Supramolecular Chemistry-I

Prof. Parimal Kanti Bharadwaj

Department of Chemistry

IIT Kanpur

Week - 07

Lecture - 32

Good morning. So, I just started talking about optical non-linearity. Let me now start it all over again. Optical non-linearity is a field which is of tremendous technological importance. It is useful in engineering, physics as well as in chemistry. The optical non-linearity is also known as photonics. Or, I can say that photonics uses optical non-linearity.

In electronics, electrons are used to acquire, store, transmit and process information. In an analogous way, in photonics, photons are used in place of electrons to carry out the above tasks. Nonlinear optics is expected to play a major role in the technology based on photonics. We would like to have a rudimentary idea about what is optical non-linearity excluding mathematical derivations that are quite difficult. And for chemists, not needed for most part. Engineering researchers and physicists dealing with instrumentation use optically non-linear compounds to fabricate sophisticated instruments. But they cannot do anything unless we make compounds. So, we are the main people to make optically non-linear active compounds. When a molecule is subjected to an oscillating external electric field (light), the induced change in molecular dipole moment (polarization) can be expressed by a power series in the field strength E as in Eqn. 1 where, P is the induced

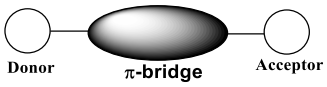
$$P = \alpha E + \beta E^2 + \gamma E^3 + \ldots \qquad (1)$$

molecular polarization, α is the linear molecular polarizability, β is the quadratic or first hyperpolarizability, and γ is the cubic or second hyperpolarizability, and so on. What is polarization? I will give a very simple example. If you take an iron ball and a rubber ball what happens is iron ball cannot be deformed, but a rubber ball I can squeeze and deform it from a spherical shape. So, I will say rubber ball is much more polarizable compared to an iron ball.

In a chemical compound, if the electron density can be deformed on interacting with electromagnetic radiation, we say the compound is polarizable. It is important to realize

that we will not use ordinary light but very intense laser light. So, most chemical compounds where polarizability varies linearly with E , we say the compound is optically linear. That is, P = αE , where α is the proportionality constant known as linear proportionality constant. However, there are some compounds, whose polarizability varies by a power series in the field strength E as in Eqn. 1 and those compounds are known as compounds having optical nonlinearity. The question is now what should be the structural characteristics of the compound that will make it optically non-linear?

First, we talk about second order optical non-linearity. Our concern now about the term βE^2 where β is the quadratic or first hyper polarizability. Now, the question is which molecules are expected to give high β values? That is a question for a chemist. The compounds that are expected to give high β values should have following type of structure:



The molecules with high beta values, should have:

i) electronically excited states close in energy to the ground state; because if the excited state and ground state are closer in energy then this energy should come in the infrared or visible light. That means I can take infrared laser or visible laser which are easily available to make electrons excited or deformed.

ii) It should have a large oscillator strength for the transition. Large oscillator strength for the transition means more number of molecules can go to the excited state and more deformation.

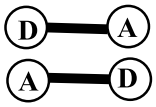
iii) A large difference between the ground and the excited state dipole moments. What is meaning of this excited state dipole moment if it is large? It means charge separation is large ok then what will happen if charge separation is large. So, electrical component of the electromagnetic radiation will interact much stronger because dipole moments are large. If the dipole moment is low that means electrical component will not be able to interact very strongly. These three criteria are very important to understand before you embark on synthesizing molecules.

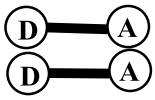
There is another important thing. Thus far, I was talking at the molecular level, but when I am trying to go to say some practical uses, I cannot work with one single molecule, but I will work with little bit powder or some solid. In that case of course, you will know that optical activity works both in the solid state in the liquid state as well as in the gaseous state. But for practical uses we need bulk. So, bulk polarizability P can be expressed as:

$$P = \chi^{(1)}E + \chi^{(2)}EE + \chi^{(3)}EEE + \ldots \qquad (2)$$

where the coefficients $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order bulk polarizability, respectively. So, β is a molecular and $\chi^{(2)}$ is the macroscopic or bulk second order optical non-linearity.

So, first we have to make β values high because we want $\chi^{(2)}$ to be high and we will assume that β value high means $\chi^{(2)}$ is also high. Unfortunately, that is right, but not always right. A large β value does not guarantee $\chi^{(2)}$ to be large. The essential condition for non-zero bulk second order nonlinearity, the molecule must crystallize in a non-centrosymmetric space group. Strongly dipolar compound such as the following will crystallize in a centrosymmetric space group. There are ways to crystallize dipolar compounds innon-centrosymmetric space group.





Centrosymmetric Non-centrosymmetric

Anti-Parallel mode Parallel mode

Therefore, the molecules should crystallize in the parallel mode for non-zero bulk susceptibility, ($\chi^{(2)}$). In the first case i.e., anti-parallel mode of crystallization will give $\chi^{(2)}$ =0.

For non-zero $\chi^{(2)}$ value, we can go from dipolar to multipolar molecules as they will have less probability to crystallize in anti-parallel mode. I stop here to-day for taking it up in the next class.