

Module 3 : Nonlinear susceptibilities of materials

Lecture 18 : Organic Nonlinear Optical Materials

Objectives

In this lecture you will learn the following

- An introduction to organic nonlinear optical materials.
- Relation between molecular polarizability and susceptibility.
- Simple models for p-electrons.
- Crystals.

The Organic materials are molecular in nature and their nonlinear susceptibilities can be understood in terms of molecular hyper-polarizabilities. The relation between condensed phase susceptibilities and molecular hyper-polarizabilities is discussed first followed by main ideas in the development of molecules with very high nonlinear susceptibilities. One of the major attractions of organic materials is the enormous variety of possible materials. Most of the nonlinear optical materials have their nonlinearity attributed to conjugated π electrons - a very important exception being urea and its derivatives. For an ideal molecular crystal, it is expected that the molecular response does not depend strongly on the environment, i.e. molecular properties are transferable. Then, to know the nonlinear susceptibilities for a molecular crystal all we need to know are the molecular polarizabilities and their relative orientation in the condensed phase.

The dipole moment of a molecule placed in an electric field is given by

$$\mu_i = \mu_i^{(0)} + \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \dots \quad (18.1)$$

where i, j, k and l are cartesian components and summation over repeated indices is implied. $\mu_i^{(0)}$ is the permanent dipole of the molecule, α_{ij} the linear polarizability tensor, β_{ijk} and γ_{ijkl} the second and third order nonlinear polarizabilities, respectively. Sometimes, in literature β is referred to as first hyperpolarizability and γ the second hyperpolarizability.

For an ideal molecular crystal, i.e. one in which the intermolecular forces can be neglected, the linear and nonlinear susceptibilities are given by

$$\chi_{IJK}^{(2)}(-\omega, \omega_1, \omega_2) = \frac{1}{V} f_I(\omega) f_J(\omega_1) f_K(\omega_2) \sum_{s,j,k} \cos \theta_{Is}^j \cos \theta_{Js}^k \cos \theta_{Ks}^l \beta_{ijk}(-\omega, \omega_1, \omega_2) \quad (18.2)$$

where by I, J, K , we denote the crystallographic axes, and by i, j, k the molecular principal axes, and θ_{Is}^j is the angle between the crystallographic axis I and the molecular axis i . The index s goes over all the molecules in a unit cell and V is the volume of the unit cell. $f_j(\omega)$ are the components of the local field factor which arise because the field experienced by a molecule in a condensed medium differs from the applied field due to fields radiated by other induced dipoles. The most common model used to estimate the local field is the Lorentz model in which in the quasi-static approximation:

$$f_I(\omega) = 1 + (\epsilon_\infty(\omega) - 1) L_I \quad (18.3)$$

with L_I denoting the depolarization factor which depends on the form of cavity surrounding the molecule. When orientation of permanent dipoles in the fluids are included in the local field calculation, another local field correction factor called Onsager correction factor is more appropriate. It is given by

$$f(0) = \epsilon(0)(\epsilon(\omega) + 2) / (2\epsilon(0) + (\epsilon(\omega))) \quad (18.4)$$

It should be emphasized that the understanding of local fields is still quite rudimentary and depends on many approximate pictures. The main thrust in the search for more efficient molecular nonlinear media is to find the molecules with largest nonlinear polarizabilities.

MOLECULAR POLARIZABILITIES:

The most important organic molecules are organic dyes which have conjugated double or triple bonds i.e. double or triple bonds separated only by one single bond. The benzene molecule is the best example of such molecules. Now, a single C-C bond is ~ 1.54 Å in length while a double bond is ~ 1.33 Å long. In benzene all C-C distances are equal and 1.39 Å. In traditional chemistry language, we say that the benzene molecule resonates between two equivalent structures so that all bonds are equal. If we write the wavefunction of carbon atoms, the geometry of the structure suggests that 3 hybridized atomic orbitals are

$$|\sigma 1\rangle = \frac{1}{\sqrt{3}}|s\rangle + \frac{1}{\sqrt{2}}|p_x\rangle - \frac{1}{\sqrt{6}}|p_y\rangle \quad (18.5)$$

$$|\sigma 2\rangle = \frac{1}{\sqrt{3}}|s\rangle - \frac{1}{\sqrt{2}}|p_x\rangle - \frac{1}{\sqrt{6}}|p_y\rangle \quad (18.6)$$

$$|\sigma 3\rangle = \frac{1}{\sqrt{3}}|s\rangle + \frac{1}{\sqrt{2}}|p_y\rangle \quad (18.7)$$

