

Quantum Chemistry

Lecture 31

Electrostatics
Multipole expansion
Polarizability
Lorentz model

NC State University

Review of Electrostatics

The Coulombic force on charge j due to charge i is:

$$\vec{F}_j = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}^2} \vec{r}_{ij}$$

The Coulombic force is additive. The combined force is a superposition. The force on charge k due to a number of charges with the index j is:

$$\vec{F}_k = \frac{1}{4\pi\epsilon_0} \sum_{j \neq k} \frac{q_j q_k}{r_{jk}^2} \vec{r}_{jk}$$

The constant ϵ_0 is the permittivity of vacuum. In MKS units the value is $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$. In the cgs-esu unit system the permittivity of free space is $1/4\pi$ and the constant $1/4\pi\epsilon_0$ does not appear in the Coulomb force.

Electric Field

The electric field is the force per unit charge. The most precise statement is that it is the force per unit charge in the limit that the charge is infinitesimally small:

$$\vec{E}_j = \frac{\partial \vec{F}_j}{\partial q}$$

When applied to the Coulomb force the electric field becomes:

$$\vec{E}_k = \frac{1}{4\pi\epsilon_0} \sum_{j \neq k} q_j \frac{\vec{r}_{jk}}{r_{jk}^2}$$

Electrostatic Potential

The electric field is the negative gradient of the scalar potential:

$$\vec{\mathbf{E}} = - \nabla \phi$$

The potential at a distance r from a charge is:

$$\phi = - \frac{q}{4\pi\epsilon_0 r}$$

The electric field represents the force per unit charge.
The potential is the work per unit charge.

$$W_{12} = \phi(q_2 - q_1)$$

In MKS units the potential has units of V where $1 \text{ V} = 1 \text{ J/C}$.

Potential and Field due to a Dipole

The potential due to a dipole is:

$$\phi(r) = \frac{\vec{\mu} \cdot \vec{r}}{4\pi\epsilon_0 r^3}$$

The assumption in this equation is that the distance between the charge and dipole, r , is large relative to the separation of charges in the dipole, d , $r \gg d$.

The electric field due to a dipole is:

$$\vec{E} = \frac{1}{4\pi\epsilon_0} \left(\frac{3(\vec{\mu} \cdot \vec{r})\vec{r}}{r^5} - \frac{\vec{\mu}}{r^3} \right)$$

Using the expression $W = -\vec{\mu} \cdot \vec{E}$ we can calculate the interaction energy of two dipoles.

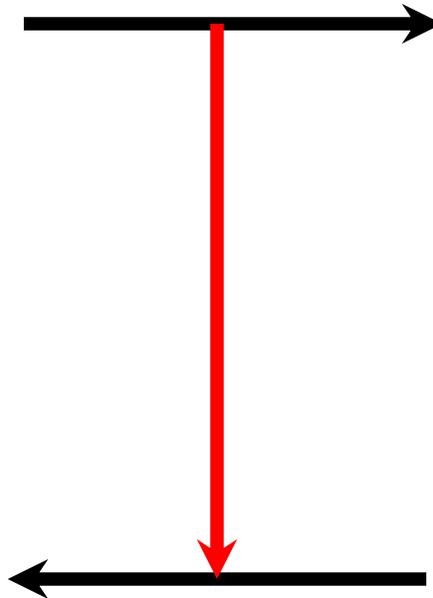
$$W = \frac{1}{4\pi\epsilon_0} \left(\frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{r^3} - \frac{3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r})}{r^5} \right)$$

Example: Effect of Dipole Orientation

Consider two dipoles, which have the orientations below that we can call aligned



and head-to-tail



Aligned: $\mu_1 \cdot \mu_2 = \mu^2$, $\mu_1 \cdot r = \mu r$, $\mu_2 \cdot r = \mu r$, $W = -2\mu^2/4\pi\epsilon_0 r^3$
Head-to-tail: $\mu_1 \cdot \mu_2 = -\mu^2$, $\mu_1 \cdot r = 0$, $\mu_2 \cdot r = 0$, $W = -\mu^2/4\pi\epsilon_0 r^3$

Electric moments

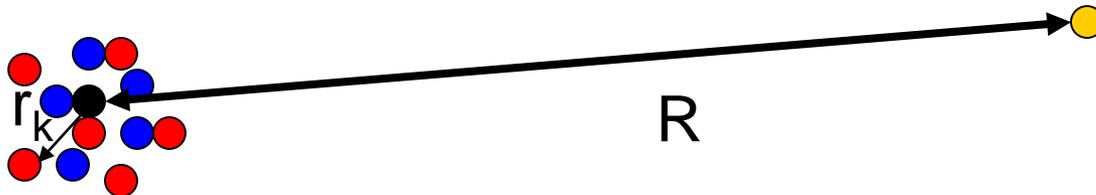
The potential due to discrete charge distribution is:

$$\phi(\mathbf{R}) = \frac{1}{4\pi\epsilon_0} \sum_k \frac{q_k}{|\mathbf{R} - \mathbf{r}_k|}$$

If the distance R of the test charge is large relative to the distances between the charges then the expansion:

$$\frac{1}{|\mathbf{R} - \mathbf{r}_k|} = \frac{1}{R} + r_k \cdot \nabla \left(\frac{1}{R} \right) + \frac{1}{2} r_k \cdot r_k : \nabla \nabla \left(\frac{1}{R} \right) + \dots$$

can be made



Electric moments

The potential is then given by:

$$4\pi\epsilon_0\phi(\mathbf{R}) = \frac{q}{R} + \mu \cdot \nabla \left(\frac{1}{R} \right) + \frac{1}{2} \Theta : \nabla \nabla \left(\frac{1}{R} \right) + \dots$$

This is the multipole expansion. The terms are the charge (also called the monopole), q , the dipole, μ , the quadrupole, Θ , and higher order terms.

$$q = \sum_i q_i = \int \rho(\vec{r}) d\vec{r}$$

$$\mu = \sum_i q_i \vec{r}_i = \int \rho(\vec{r}) \vec{r} d\vec{r}$$

$$\Theta = \sum_j \sum_i q_i \vec{r}_i \vec{r}_j = \int \rho(\vec{r}) \vec{r} \vec{r} d\vec{r}$$

q is a scalar,

μ is a vector (a first rank tensor)

Θ is a matrix (a second rank tensor)

Interaction of electric moments with the electric field

The interaction of a collection of charges subjected to an electric field is given by:

$$W = q\phi - \boldsymbol{\mu} \cdot \mathbf{E} + \frac{1}{2} \Theta : \nabla \mathbf{E} + \dots$$

The picture is that of a charge interacting with the potential, the dipole interacting with a field, the quadrupole interacting with the field gradient etc.

An electric field can exert a force:

$$\mathbf{F} = \sum_i q_i \mathbf{E}(r_i)$$

or a torque:

$$\mathbf{T} = \sum_i \mathbf{r}_i \times q_i \mathbf{E}(r_i)$$

on a collection of charges.

Polarizability

In the presence of an externally applied electric field the dipole moment of the molecule can also be expressed as an expansion in terms of moments:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 - \boldsymbol{\alpha} \cdot \mathbf{E} + \frac{1}{2} \boldsymbol{\beta} : \mathbf{E}\mathbf{E} + \dots$$

The leading term in this expansion is the permanent dipole moment, $\boldsymbol{\mu}_0$. The polarizability is a tensor whose components can be described as follows:

$$\alpha_{xy} = \left(\frac{\partial \mu_x}{\partial E_y} \right)_0$$

Where the 0 subscript refers to the fact that the derivative is evaluated at zero field. The $\boldsymbol{\beta}$ tensor is called the hyperpolarizability and is third ranked tensor.

