

Recent Advances in Spectroscopic Techniques

Presented by

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ATOMIC AND MOLECULAR SPECTROSCOPY

Spectroscopy

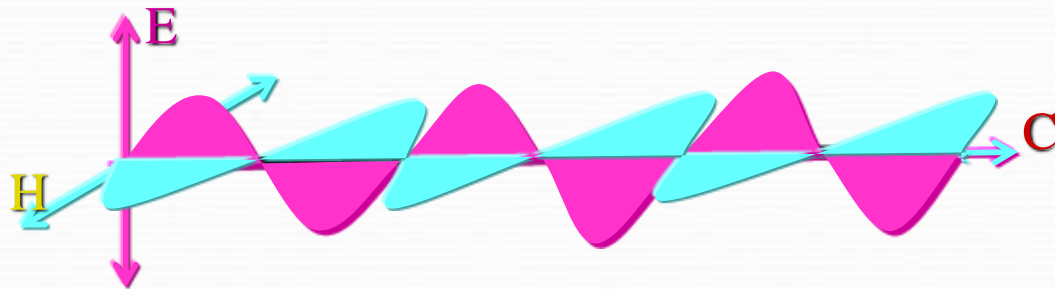
Spectroscopy involves the investigation of the interaction of electromagnetic radiation with matter and explanation of the spectral pattern.

Spectra show how the interaction between electromagnetic radiation and the matter varies with the frequency of this electromagnetic radiation.

Electromagnetic Radiation: consists of orthogonal oscillating electric (**E**) and magnetic (**H**) fields propagating through space with velocity (**C**)

$$C = 2.998 \times 10^8 \text{ m/s}$$

$$= 2.998 \times 10^{10} \text{ cm/s (in vacuum).}$$



Electromagnetic Radiation

- c** speed of light, m/sec
- ν** frequency, the number of waves that pass a fixed point in a second, sec⁻¹
- λ** wavelength, the length of a single wave, m

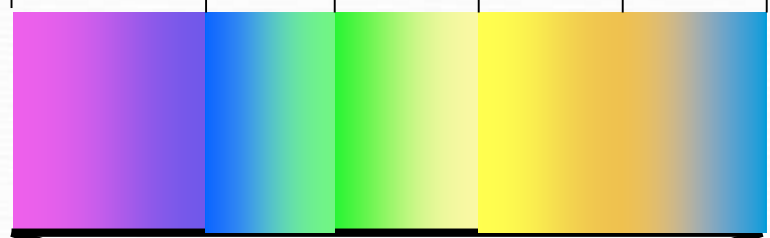
$\tilde{\nu} = 1/\lambda$ (in cm) wavenumber = a number of waves that fit a centimetre, **units = cm⁻¹**

$$E = h \cdot \nu$$
$$= h \cdot c / \lambda = h \cdot c \cdot \tilde{\nu}$$

$$c = \nu \cdot \lambda$$

h - Planck constant, 6.626 · 10⁻³⁴ J · sec

420 470 530 580 620 700 nm

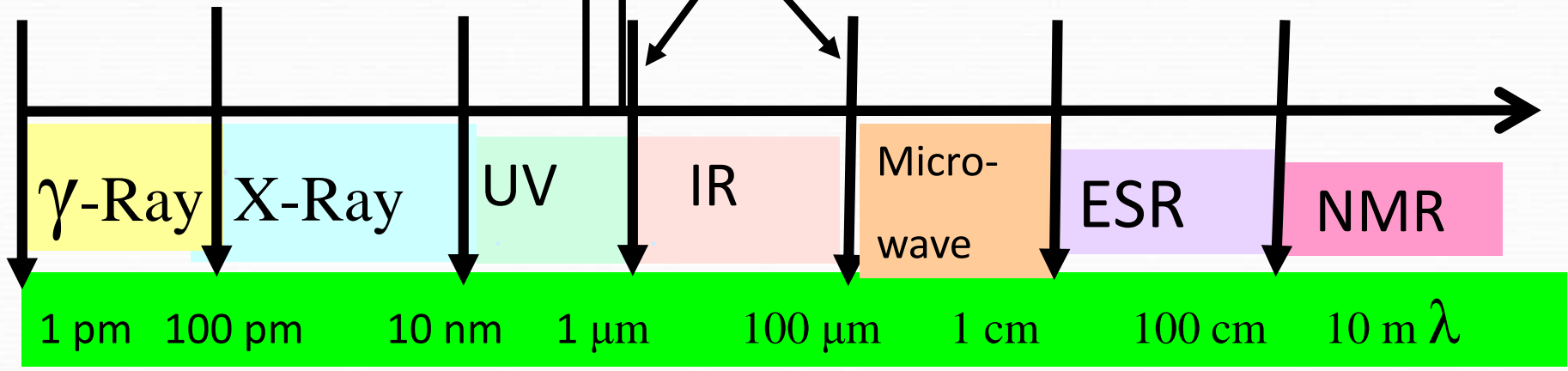


12800 3333 333 33 cm⁻¹

NIR Mid IR Far IR

Visible

Spectral Regions



$$E = h \cdot \nu = h \cdot c / \lambda = h \cdot c \cdot \tilde{\nu}$$

How Light Interacts with Matter

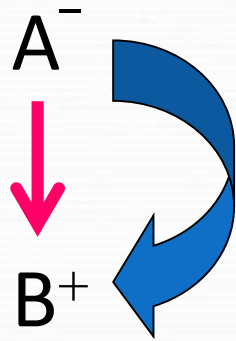
- An electron will interact with a photon.
- An electron that **absorbs** a photon will **gain** energy.
- An electron that **loses** energy must **emit** a photon.
- The total energy (electron plus photon) remains constant during this process.

Molecular Absorption

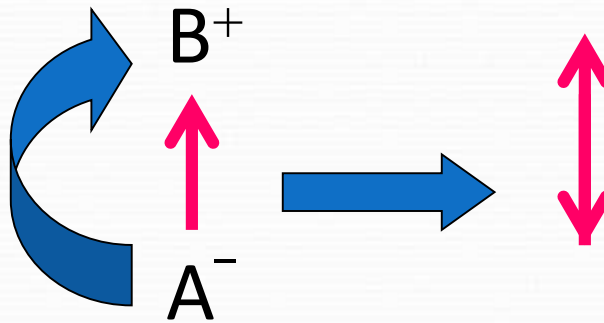
- More complex than atomic absorption because many more potential transitions exist
 - Electronic energy levels
 - Vibrational energy levels
 - Rotational energy levels
- $E_{\text{molecule}} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$
 $E_{\text{electronic}} > E_{\text{vibrational}} > E_{\text{rotational}}$
- Result - complex spectra

- ❖ Transition between electronic energy levels give the spectrum in the **visible or UV region**- Electronic spectra
- ❖ Transition between vibration levels gives the spectra in the **IR region** – Vibrational spectra
- ❖ Transition between rotational levels gives the spectra in the **Far IR or microwave region**- Rotational spectra
- ❖ **Electron** can give interaction energies when placed in a magnetic field –**ESR spectra (Microwave region)**
- ❖ Transition between energy levels that arise from the different orientations of magnetic moment of nuclei placed in a magnetic field **Nucleus- NMR spectra (Radio frequency region)**

Molecule give a rotational spectrum only if it has a permanent dipole moment:



Rotating molecule



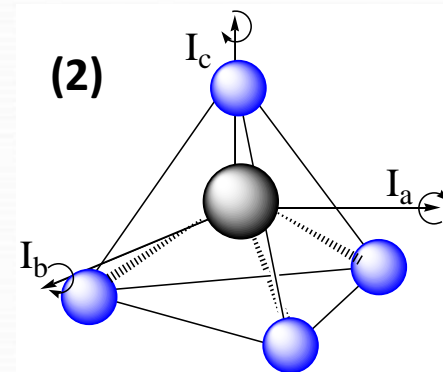
Oscillating dipole

- H-Cl, and C=O give rotational spectrum.
- H-H and Cl-Cl don't give rotational spectrum.

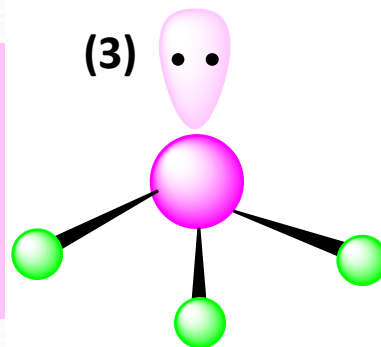
Rigid rotors are classified into four groups according to the relative values of their moment of inertia:

1- Linear rotators: such as diatomic molecules or linear molecules. As H-Cl and O=C=S, acetylene and O=C=O , $I_a=0$ and $I_b=I_c$.

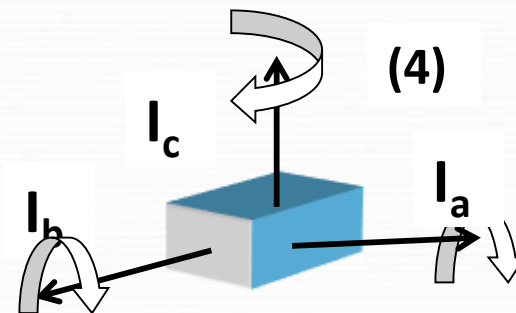
2-Spherical tops rotators: They have three equals moment of inertia. e.g. CH₄, SiH₄ and SF₆. $I_a=I_b=I_c$.