These orbitals are symmetric about the $z=0$ plane in which all the nuclei lie. The fourth orbital normal to these is the π orbital

$$|\pi\rangle = |p_z\rangle \quad (18.8)$$

These π -electrons overlap with other π -electrons on either side and are thus free to move on above and below the plane of the molecule as illustrated in the figure 18.1 below. The π -electrons contribute significantly to the chemical and optical properties of these molecules.

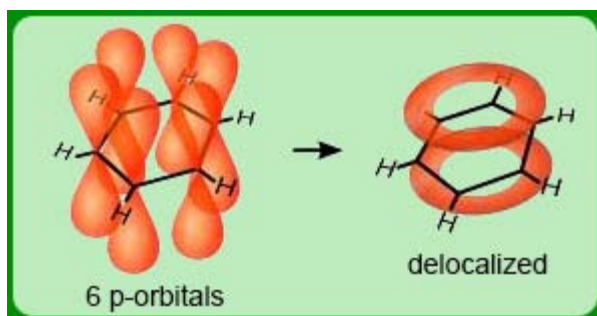


Figure 18.1 p-electron cloud in benzene.

The simplest and as we shall see the most interesting π -electron systems are one-dimensional π -electrons chains called cyanine dyes and polyenes shown in Figures 18.2 and 18.3, respectively.

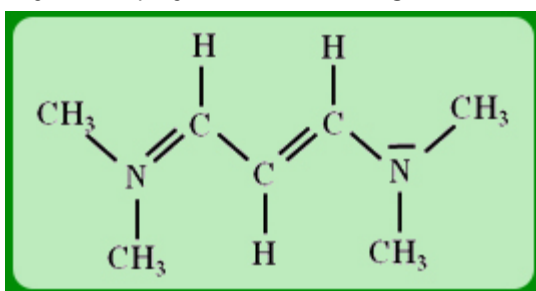


Figure 18.2 A symmetric cyanine dye with 2 conjugated p-electrons.

Additional $C=C$ pairs can be added to form longer chains. Bar on the N atom denotes that the atom contributes 2 electrons to the p electron chain (since of the 5 valence electrons of N only 3 are used in forming the 3 s bonds.) The molecule shown is a positive ion implying that the other N atom has only 4 valence electrons.

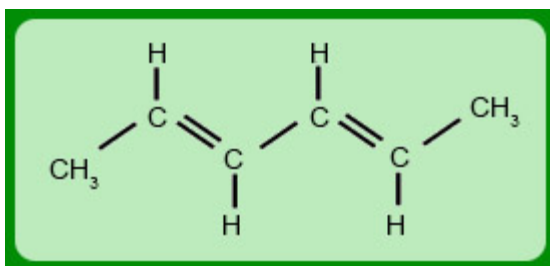


Figure 18.3 A polyene dye with 2 conjugated double bonds.

In all these molecules, the CH_3 groups can be replaced by other monovalent groups without significantly changing the optical spectra of the molecule.