Polarizability as second rank tensor

The dipole moment components each can depend on as many as three different polarizability components as described by the matrix:

$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

If a molecule has a center of symmetry (e.g. CCl_4) then the polarizability is a scalar (i.e. the induced dipole moment is always in the direction of the applied field). However, for non-centrosymmetric molecules components can be induced in other directions. The directions are often determined by the directions of chemical bonds, which may not be aligned with the field. This is the significance of the tensor.

Dielectric polarization

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Dielectric Polarization

We divide matter into two categories: conductors and insulators. Free charges in a conductor will respond to exactly cancel an applied field. The charges in an insulator will respond to an applied field in such a way as to partially cancel an applied electric field. The situation in an insulator is more complicated, however, since a molecule in the insulator will also experience a field due to the response of the insulator. There is a reaction field due to the response of the medium to charges on the molecule and there is a local field due to polarization of the solvent in the applied field. These issues are important for relating the molecular polarizability to the bulk polarization. Here we shall demonstrate the role of the dielectric constant (also called the relative permittivity) as a factor that relates the polarization of an insulator to an applied electric field.

The Electric Field in a Capacitor

The experimental geometry that is most convenient for the purpose of demonstrating the dielectric constant is the parallel plate capacitor. We compare a capacitor with vacuum between the charged plates to one with a dielectric. In the case of vacuum the field is:

$$\vec{E}_0 = \frac{\sigma}{\epsilon_0} \hat{z} = \frac{\phi}{d} \hat{z}$$

Notice that the way the field is defined, it is independent of what is placed in the capacitor. Field calculations are simple. Just use the voltage and divide by the separation distance. Common units of field are V/cm or V/m.

Illustration of the parallel plate capacitor

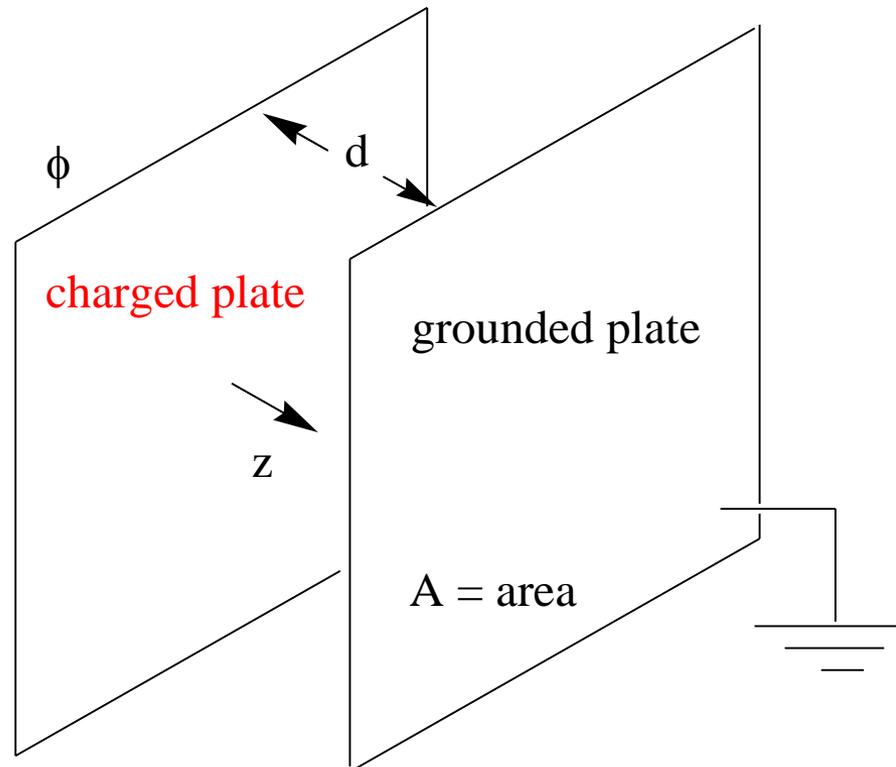
The surface charge density is $\sigma = q/A$.

The vacuum permittivity is ϵ_0 .

The potential is ϕ and the distance between the plates is d .

The unit vector z is normal to the capacitor plates.

These features are illustrated below.



Definition of the Dielectric Constant

If we now place a dielectric medium between the plates at constant voltage we have:

$$\vec{E} = \frac{\sigma}{\varepsilon} \hat{z} = \frac{\sigma}{\varepsilon_r \varepsilon_0} \hat{z} = \frac{\phi}{d} \hat{z}$$

Note that the field is unchanged. It is still the voltage divided by the distance. However, the surface charge density required to attain this field is different (σ' instead of σ) because the medium has a permittivity ε . Note that since the surface charge density increases when the dielectric is present the capacitance also increases.

The relationship between the dielectric constant and the permittivity of vacuum is $\varepsilon = \varepsilon_r \varepsilon_0$. The relative permittivity ε_r is commonly called the dielectric constant. The dielectric constant is greater than 1 and can be as large 111.0 for formamide (see Table 3.1 in Mol. Spectroscopy by McHale).

Dielectric Polarization

The larger the dipole moment the greater the tendency of the solvent to respond to an applied field by reorientation of the microscopic dipoles. However, inspection of Table 3.1 shows that there are exceptions and that liquid structure and collective dynamics also play a role.

To see the connection between the dielectric constant and the polarization we perform an experiment. We charge up the capacitor in vacuum. The field is $E_0 = \sigma/\epsilon_0$. Then we add an insulating medium with dielectric constant ϵ_r leaving the charges constant. Now the field is $E = \sigma/\epsilon = \sigma/\epsilon_r\epsilon_0$. The field is reduced in this case because the amount of charge is kept constant. The difference between E and E_0 is due to the polarization of the medium, P .

$$\vec{E} = \vec{E}_0 - \frac{\vec{P}}{\epsilon_0}$$

Dielectric Polarization

We call E the macroscopic field. The relationship between E and E_0 is:

$$\vec{E}_0 = \epsilon_r \vec{E}$$

Solving for the polarization we find:

$$\vec{P} = \epsilon_0 (\vec{E}_0 - \vec{E})$$

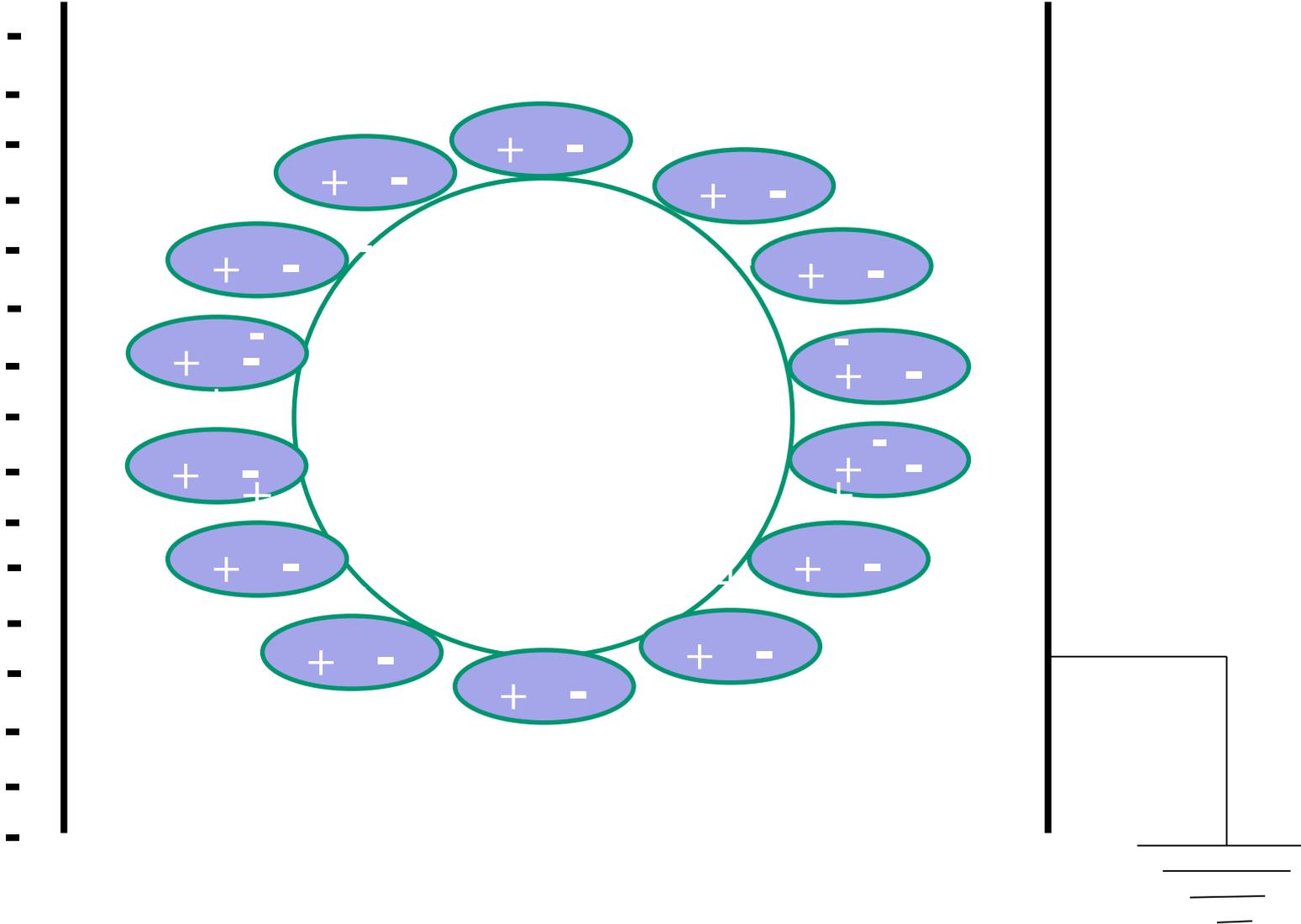
Thus, the polarization is proportional to macroscopic field:

$$\vec{P} = \epsilon_0 (\epsilon_r - 1) \vec{E} = \epsilon_0 \chi_e \vec{E}$$

where χ_e is the electric susceptibility.

One main goal of studies of dielectric polarization is to relate macroscopic properties such as the dielectric constant to microscopic properties such as the polarizability.

The spherical cavity approximation



Non-polar gas phase molecules

The relationship between polarizability and susceptibility is simple for non-polar molecules in the gas phase where intermolecular interactions can be ignored. The polarization can be immediately expressed in terms of both electric susceptibility (macroscopic) and polarizability (microscopic).

$$\vec{P} = \epsilon_0 \chi_e \vec{E} = \frac{N}{V} \alpha \vec{E}$$

We can see that

$$\chi_e = \frac{N\alpha}{V\epsilon_0}$$

and since $\epsilon_r = 1 + \chi_e$

$$\epsilon_r = 1 + \frac{N\alpha}{V\epsilon_0}$$

Furthermore since $\epsilon_r = n^2$ we have $n = \sqrt{1 + \frac{N\alpha}{V\epsilon_0}} \approx 1 + \frac{N\alpha}{2V\epsilon_0}$

Non-polar molecules in condensed phase

Interactions between non-polar molecules cannot be neglected in condensed phases. The treatment considers a local field \mathbf{F} inside the dielectric and its relation to an applied field \mathbf{E} . The Lorentz local field considers a spherical region inside a dielectric that is large compared to the size of a molecule. The field inside this uniformly polarized sphere behaves as if it were due to a dipole given by:

$$\vec{\mu} = \frac{4\pi a^3}{3} \vec{P}$$

Since P is the polarization per unit volume and $4\pi a^3/3$ is the volume of the sphere we see that μ is the induced dipole moment or polarization (these are equivalent). The local field is the macroscopic field \mathbf{E} minus the contribution of the due to the matter in the sphere:

$$\vec{F} = \vec{E} - \vec{E}_{int} = \vec{E} + \frac{\vec{P}}{3\epsilon_0}$$

Lorentz local field

Since $\vec{P} = \epsilon_0(\epsilon_r - 1)\vec{E}$

the Lorentz local field is $\vec{F} = \frac{1}{3}(\epsilon_r + 2)\vec{E}$

Since $\epsilon_r = 1$ for vacuum and $\epsilon_r > 1$ for all dielectric media it is apparent that the local field is always larger than the applied field. This simple consequence of the theory of dielectric polarization causes confusion. We usually think of the dielectric constant as providing a screening of the applied field. Therefore, we might be inclined to think of a local field as smaller than the applied field. However, this naïve view ignores the role of the polarization of the dielectric itself. Inside the sphere we have carved out of the dielectric we observe the macroscopic (applied) field *plus* the field due to the polarization of the medium. The sum of these two contributions leads to a field that is always larger than the applied electric field.

The Clausius-Mosotti Equation

The polarization is the number density times the polarizability times the local field.

$$\vec{P} = \frac{N\alpha}{V} \vec{F} = \frac{N\alpha}{3V} (\epsilon_r + 2) \vec{E}$$

We have already seen that

$$\vec{P} = \epsilon_0 (\epsilon_r - 1) \vec{E}$$

We eliminate E to obtain the Clausius-Mosotti equation.

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{N\alpha}{3\epsilon_0 V}$$

This equation connects the macroscopic dielectric constant ϵ_r to the microscopic polarizability. Since $\epsilon_r = n^2$ we can replace these to obtain the Lorentz-Lorentz equation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N\alpha}{3\epsilon_0 V}$$

Lorentz-Lorentz Equation

Again here the equation connects the index of refraction (macroscopic property) to the polarizability (microscopic property). The number density N/V can be replaced by the bulk density ρ (gm/cm³) through

$$\frac{N}{V} = \frac{N_A \rho}{M}$$

where N_A is Avagadro's number and M is the molar mass. Thus, the Lorentz-Lorentz equation that connects the index of refraction with the polarizability is:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N_A \alpha}{3\epsilon_0 M} \rho$$

Polar molecules

The polarization we have discussed up to now is the electronic polarization. If a collection of non-polar molecules is subjected to an applied electric field the polarization is induced only in their electron distribution. However, if molecules in the collection possess a permanent ground state dipole moment, these molecules will tend to reorient in the applied field. The alignment of the dipoles will be disrupted by thermal motion that tends to randomize the orientation of the dipoles. The nuclear polarization will then be an equilibrium (or ensemble) average of dipoles aligned in the field.

$$\vec{P}_0 = \frac{N\langle\vec{\mu}\rangle}{V}$$

Equilibrium averaged dipole moment

The angle brackets indicate the equilibrium average. If the permanent dipole moment is μ_0 , then the interaction with the field is $W = -\mu_0 \times \mathbf{F} = -\mu_0 F \cos\theta$ where θ is the angle between the dipole and the field direction. Thus, the average dipole moment is

$$\langle \vec{\mu} \rangle = \mu_0 \langle \cos\theta \rangle$$

The average indicated is an average over a Boltzmann distribution.

$$\langle \cos\theta \rangle = \frac{\int_0^\pi \cos\theta \exp\left\{-\frac{W}{k_B T}\right\} \sin\theta d\theta}{\int_0^\pi \exp\left\{-\frac{W}{k_B T}\right\} \sin\theta d\theta}$$

Equilibrium averaged dipole moment

Substituting in for the interaction energy W we find

$$\langle \cos \theta \rangle = \frac{\int_0^\pi \cos \theta \exp \left\{ \frac{\mu_0 F \cos \theta}{kT} \right\} \sin \theta d\theta}{\int_0^\pi \exp \left\{ - \frac{\mu_0 F \cos \theta}{kT} \right\} \sin \theta d\theta}$$

We make the substitutions

The integral is $u = \frac{\mu_0 F}{kT}$, $x = \cos \theta$

The Langevin Function

And the integral becomes:

$$\begin{aligned}\cos \theta &= \frac{\int_{-1}^1 x \exp\{ux\} dx}{\int_{-1}^1 \exp\{ux\} dx} = \frac{\frac{e^u(u-1)}{u^2} + \frac{e^{-u}(u+1)}{u^2}}{\frac{e^u}{u} - \frac{e^{-u}}{u}} \\ &= \frac{e^u + e^{-u} - \frac{(e^u - e^{-u})}{u}}{e^u - e^{-u}} = \coth(u) - \frac{1}{u}\end{aligned}$$

The function $\coth(u) - 1/u$ is known as the Langevin function. It approaches $u/3$ for $u \ll 1$ and 1 when u is large. The limit for large u is easy to see. The limit for small u requires carrying out a Taylor's series expansion of the function to many higher order terms.