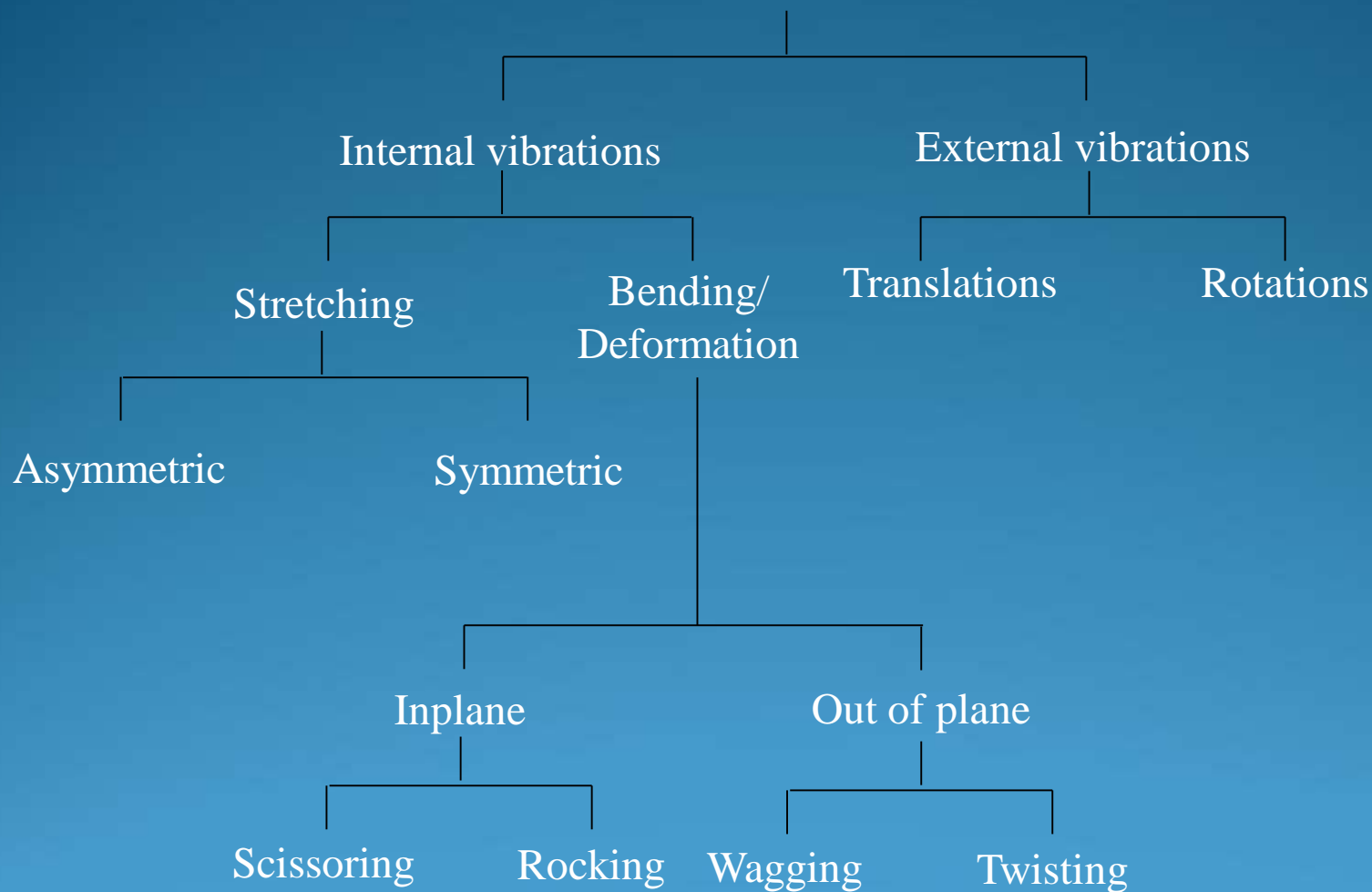
3- Symmetric tops rotators: They have Two equals moment of inertia. e.g. NH₃, CH₃CN and CH₃Cl , $I_a=I_b \neq I_c$.



4- Asymmetric tops rotators: Have three different moment of inertia e.g. H₂O, CH₃OH and vinyl chloride and formaldehyde. $I_a \neq I_b \neq I_c$.



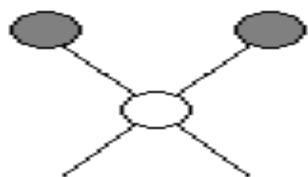
Molecular Vibrations



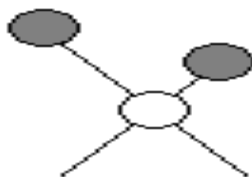
❖ Polyatomic molecule of n atoms have $(3n-6)$ vibrational degrees of freedom

❖ $(n-1)$ bond stretching vibrations

Stretching vibrations



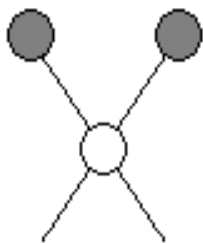
Symmetric



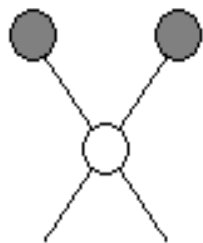
Asymmetric

❖ $(2n-4)/(2n-5)$ deformation vibrations (linear) / (non-linear)

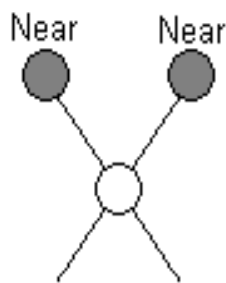
Bending vibrations



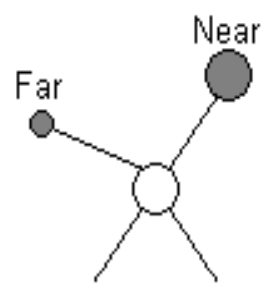
In-plane rocking



In-plane scissoring



Out-of-plane wagging



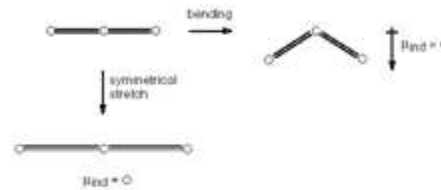
Out-of-plane twisting

Vibrational Spectroscopy

- ❖ **Atoms in a molecule vibrate even at absolute zero about some mean position.**
- ❖ **A vibrating molecule interacts with electromagnetic radiation of suitable frequency and when the frequency matches with one of the normal modes of vibration, the molecule may either absorb or emit the radiation.**
- ❖ **Another way of interaction with molecule is scattering, with or without change of frequency.**

Vibrational Spectroscopy

- CO₂ Example



- Infrared active is permanent dipole moment changes as in bending
- Raman active if polarizability changes as in symmetric stretch

- Raman and Infrared spectroscopy are complementary due to selection rules
 - Highly symmetric polyatomic molecules with center of inversion are IR active
 - Homonuclear diatomic molecules are Raman active
 - Non-symmetric molecules demonstrate both modalities

Infrared spectroscopy

- ❑ If the radiation has the same frequency as one of the normal modes of vibration, it may be possible for the molecule to absorb the radiation. A molecule absorbs infrared radiation when the vibration of the atoms in the molecule produces an oscillating electric field with the same frequency as the frequency of incident infrared radiation.
- ❑ The molecule absorbing a quantum of energy give rise to bands about 200 to 4000 cm^{-1} .
- ❑ IR is generally subdivided into three regions
 - Near IR (12,500- 4000 cm^{-1})
 - Middle IR (4000-400 cm^{-1})
 - Far IR (400-50 cm^{-1}).
- ❑ The middle IR is the region most commonly employed for standard laboratory investigations as it covers most of the vibration transactions.
- ❑ The far IR region is also important when we deal with solid samples. Studies below 400 cm^{-1} require special instruments and technique.

Infrared selection rules

- ✍ For a molecule to absorb infrared light it must have a vibration during which the change in dipole moment with respect to distance is non-zero.

$$\left(\frac{\partial \mu}{\partial Q} \right) \neq 0$$

$\partial \mu$ = change in dipole moment

∂Q = change in bond distance

- ✍ The energy of the infrared light must be equal to a vibration energy level difference in the molecule.

$$\Delta E = hc \nu$$

ΔE = vibration energy level difference in a molecule

ν = wave number in cm^{-1}

Fourier transform infrared (FT-IR) spectroscopy

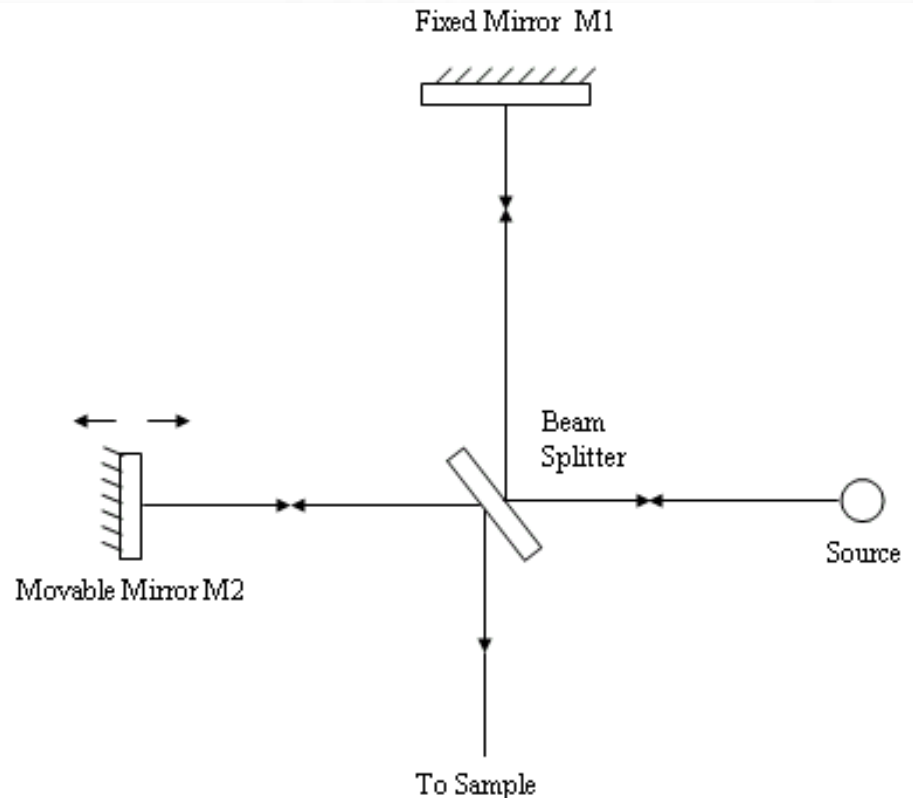
- FT-IR is a simple mathematical technique to resolve a complex wave into its frequency components.
- A time domain plot is converted into a frequency domain spectrum. The whole spectrum can be obtained as a function of wavenumber.

