perfluoroether
  - –A/cm at 157 nm = 1.1/cm
  - –Index at 31.5 °C = 1.360

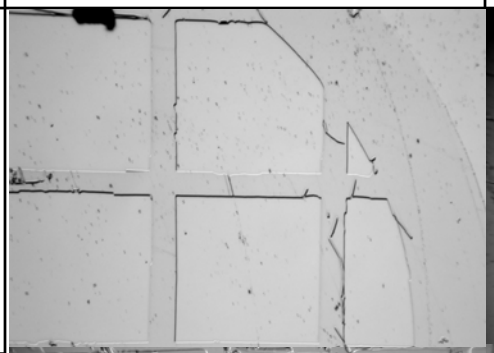
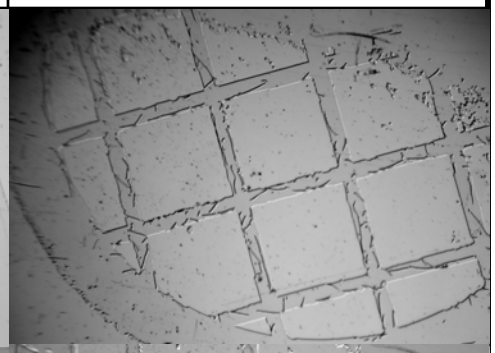
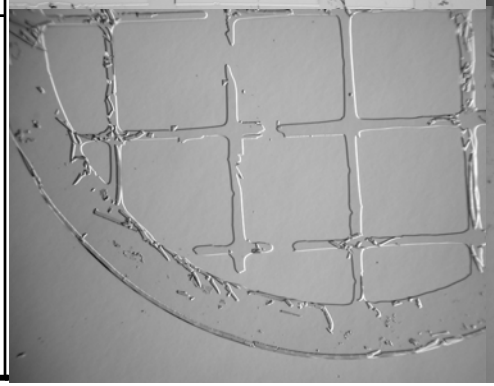
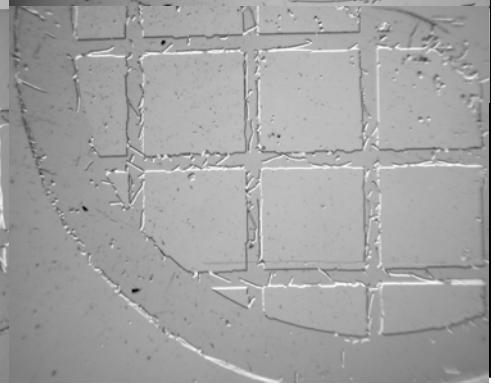
- Krytox n(21.5 °C) ~ 1.366
  - –Assuming dn/dT = -6 x 10-4
  - – $\lambda_{effective}$ = 115.4 nm



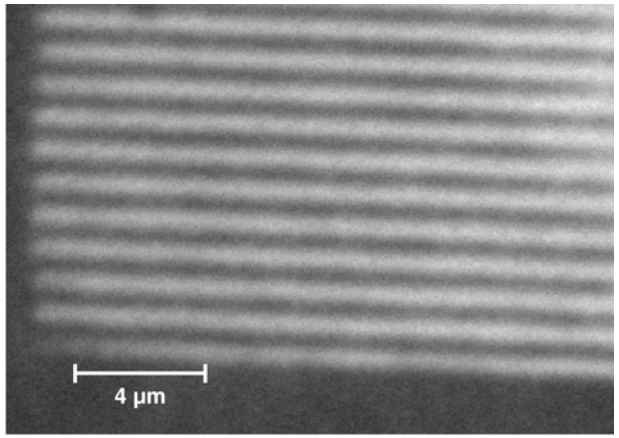
Sample	*n* (21.5 °C)	d*n*/d*T* (°C) (21.5 °C)
IF24 (157 nm)	$1.315{,}62 \pm 1 \times 10^{-4}$	-5.83×10^{-4} / °C
IF26 (157 nm)	$1.329{,}46 \pm 1 \times 10^{-4}$	-7.63×10^{-4} / °C
IF48 (157 nm)	$1.326{,}34 \pm 1 \times 10^{-4}$	-6.45×10^{-4} / °C
Water (193 mm)	$1.436{,}62 \pm 2 \times 10^{-5}$	-1.00×10^{-4} / °C

157*i* Contact Printing: IF/Resist Compatibility

- Multiple Property Requirements
  - –For Immersion
- Simple Test Of Compatibility
  - –IF/Resist Compatibility
  - –IF Removal From Wafer
  - –Resist Development
- Method
  - –Use TEM Grid Contact Mask
    - »3mm Diameter
  - –157 nm Exposure
  - –IF Removal
  - –Resist PEB
  - –Resist Develop

Fluid	157*i* Immersion	Dry
PFH IF24		
PFE Krytox ® IF43		

- **Next MIT-LL 157*i* MicroStepper**
  - –More Detailed Imaging Results
- **0.5 μm 1:1 Dense Lines**
  - –Optical Micrograph .
  - –Initial Results .