The Langevin Function

For typical fields employed $\mu_0 F/kT \ll 1$. You can convince yourself of this using the following handy conversion factors

$$\mu_0 F = 1.68 \times 10^{-5} \text{ cm}^{-1}/(\text{DV}/\text{cm})$$

$$k = 0.697 \text{ cm}^{-1}/\text{K}$$

For example, at 300 K, thermal energy is 209 cm^{-1} . For liquid water ($\mu_0 \approx 2.4 \text{ D}$) in a $10,000 \text{ V}/\text{cm}$ field we have $W = 0.4 \text{ cm}^{-1}$. Here $u = \mu_0 F/kT$ is of the order of $1/1000$. Thus, we can express the orientational polarization as

$$P_0 = \frac{N\mu_0 \cos \theta}{V} = \frac{N\mu_0^2}{3VkT} F$$

The total polarization is the sum of the electronic and orientational polarization terms

$$\vec{P}_{tot} = \vec{P}_e + \vec{P}_0 = \frac{N}{V} \left(\alpha + \frac{\mu_0^2}{3k_B T} \right) \vec{F}$$

The Debye Equation

Following the same protocol used above to derive the Clausius-Mossotti equation, we obtain the Debye equation for the molar polarization

$$\vec{R} = \frac{M}{\rho} \left(\frac{\epsilon_r - 1}{\epsilon_r + 2} \right) = \frac{N_A}{3\epsilon_0} \left(\alpha + \frac{\mu_0^2}{3k_B T} \right) \vec{F}$$

This equation works reasonable well for some organics, however, it fails for water. The reason for the failure of the Debye model is that the Lorentz local field correction begins with a cavity large compared to molecular dimension and thus ignores local interactions of solvent dipoles.

The Local Field Problem

The local field problem is one of the most vexing problems of condensed phase electrostatics. Following Lorentz there are two models, the Onsager model and the Kirkwood model that attempt to account for the local interactions of solvent molecules in an applied electric field. The approaches discussed here are all continuum approaches in that there is a cavity and outside that cavity the medium is treated as a continuum dielectric with dielectric constant ϵ_r . The models differ in how they define the cavity. As stated above, Lorentz model assumes a large cavity (a is much larger than the molecule size). The Onsager model focuses on the creation of a cavity around a single molecule of interest (a is equal to the molecule size). The Kirkwood model includes a cluster around the molecule to account for local structure.

The Onsager Model

The Debye model assumes that the dipole μ_0 is not affected by the solvation shell. Yet consider water which has a gas phase dipole moment of 1.86 D and in condensed phase has a dipole moment in the range 2.3 - 2.4 D. The neighboring water molecules have a large effect inducing a dipole moment more than 25% larger than the gas phase dipole moment.

The dipole moment \mathbf{m} is the sum of the permanent and induced parts

$$\mathbf{m} = \mu_0 + \alpha \mathbf{F}$$

The local field \mathbf{F} has two contributions, the cavity field \mathbf{G} and the reaction field \mathbf{R} .

$$\mathbf{F} = \mathbf{G} + \mathbf{R}$$

The cavity field is given the spherical cavity approximation in terms of the applied field

$$\mathbf{G} = \frac{3\varepsilon_r}{2\varepsilon_r + 1} \mathbf{E}$$

The Onsager Model

Notice that the cavity field is always greater than one. This is exactly analogous to the Lorentz local field. However, the Lorentz local field increases without bound as ϵ_r increases. The Onsager cavity field increases from 1 to 1.5 as ϵ_r approaches ∞ . The reaction field is proportional to the dipole moment of the molecule in the cavity:

$$\mathbf{R} = \left(\frac{\epsilon_r - 1}{2\epsilon_r + 1} \right) \left(\frac{\mathbf{m}}{2\pi a^3 \epsilon_0} \right) \equiv g\mathbf{m}$$

The reaction field is always parallel to the permanent dipole moment. Only the cavity field can exert a torque on the dipole and cause it to align in the applied field. By separating these two effects the Onsager model improves upon the Debye equation..

The Onsager Model

The Onsager reaction field is also an important relation for understanding the effect of solvents on the absorption and emission spectra of polar and polarizable molecules.

Solvatochromism is the measurement of the effect of the solvent on the maximum position of the absorption band.

Relaxation dynamics are also measured by determining the change in fluorescence maximum in fluorescent dyes in order to obtain an estimate of the reorientational dynamics of solvents.

Frequency dependent dielectric function

Viewed from a microscopic perspective we know that the molecular polarizability is frequency dependent. Electronic polarizability is present in all molecules and has a response time that is rapid ($> 10^{14} \text{ s}^{-1}$). The high frequency response can follow the undulations of electromagnetic radiation in the visible region and hence this response gives rise to refraction of light. This contribution is the high frequency or optical dielectric constant, ϵ_{∞} . There is a nuclear polarizability in polar molecules due to their tendency to align in an applied electric field due to the torque of the applied field in the frequency range from 10^6 to 10^{10} s^{-1} . These motions give rise to absorption and dispersion in the microwave region. They also contribute to the low frequency or static dielectric constant, ϵ_r . The static dielectric constant is not really static, but rather is due to changes in the electrical response due to dipolar reorientation.

Complex dielectric function

We shall dissect the relative permittivity, ϵ_r into real and imaginary parts:

$$\epsilon_r(\omega) = \epsilon_r'(\omega) + i\epsilon_r''(\omega)$$

These two contributions represent the in-phase (ϵ_r') and out-of-phase (ϵ_r'') components of the frequency response of the medium. The in-phase component results in dispersion. Physically this means refraction of the electromagnetic radiation as it passes through the medium. The out-of-phase component gives rise to absorption. Absorption occurs in the visible (electronic state transitions), infrared (vibrational transitions), and microwave (rotational transitions). The real and imaginary parts of the frequency dependence dielectric response are related to one another by Kramers-Kronig relations.

Kramers-Kronig Relations

$$\varepsilon_r'(\omega) = \varepsilon_\infty + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_r''(s) s ds}{s^2 - \omega^2}$$

$$\varepsilon_r''(\omega) = \frac{-2\omega}{\pi} \int_0^\infty \frac{\varepsilon_r' - \varepsilon_\infty}{s^2 - \omega^2} ds$$

The importance of these equations for spectroscopy is that we can obtain information on absorptive processes by measuring dispersion. For example, diffuse reflectance spectra from crystals can be transformed into absorption spectra.