Michelson interferometer in which an interferogram is taken. Applying Fourier transform to the interferogram.

$$G(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t) e^{i\omega t} dt$$

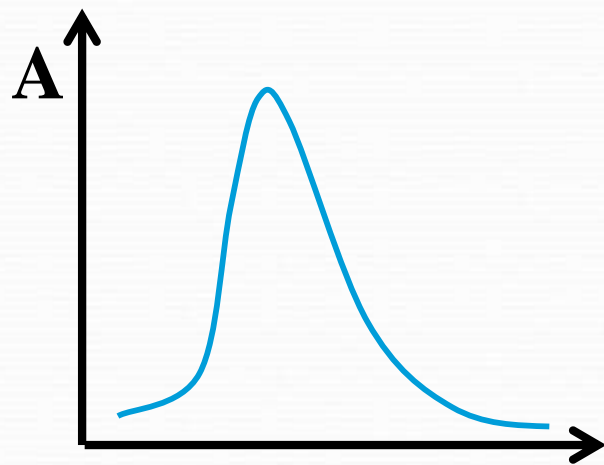
FT-IR improves

- ✦ Sensitivity
- ✦ Rapid scanning
- ✦ Resolution and
- ✦ Signal to noise ratio

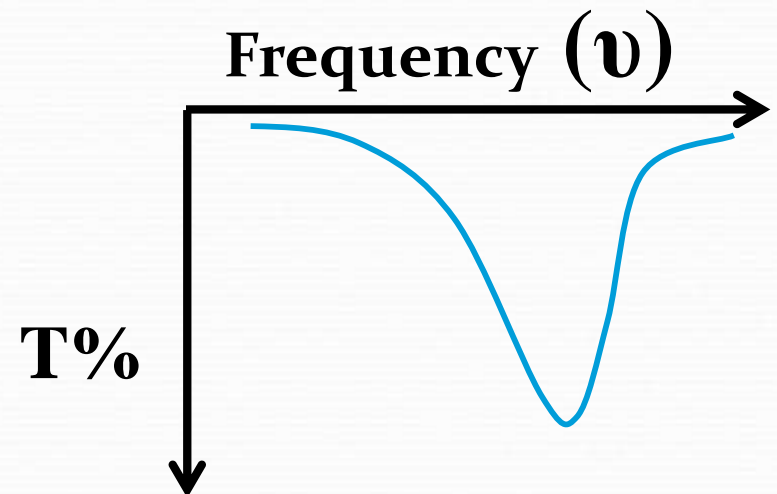


Basic components of Spectrometer

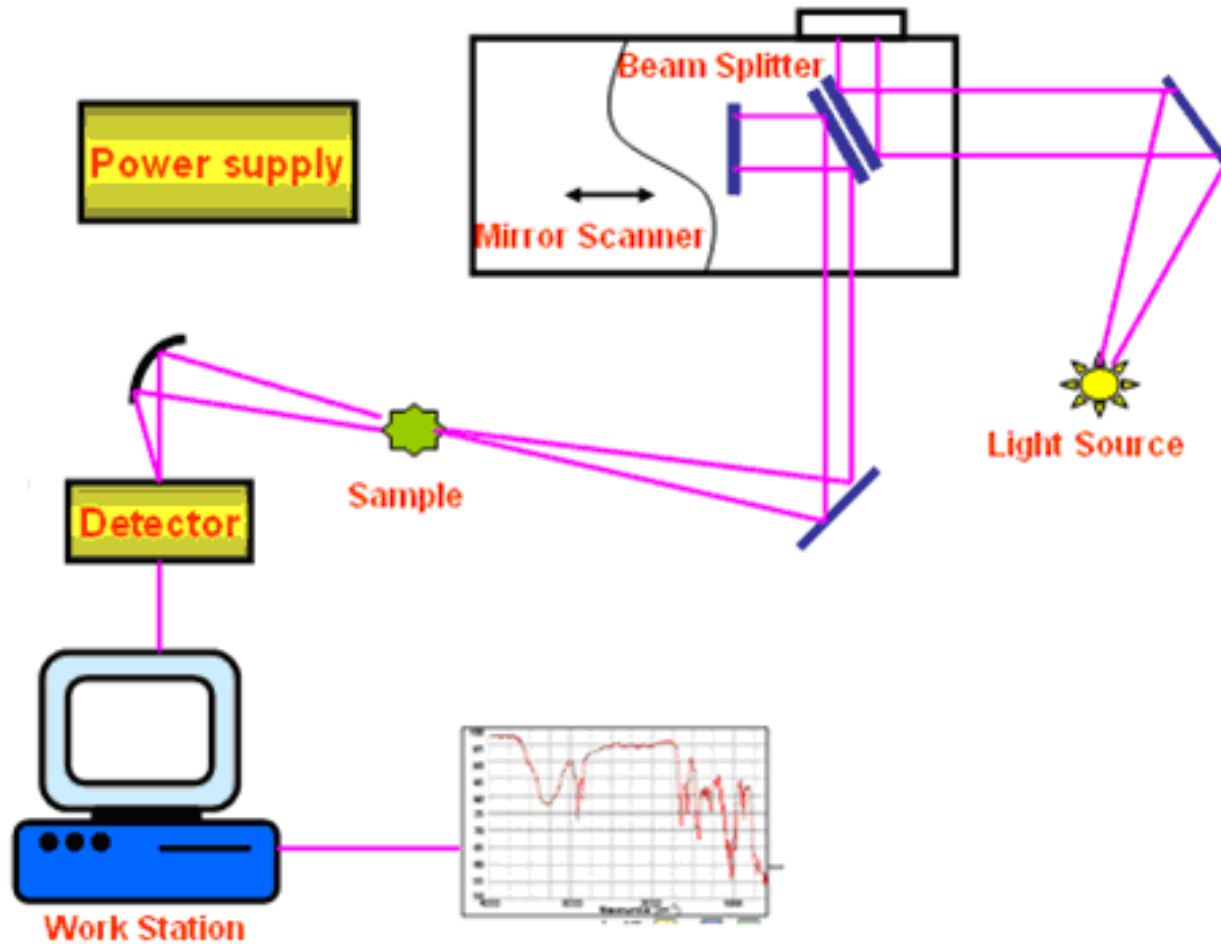
White-light covering a wide range of frequencies is passed through a sample cell and then to a polychromator (a prism or grating). Detector (photodiode array) records the intensity of transmitted light as a function of frequency or records the absorbance as a function of wavelength or wavenumber.



λ = Wavelength.



FTIR spectrometer



What is Raman Scattering?

- Scattering of incident light – inelastic
- Rayleigh vs. Raman scattering

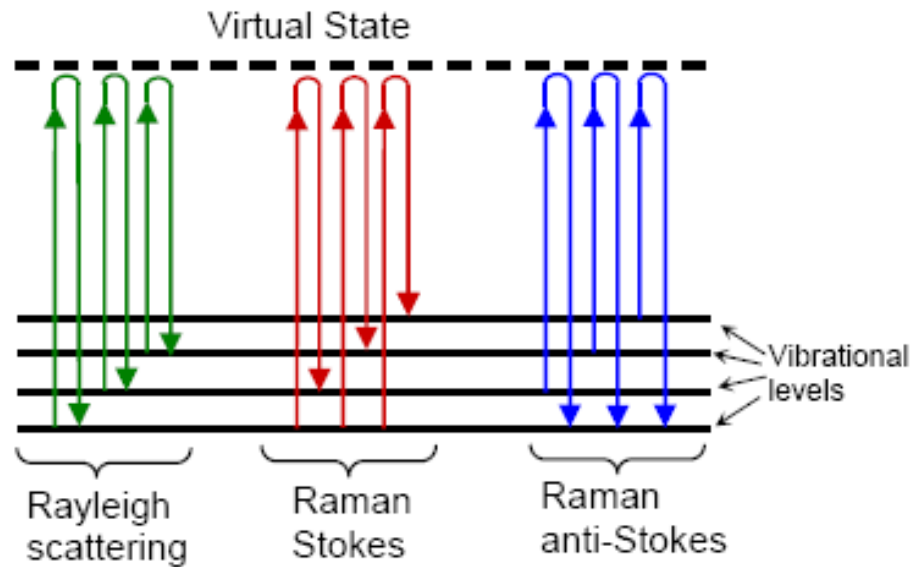


Diagram of Rayleigh and Raman Scattering

Raman Spectroscopy

Raman effect is a 2-photon scattering process

These processes are inelastic scattering:

Stokes scattering: energy lost by photon:



Anti-Stokes scattering: energy gained by photon:



Selection rule for Raman spectrum

- Vibration is active if it has a change in polarizability, α . Polarizability is the ease of distortion of a bond. For Raman-active vibrations, the incident radiation does not cause a change in the dipole moment of the molecule, but instead a change in polarizability.
- In starting the vibration going, the electric field of the radiation at time t , E , induces a separation of charge (i.e. between the nuclear protons and the bonding electrons). This is called the induced dipole moment, P . (Don't confuse it with the molecule's dipole moment, or change in dipole moment, because this is often zero).

$$P = \alpha E$$

Example: There are 4 normal modes of CO₂. Only ν_1 is Raman active

μ is dipole moment;

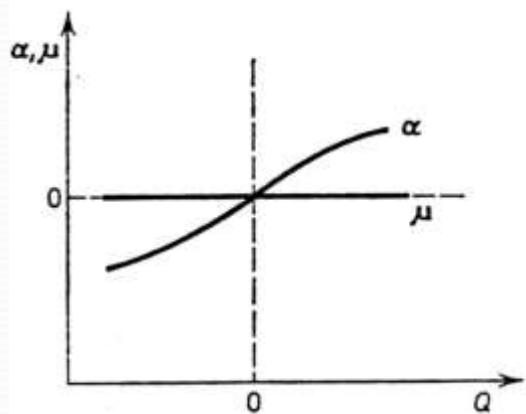
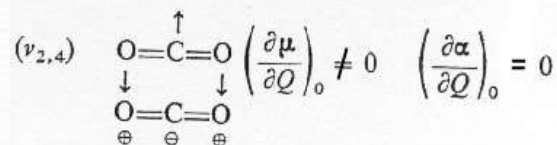
α is polarizability;

