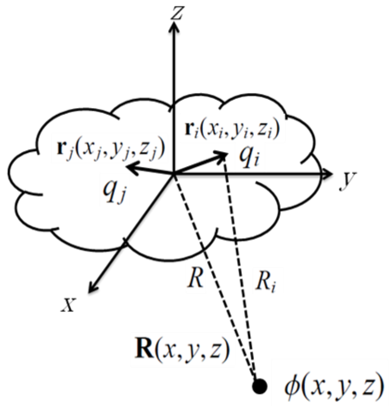
4. Electric Dipole Moment and Molecular Structure

4.1 Electric dipole moment（電偶極子效率）



Definition of electric dipole moment

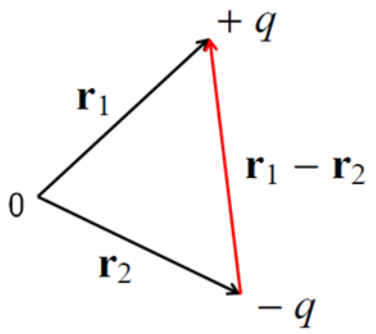
Electrical potential $\phi(x,y,z)$ at position $\mathbf{R}$

$$\phi(x,y,z) = \sum_i \phi_i(x,y,z,x_i,y_i,z_i)$$
$$= \frac{1}{4\pi\epsilon_0}\sum_i \frac{q_i}{\sqrt{(x-x_i)^2+(y-y_i)^2+(z-z_i)^2}}$$

$$x_i << x \quad y_i << y \quad z_i << z$$

$$\phi_i(x,y,z,x_i,y_i,z_i)$$
$$= \frac{q_i}{4\pi\epsilon_0}\frac{1}{R} - \frac{q_i}{4\pi\epsilon_0}\left\{\frac{\partial}{\partial x}\left(\frac{1}{R_i}\right)x_i + \frac{\partial}{\partial y}\left(\frac{1}{R_i}\right)y_i + \frac{\partial}{\partial z}\left(\frac{1}{R_i}\right)z_i\right\}$$
$$+\frac{q_i}{8\pi\epsilon_0}\left\{\frac{\partial^2}{\partial x^2}\left(\frac{1}{R_i}\right)x_i^2 + \frac{\partial^2}{\partial y^2}\left(\frac{1}{R_i}\right)y_i^2 + \frac{\partial^2}{\partial z^2}\left(\frac{1}{R_i}\right)z_i^2\right\} + \cdots$$

$$\phi = \sum_i \phi_i$$
$$= \frac{1}{4\pi\epsilon_0 R}\sum_i q_i \quad \longrightarrow \text{Electric charge}$$
$$+\frac{1}{4\pi\epsilon_0 R^3}\left(\sum_i q_i\mathbf{r}_i\right)\mathbf{R} \quad \longrightarrow \text{Dipole moment} \qquad \sum_i q_i\mathbf{r}_i \equiv \mu_i$$
$$+\frac{1}{8\pi\epsilon_0 R^5}\left(\qquad \right) \quad \longrightarrow \text{Quadrupole moment}$$
$$+ \cdot \cdot \cdot$$



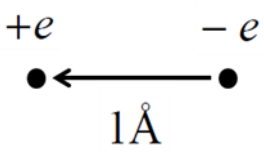
$$\vec{\mu} = q(\mathbf{r}_1 - \mathbf{r}_2)$$

Dipole moment directs from – to + !!!

Units of electric dipole moment

Cm　or　D (Debye)

1D ≡ 1 cgs esu = 3.336×10^{-30} Cm



$\mu = 1.6 \times 10^{-29}$ Cm = 4.76 D
$e = 1.6 \times 10^{-19}$ C
$r = 10^{-10}$ m

Electric dipole moment and intermolecular interactions（分子間相互作用）

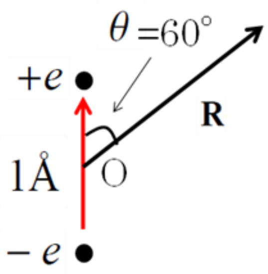
$\sum_i q_i$　　　　$\vec{\mu}$

Charge term $\propto 1/R$　　Dipole term $\propto 1/R^2$　　Quadruple term $\propto 1/R^3$

Long range force

Short range force

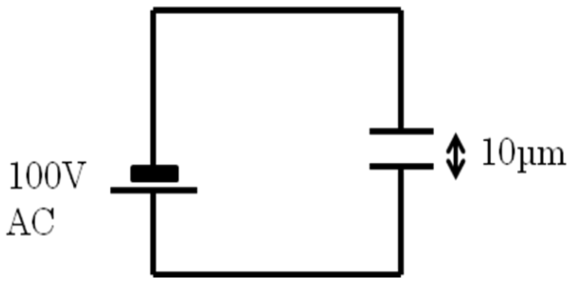
Intermolecular interactions （分子間相互作用）



$$\phi = \frac{1}{4\pi\epsilon_0 R^3}\vec{\mu}\cdot\mathbf{R} = \frac{1}{1.11\times10^{-10}}\cdot\frac{1}{2}\cdot\frac{\mu}{R^2} \approx \frac{1.6\times10^{-29}}{2\times10^{-10}}\frac{1}{R^2}$$

$$E_R = \frac{\partial\phi}{\partial R} = 0.8\times10^{-19}\left(-\frac{2}{R^3}\right) = -1.3\times10^{9}\ \mathrm{Vm^{-1}}\ (R = 5\text{Å})$$

Cf. Infrared electroabsorption spectroscopy



$$E = \frac{100}{10^{-5}} = 10^{7}\mathrm{Vm^{-1}}$$

Observed electroabsorption shift 0.01～0.1cm^{-1}

Solvent shift 10cm^{-1}

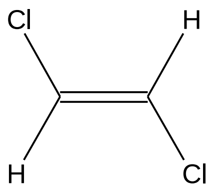
Solvent field is much higher than the external field !!!