In the symmetric cyanines the exchange of single and double bonds still satisfies all the valence of all atoms, so as in the case of benzene the conjugated bond chain is expected to have all bonds of equal

length the effective potential seen by p electrons then is periodic with a period equal to one bond length. However, in polyenes, this is not true and thus single and double bonds have different lengths and the effective potential seen by n electrons is periodic with period equal to the sum of single bond length+ double bond length. This has important consequences for their optical properties. In the spirit of empirical pseudo-potential theory of semiconductors, we can say that cyanines are like a 1-dimensional free electron gas with periodic potential with period $\bar{l} = (l_{\text{single-bond}} + l_{\text{double-bond}})/2$ whereas polyenes are like a 1-dimensional free electron gas with periodic potential with period $2\bar{l}$. Thus, for infinite length a cyanine is like a one dimensional metal while a polyene is like a semiconductor because for cyanines there is one n-electron per unit cell while for polyenes there are two (because the unit cell has two atoms and each atom contributes one n-electron). The n-electrons in a cyanine with j conjugated double bonds can thus be represented by $2j+2$ free electrons in a box of length $2L = 2(j+1)\bar{l}$. A polyene with j conjugated double bonds is similarly represented by a box of length $2L = 2(j+1)\bar{l}$. This model for dyes has been in use for a long time and was first described elegantly by Kuhn [H. Kuhn, Fortsch. Chem. Org. Nat. 16 (1958) 169; ibid, 17 (1959)404]. He also showed that the model gives a good account of absorption maxima and their strengths. Calculations of linear and nonlinear polarizabilities based on this model provided interesting insights into the nature of nonlinear polarizabilities. We discuss this now.

FREE ELECTRON MODEL FOR NONLINEAR RESPONSE

The Hamiltonian is

$$H_0 = (-\hbar^2 / 2m)(\partial^2 / \partial x^2) \quad (18.9)$$

and the interaction with the field is represented by

$$H_1 = -eEx \quad (18.10)$$

The change in energy caused by this perturbation is expanded in a series

$$\Delta \mathcal{E} = -\frac{1}{2} \alpha E^2 - \frac{1}{3} \beta E^3 - \frac{1}{4} \gamma E^4 - \dots \quad (18.11)$$

The wave equations in successively higher orders are described in the following. In the zeroth order

$$(H_0 - \mathcal{E}_n^{(0)})\psi_n^{(0)} = 0 \quad (18.12)$$

has the solutions

$$\psi_n^{(0)} = \sqrt{L} \sin(n\pi(x+L)/L) \quad (18.13)$$

with

$$\mathcal{E}_n^{(0)} = \frac{\hbar^2 n^2}{8mL^2} \quad (18.14)$$

In the first order, we need to solve the equation

$$(H_0 - \mathcal{E}_n^{(0)})\psi_n^{(1)} = (\mathcal{E}_n^{(1)} - H_1)\psi_n^{(0)} \quad (18.15)$$

with

$$\mathcal{E}_n^{(1)} = \langle \psi_n^{(0)} | H_1 | \psi_n^{(0)} \rangle \quad (18.16)$$

Instead of using the usual expansion of the first order wave-function in terms of unperturbed wave functions we can solve the equation as an inhomogenous differential equation. The solution is arbitrary to the extent that a constant multiple of unperturbed wave function can be added. We fix this constant such that

$$\langle \psi_n^{(r)} | \psi_n^{(0)} \rangle = \delta_{r,0} \quad (18.17)$$

This gives an advantage that eigen values to order $(2n+1)$ can be obtained from wavefunction to order n . [L.I. Schiff, Quantum Mechanics, I II edition, (McGraw Hill, New York, 1968) p. 296].

In the second order,

$$(18.18)$$

$$(H_0 - \mathcal{E}_n^{(0)})\psi_n^{(2)} = (\mathcal{E}_n^{(1)} - H_1)\psi_n^{(1)} + \mathcal{E}_n^{(2)}\psi_n^{(0)}$$

Since $\mathcal{E}_n^{(2)}$ is known in terms of the first order wave functions, Eq (18.18) can be solved again as an inhomogenous differential equation. This yields energies upto 5th order in the imposed electric field. Then using the eq (18.11) we obtain closed form expressions for linear and third order polarizabilities:

$$\alpha = \frac{4L^4}{a_0} \sum_{n=1}^N \left\{ \frac{-2}{3\pi^2 n^2} + \frac{10}{3\pi^4 n^4} \right\} \quad (18.19)$$

and

$$\gamma = \frac{128L^{10}}{a_0^3 e^2} \sum_{n=1}^N \left\{ \frac{-2}{9\pi^6 n^6} + \frac{140}{3\pi^8 n^8} - \frac{440}{\pi^{10} n^{10}} \right\} \quad (18.20)$$

where a_0 is the Bohr radius. These results reveal several interesting aspects.