The refractive index can also be represented as a complex quantity.

$$N(\omega) = n_r(\omega) + i\kappa(\omega)$$

Relationship to index of refraction

The high frequency part of the dielectric response is equal to the square of the index of refraction, $\epsilon_r(\omega) = N(\omega)^2$. Equating real and imaginary parts leads to

$$\begin{aligned}\epsilon'_r(\omega) &= n_r^2(\omega) - \kappa^2(\omega) \\ \epsilon''_r(\omega) &= 2n_r(\omega)\kappa(\omega)\end{aligned}$$

The real part of the index of refraction, $n_r(\omega)$ is the factor by which the speed of light is reduced as it traverses a medium. The imaginary part of the index of refraction, $\kappa(\omega)$ is an absorption coefficient. To understand the effects of these two terms, consider an electric field

$$E = \text{Re } E_0 \exp \left\{ i(kx \pm \omega t) \right\}$$

Absorption

The wavevector in vacuum is $k = \frac{2\pi}{\lambda}$

and in a dielectric medium it is $k = \frac{2\pi N}{\lambda}$

Considering both the real and imaginary parts of the index of refraction we have

$$E = \text{Re } E_0 \exp \left\{ i \left(\frac{2\pi n_r x}{\lambda} \pm \omega t \right) \right\} \exp \left\{ - \frac{2\pi \kappa x}{\lambda} \right\}$$

The exponentially decaying term represents the attenuation of radiation as it passes through an absorptive medium. Since the intensity is proportional to the square of the amplitude of the electric field

$$I = I_0 \exp\{-\gamma x\} = I_0 \exp \left\{ - \frac{4\pi \kappa x}{\lambda} \right\}$$

The absorption coefficient

The absorption coefficient γ is

$$\gamma(\omega) = \frac{\omega \epsilon''(\omega)}{n_r c}$$

The absorption coefficient can be related to the molar absorptivity ϵ (units of $\text{L mol}^{-1} \text{cm}^{-1}$) by comparing Beer's law to the above expression

$$I = I_0 10^{-\epsilon(\omega) C x}$$

The exponential can be converted to base e:

$$I = I_0 \exp\{-2.303 \epsilon(\omega) C x\}$$

In the above expression x is the pathlength and C is the concentration. Using these relations we can establish the connection between the imaginary part of the dielectric constant and the molar absorptivity.

Relationship to extinction coefficient

The imaginary part of the dielectric function is related to the extinction coefficient as follows:

$$\epsilon''(\omega) = \frac{2303Ncn_r\epsilon(\omega)}{\omega V N_A}$$

where N/V is the number of absorbing molecules per cm^3 . This can also be expressed as the number of moles per L.

$$\epsilon''(\omega) = \frac{2.303Ccn_r\epsilon(\omega)}{\omega}$$

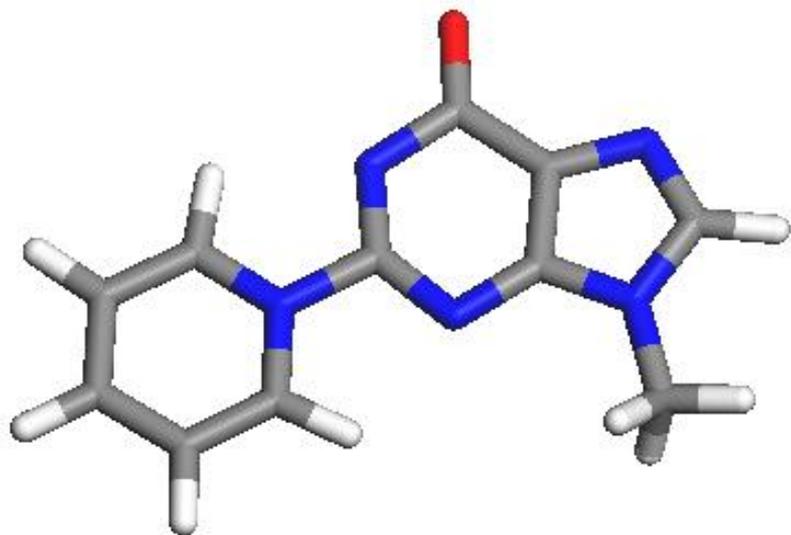
Which can be solved for a definition of the extinction coefficient:

$$\epsilon(\omega) = \frac{\omega\epsilon''(\omega)}{2.303Ccn_r}$$

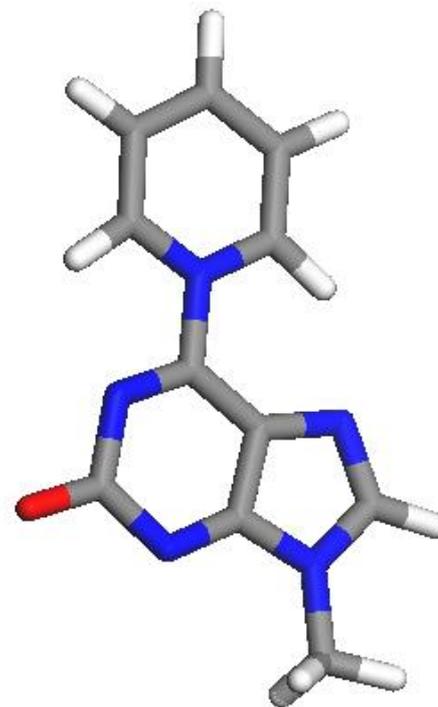
Solvatochromism and Electrochromism by DFT

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Xanthine Pyridinium Betaines



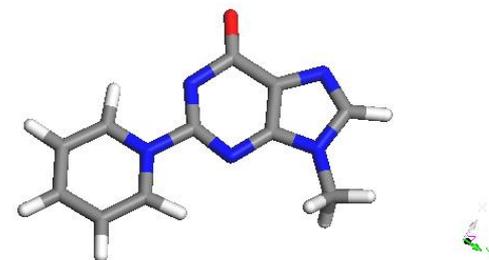
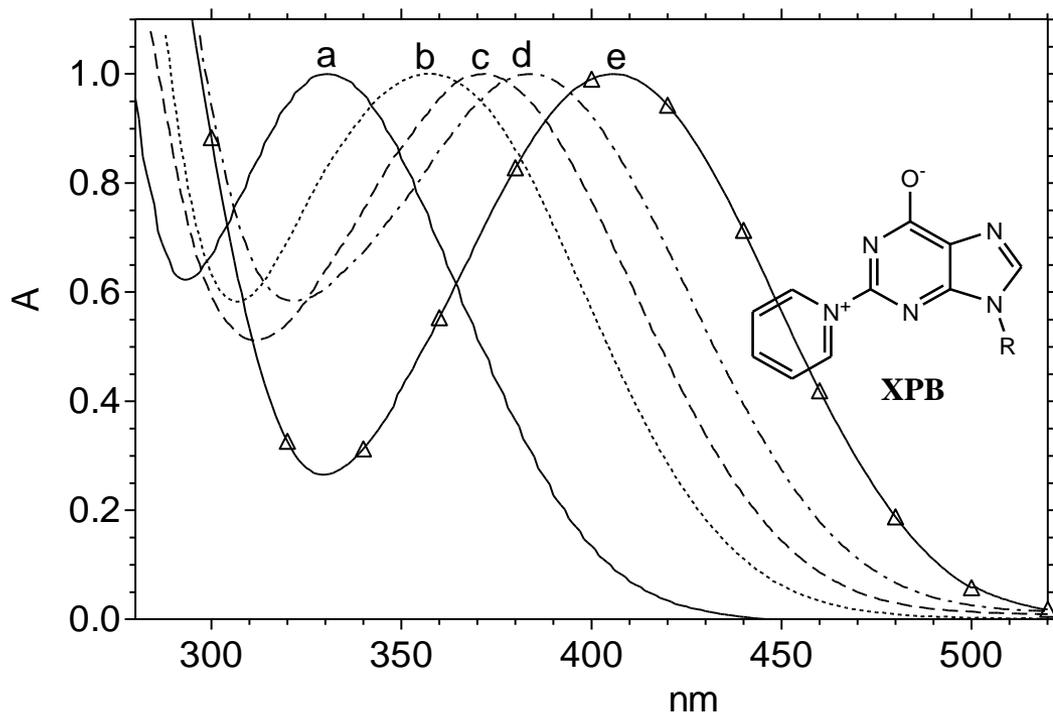
XPBM