Optical Perspective: High Index & Low Absorbance

Optical Properties & Electronic Structure

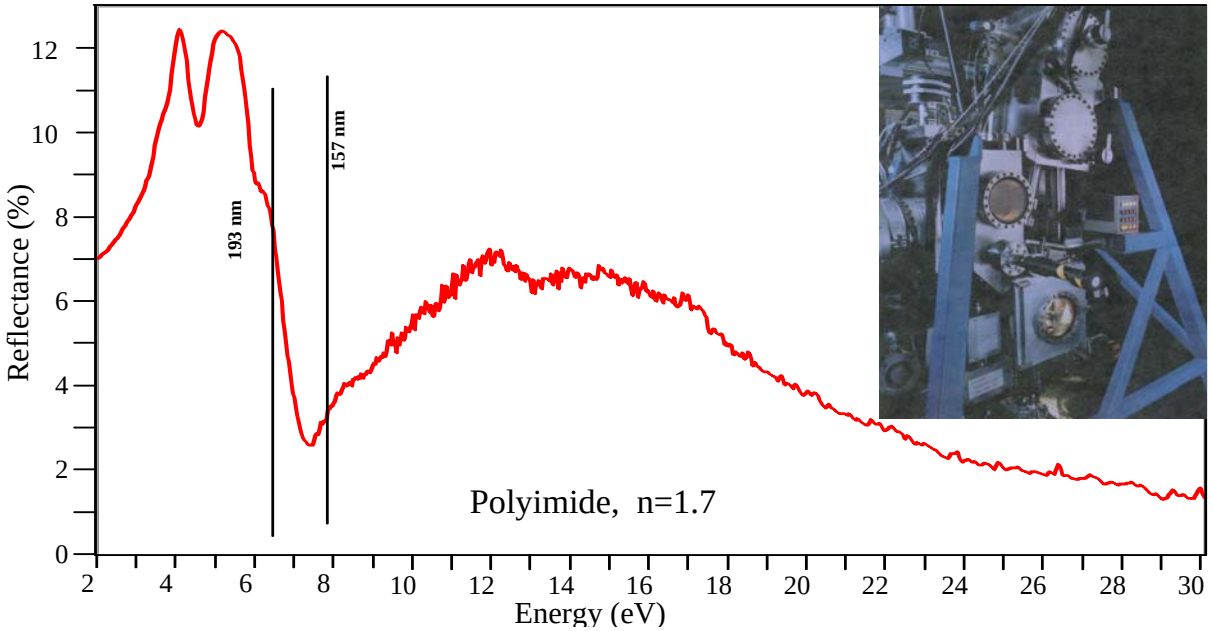
- **VUV Reflectance**
  - –2 to 40 eV
  - –600 nm to 30 nm

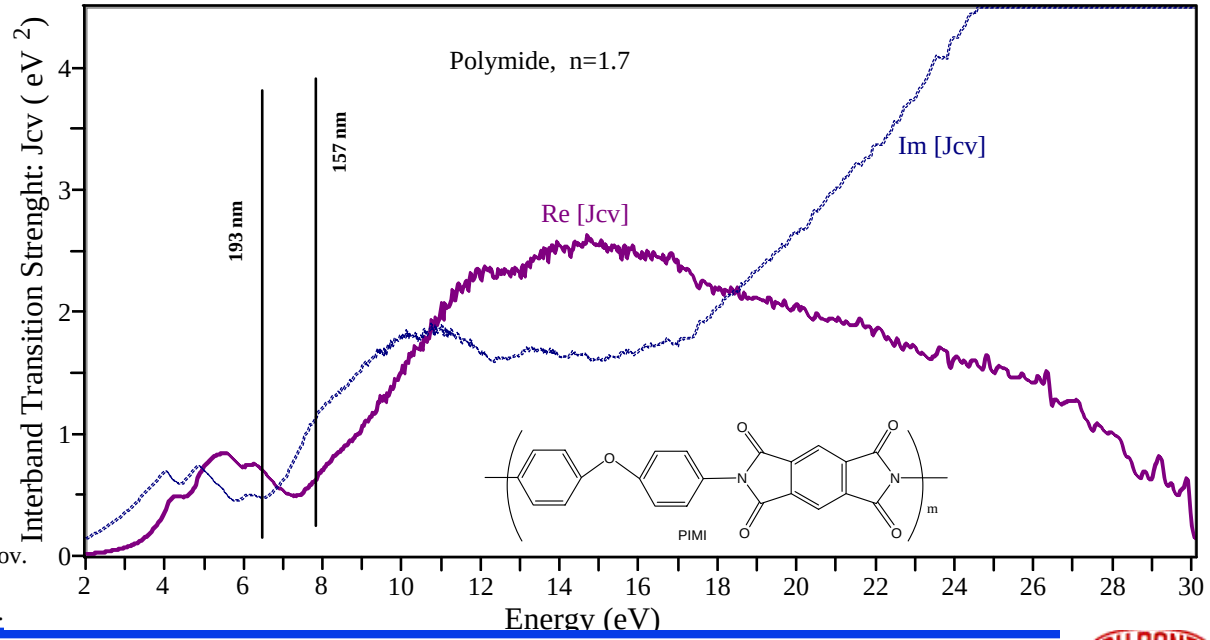
- **Kramers Kronig Dispersion Analysis**
  - –Recover Reflected Phase

$$\theta(E) = -\frac{2E}{\pi} \mathrm{P} \int_0^\infty \frac{\ln\{\rho(E')\}}{E'^2 - E^2} dE'$$