Molecular symmetry and electric dipole moment

Molecules with inversion symmetry i (对称中心)

$$\vec{\mu} = \sum_i q_i \mathbf{r}_i \xrightarrow[\text{inversion}]{} -\vec{\mu} \qquad \vec{\mu} = -\vec{\mu} = 0$$

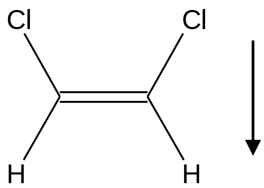
trans-1,2-dichloroethylene



$\mu = 0$

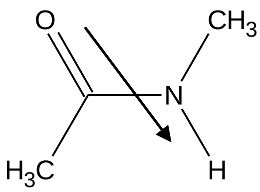
無極性 non-polar

cis-1,2-dichloroethylene



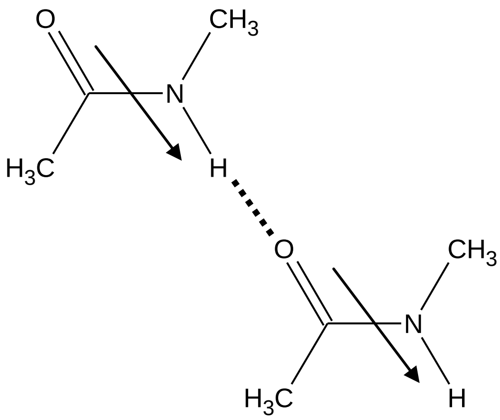
有極性 polar

N-methylacetoamide



4.4 D

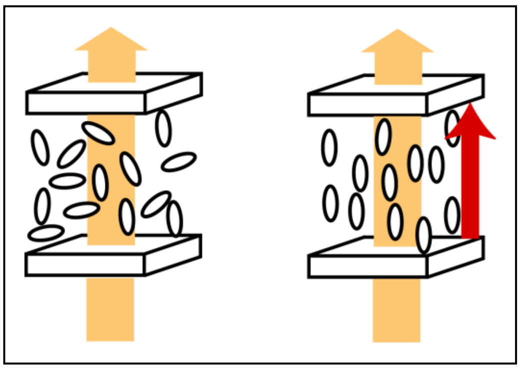
monomer



4.4 D × 2

dimer

A head-to-tail structure determined with infrared electroabsorption spectroscopy !!

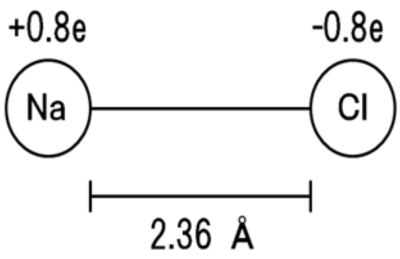


4.2 Electric dipole moments of diatomic molecules

a) NaCl (a high temperature molecule 高温分子)

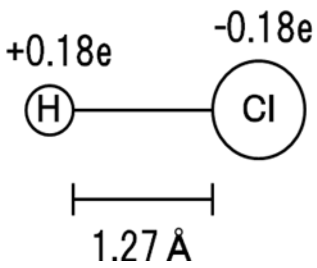
$$\begin{cases} \mu_{obs} = 30.02 \times 10^{-30}\ \mathrm{Cm} & \leftarrow \text{determined with microwave spectroscopy} \\ r_{obs} = 2.36\text{Å} = 2.36 \times 10^{-10}\ \mathrm{m} & \leftarrow \text{determined with microwave spectroscopy} \end{cases}$$

$$q = \frac{\mu}{r} = \frac{30.02 \times 10^{-30}}{2.36 \times 10^{-10}} = 1.27 \times 10^{-19}\mathrm{C} \sim 0.8e$$



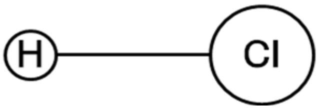
b) HCl

$$\left.\begin{array}{l} \mu = 3.70 \times 10^{-30}\mathrm{Cm} \\ r = 1.27\text{Å} \end{array}\right\} \quad q = 2.91 \times 10^{-20}\mathrm{Cm} = 0.18e$$

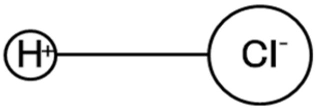


c）Ionicity of a bond （離子度）

$$\psi(\mathrm{HCl}) = \underbrace{a\psi(\mathrm{H:Cl})}_{\text{covalency（共價鍵度）}} + \underbrace{b\psi(\mathrm{H^+Cl^-})}_{\text{iconicity（離子度）}}$$



H:Cl $\quad \mu_c = \int \psi^*(\mathrm{H:Cl})\,\tilde{\mu}\,\psi(\mathrm{H:Cl})d\tau = 0$



