

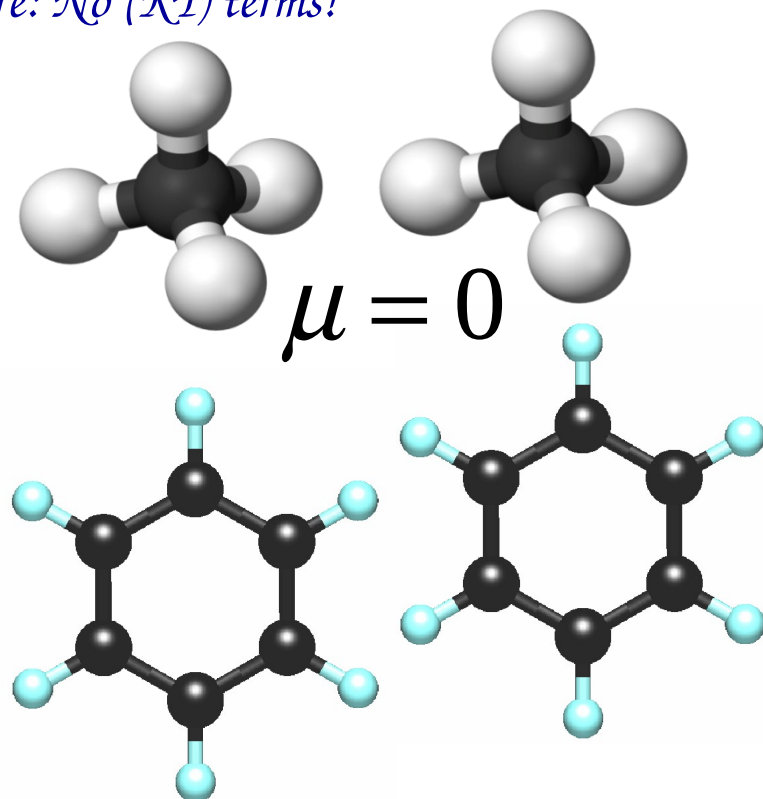
Induced Dipole-Induced Dipole Interaction (Dispersion force)

*Transient induced-dipole moments – electronic polarizabilities
has to be involved - Due to correlated motion of electrons*

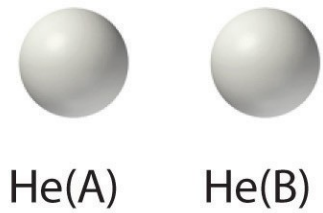
$$V_{id-id}(r) \sim \frac{\alpha_i \alpha_j}{r^6}$$

*Independent of Orientation and
Temperature: No (kT) terms!*

*Termed London Forces, or dispersion!
core of a quantum-mechanical effect!
Can be extremely strong force if a large
number of molecules are involved –
higher alkanes are solid at 300K*



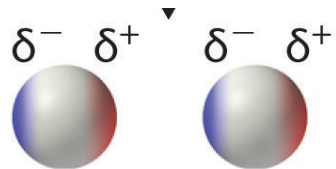
Instantaneous electronic fluctuations – transient dipoles!



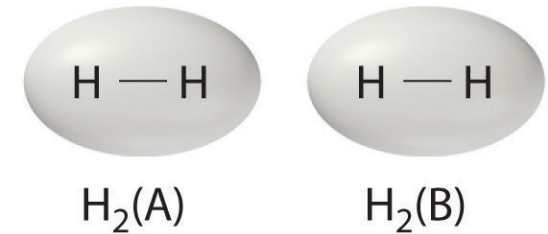
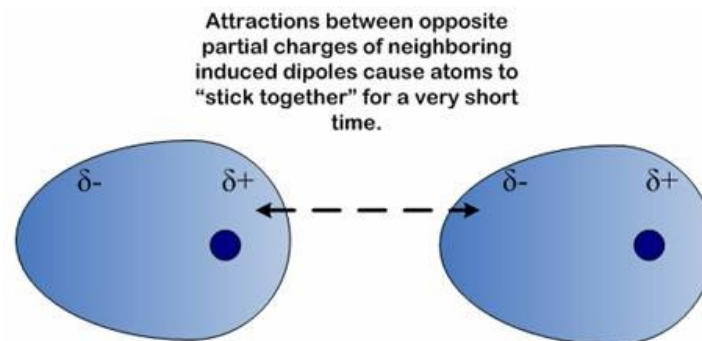
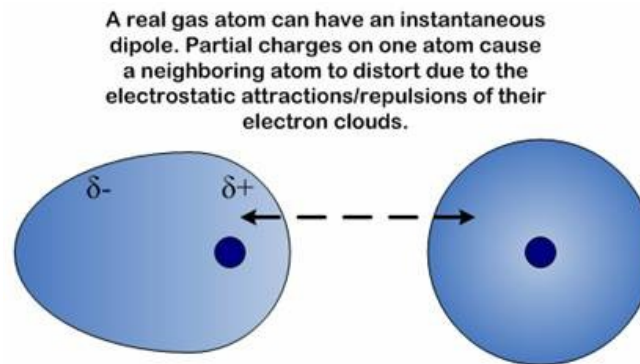
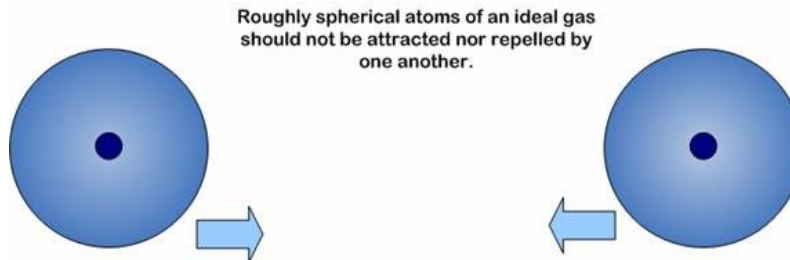
No polarization