Q is vibration coordinate, The slopes

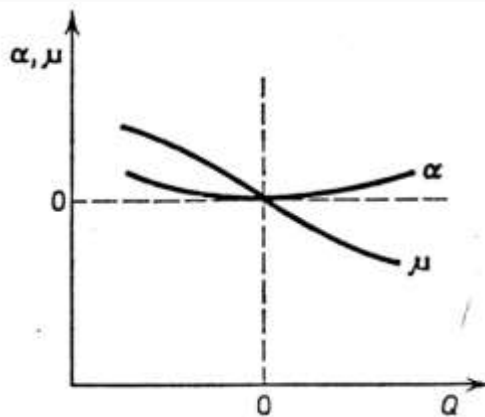
are measured at $Q = 0$ (I.e. at the equilibrium position).

$$(\nu_1) \quad \overset{\leftarrow}{\text{O}}=\text{C}=\overset{\rightarrow}{\text{O}} \left(\frac{\partial \mu}{\partial Q} \right)_0 = 0 \quad \left(\frac{\partial \alpha}{\partial Q} \right)_0 \neq 0$$

$$(\nu_3) \quad \overset{\leftarrow}{\text{O}}=\overset{\rightarrow}{\text{C}}=\overset{\leftarrow}{\text{O}} \left(\frac{\partial \mu}{\partial Q} \right)_0 \neq 0 \quad \left(\frac{\partial \alpha}{\partial Q} \right)_0 = 0$$



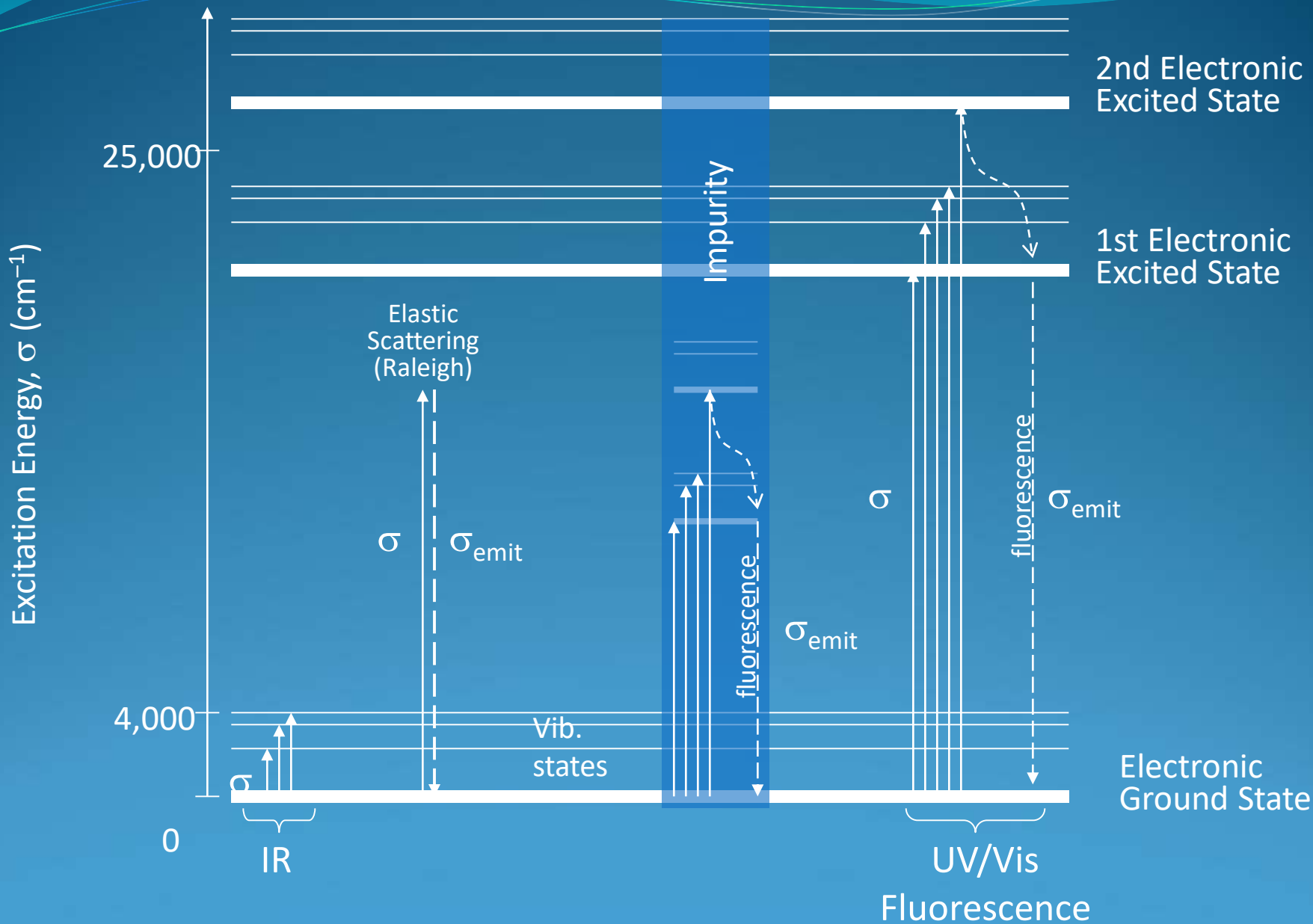
ν_1



ν_3

Change in dipole moment, μ , and polarizability, α , during CO₂ vibrations

Main Optical Transitions: Absorption, Scattering, and Fluorescence



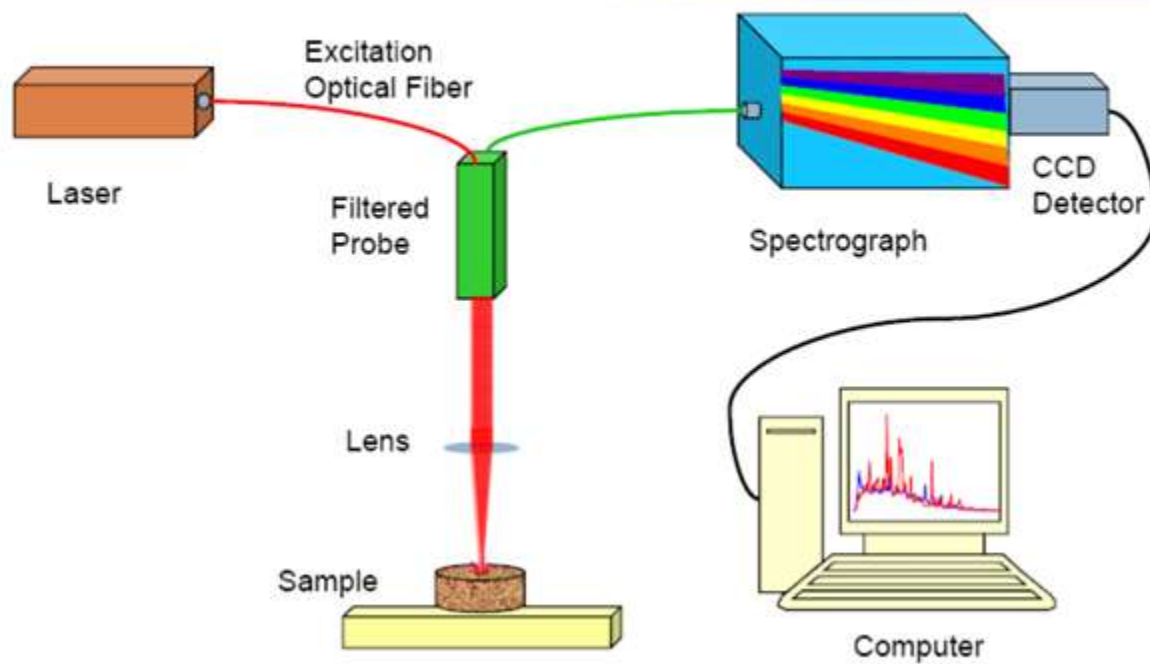
Fourier transform Raman spectrometer

The Raman instrument can be on the same bench as the FTIR.

Often, a YAG:Nd³⁺ laser (1064 nm) is used to excite the sample, so that the excitation energy is lower than the absorption band energies of organic systems. Fluorescence is then minimized.

Instruments may be combined with a microscope, or optical fiber, so that scanning over a few (microns)² of surface area, and Raman mapping is easily performed.

Raman Instrument



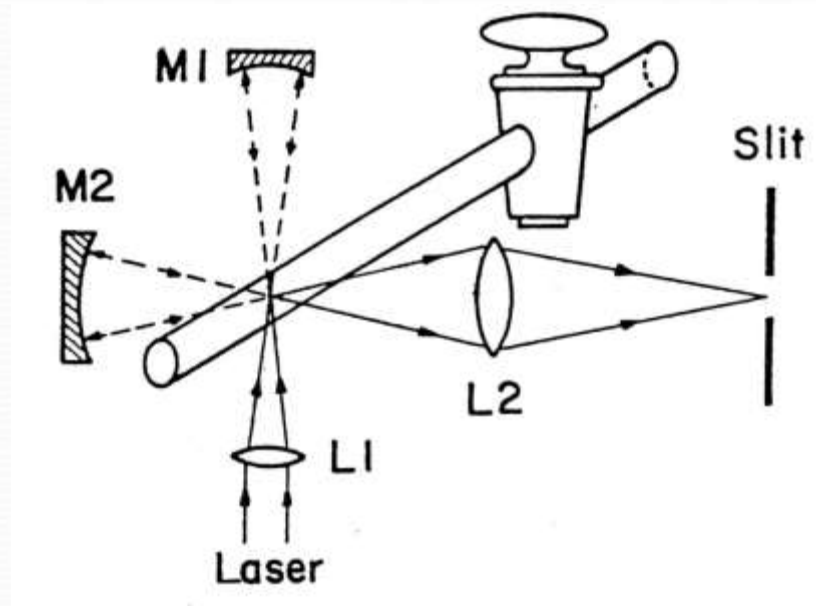
Sampling techniques for Raman spectroscopy

If the sample is colourless, it does not absorb a visible laser

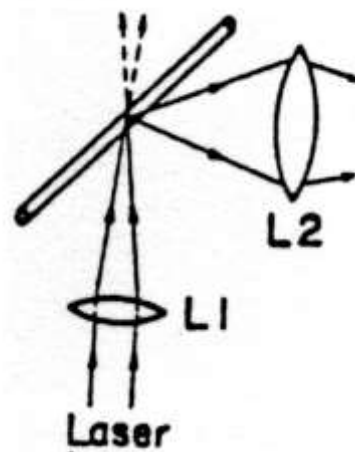
Raman spectroscopy is applicable to solids, liquids or gases.