$\mathrm{H^+Cl^-}$ $\quad \mu_i = \int \psi^*(\mathrm{H^+Cl^-})\,\tilde{\mu}\,\psi(\mathrm{H^+Cl^-})d\tau = eR$

$$\begin{aligned}
\mu &= \int \psi^*(\mathrm{HCl})\,\tilde{\mu}\,\psi(\mathrm{HCl})d\tau \\
&= a^2 \int \psi^*(\mathrm{H:Cl})\,\tilde{\mu}\,\psi(\mathrm{H:Cl})d\tau \\
&+ ab \int \psi^*(\mathrm{H:Cl})\,\tilde{\mu}\,\psi(\mathrm{H^+Cl^-})d\tau \\
&+ ba \int \psi^*(\mathrm{H^+Cl^-})\,\tilde{\mu}\,\psi(\mathrm{H:Cl})d\tau \\
&+ b^2 \int \psi^*(\mathrm{H^+Cl^-})\,\tilde{\mu}\,\psi(\mathrm{H^+Cl^-})d\tau
\end{aligned}$$

} Neglect these cross terms (the ab and ba terms)

$$\mu = b^2 eR \qquad b^2 = \frac{\mu}{eR}$$

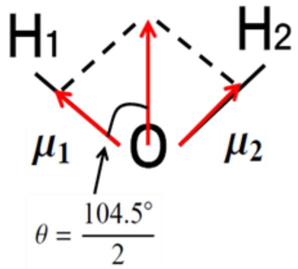
	$\mu/10^{-30}\mathrm{Cm}$	$R/\text{Å}$	b^2
HF	6.09	0.917	0.41
HCl	3.70	1.274	0.18
HBr	2.76	1.414	0.12
HI	1.49	1.609	0.057

Ionicity b^2 decreases on going from HF to HI. HI is almost completely covalent !!

4.3 Electric dipole moments of polyatomic molecules and bond moments

a) H_2O

$$\mu_{\rm obs} = 6.46 \times 10^{-30}\ {\rm Cm}$$



$$\boldsymbol{\mu}_{\rm obs} = \boldsymbol{\mu}_1 + \boldsymbol{\mu}_2$$

$$\mu_{\rm HO} = 5.2 \times 10^{-30}\ {\rm Cm}$$

bond moment of HO

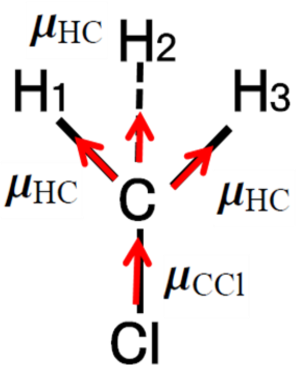
b) Bond moments (positive atom first like HO and C=N)

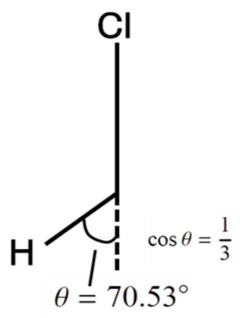
HC	1.3×10^{-30} Cm
CN	$0.7 \times$
CO	2.5
CS	3.0
CI	4.0
CBr	4.6
CCl	4.9
CF	4.7
C=N	3.0
C=O	7.7
C=S	8.7
C≡N	11.7

CH_3Cl $$\mu_{\rm obs} = 6.31 \times 10^{-30}\ {\rm Cm}$$

$$\boldsymbol{\mu} = \boldsymbol{\mu}_{\rm CCl} + \boldsymbol{\mu}_{\rm HC} + \boldsymbol{\mu}_{\rm HC} + \boldsymbol{\mu}_{\rm HC}$$

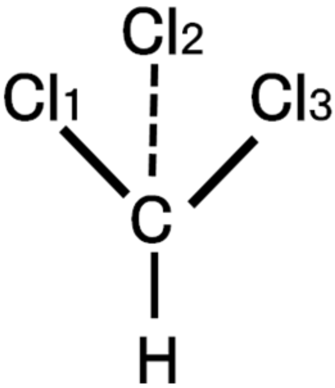
$$\mu = \mu_{\rm CCl} + \mu_{\rm HC} = 4.9 + 1.3 = 6.2$$





$CHCl_3$

$$\mu_{obs} = 3.47 \times 10^{-30}\ \mathrm{Cm}$$

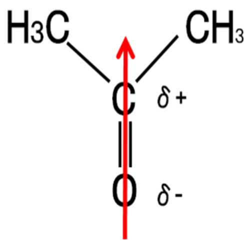


$$\boldsymbol{\mu} = \boldsymbol{\mu}_{HC} + \boldsymbol{\mu}_{CCl} + \boldsymbol{\mu}_{CCl} + \boldsymbol{\mu}_{CCl}$$

$$\mu = \mu_{CCl} + \mu_{HC} = 4.9 + 1.3 = 6.2$$

Cl-C-Cl angle is much larger than the tetrahedral angle !!!