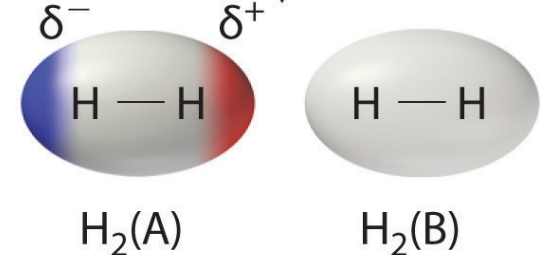
Instantaneous dipole on atom A



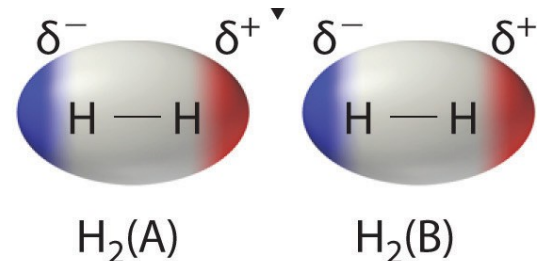
Induced dipole on atom B



No polarization

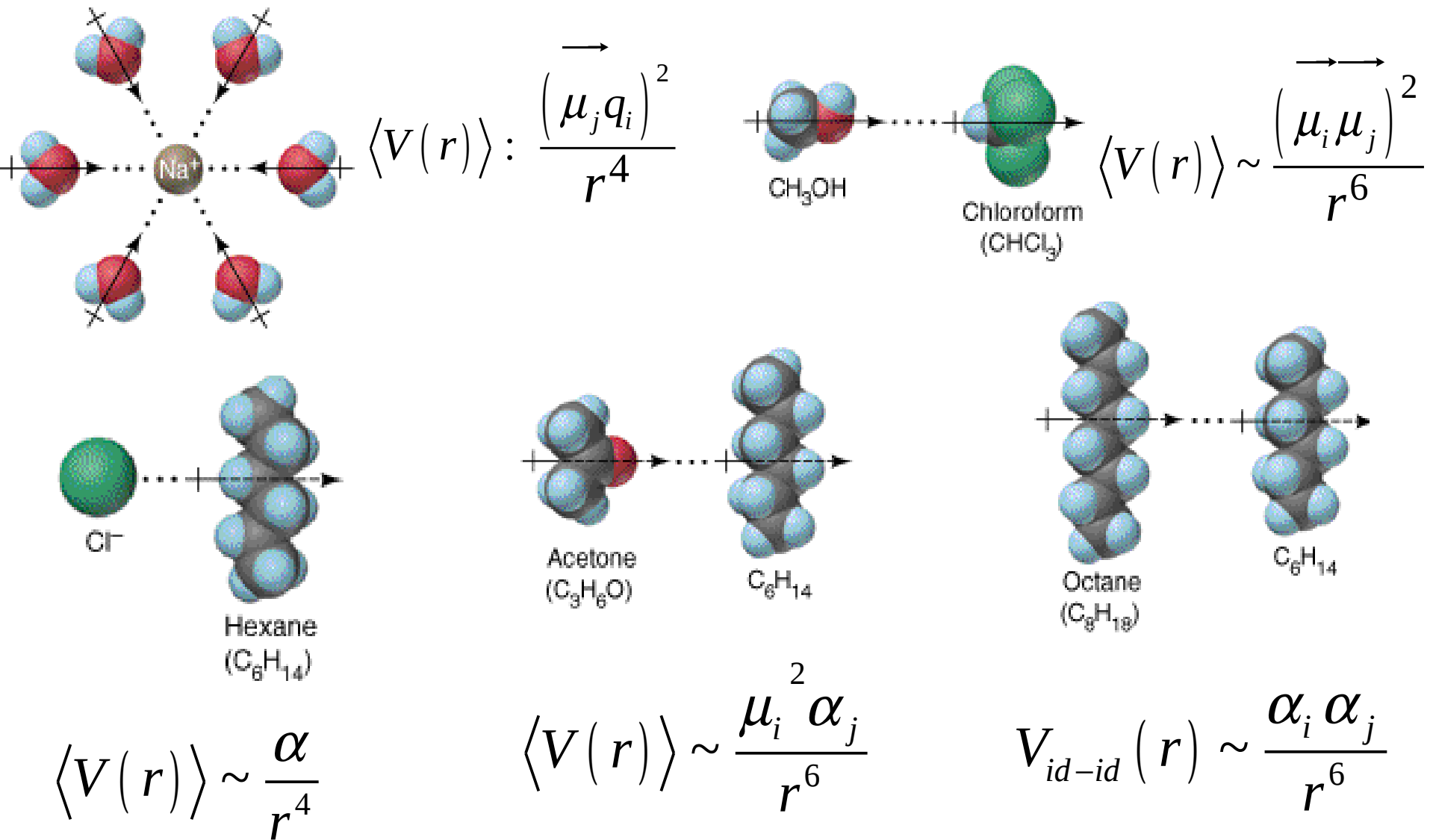


Instantaneous dipole on molecule A

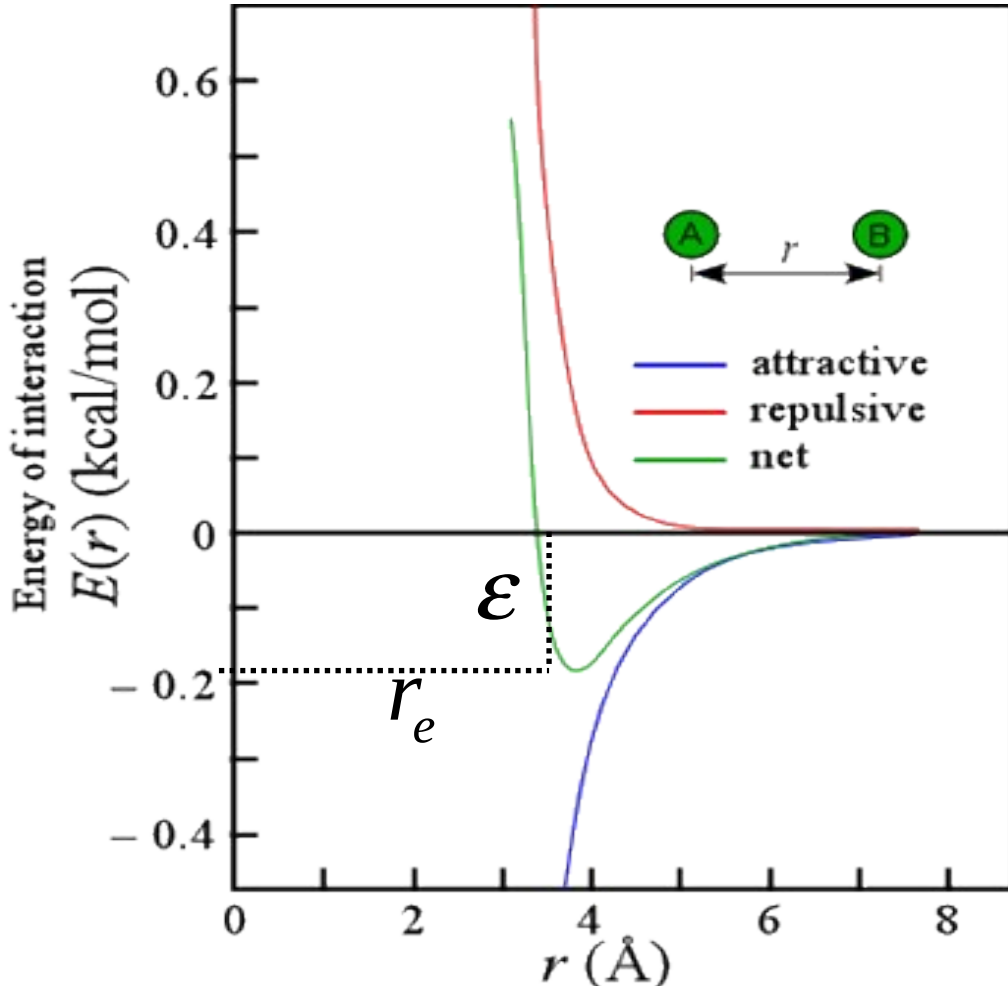


Induced dipole on molecule B