Gases:

use gas cell



Liquids and solids can be sealed in a glass capillary:
sealed in a glass capillary:



If the compound is colored, it can absorb the laser, get hot and decompose. Some techniques are:

- Reduce the laser power (defocus) and/or change wavelength;
- Dilute the sample into a KBr pellet;
- Cool the sample
- Rotate or oscillate the laser beam on the sample

Number of bands in a Raman spectrum

As for an IR spectrum, the number of bands in the Raman spectrum for an N-atom non-linear molecule is seldom $3N-6$, because:

polarizability change is zero or small for some vibrations;

bands overlap;

combination or overtone bands are present;

Fermi resonances occur;

some vibrations are highly degenerate; etc...

Depolarization ratio of a vibrational mode in the Raman spectrum

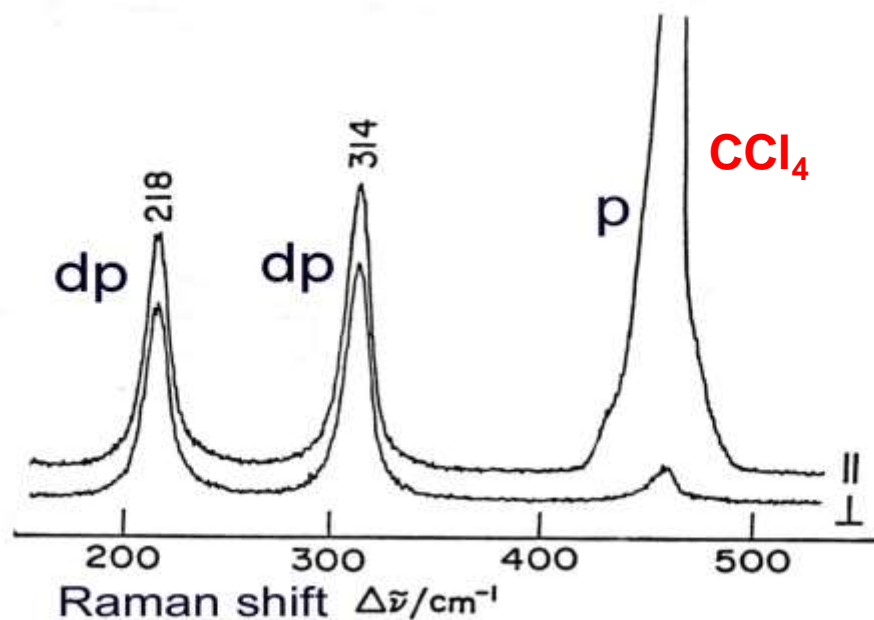
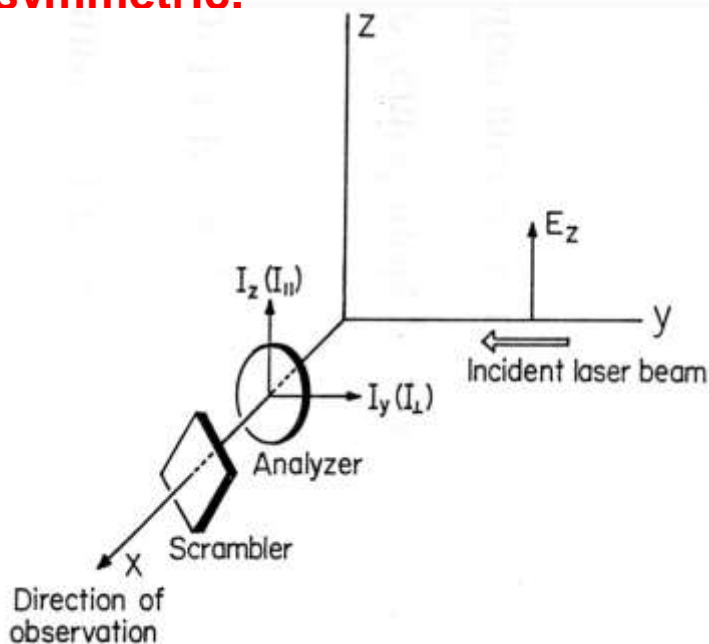
may give information about the symmetry of a vibration.

$$\rho_p = \text{depolarization ratio for polarized light} = I_y/I_z = I_{\perp}/I_{\parallel}$$

This is different from the depolarization ratio for unpolarized light, see Infrared and Raman Spectra...Part A., K. Nakamoto 5th Ed. Wiley 1997. Pp. 97-101.

$0 \leq \rho_p < 0.75$; Raman line is polarized (p). Vibration is totally symmetric

$\rho_p = 0.75$. Raman line is depolarized (dp). Vibration is not totally symmetric.



Special types of Raman spectroscopy

(see Hollas, Modern Spectroscopy, Wiley)

Resonance Raman (RR) scattering

When the laser excitation frequency is near (or coincident) with an electronic absorption band, intensity enhancement can occur by a factor of 10^2 - 10^6 , compared with normal Raman scattering.

Electronic transitions are often localized in one part of a molecule, so that RR provides information about vibrations of the chromophore, especially those exhibiting a large change in geometry between the two electronic states.

RR is used in analytical chemistry to achieve detection limits 10^{-6} - 10^{-8} M.

Surface enhanced Raman spectroscopy (SERS):

Raman scattering is enhanced (typically by 10^3 - 10^6 times) when the analyte is adsorbed on colloidal metallic surfaces,

e.g. on colloidal Ag prepared by reduction of Ag^+ with citrate, in particle size range 25-500 nm.

Stimulated Raman scattering (SRS)

The Raman scattering from a laser is observed in the forward direction from the sample (i.e. in the same direction, or at a small angle to the incident laser radiation).

Vibrational progressions are observed for certain modes.

Coherent anti-Stokes Raman spectroscopy (CARS)

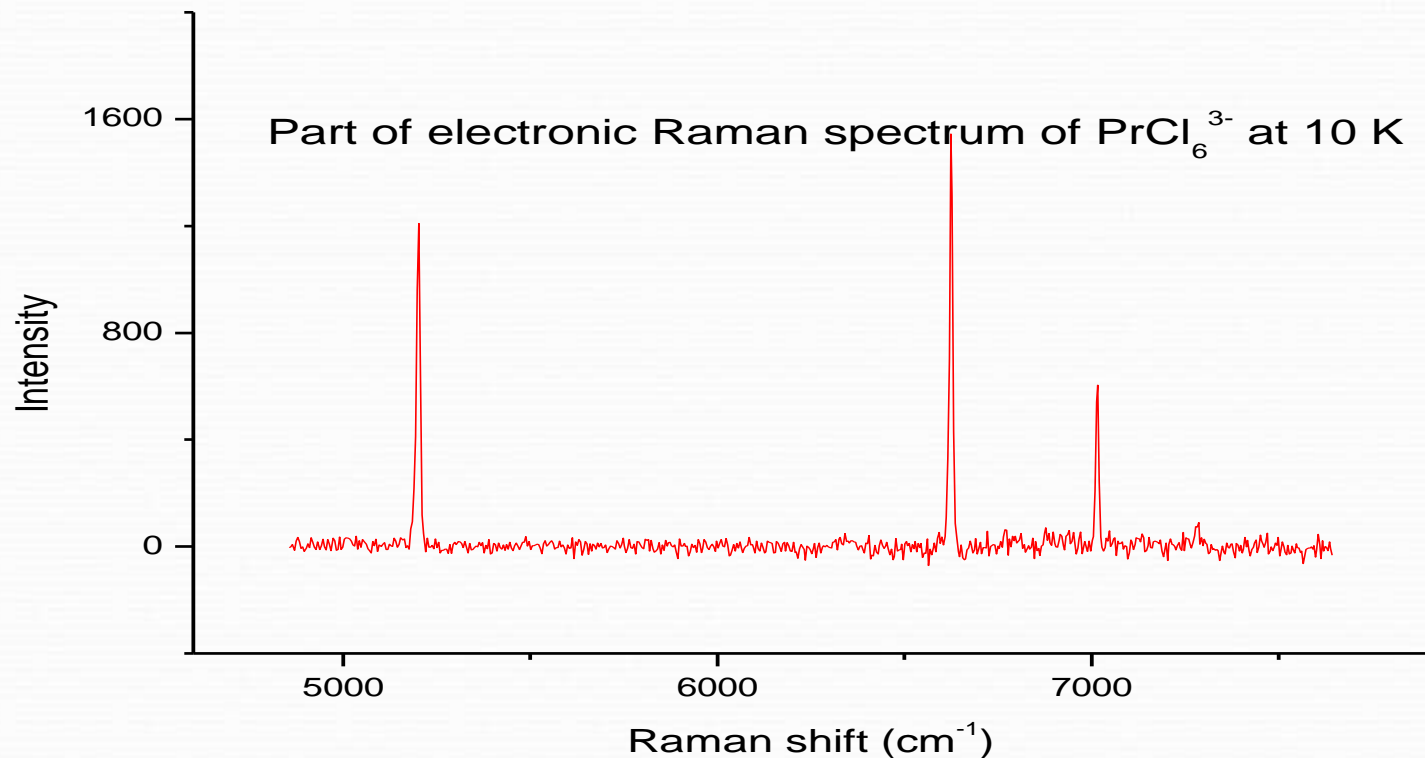
Radiation from two lasers is incident on the sample, and the intensity of the outgoing wave energy gives information about the vibrational modes of the sample.