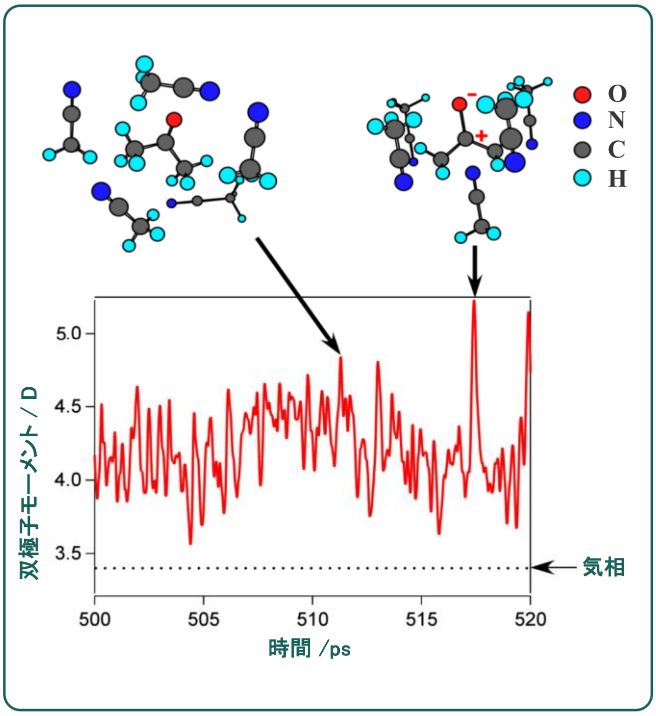
c) Dynamic polarization and fluctuating dipole moments（動態分極）



$$\mu_{obs} = 1.2 \times 10^{-29}\ \mathrm{Cm}$$

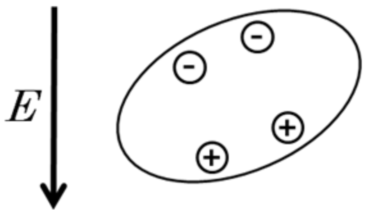
in the gaseous phase

MD simulation of acetone in acetonitrile

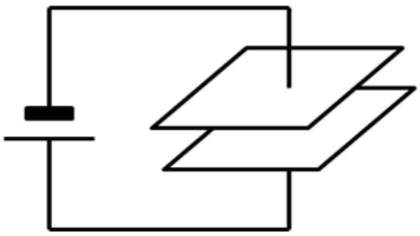


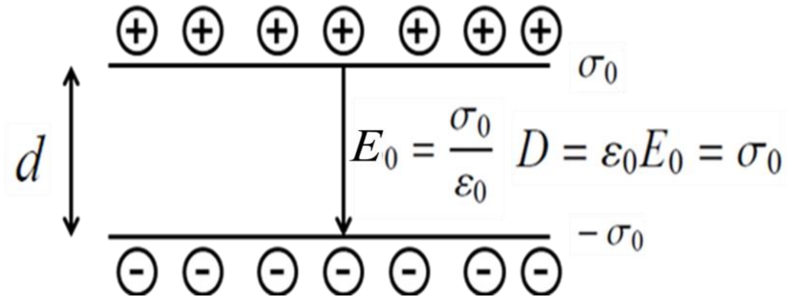
5. Dielectric Polarization and Dielectric Constant

5.1 Dielectric material and dielectric constant

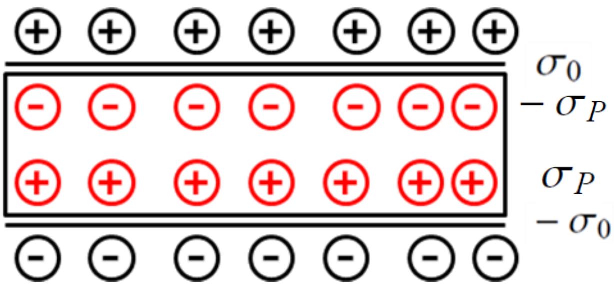


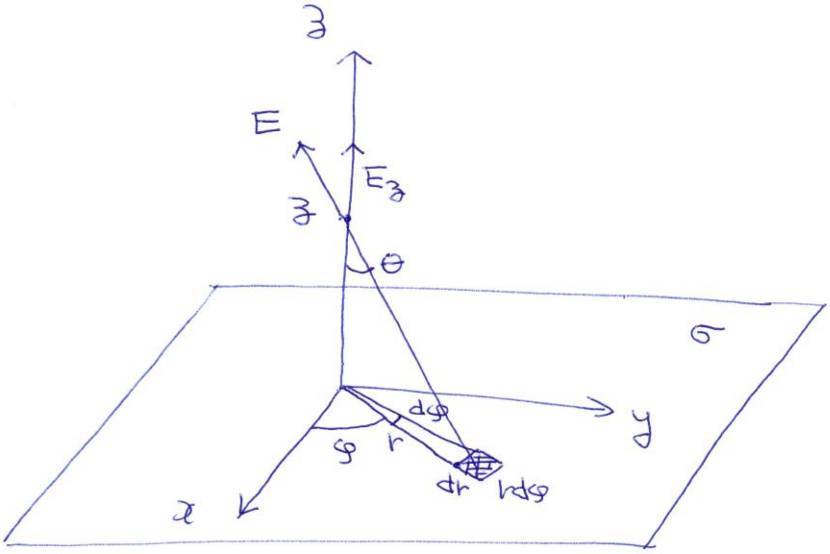
A capacitor in vacuo





A capacitor with dielectric material





$$dA = r\,dr\,d\varphi$$

$$q = \sigma\,dA = \sigma\,r\,dr\,d\varphi$$

$$E = \frac{1}{4\pi\varepsilon_0}\,\frac{q}{r^2+z^2} = \frac{1}{4\pi\varepsilon_0}\,\frac{\sigma\,r\,dr\,d\varphi}{r^2+z^2}$$

$$E_z = E\cos\theta = E\cdot\frac{z}{\sqrt{r^2+z^2}} = \frac{\sigma}{4\pi\varepsilon_0}\,z r\,(r^2+z^2)^{-\frac{3}{2}}\,dr\,d\varphi$$

$$\iint E_z = \int_0^{2\pi}\!\!\int_0^{\infty} \frac{\sigma}{4\pi\varepsilon_0}\,z r\,(r^2+z^2)^{-\frac{3}{2}}\,dr\,d\varphi$$

$$= \frac{\sigma}{2\varepsilon_0}\int_0^{\infty} z r\,(r^2+z^2)^{-\frac{3}{2}}\,dr$$