Attractive Potentials for Various Intermolecular forces



LJ: Good potential to model intermolecular interactions



Lennard-Jones Potential very suitable as a model for van der waals' forces*

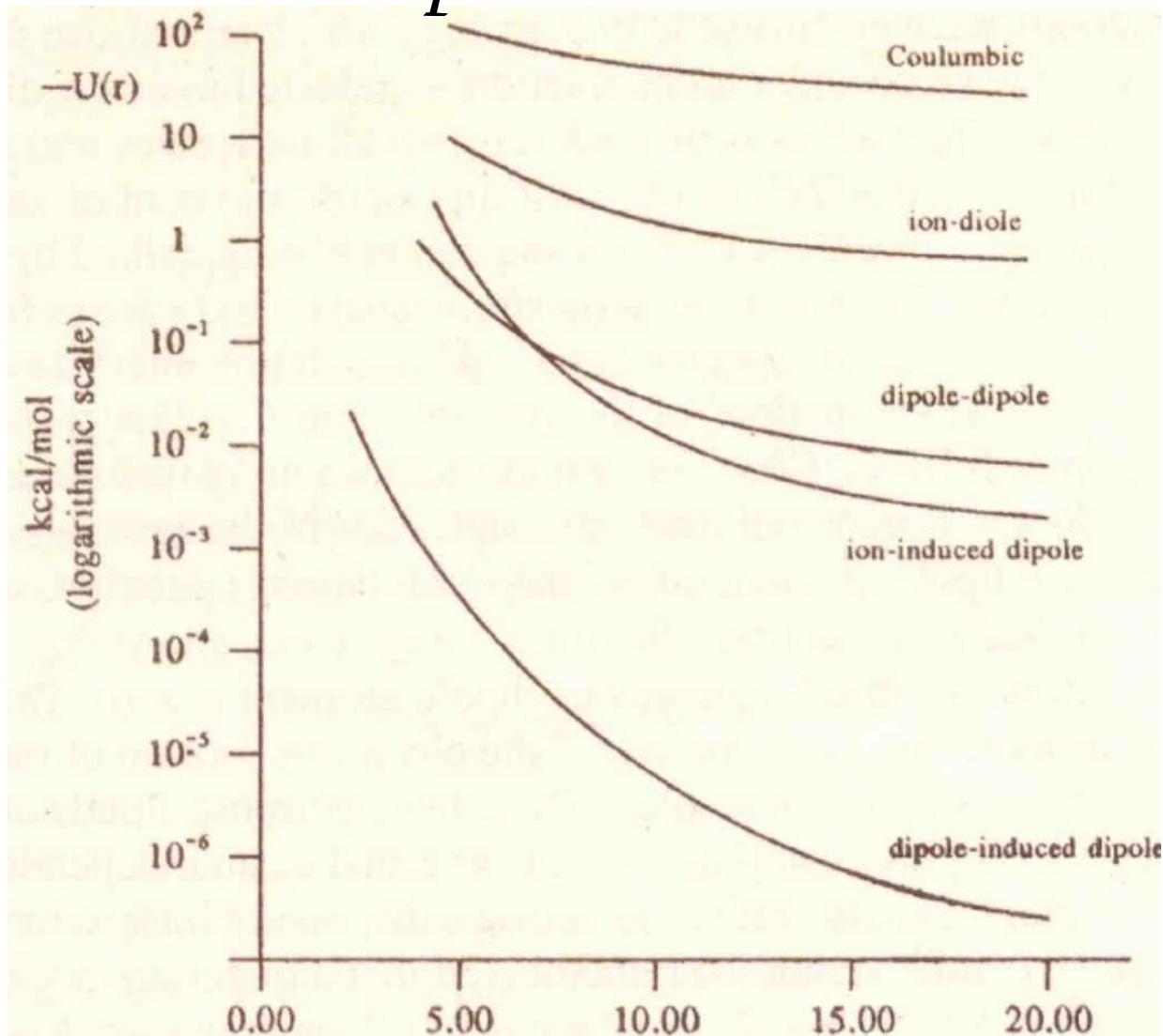
$$V_{LJ} = \epsilon \left[\left(\frac{r_e}{r} \right)^{12} - 2 \left(\frac{r_e}{r} \right)^6 \right]$$