- **Interband Transition Strength**

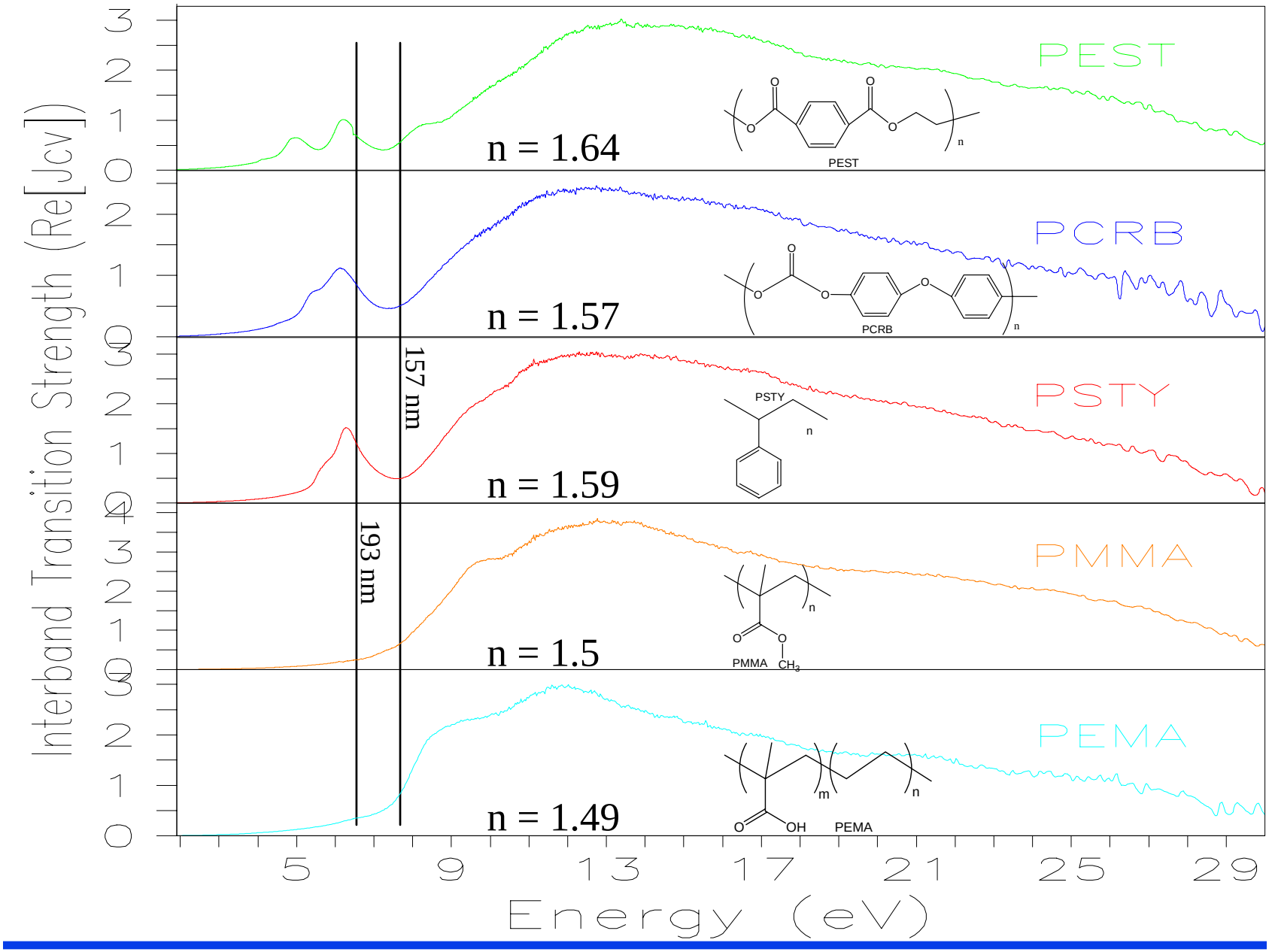
$$J_{cv} = i \frac{E^2}{8\pi^2} (\varepsilon_1 + i\varepsilon_2)^*$$



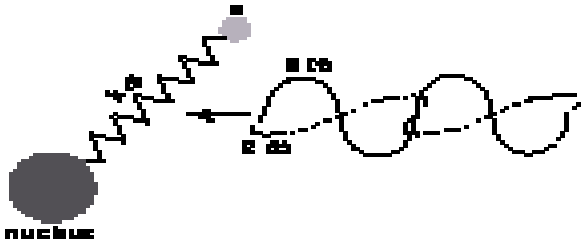


M. L. Bortz, R. H. French, Applied Physics Letters, 55, 19, 1955-7, Nov. 8, (1989). R. H. French, Physica Scripta, 41, 4, 404-8, (1990). M. L. Bortz, R. H. French, , Applied Spectroscopy, 43, 8, 1498-1501, (1989).