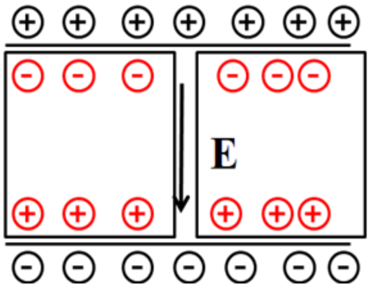
$$r^2+z^2=t \qquad 2r\,dr = dt \qquad r\,dr = \frac{dt}{2}$$

$$= \frac{\sigma}{2\varepsilon_0}\int_{z^2}^{\infty} \frac{1}{2} z\,t^{-\frac{3}{2}}\,dt \qquad \begin{matrix} r=0 & t=z^2 \\ r=\infty & t=\infty \end{matrix}$$

$$= \frac{\sigma}{2\varepsilon_0}\,\frac{z}{2}\left(-\frac{1}{\frac{1}{2}}\left[t^{-\frac{1}{2}}\right]_{z^2}^{\infty}\right)$$

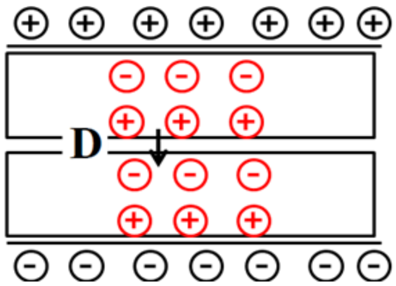
$$= \frac{\sigma}{2\varepsilon_0}$$

E : **canal field**



$$E = \frac{\sigma_0 - \sigma_P}{\varepsilon_0}$$

D : **gap field**



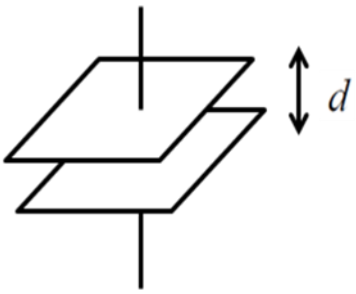
$$\mathrm{div}\mathbf{D} = \rho \quad \text{(Maxwell eq.)}$$

$$DA = \sigma_0 A$$

$$D = \sigma_0$$

$$= \varepsilon_0 E + \sigma_P$$

Total polarization



$$P \times Ad = \sigma_P A \times d$$

$$P = \sigma_P$$

Polarization:

Dipole moment induced in a unit volume

$$\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P}$$

Dielectric constant : **proportional constant between** **D** and **E**

$$\mathbf{D} = \varepsilon \mathbf{E}$$

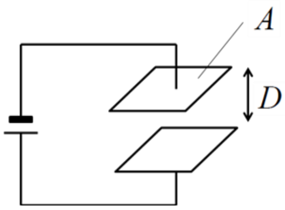
$$= \varepsilon_0 \mathbf{E} + \mathbf{P}$$

$\mathbf{P} \propto \mathbf{E}$ (linear polarization)

Relative permeability or dielectric constant

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \qquad \varepsilon_r > 1$$

Measurement of dielectric constant



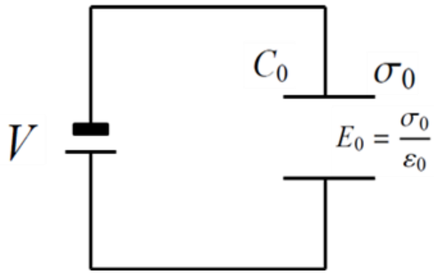
$$q = CV$$

q : charge （電荷） C

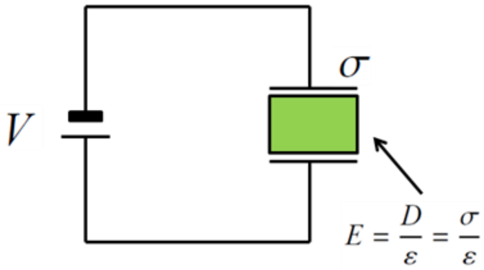
C : capacity （容量） $F = CV^{-1}$

V : potential difference （電位差、電壓） $V = ED$

In vacuo



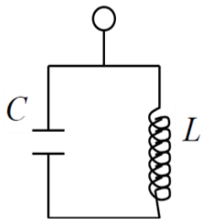
With dielectric medium



$$\frac{\sigma_0}{\varepsilon_0} = \frac{\sigma}{\varepsilon}$$

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = \frac{\sigma}{\sigma_0} = \frac{C}{C_0}$$

Resonant circuit to measure C



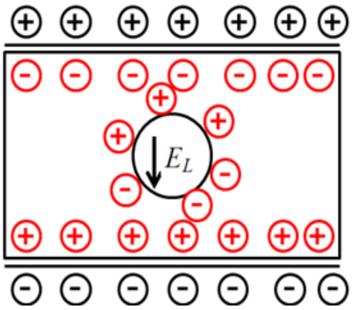
$$\omega = \frac{1}{\sqrt{CL}}$$

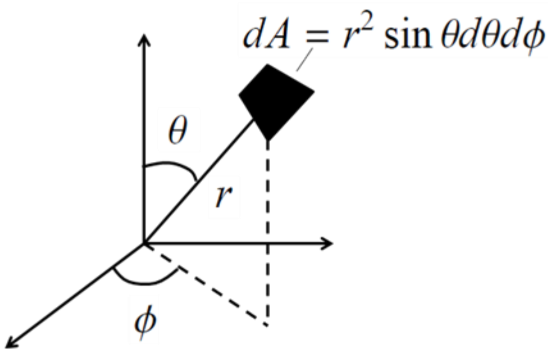
L : inductance

Measurement of ω with a resonant circuit with known L gives the value of C.