- The two sums in Eqs (18.19) and (18.20) both can be evaluated exactly in the limit $N \rightarrow \infty$ and vanish in that limit. Physically, this happens because for a fixed L, if we keep filling the states with more and more electrons the HOMO-LUMO gap keeps increasing. As $N \rightarrow \infty$, the system approaches a filled Fermi sea with infinite gap. Such a system is of course unpolarizable.
- This means that for moderately large lengths of the p-electron cloud we can approximate them as

$$\alpha \cong \frac{8L^4}{3a_0\pi^2 N}. \quad (18.21)$$

and

$$\gamma \cong \frac{256N^5 a^{10}}{45a_0^3 e^2 \pi^6} \quad (18.22)$$

Since the length of the box $2L$ and N the number of levels occupied both increase as j , the number of double bonds, we expect α to increase as j^3 and γ to increase as j^5 .

- For $\chi^{(1)}$ this means only a modest increase since the density for random packing will go like $\sim 1/j^3$.
- For $\chi^{(3)}$ a substantial increase is expected.
- Since transition dipole moments $\sim L$ and energy differences between highest occupied and lowest unoccupied levels $\sim 1/L$, the sum-over-states expressions imply that α should increase as L^3 as obtained by the exact calculation while γ should increase as $\sim L^7$ while it actually increases as L^5 .
- The reason for this is very interesting. In one dimensional case the energy levels of electrons at the Fermi level are very similar for a particle in a box and a harmonic oscillator. For a harmonic oscillator, of course, the hyper-polarizabilities are all zero.
- This happens because there are only 3 nonzero terms in the expression for γ and they cancel exactly. For particle in a box model too, there is a substantial cancellation, reducing the value of γ much below the three terms which do indeed go as L^7 .

An important consequence of this is that if one could somehow alter the energy levels selectively, one could substantially increase γ . Azo-cyanine dyes obtained by replacing the central $-\text{CH}$ by N atom (See figure 18.4) is one such perturbation that has been shown to be effective in increasing the anharmonicity. [See S.C. Mehendale and K.C. Rustagi, Opt. Comm, (1979) for theoretical prediction and S H Stevenson, D.S.Donald and G.R.Meredith, *Mat. Res. Soc. Symp. Proc.* 109. 1988 for experimental verification.]

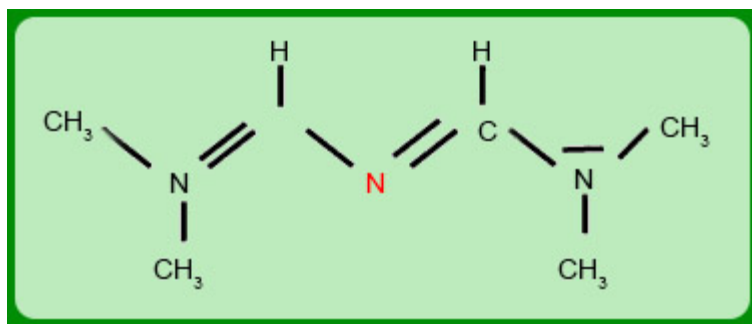


Figure 18.4 A azo-cyanine dye in which the central C-H moiety is substituted by a N atom

For polyenes the periodic potential acts to increase the anharmonicity but it also reduces the delocalization. The theoretical estimates obtained by direct diagonalization of the unperturbed matrix are shown in Figure 18.5 along with the experimental results. The agreement is remarkable in view of the simplicity of the model. There have been many more sophisticated calculations using various versions of molecular orbital models, claiming the importance of electron-electron interaction in determining the observed highly nonlinear dependence on the number of double bonds.