Hyper-Raman spectroscopy

Very weak scattering at twice the laser frequency, $2\nu_0$, is called Hyper-Rayleigh scattering. Similarly, Stokes and anti-Stokes hyper-Raman scattering occur at $2\nu_0 \pm \nu_{\text{vib}}$, where ν_{vib} is a vibration frequency. The selection rules differ from those of Raman scattering.

Electronic Raman scattering

Raman scattering can occur from electronic states, as well as from vibrations. At room temperature the bands are very broad, and merge into the background. At low temperatures (<80 K), the bands sharpen, and give information about the energies of electronic states of the molecule.



Applications of vibrational spectroscopy

Vibrational spectroscopy has been widely used in

- **Nonlinear optics**
- **Astronomy**
- **Planetary sciences**
- **Single molecule detection**
- **Remote sensing and mineralogy**
- **Geology**
- **Polymer chemistry**
- **Forensic science**
- **Medical diagnosis**
- **Pharmaceutical and biopharmaceutical industry**
- **Biochemical analysis**
- **Food and dye industries**
- **Petroleum industries**

Surface Enhanced Raman

- In the 1970's, it was observed that rough metal surfaces produced enhanced Raman signals (up to 10^6)
- Observations:
 - Required roughened (10-100nm) surface of highly reflective metals
 - Raman intensity generally falls off with increasing vibrational frequency
 - Raman shifts are sometimes shifted from standard Raman and new peaks appear

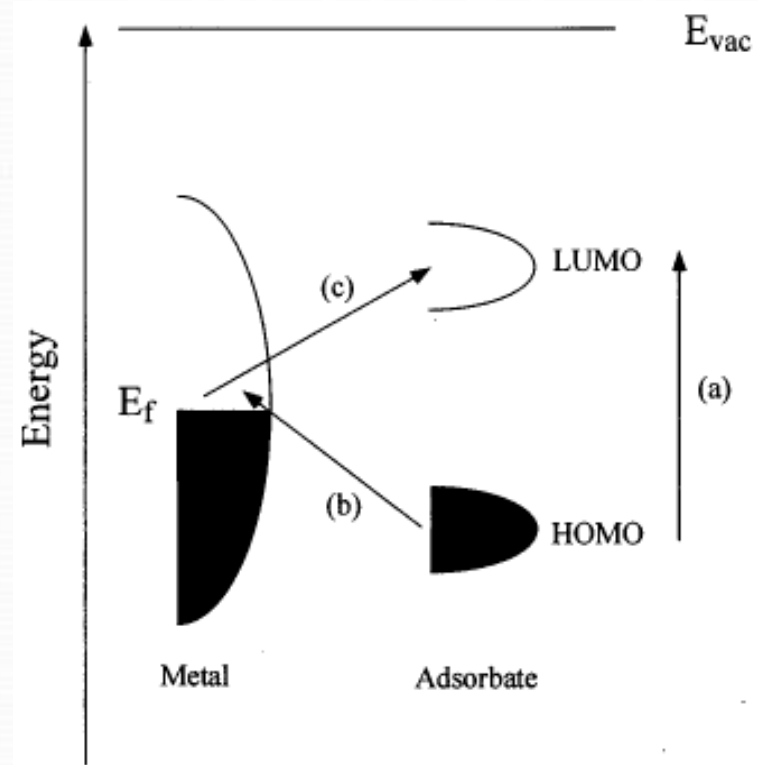
Theoretical explanations for SERS

- A. Electromagnetic field enhancement mechanism
excitation of surface plasmon
tends to form spatially localized “hot areas”
the magnitude of enhancement $\sim 10^6$ - 10^7 times for
single colloidal silver, and $\sim 10^8$ for the gap between two
coupled particles

- B. Chemical enhancement
due to specific interactions, forming charge-
transfer complexes
the magnitude of chemical enhancement ~ 10 - 100
times

Chemical Enhancement

- When molecules are adsorbed to the surface, their electronic states can interact with the states in the metal and produce new transitions
- True nature of this still not fully understood



SERS applications

classical electrochemical studies
e.g. corrosion processes, film
growth, self-assembled monolayers

trace analysis approaching single
molecule detection limit e.g. 100
pyridine molecules on Ag electrode

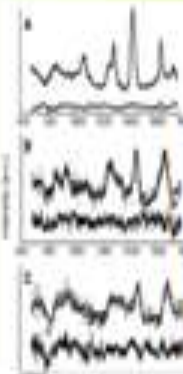
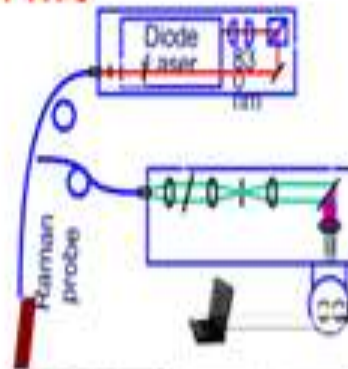
**Efficient enhancing substrates: Ag,
Au and Cu, rough surfaces or
colloidal particles with the size of
tens of nanometers**

biological samples
e.g. DNA/protein detection

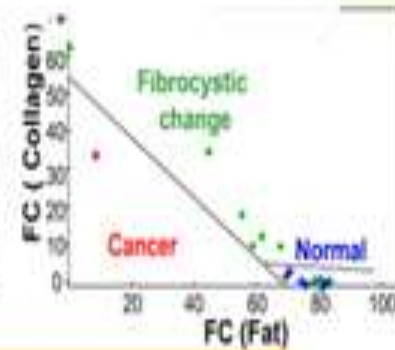
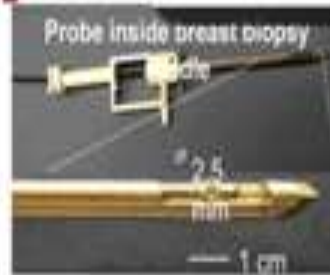
surface enhanced anti-stokes
Raman scattering surface enhanced
resonance Raman scattering (SERRS)



In vivo



- Cholesterol-like
- Fat
- Collagen
- Cell Nucleus
- Cell Cytoplasm
- NIC Parameter



Features

Simple
High sensitivity

Non-invasive
High specificity

- SERS techniques Can be used to
 - Identify molecules using the “molecular fingerprint” provided by the Raman signal
 - Perform single molecule detection due to high signal amplification
- Besides roughened metal surfaces, you may also use nanoparticles as SERS substrate
 - Colloidal nanoparticles
 - Microsphere lithography

Nanoparticle Advantages

- Using a “resonant” nanoparticle provides several advantages for SERS
 - Large absorption cross section - bright
 - Much smaller than cells/tissue – can move and sample in cells/tissue
 - Surface can be modified – linking to molecular probes
 - No photobleaching – longterm monitoring
 - Tuning of resonance possible – optimize for environment or spectral multiplexing

Single Particle SERS

- Due to the large SERS enhancement, can see single particles if they are between the nanoparticles

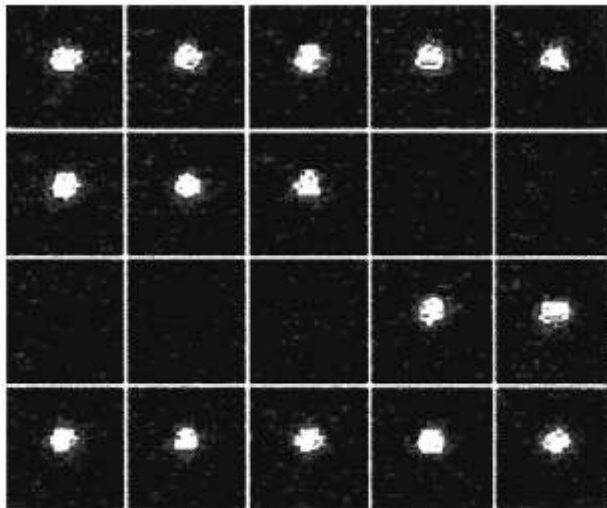


Figure 6. Intermittent SERS signal from R6G adsorbed on a single Ag nanoparticle. The integration time per frame is 1 s, and the rate of acquisition is 0.5 Hz. For this particle, the peak intensity for the “on” time is ~ 150 cps. When the particle blinks “off”, this intensity drops to ~ 1 cps (the background count rate).

Micheals, J. Am. Chem. Soc. **121**, 9932 (1999)