** Did Lennard and Jones come up with this potential function independently or they worked together??*

Comparison of Various Interactions

Ion-dipole		Ion charge— dipole charge	40–600	$\text{Na}^+ \cdots \text{O} \begin{array}{l} \text{H} \\ \diagup \\ \diagdown \\ \text{H} \end{array}$
Dipole-dipole		Dipole charges	5–25	$\text{I}-\text{Cl} \cdots \text{I}-\text{Cl}$
Ion-induced dipole		Ion charge— polarizable e^- cloud	3–15	$\text{Fe}^{2+} \cdots \text{O}_2$
Dipole-induced dipole		Dipole charge— polarizable e^- cloud	2–10	$\text{H}-\text{Cl} \cdots \text{Cl}-\text{Cl}$
Dispersion (London)		Polarizable e^- clouds	0.05–40	$\text{F}-\text{F} \cdots \text{F}-\text{F}$
H bond	$\overset{\delta^-}{\text{A}}-\overset{\delta^+}{\text{H}} \cdots \overset{\delta^-}{\text{B}}$	Polar bond to H— dipole charge (high EN of N, O, F)	10–40	$\begin{array}{c} \text{:}\ddot{\text{O}}-\text{H} \\ \\ \text{H} \end{array} \cdots \begin{array}{c} \text{:}\ddot{\text{O}}-\text{H} \\ \\ \text{H} \end{array}$

Distance dependence of intermolecular potentials



After modification by all the constants involved

Distance dependence of various intermolecular potentials

Typical Energies / kcal mol⁻¹

Type of interaction	$r_{ij} = 5 \text{ \AA}$	$r_{ij} = 10 \text{ \AA}$	$r_{ij} = 15 \text{ \AA}$
ion-ion	- 66.41		- 22.14
ion-dipole	- 4.15		- 0.46
dipole-dipole	- 0.52		- 0.019
ion-induced dipole	- 0.79		- 0.0098
dipole-induced dipole	- 0.0124		- 0.000017

$$\langle V \rangle_{\text{Ion-Dip}} : \frac{1}{r^4}$$

$$\langle V \rangle_{\text{dip-dip}} \sim \frac{1}{r^6}$$

$$\langle V \rangle_{\text{ion-ind_dip}} \sim \frac{1}{r^4}$$

$$\langle V \rangle_{\text{dip-ind_dip}} \sim \frac{1}{r^6}$$

Revisiting Electronic Polarizability!

Induced dipole moment in a atom or molecule
due to the polarization of charge distribution

$$\mu_{\text{Induced}} \left(E \right) = \alpha E$$

$\alpha \rightarrow$ Electronic Polarizability (molecular property)

Polarizability of a molecule (or atom) is a measure of its ability to respond to an uniform electric field and acquire an (induced) dipole moment (a vector!)

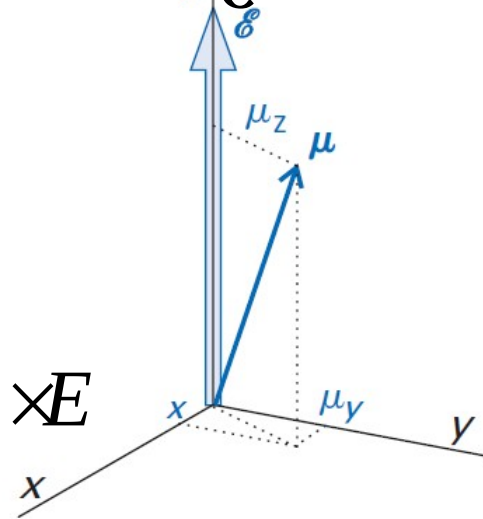
$$\mu_I^2 = \mu_{Ix}^2 + \mu_{Iy}^2 + \mu_{Iz}^2$$

While (induced) dipole moment is a vector, Polarizability is a tensor - No specific direction, but has directionality !!

The Polarizability tensor: 3x3 matrix

$\mu_{Ix}, \mu_{Iy}, \mu_{Iz}$: may not be the same

$$\langle \mu_{Iz} \rangle = \alpha_{zz} \times E \quad \langle \mu_{Ix} \rangle = \alpha_{xx} \times E \quad \langle \mu_{Iy} \rangle = \alpha_{yy} \times E$$



Applied electric field can induce a dipole moment which may not be parallel to the field. Induced dipole depends on all the elements of the polarizability matrix!

$$\bar{\alpha} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \quad \begin{array}{l} \text{Non-centrosymmetric} \\ \text{molecules} \\ \alpha_{xx} \neq \alpha_{yy} \neq \alpha_{zz} \end{array}$$

Polarizability is a 3x3 matrix (tensor or rank 2)

Estimate relative magnitudes of polarizability components

$$\mu_{\text{Ind}} = \mu^E - \mu^{E=0} = \bar{\alpha} E$$

$$\begin{pmatrix} \mu_{Ix} \\ \mu_{Iy} \\ \mu_{Iz} \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