5.2 Lorentz field E_L

A field that is experienced by a molecule in a dielectric medium





Electric field for –z direction that is produced by the charge induced on an area element dA

$$\frac{1}{4\pi\varepsilon_0} \cdot \frac{\sigma_P \cos\theta dA}{r^2} \cos\theta$$

Electric field for –z direction that is produced by the charge induced on the total sphere

$$E' = \frac{1}{4\pi\varepsilon_0} \int_0^{\pi} \int_0^{2\pi} \frac{\sigma_P \cos^2\theta r^2 \sin\theta d\theta d\phi}{r^2} = \frac{\sigma_P}{3\varepsilon_0} = \frac{P}{3\varepsilon_0}$$

$$E_L = E + \frac{P}{3\varepsilon_0}$$ ← Lorentz field

$$E_L = \frac{2}{3}E + \frac{1}{3}\frac{D}{\varepsilon_0} \qquad D = \varepsilon_0 E + P$$

E $\frac{D}{\varepsilon_0}$

Lorentz field is in between and !!

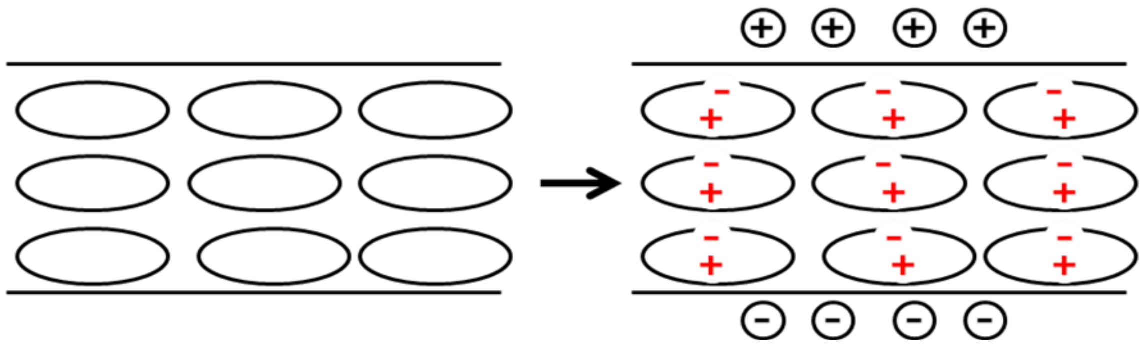
5.3 Molecular polarization（分子極化）

Molecular polarization

$$P = P_E + P_A + P_O \quad \mathrm{cm}^{-2} \quad \mathrm{cm}\cdot\mathrm{m}^{-3}$$

P_E : Electronic polarization （電子極化）
P_A : Atomic polarization （原子極化）
P_O : Orientational polarization （方向極化）

Electronic polarization: polarization due to the distortion of the electron cloud

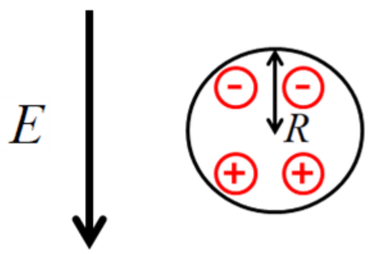


Dipole moment induced on one molecule μ

$$\mu = \varepsilon_0 \alpha_E E_L$$

α_E : electronic polarizability m^3
μ : Cm
$\varepsilon_0 E_L$: Cm^{-2}

A metal sphere in a uniform electric field

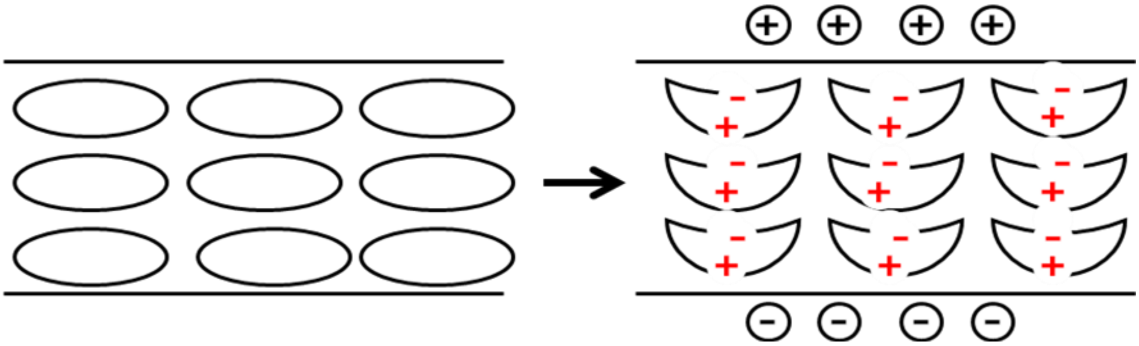


$$\mu = \frac{4}{3}\pi\varepsilon_0 R^3 E$$

$$\alpha_E = \frac{4}{3}\pi R^3 \quad \mathrm{m}^3$$

$P_E = N\varepsilon_0 \alpha_E E_L$ $\quad N$: number of molecule in a unit volume