XPBRM

A new class of solvatochromic molecules

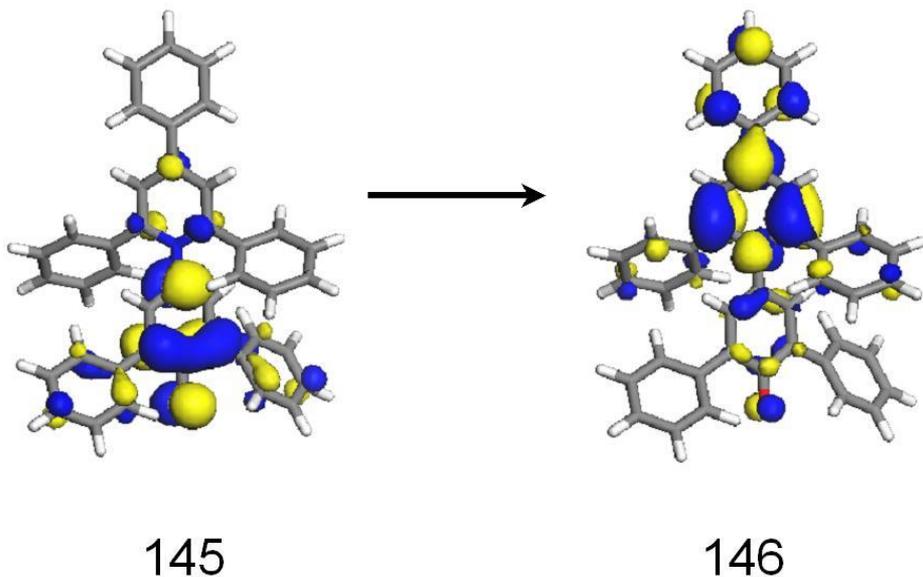
Solvatochromism: solvent effect on absorption spectrum



- a Water
- b Ethanol
- c Butanol
- d Dimethylsulfoxide
- e Chloroform

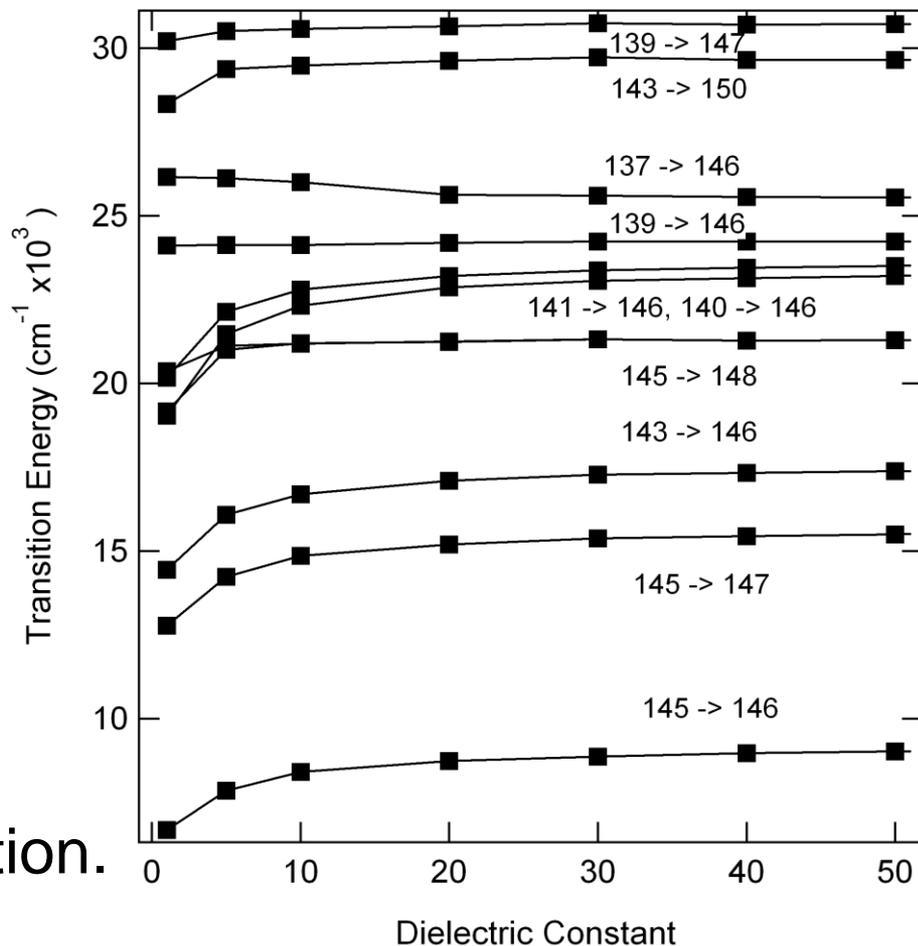
XPBs, a new class of solvatochromic molecules.

Origin of Solvatochromism

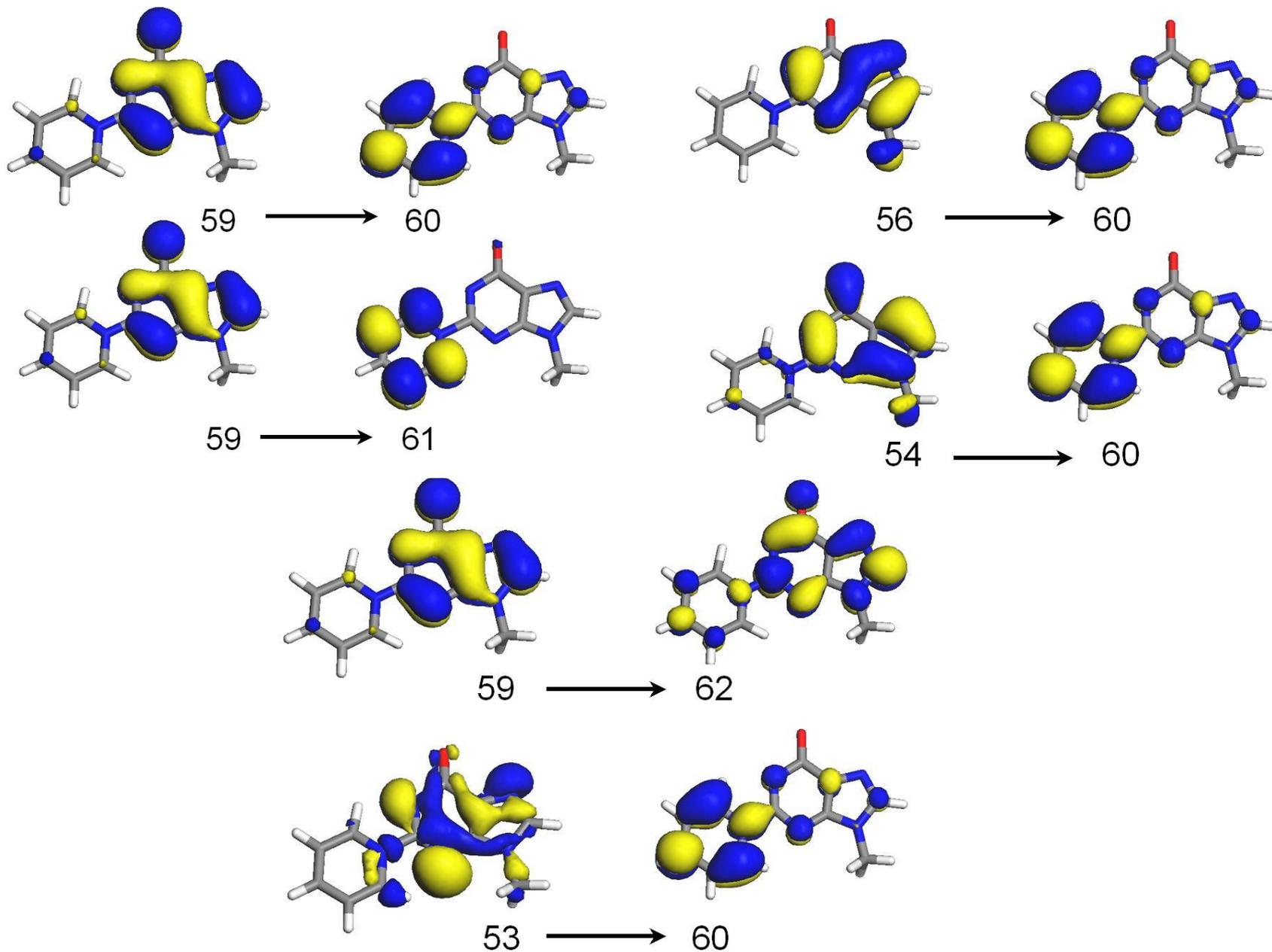


TD-DFT calculation shows that this is the intense transition. Energy is $11,871 \text{ cm}^{-1}$.