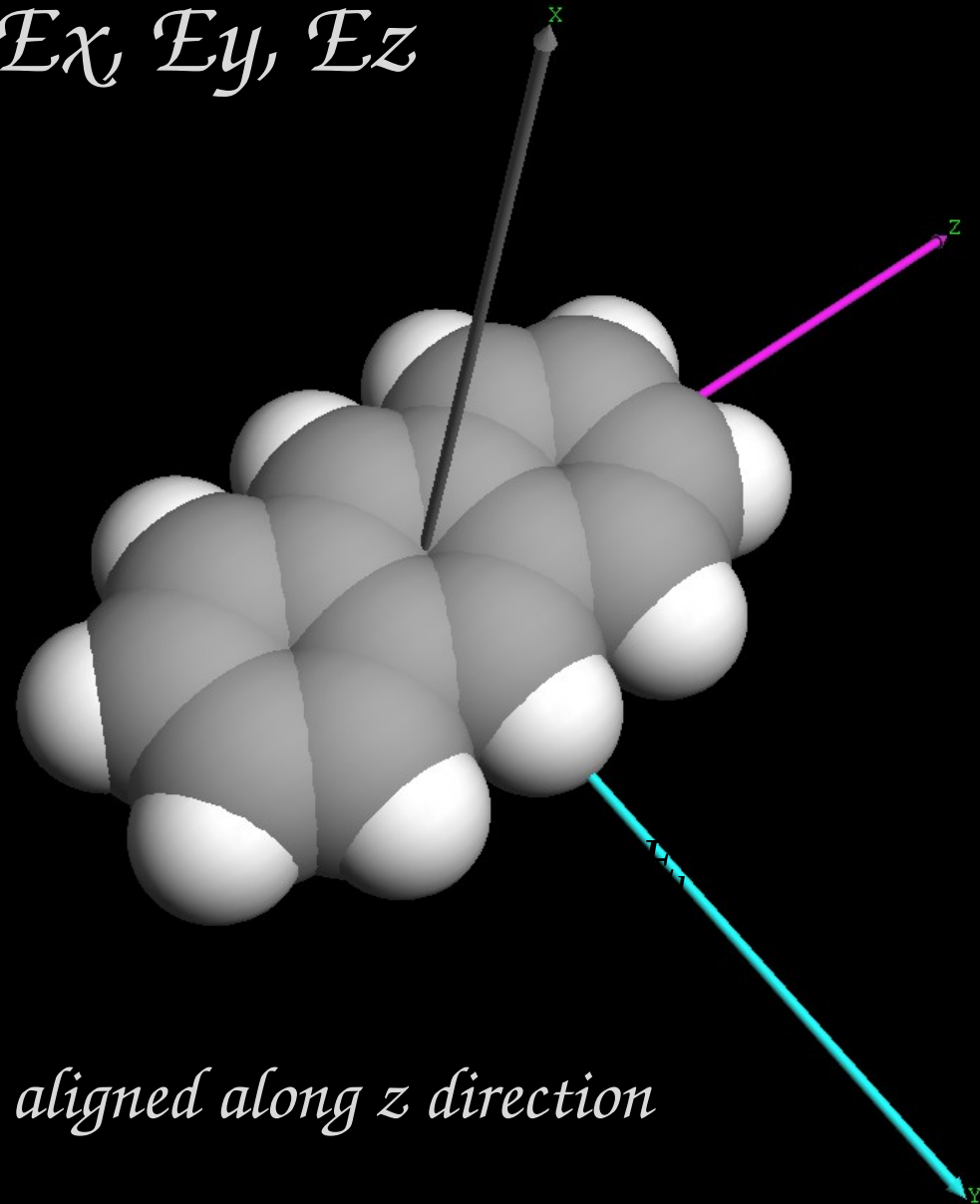
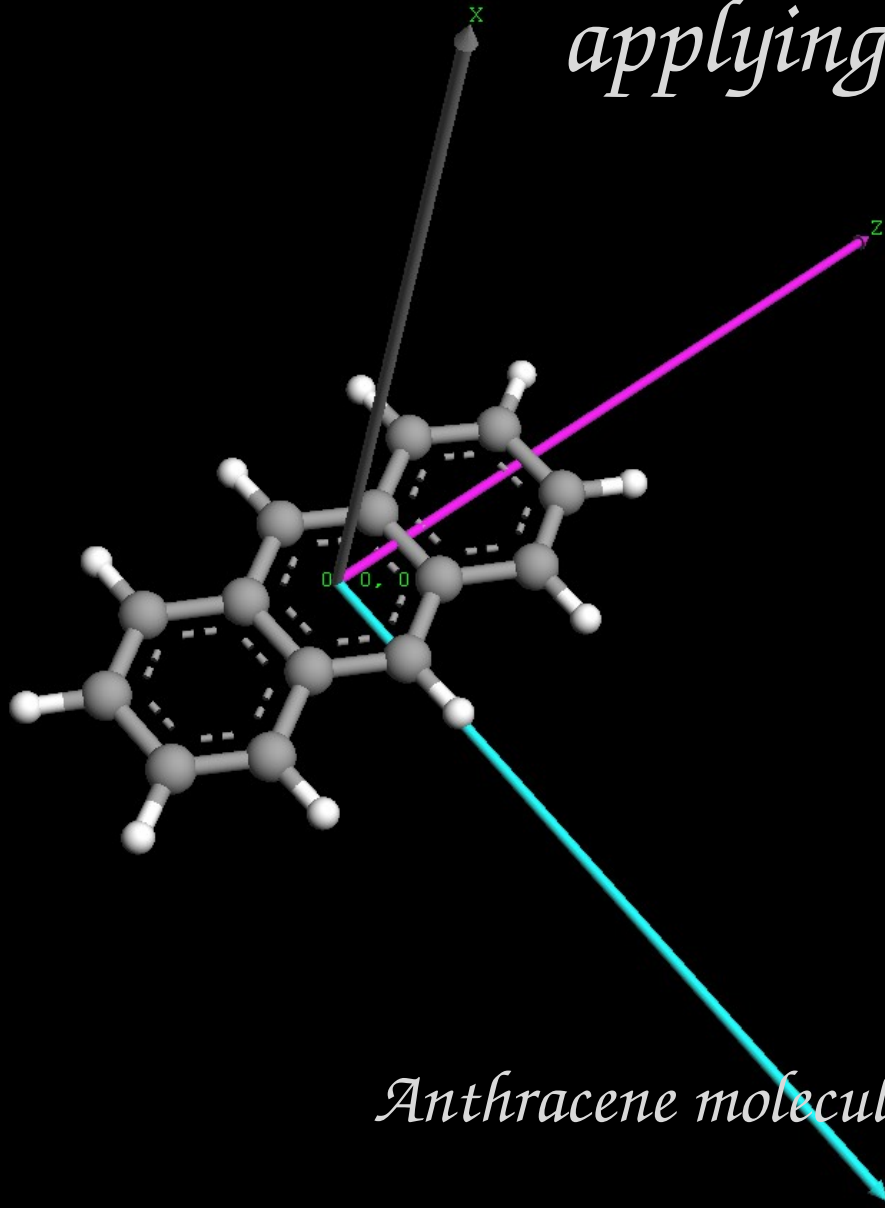
Average of the electronic Polarizability ~ 1/3 Trace of matrix – sum of diagonal elements. (considering off-diagonal elements relatively small)