Atomic polarization: polarization due to the distortion of molecular structure



$$P_A = N\varepsilon_0\alpha_A E_L$$

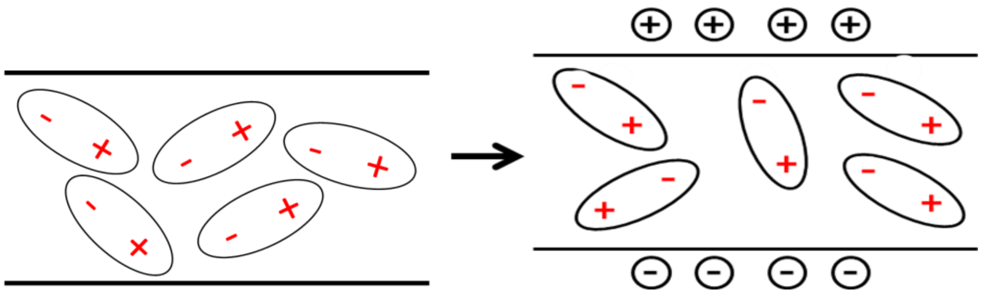
α_A : atomic polarizability

$\alpha_A << \alpha_E$

$(\alpha_A = 0.05\alpha_E)$

Orientational polarization: polarization due to molecular orientation

Only for polar molecules

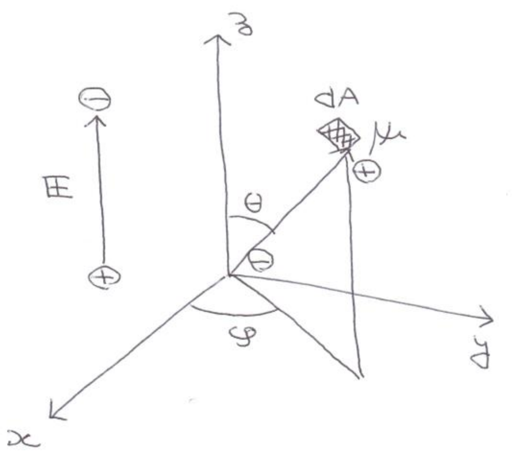


$$P_O = N\frac{\mu^2}{3kT}E_L$$

μ : molecular dipole moment

$$\alpha_0 = \frac{\mu^2}{3\varepsilon_0 kT}$$

http://zh.wikipedia.org/wiki/%E4%BB%8B%E9%9B%BB%E8%B3%AA



$dA = \sin\theta \, d\theta \, d\varphi$

$$\Delta E = -\mu E \cos\theta \qquad \begin{cases} E = -\mu E & \text{for } \theta = 0 \\ E = +\mu E & \text{for } \theta = \pi \end{cases}$$

$$\overline{\mu_z} = \frac{\int_0^{2\pi}\int_0^{\pi} \mu \cos\theta \, e^{-\frac{\Delta E}{kT}} \sin\theta \, d\theta \, d\varphi}{\int_0^{2\pi}\int_0^{\pi} e^{-\frac{\Delta E}{kT}} \sin\theta \, d\theta \, d\varphi}$$

$$= \frac{\int_0^{\pi} \mu \cos\theta \, e^{\frac{\mu E \cos\theta}{kT}} \sin\theta \, d\theta}{\int_0^{\pi} e^{\frac{\mu E \cos\theta}{kT}} \sin\theta \, d\theta}$$

$\cos\theta = t$

$-\sin\theta \, d\theta = dt$

$$= \frac{\int_1^{-1} \mu t \, e^{\frac{\mu E}{kT} t} \, dt}{\int_1^{-1} e^{\frac{\mu E}{kT} t} \, dt}$$

$\frac{\mu E}{kT} \ll 1$

$$\sim \frac{\int_{-1}^{1} \mu t \left(1 + \frac{\mu E}{kT} t\right) dt}{\int_{-1}^{1} \left(1 + \frac{\mu E}{kT} t\right) dt}$$

$$= \frac{\left[\frac{1}{2}\mu t^2 + \frac{1}{3}\frac{\mu^2 E}{kT}\right]_{-1}^{1}}{\left[t + \frac{\mu E}{2kT} t^2\right]_{-1}^{1}} = \frac{\mu^2 E}{3kT}$$

μ=10^{-30} Cm, E=10^{7} Vm^{-1}=NC^{-1} → μE=10^{-23} Nm=10^{-23} J

K=1,38x10^{-23} JK^{-1}, T=300 K → kT=4x10^{-20} J

Molecular polarization and dielectric constant (Clausius-Mossoti formula)

$$P = P_E + P_A + P_O = N\varepsilon_0\alpha E_L$$
$$\alpha = \alpha_E + \alpha_A + \alpha_O$$

$$\begin{cases} \mathbf{D} = \varepsilon\mathbf{E} = \varepsilon_0\mathbf{E} + \mathbf{P} \\ \mathbf{P} = N\varepsilon_0\alpha\mathbf{E_L} \end{cases}$$