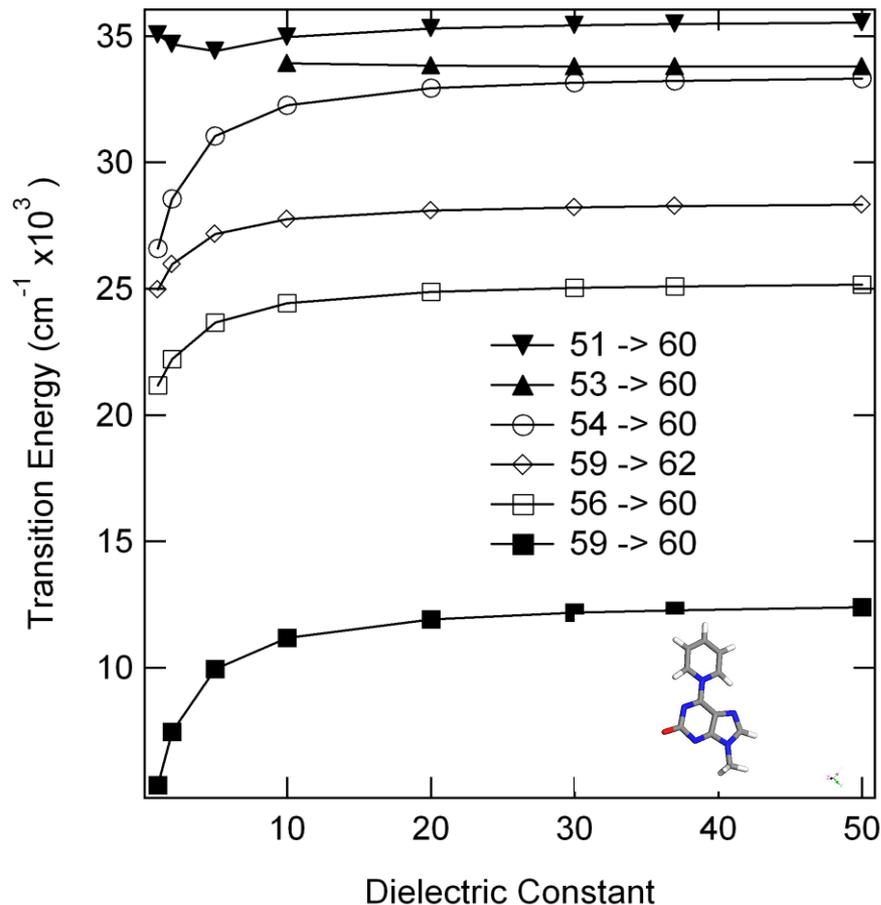
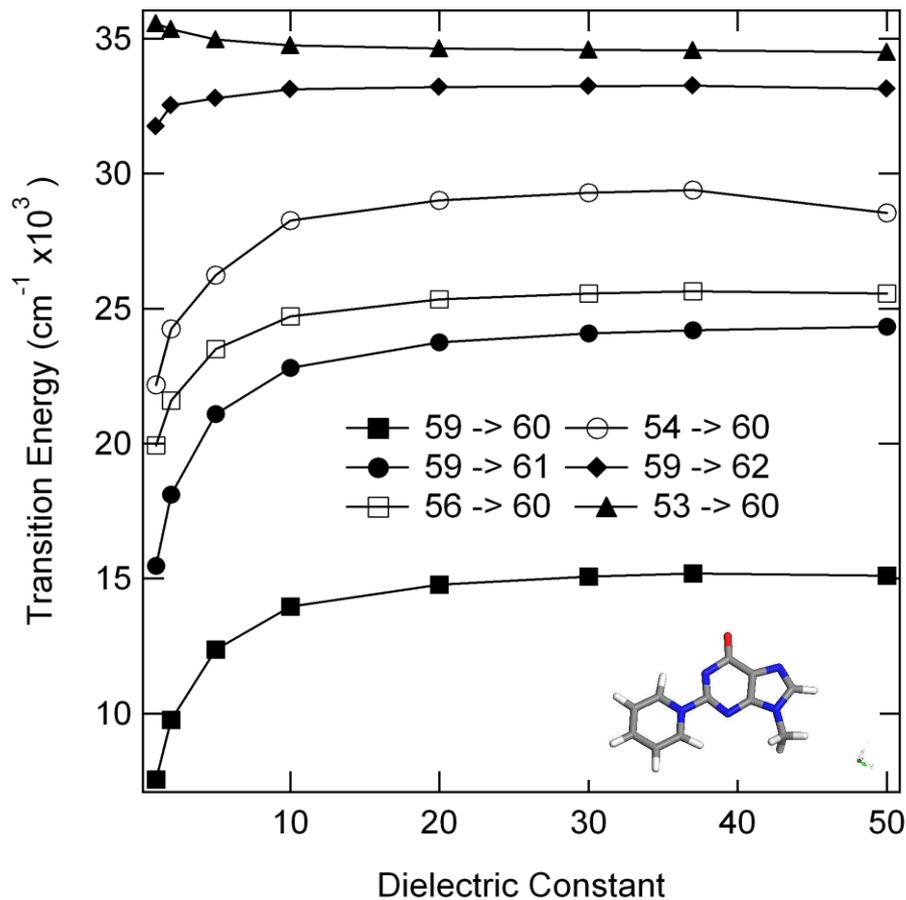
Classic solvatochromic molecule: Reichardt's dye
Basis for the $E_T(30)$ solvent polarity scale



Calculated transitions for XPBM

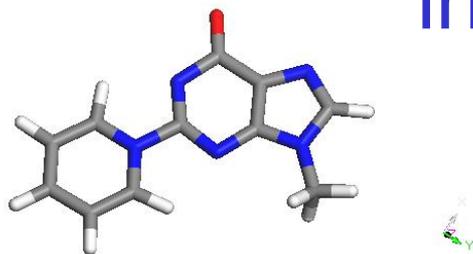


DFT calculation of solvatochromism



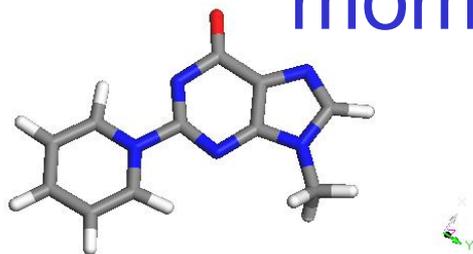
Use COSMO continuum dielectric model to obtain absorption spectra as a function of ϵ . This is a model for solvatochromism.