$$\alpha_{ii} = \frac{\mu_i^{E_i} - \mu_i^{E_i=0}}{E_i}$$

$$\alpha_{ji} = \frac{\mu_j^{E_i} - \mu_j^{E_i=0}}{E_i}$$

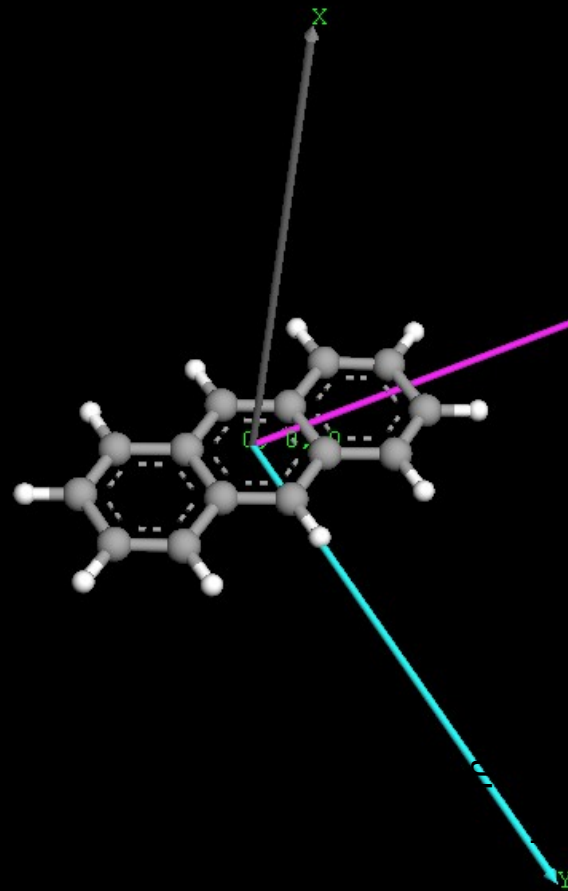
$$\mu_i^{E_i} = \mu_i^{E_i=0} + \alpha_{ii} E_i \quad \text{and} \quad \mu_j^{E_i} = \mu_j^{E_i=0} + \alpha_{ji} E_i$$

*Test case using Anthracene: Calculate μ_{ind} by
applying E_x, E_y, E_z*



Anthracene molecule aligned along z direction

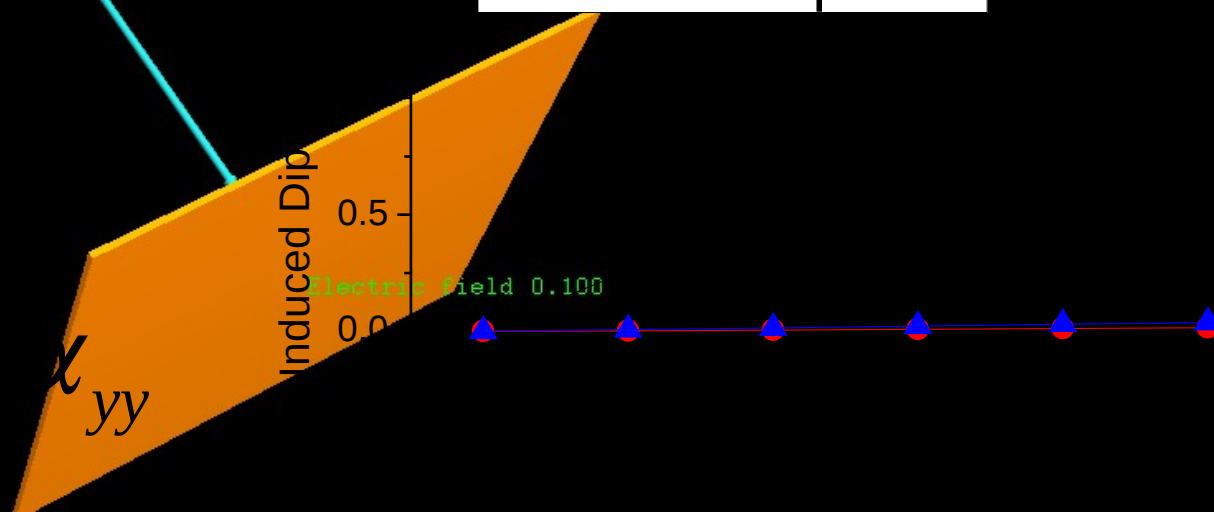
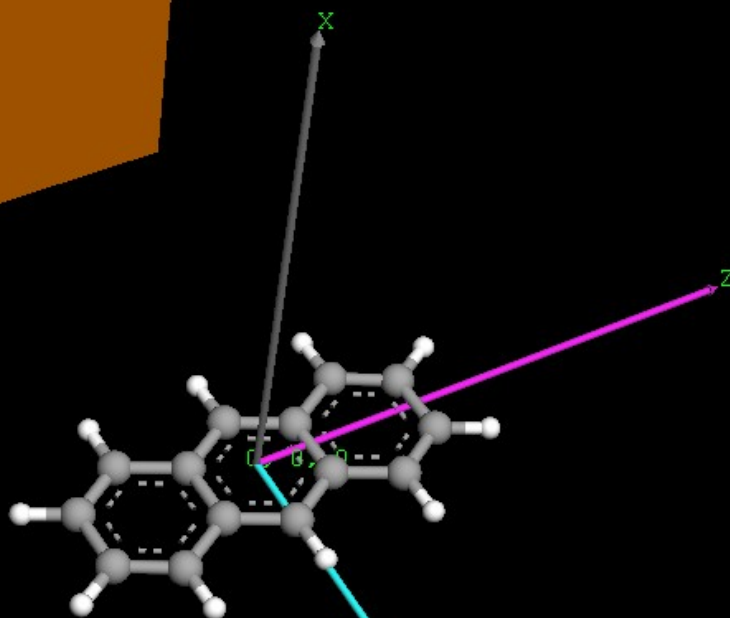
Apply E_z : Calculate $\mu_{Iz}, \mu_{Iy}, \mu_{Ix}$