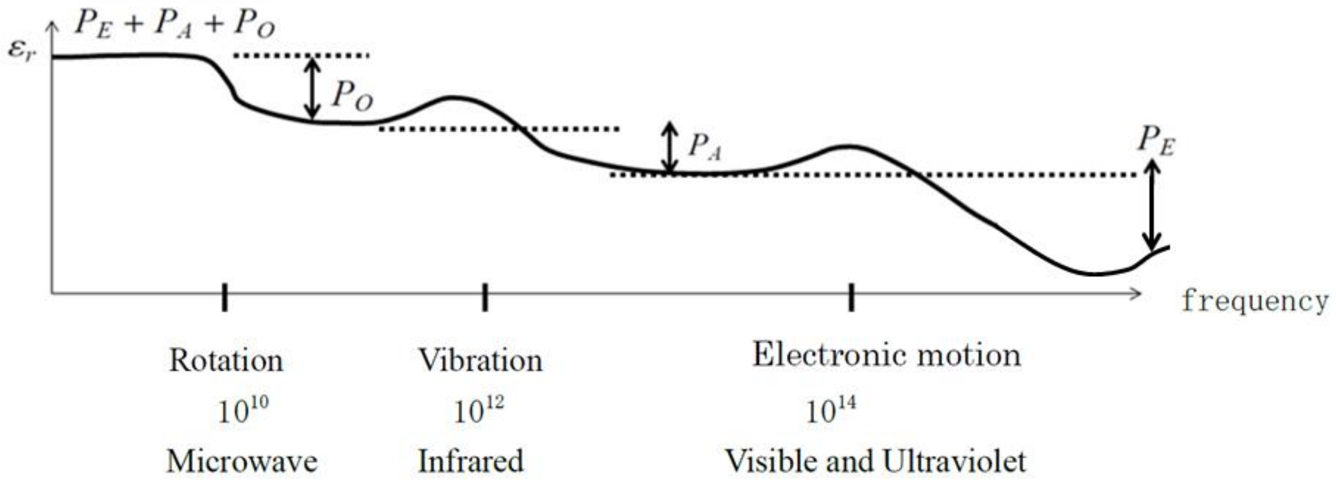
$$\begin{aligned} P &= (\varepsilon - \varepsilon_0)E \\ &= N\varepsilon_0\alpha E_L \\ &= N\varepsilon_0\alpha\left(\frac{2+\varepsilon_r}{3}\right)E \\ \varepsilon - \varepsilon_0 &= N\varepsilon_0\alpha\left(\frac{2+\varepsilon_r}{3}\right) \\ \varepsilon_r - 1 &= N\alpha\left(\frac{2+\varepsilon_r}{3}\right) \\ \underbrace{\frac{\varepsilon_r - 1}{\varepsilon_r + 2}}_{\text{Macro}} &= \underbrace{\frac{1}{3}N\alpha}_{\text{Micro}} \end{aligned}$$

Temperature dependence of ε_r

$$\begin{aligned} \frac{\varepsilon_r(T) - 1}{\varepsilon_r(T) + 2}\frac{3}{N} &= \alpha \\ &= \alpha_E + \alpha_A + \frac{\mu^2}{3\varepsilon_0 RT} \end{aligned}$$

Determination of dipole moments !!!

4.4 Dielectric dispersion



4.5 Non-linear polarization

$$P = \underbrace{\chi_1 E}_{\text{Linear}} + \underbrace{\chi_2 E^2 + \chi_3 E^3}_{\text{Non-linear}}$$

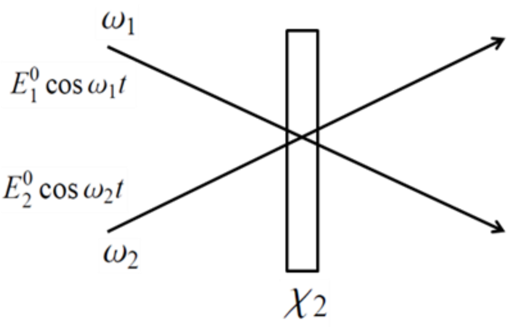
Vibration

Linear optics $\leftarrow$ $\chi_1 \sim \varepsilon_r$

Light propagation, emission, absorption

Non-linear optics $\leftarrow$ χ_2, χ_3

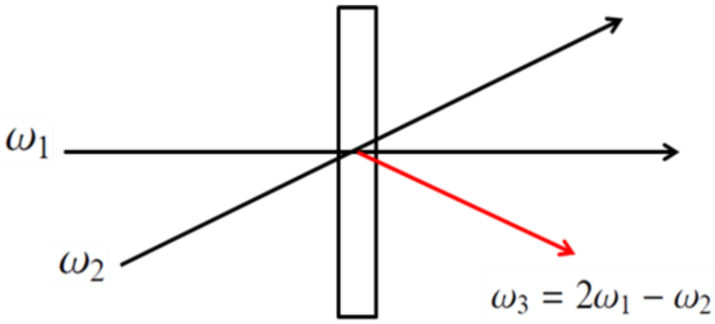
Sum and difference frequency generation: X_2



$$
\begin{aligned}
P_2 &= \chi_2 E_1 E_2 \\
&= \chi_2 E_1^0 E_2^0 \cos \omega_1 t \omega_2 t \\
&= \frac{1}{2}\chi_2 E_1^0 E_2^0 \{\cos(\omega_1 + \omega_2)t + \cos(\omega_1 - \omega_2)t\}
\end{aligned}
$$

CARS χ_3

Coherent Anti-Stokes Raman Scattering



$$P_3 = \chi_3 E_1^2 E_2$$