Calculated electrochromism using DFT: Obtain the shift in wavenumber in an applied field



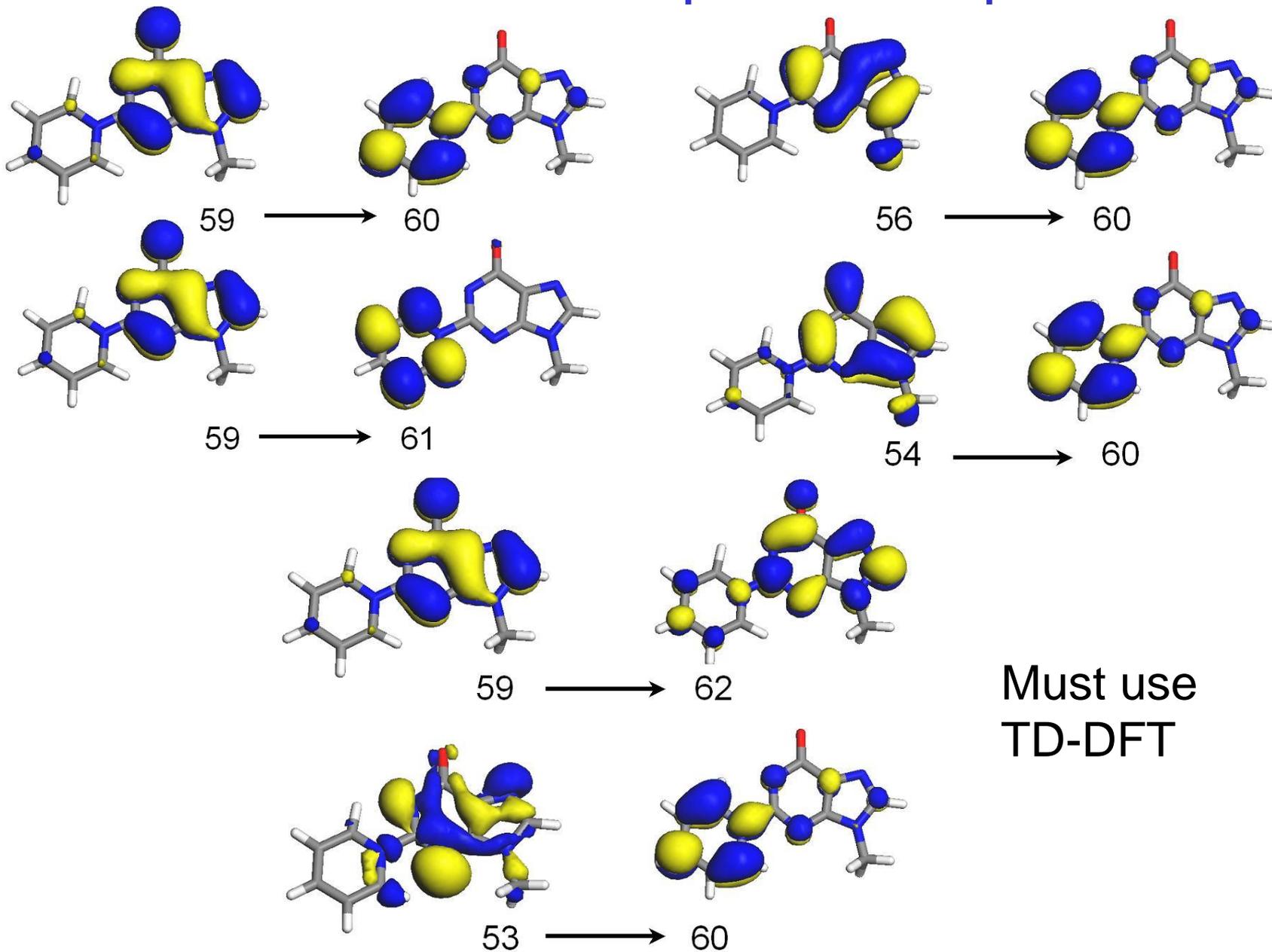
Transition	$\epsilon = 1$	$\epsilon = 5$	$\epsilon = 10$	$\epsilon = 15$	$\epsilon = 20$	$\epsilon = 30$
59 → 60	605.5	1215.1	1333.7	1373.4	1393.2	1413.0
59 → 61	726.1	1411.0	1542.3	1588.0	1610.9	1633.7
56 → 60	703.1	1342.3	1469.5	1509.5	1529.5	1549.4
54 → 60	759.2	1322.2	1390.1	1416.8	1429.2	1440.5
59 → 62	153.2	119.3	69.1	60.8	56.1	51.7
53 → 60	211.9	595.6	219.3	194.8	197.3	200.8
59 → 63	46.9	126.5	179.4	445.1	209.2	276.1

Calculated electrochromism using DFT: Convert the shift into a difference dipole moment using $U = -\Delta\mu \cdot F$



Transition	$\epsilon = 1$	$\epsilon = 5$	$\epsilon = 10$	$\epsilon = 15$	$\epsilon = 20$	$\epsilon = 30$
59 → 60	3.5	7.0	7.6	7.9	8.0	8.1
59 → 61	4.2	8.1	8.8	9.1	9.2	9.4
56 → 60	4.0	7.7	8.4	8.7	8.8	8.9
54 → 60	4.4	7.6	8.0	8.1	8.2	8.3
59 → 62	0.89	0.68	0.40	0.35	0.32	0.30
53 → 60	1.2	3.4	1.3	1.1	1.1	1.2
59 → 63	0.27	0.73	1.0	2.5	1.2	1.6

Which transitions correspond to experiment?

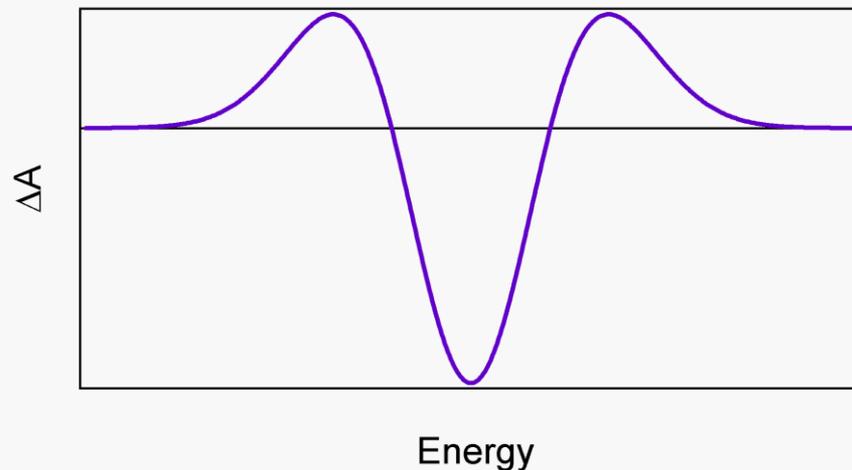
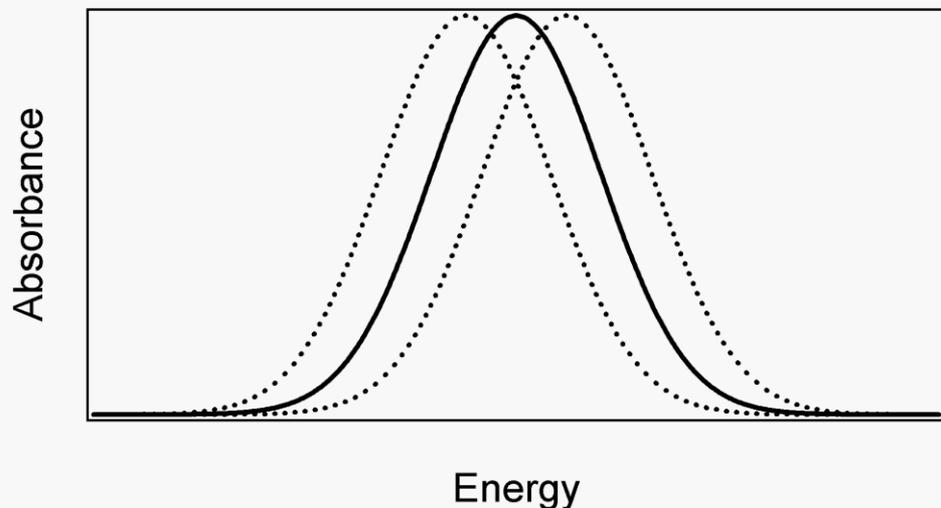


Must use
TD-DFT

Electroabsorption

NC State University

Band broadening due to difference dipole moment $\Delta\mu_A$



Band shift due to difference dipole moment $\Delta\alpha$