[See e.g. C Bubeck in K.Müllen and G Wegner. *Electronic materials: the oligomer approach*. Weinheim: Wiley-VCH, 1998].

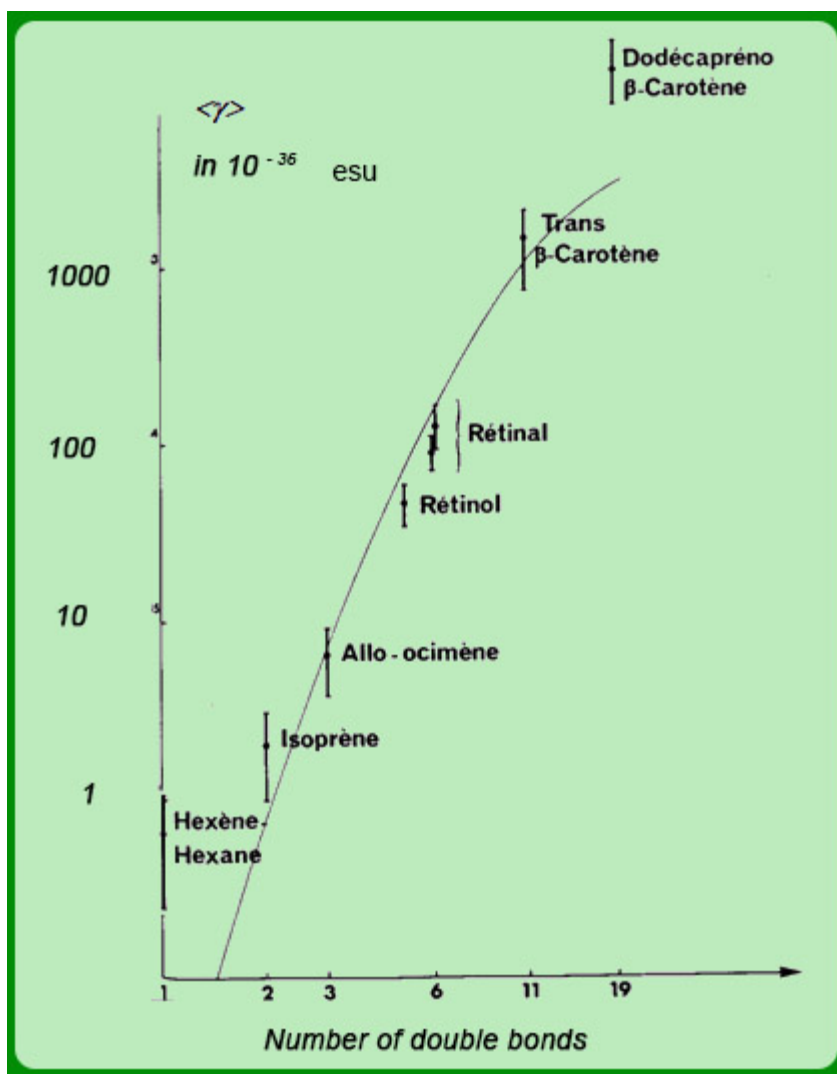


Figure 18.5 Orientation averaged third order polarizability $\langle \chi \rangle$ for polyenes.

(Adopted from J-P Hermann D.Sc Thesis (Orsay 1974))

To clarify the importance of e-e interaction in determining the nonlinearity let us consider the following system of N electrons in a harmonic potential with the Hamiltonian given by

$$H = \sum_{i=1}^N \left(\frac{\vec{p}_i^2}{2m} + \frac{1}{2} m \omega_0^2 r_i^2 \right) + \sum_{i < j=1}^N \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (18.23)$$