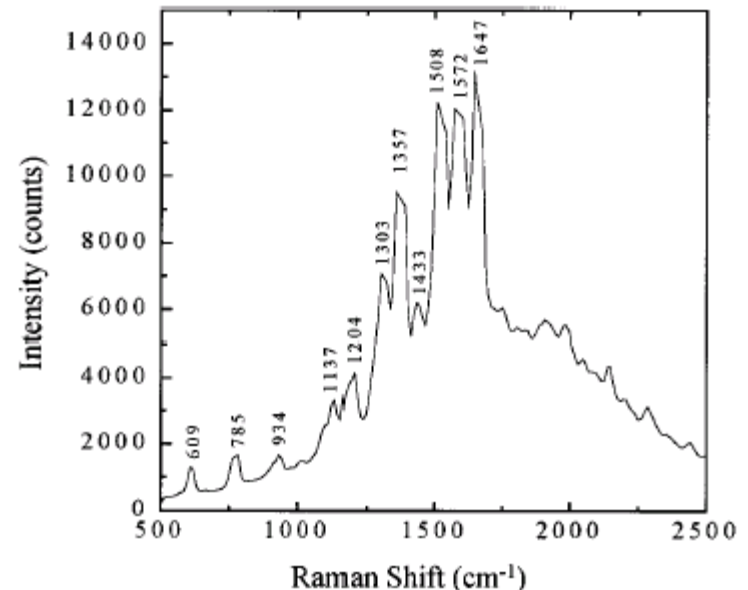
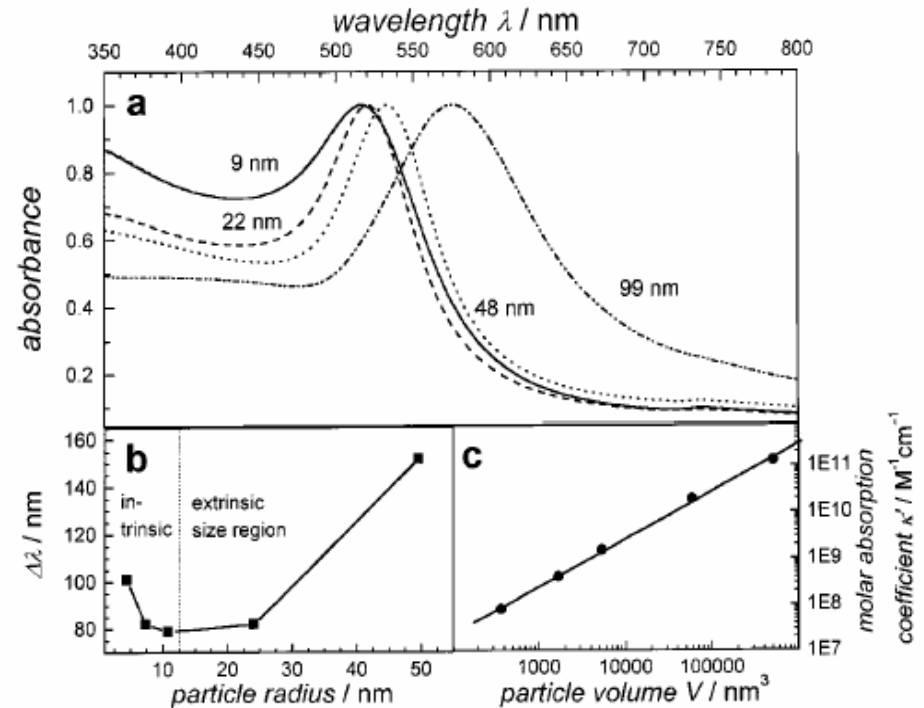


Figure 8. SERS spectrum for R6G adsorbed on a single Ag nanoparticle. NaCl was added at a concentration of 1 mM, and R6G was added at a concentration of 7×10^{-10} M. The integration time was 60 s at ~ 30 W/cm². The spectral resolution is 50 cm⁻¹. The Raman line widths are instrument-limited.

Single Nanoparticles

Recall the extinction coefficient for gold nanoparticles

- Need to excite the nanoparticles at the absorption peak for best enhancement – 517nm for 30nm gold particles
- Argon laser line at 514.5nm



Link et al., J. Chem. Phys B 103, 8410 (1999).

NLO Materials

- **The ever-increasing speed of computer processors and expanding Telecommunication networks generates the need for greater bandwidth. Currently there is a growing interest in organic electro-optic (EO) materials for use as nonlinear optically active materials in devices such as electro-optic transducers, optical switches, sensors, etc**
- **Focus on new electro-optic applications has also stimulated a need for materials with larger electro-optic activities, both at the molecular level (β). Device applications require materials with larger EO coefficients, high thermal stability, and low optical loss**
- **For these material characteristics to be realized, molecules with large β , high decomposition temperatures, and low absorption at telecommunication wavelengths are required**
- **Such materials generally contain donor and acceptor groups positioned at either end of a suitable conjugation path. The magnitude of the nonlinear coefficient increases with increasing length of the Conjugation path and also with the charge state of the donor/acceptor groups.**

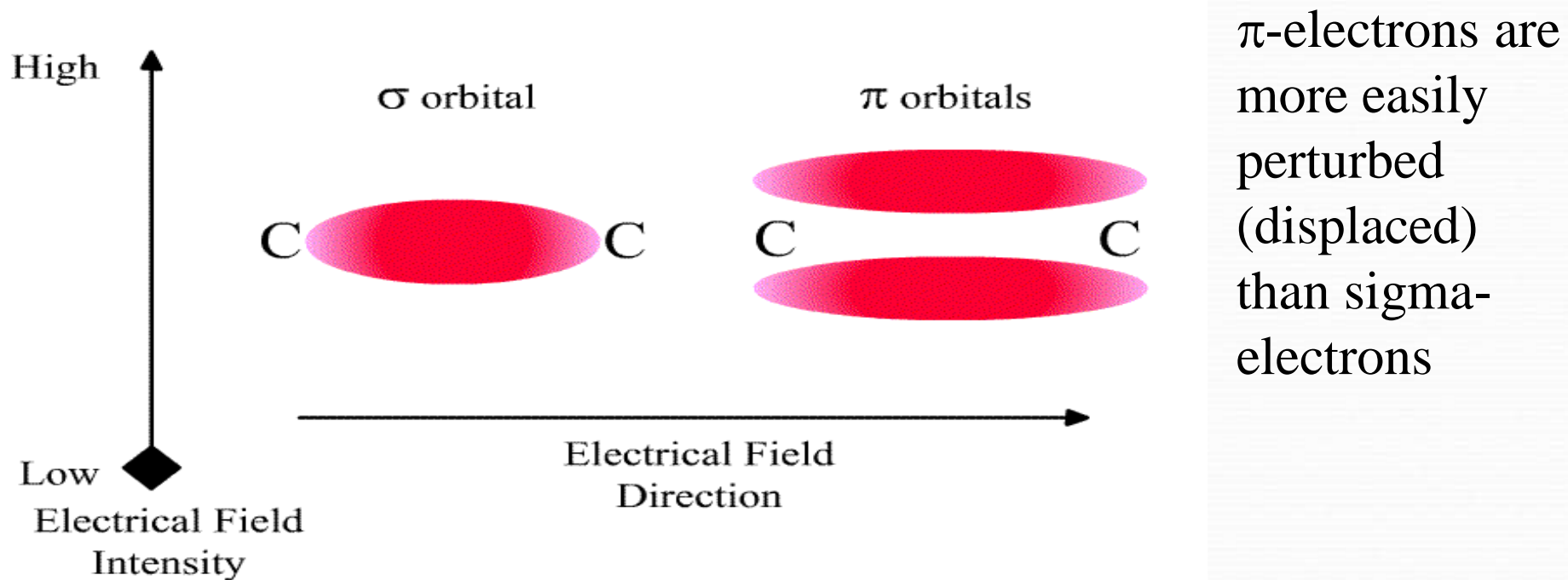
Molecular structure and NLO property of hydrogen bonded crystals

Essential requirements for the crystal to be NLO active

- a) A material must crystallize in one of the non-centrosymmetric space groups**
- b) It should have a large macroscopic second-order susceptibility**
- c) It should have proper phase-matching properties (high intrinsic birefringence and proper low dispersion)**

Origin of NLO response

Electro-Optic Behavior Depends on Orbital Type and Position

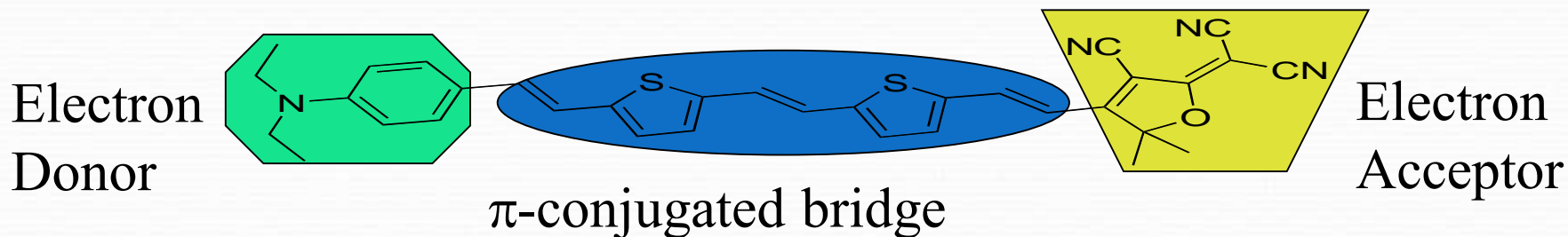


Theory and Modeling

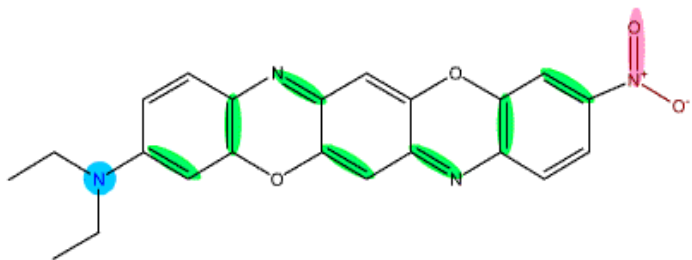
- ❖ **Theory and modeling have played an important role in many areas of science and engineering since the availability of modern computing machines.**
- ❖ **The development of new materials is driven by anticipated new technology and/or perceived improvement in existing technology. In both cases, however, two major factors, namely, improved technology and potential economic payoff, guide the search and development of new materials**
- ❖ **But the theory and modeling of new materials are not merely cost reducing tools. They provide a detailed physical understanding of the phenomenon and required materials properties for technological applications.**
- ❖ **Such an understanding, in addition to improving our fundamental knowledge of the chemistry and physics of materials, constitutes the foundation of the applications of materials to contemporary and future technologies. Therefore, the role of theory and modeling in materials development spans from providing a comprehensive understanding of the physics underlying a technologically useful or debilitating phenomenon to identifying systems exhibiting appropriate device properties.**