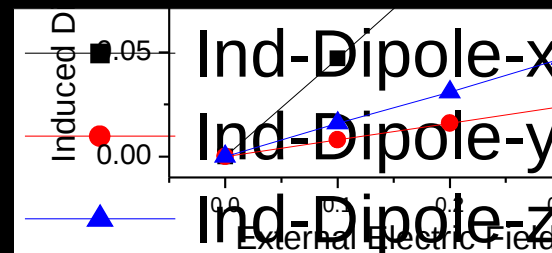
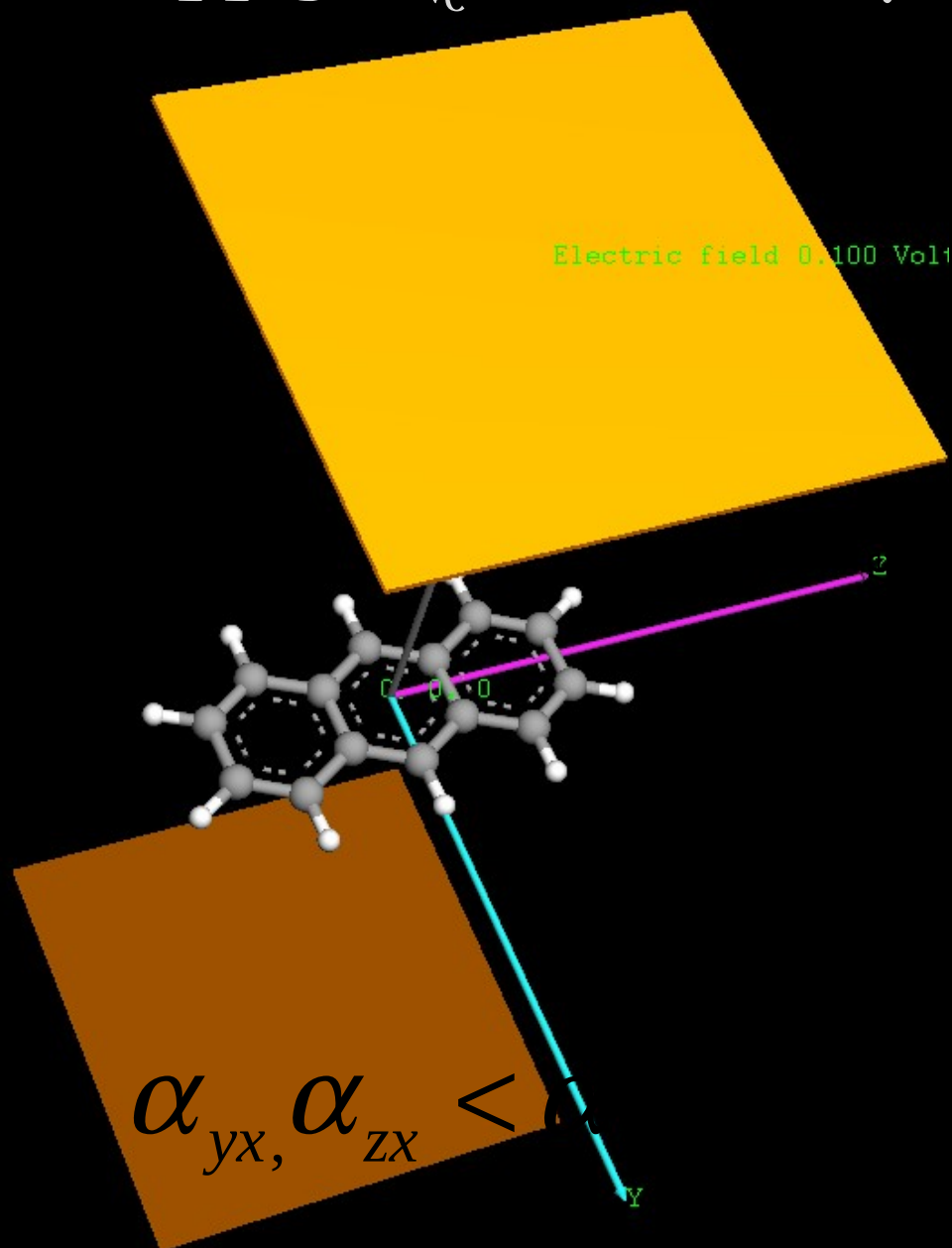
- Ind-Dipole-z
- Ind-Dipole-y
- ▲— Ind-Dipole-x



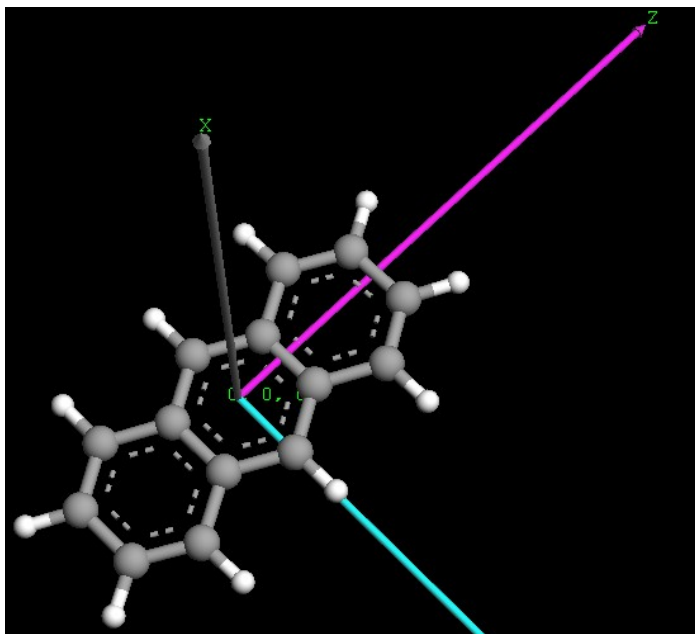
Apply E_y : Calculate μ_{Iz} , μ_{Iy} , μ_{Ix}