The energy eigen values of this Hamiltonian are obviously more complex than for the non-interacting electrons. But surprisingly, the absorption spectrum shows a resonance only at frequency ω_0 . To see this, we note that in the electric dipole approximation the interaction Hamiltonian is given by

$$H' = -e\vec{E} \cdot \sum_{i=1}^N \vec{r}_i \quad (18.24)$$

Including the interaction the total Hamiltonian is still separable into centre of mass coordinate $\vec{R} = \sum_{i=1}^N \vec{r}_i$

and relative coordinates $\vec{r}_1 - \vec{r}_2, \vec{r}_1 - \vec{r}_3, \dots$ etc. As is well known the kinetic energy term also splits into a centre of mass part and a relative motion part. The electric dipole operator involves only the centre of

mass coordinate $\vec{R} = \sum_{i=1}^N \vec{r}_i$. Thus the optical response of this Hamiltonian is exactly the same as that of

non-interacting electrons in the harmonic oscillator system. And, the response remains linear even if electron-electron interaction is included. This result, known as the generalized Kohn Theorem has interesting consequence for the nonlinear response. When anharmonic terms are included the separation is no longer valid because while the harmonic interaction term separates into a centre of mass part and a relative motion part, as $x_1^2 + x_2^2 = ((x_1 + x_2)^2 - (x_1 - x_2)^2) / 2$, the anharmonic part does not since

$$x_1^4 + x_2^4 = \frac{1}{8}(x_1 + x_2)^4 + \frac{1}{8}(x_1 - x_2)^4 + \frac{3}{4}(x_1 - x_2)^2(x_1 + x_2)^2$$

This suggests that we should be able to write

$$\beta_{ijk} = \beta_{ijk}^{\text{bare}} \times \text{screening factor}$$

and

$$\gamma_{ijkl} = \gamma_{ijkl}^{\text{bare}} \times \text{screening factor}$$

In short, we expect that the nonlinearities are not generated by the electron-electron interaction they can of course be modified by the interaction. Further, one can expect that for similar molecules the screening factor would be similar. Thus to predict which molecules have relatively large nonlinearity the noninteracting electron picture provides a good starting point. Conversely, the success of simple models such as the free electron model in predicting important trends in nonlinear response does not imply that the model describes the complete physics.

Second order response:

All the molecules considered so far have inversion symmetry. A simple model for substituted benzenes assumes that to determine β only two states are important- the ground and first excited state. The two-state model allows one to express β as

$$\beta_{mxx} = \frac{3e^2}{2\hbar^2} \frac{\omega_0 f(\mu_{ee} - \mu_{gg})}{(\omega_0^2 - \omega^2)(\omega_0^2 - 4\omega^2)} \quad (18.25)$$

where ω is the frequency of the incident laser, $\hbar\omega_0$ is the energy difference between the two states, f is the oscillator strength of the transition, and μ_{ee} and μ_{gg} are the molecular dipole moments in the excited and ground state, respectively. This model has been found to be very successful in the development of nonlinear organic materials. [See J.Zyss and D.S. Chemla eds, Academic, New York (1987) for more details].

For second order nonlinear materials, it is not sufficient to have molecules that lack inversion symmetry but also to assemble them in a structure lacking one. This is made difficult by the fact that the electrostatic interaction between two dipoles favours them to be oppositely oriented!

Several tricks have been developed which allow the crystallization of such molecules into inversion asymmetric structures. Some of these involve using chiral molecules, hydrogen bonding, modifying the molecule to cause steric hinderance, using nonpolar molecules and electric field poling.

Finally, we should mention that one of the key concerns about organic materials is that many of them

deteriorate with time.

SUGGESTED FURTHER READING:

1. J. Zyss, *Molecular Nonlinear Optics-Materials, Physics and Devices*, Academic, Boston, (1994)
2. P.N. Prasad, D.I Williams *Nonlinear Optical Effects in Molecules and Polymers*
Wiley Interscience, New York (1991)
3. F. Kajzar and I.D. Swalen eds. *Organic Thin Films for Waveguiding Nonlinear Optics*,
Gordon and Breach, Amsterdam (1996).

Recap

In this lecture you have learnt the following

- Local field effects in molecular crystals.
- Free-electron model suggests rapid increase of nonlinearities with conjugation length.
- Two state model for second order nonlinearity.
- Many tricks are used for assembling molecules into noncentro symmetric crystals.