Electronic Structure of Polymers



The Lorentz Oscillator

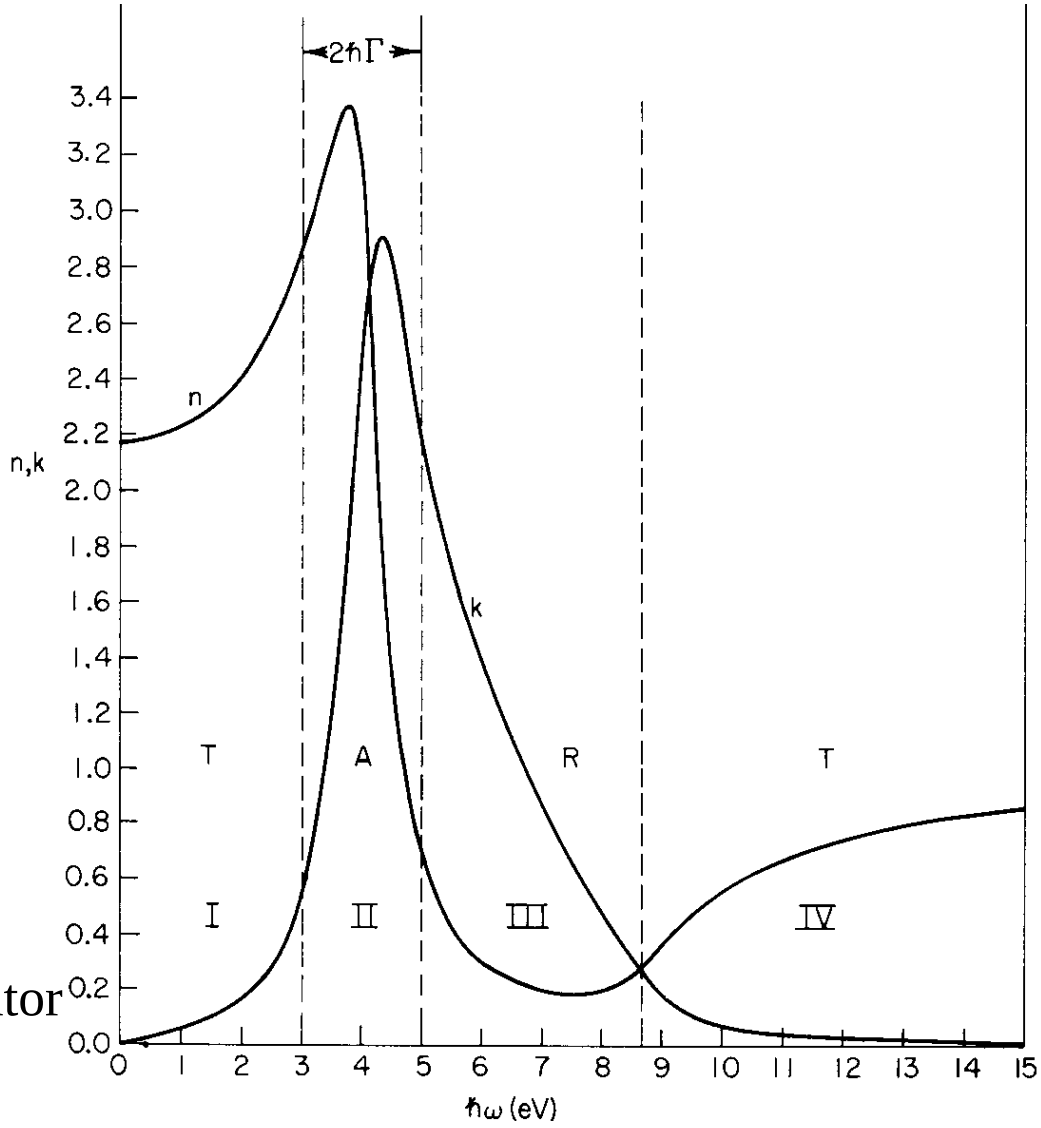


- Response of Charges To EM Wave
- Classical Lorentz Oscillator
  - –ε is Dielectric Constant
  - –ω is Frequency Variable

$$\hat{\varepsilon}(\omega) = 1 + \frac{4\pi N e^2}{m} \frac{1}{\left(\omega_o^2 - \omega^2\right) - i\Gamma\omega}$$

  - –Γ is Oscillator Width
  - –ω_o is Oscillator Frequency
  - –N is Electron Density
    - »Determines Area
- Quantum Mechanical Lorentz Oscillator
  - –f is the Oscillator Strength

$$\hat{\varepsilon}(\omega) = 1 + \frac{4\pi e^2}{m} \sum_j \frac{N f_j}{\left(\omega_j^2 - \omega^2\right) - i\Gamma_j\omega} \qquad \sum_j f_j = 1$$