Apply $\mathcal{E}_x$: Calculate μ_{Iz} , μ_{Iy} , μ_{Ix}

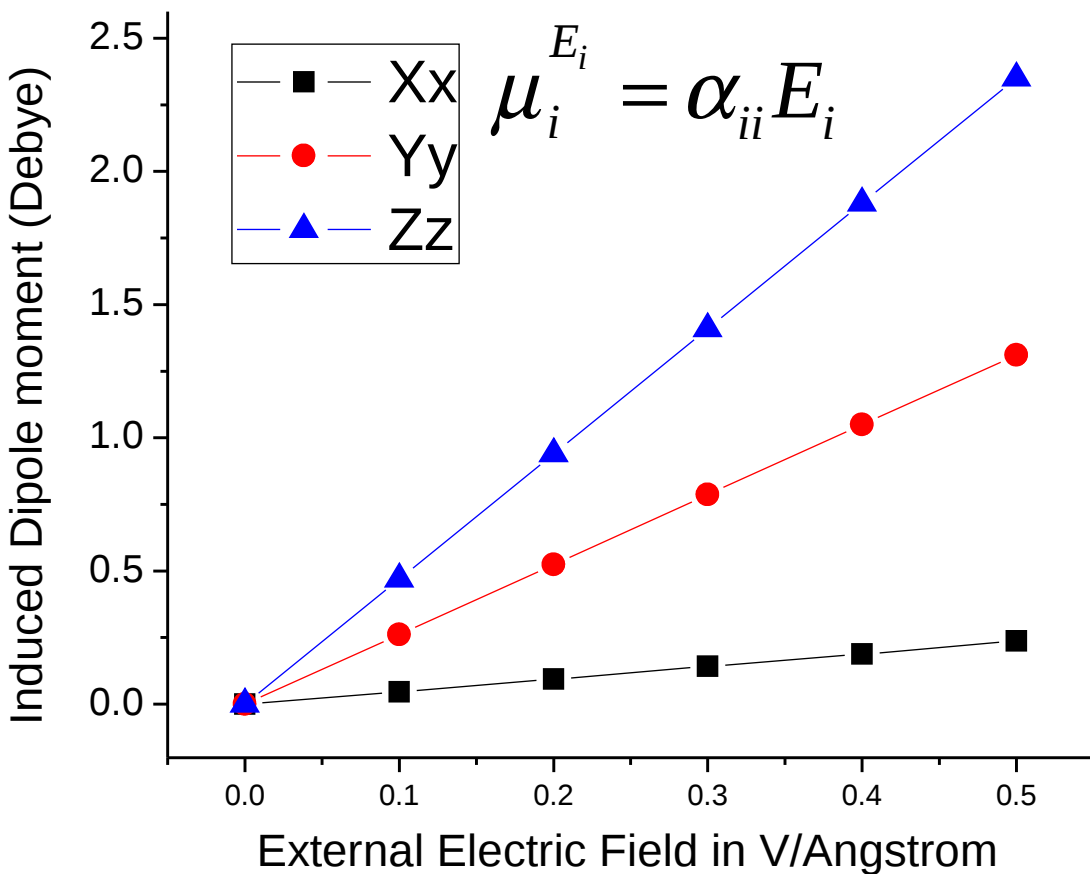


Diagonal elements of polarizability: α_{ii}



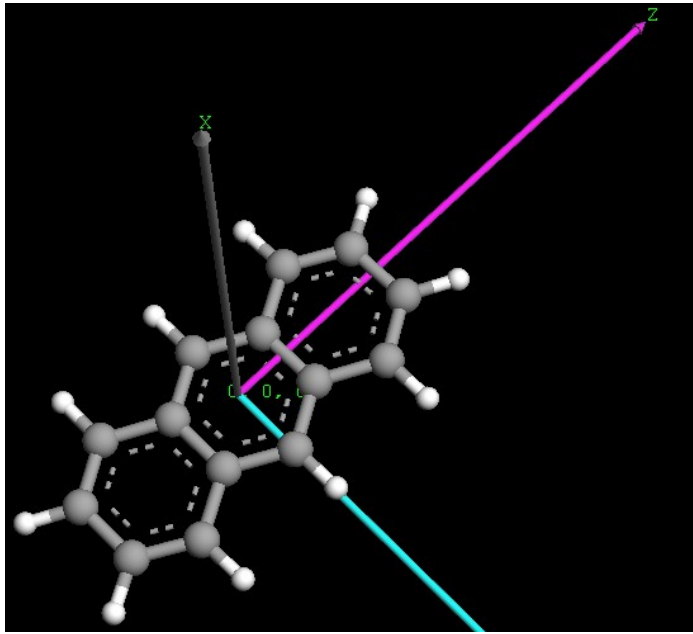
$$\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \div$$

Diagonal terms of the polarizability matrix

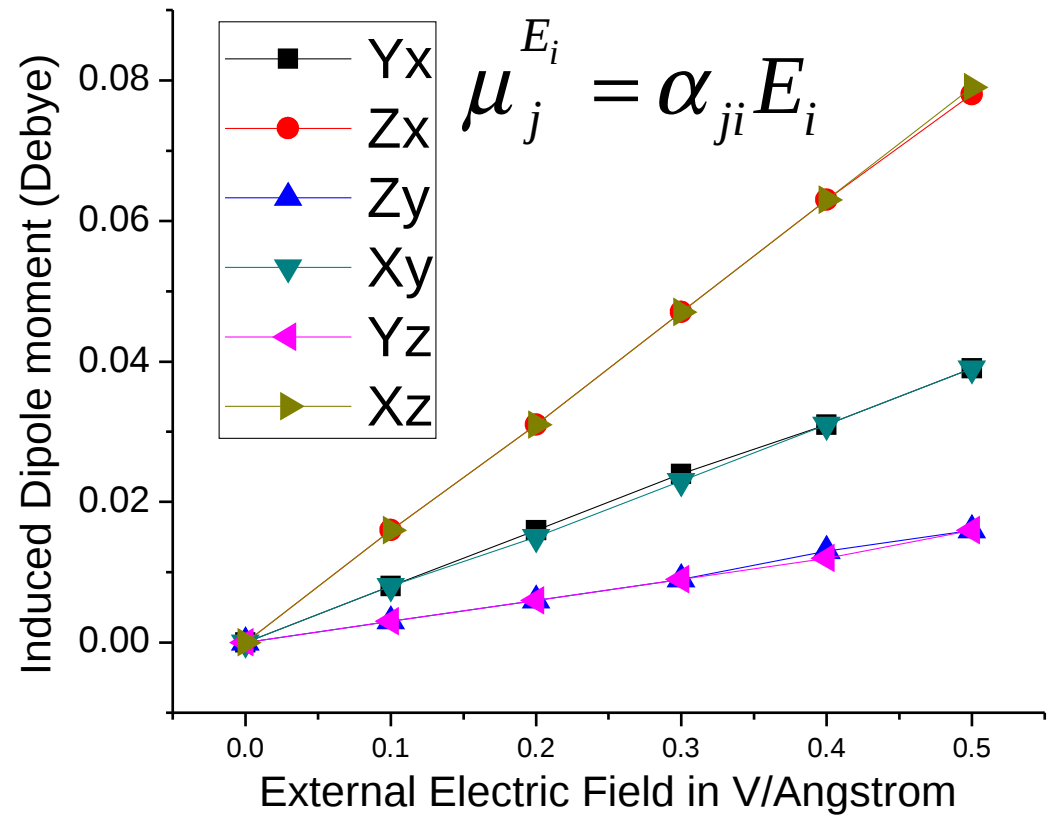


$$\alpha_{zz} > \alpha_{yy} > \alpha_{xx}$$

Off-Diagonal elements (α_{ij}) are small



Off-diagonal terms of the polarizability matrix



$$\begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \quad \alpha_{xy} = \alpha_{yx}; \alpha_{xz} = \alpha_{zx}; \alpha_{yz} = \alpha_{zy}$$