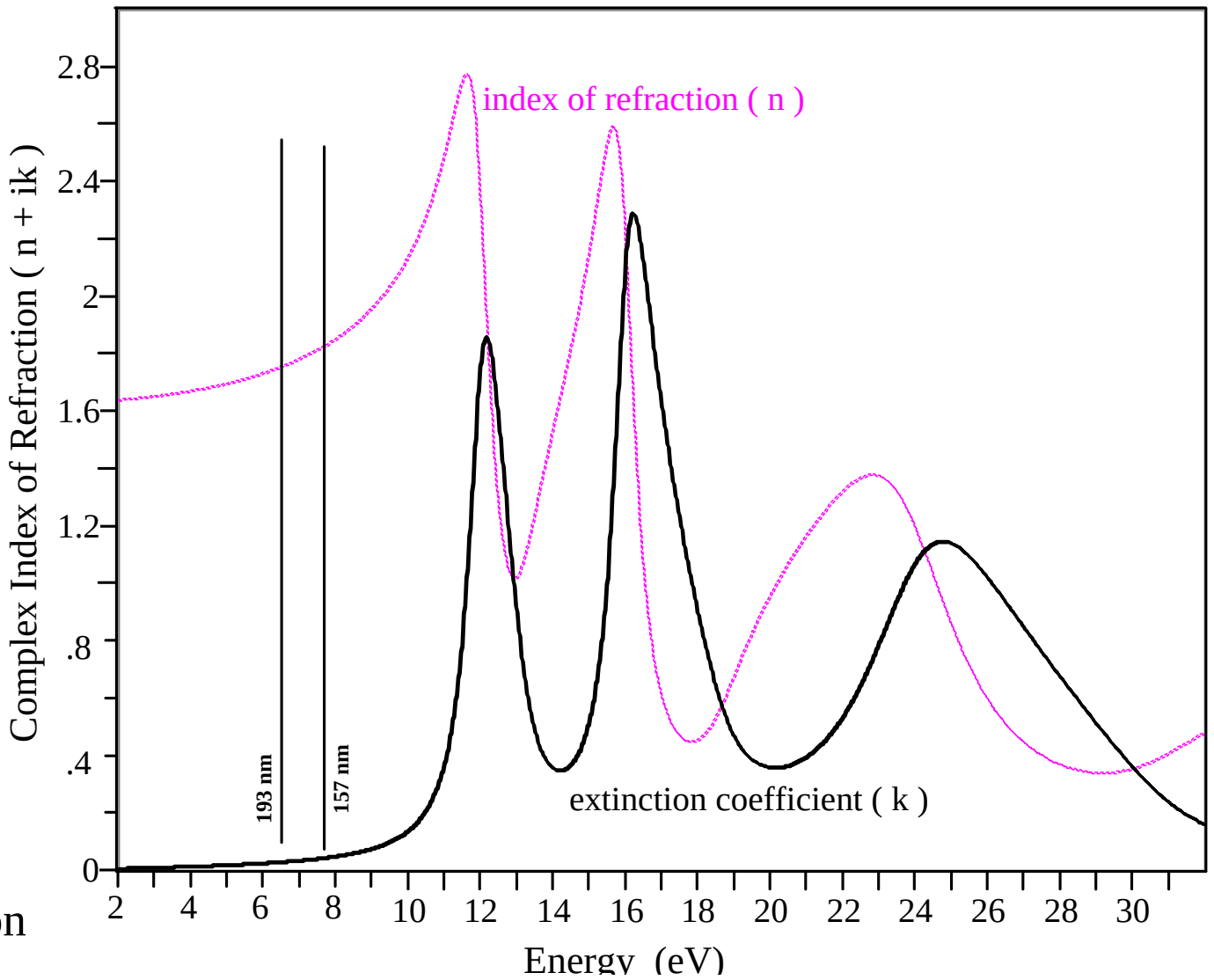
F. Wooten, **Optical Properties of Solids**, Academic Press, 1972.

Three Lorentz Oscillator Model

- LO Energies
  - –12, 16, 24 eV
- LO Widths
  - –1, 1, 4 eV
- Oscillator Strengths
  - –0.2, 0.3, 0.5
- Plasma Frequency
  - –22 eV

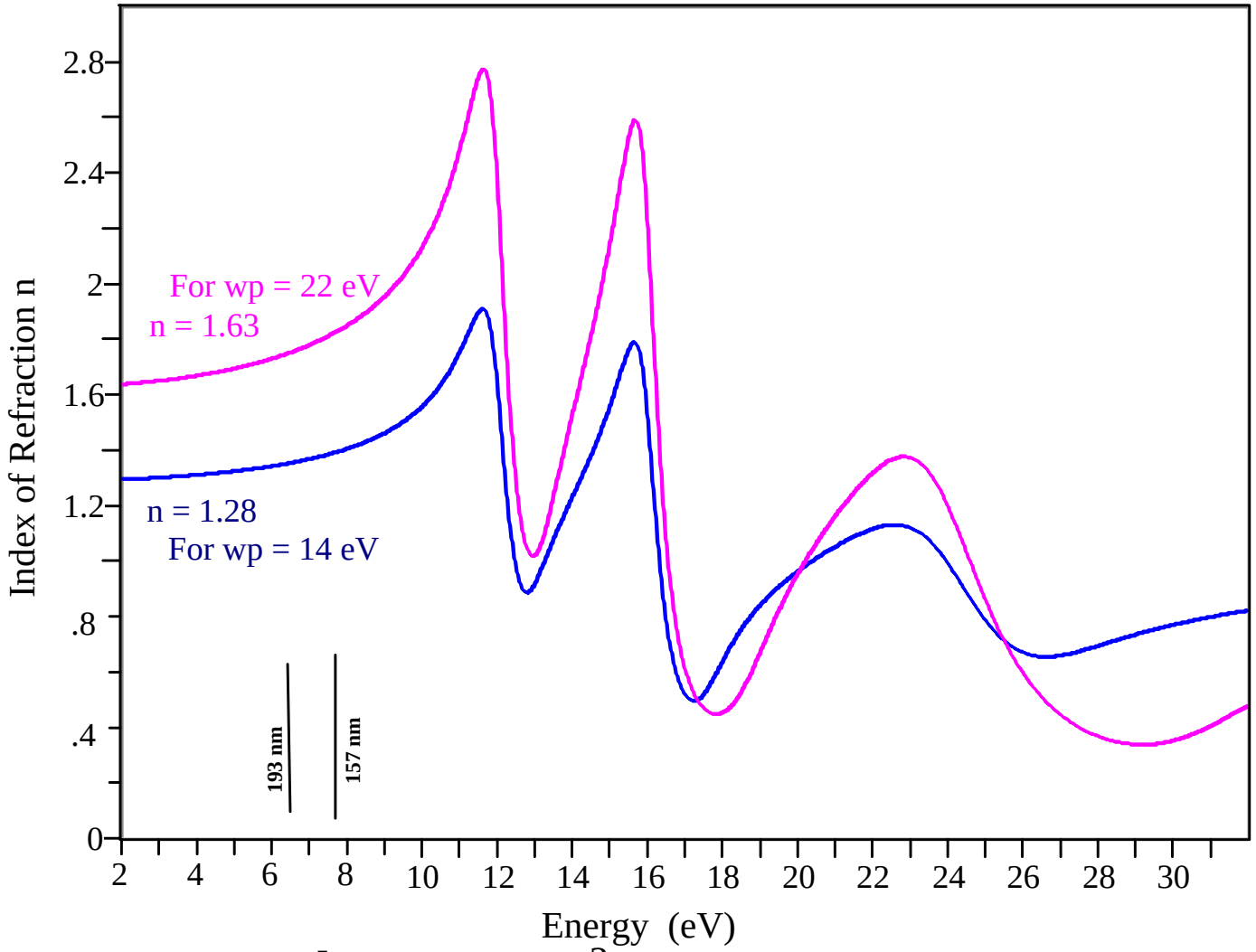
$$\omega_p = \frac{4\pi\ Ne^2}{m}$$

- Index of Refraction
  - – n = 1.63
- Regions Of Dispersion
  - –Normal
  - –Anomalous



Increase The Plasma Frequency, Density

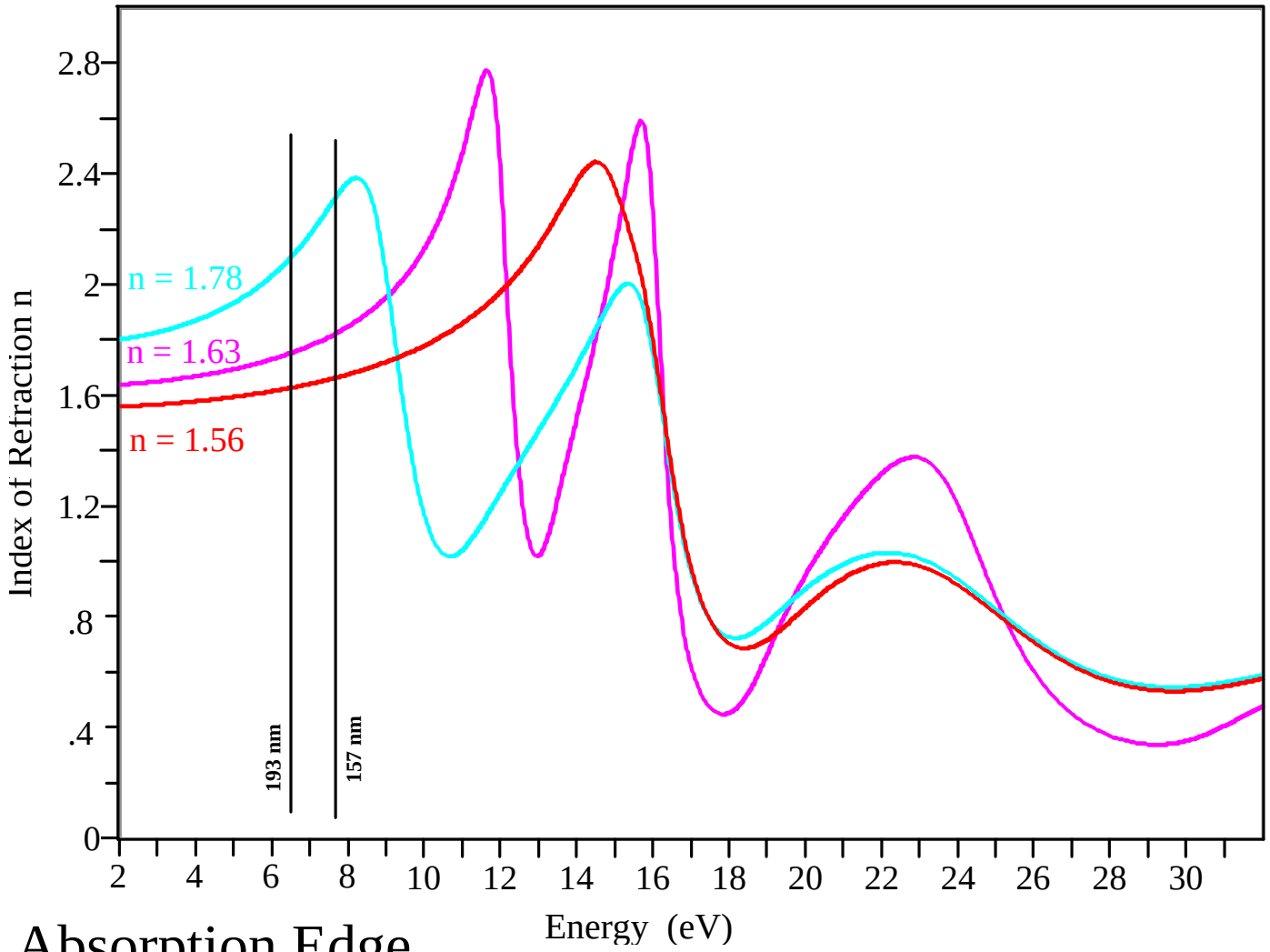
$$\omega_p = \frac{4\pi\, Ne^2}{m}$$



- Increasing Electron Density: electrons/nm^3
  - –Increases The Index of Refraction
- Difficult Synthetic Pathway: Density Is “Intrinsic”

Shift Energy Of First Oscillator

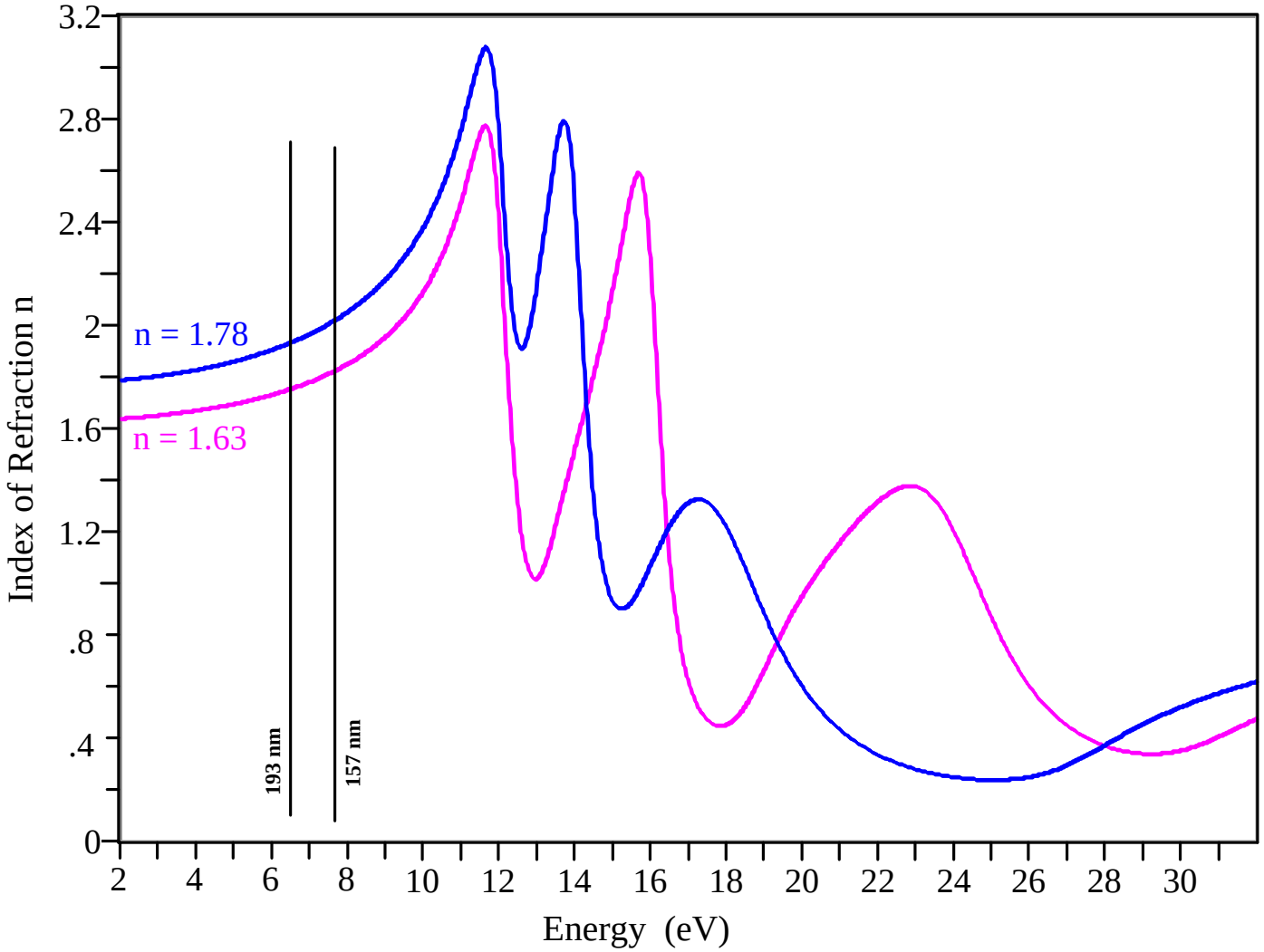
- Index Increases With Absorbance
- Shift Oscillator Down In Energy
- Should Increase Index



- But Approaching Absorption Edge
  - –Causes Optical Absorbance To Increase Rapidly
- Trade Off Of Index and Absorbance

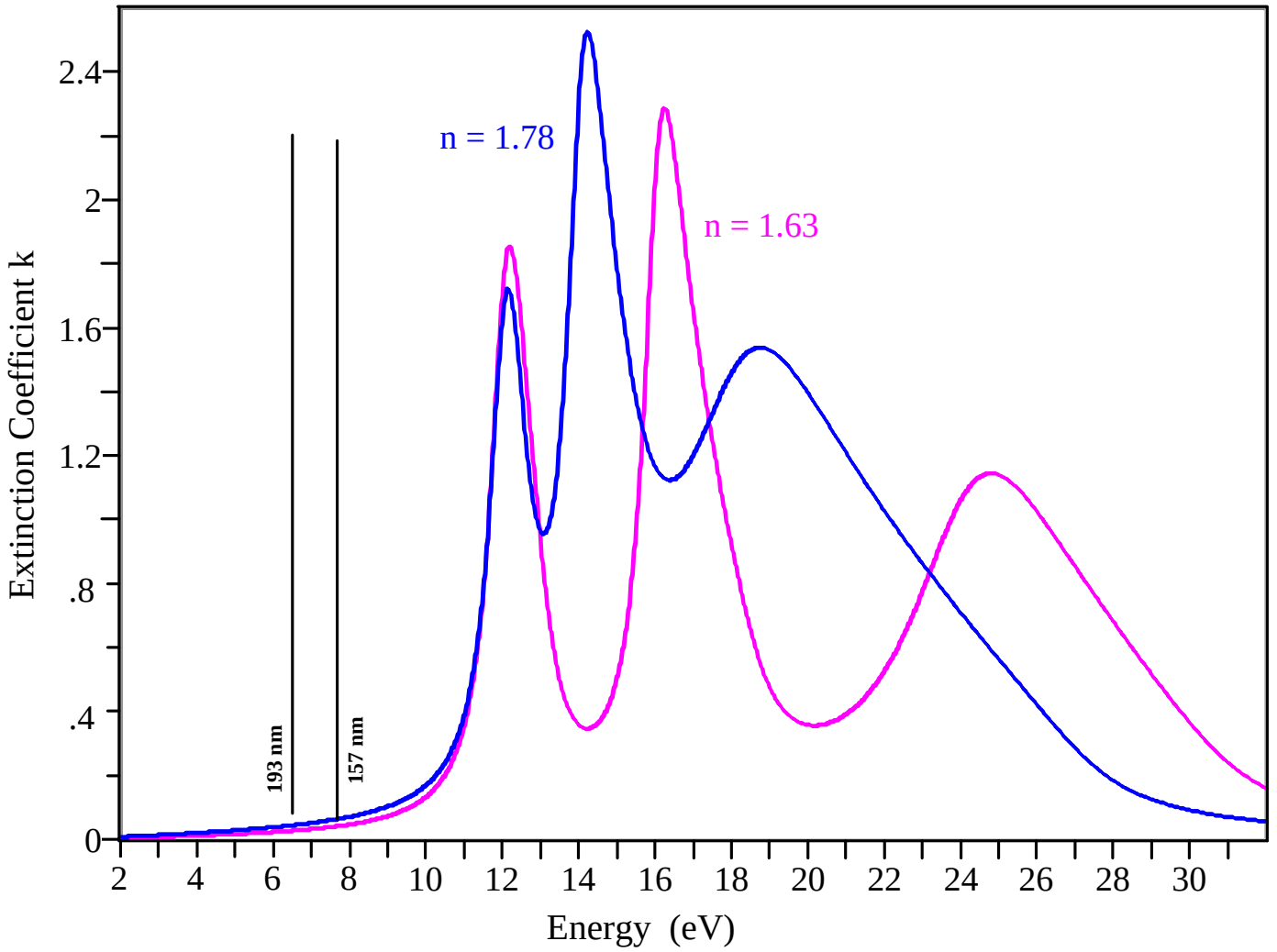
Shift Two High Energy Lorentz Oscillators

- Also Shift Higher Energy Oscillators
- Down To Lower Energies
- Increases Index
  - –But Not As Fast



- Shifting Only Two Higher Energy Oscillators
  - –Can Increase Index, While Minimizing Increase In Absorbance

Shift Two High Energy LO's, Extinction Coeff.



- Have Effectively Decoupled Index and Absorbance
  - –In This Example: n Increases, While Abs. Only Increases Slightly

Conclusions

- **Organic and Environmental Absorbers**
  - –ppm Levels of Trace Absorbers Dominate Absorbance
  - –Water and Oxygen Are Strong Trace Absorbers
- **Absorbance: Structure Property Correlations**
  - –Want Bond Alternation to Break up Conjugation
  - –Want Acyclic Fluorocarbons With Minimal Hydrogen
  - –Want Fluoroethers with Minimal Hydrogen & No H α To O
  - –Avoid 4 & 6 Member Fluorocarbon Rings
- **Current 157 nm Immersion Fluid Index ~ 1.366 At 21^{O}C**
  - –Effective Wavelength of 115.4 nm
- **High Index & Low Absorbance**
  - –Avoid Bond Absorptions Near Litho Wavelength
    - »e.g. Aromatics, Olefins etc.
  - –Increase Electron Density
  - –Tune Bond Absorptions To Increase Index