Origin of NLO response

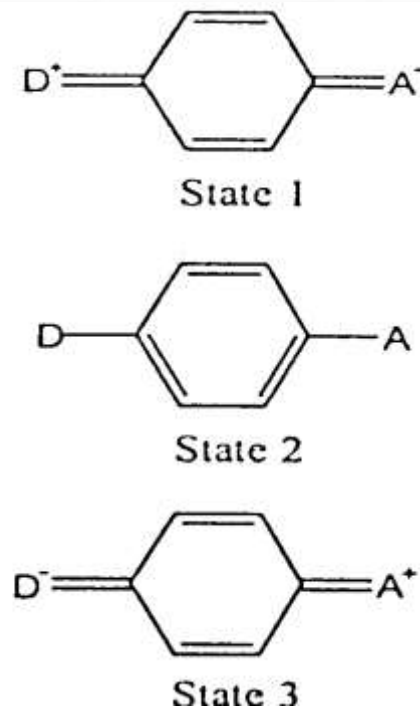
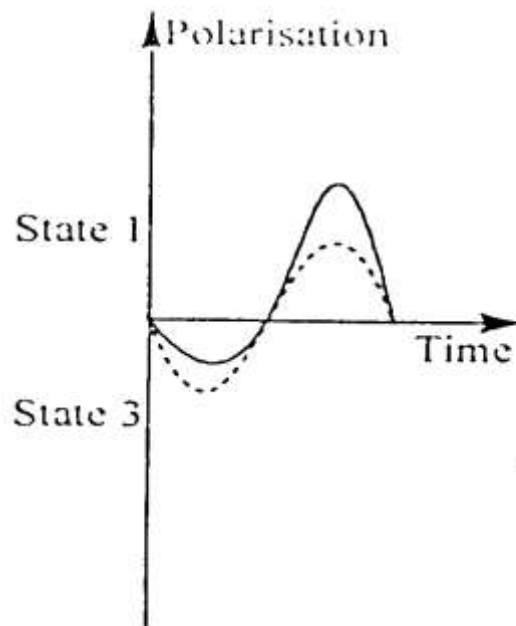
Design of NLO chromophore



Charge displacement can occur over extended distances using materials with extended π -conjugation



The charged separated form will have a larger dipole moment and thus a stronger interaction with an applied electric field



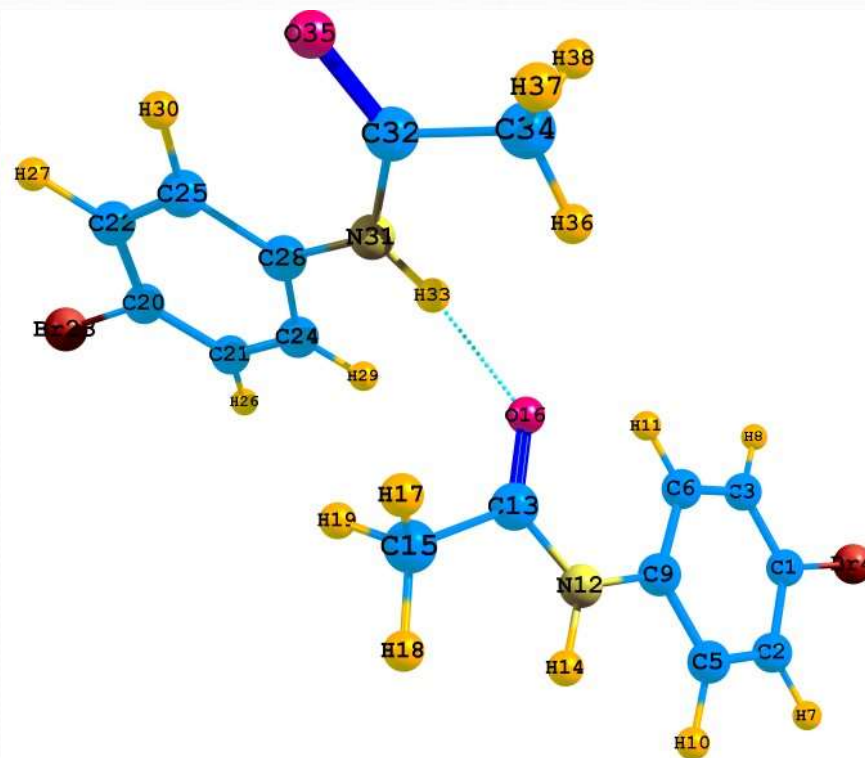
Optimization and first hyperpolarizability

The parameters influencing β are

- 1. Donor-acceptor system** (Aniline, Nitro benzene, Stilbene)
- 2. Nature of substituents** (Donor groups - NH_2 , $-\text{OCH}_3$, $-\text{N}(\text{CH}_3)_2$)
- 3. Conjugation Length** (Acceptor groups - CN , $-\text{NO}_2$, $-\text{CHO}$)
- 4. Influence of planarity**

- ❖ The large value of second order polarizability is associated with the intramolecular charge transfer (ICT), resulting from the electron cloud movement through π -conjugated frame work from electron donor to electron acceptor groups.
- ❖ The electron cloud is capable of interacting with an external electric field and thereby altering the dipole moment and the second order non-linear optical activity.

P-Bromo Acetanilide



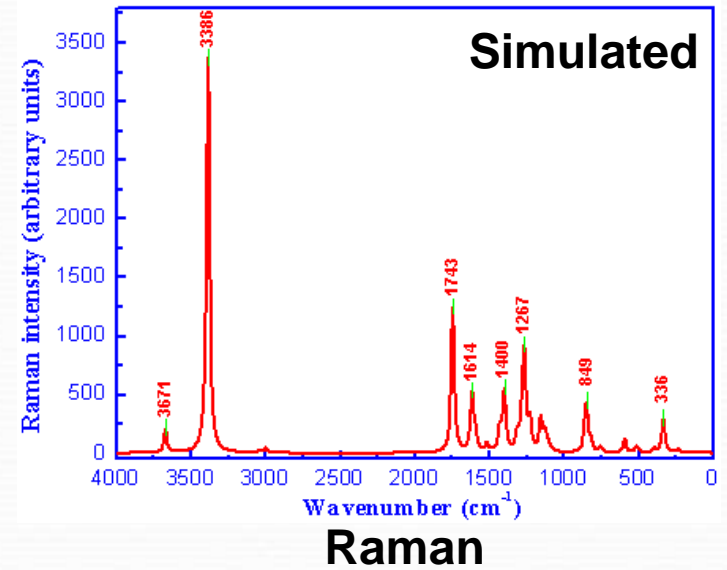
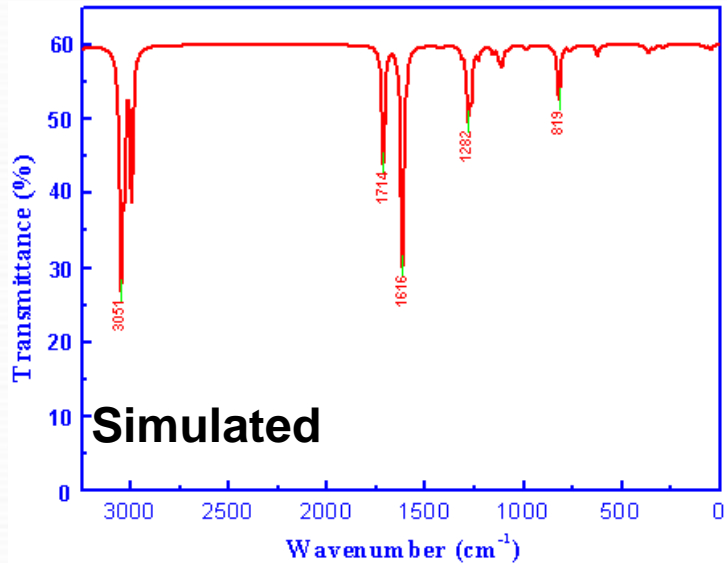
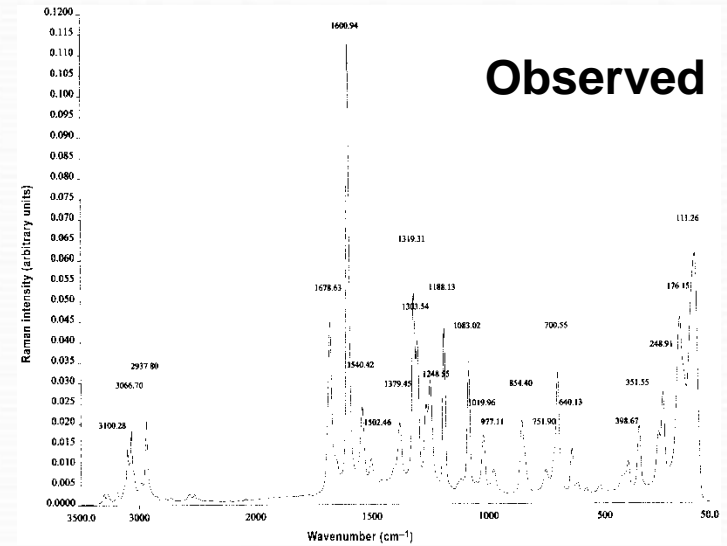
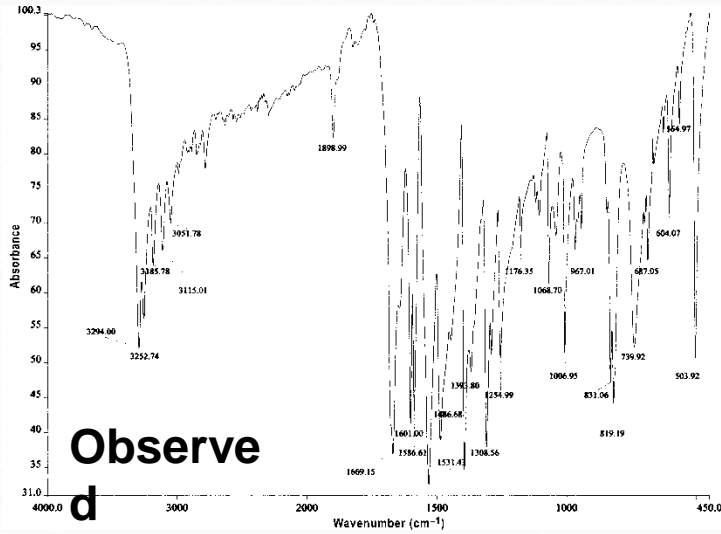
Importance

- ⌘ NLO active P-Bromo Acetanilide (PBA) single crystals are used as optical memories.
- ⌘ Used as experimental photographic developers, as an inhibitor in hydrogen peroxide and to stabilize cellulose ester varnishes.
- ⌘ Used in the intermediation in rubber accelerator synthesis, dyes and dye intermediate synthesis, and camphor synthesis.
- ⌘ It is found to possess analgesic properties and is used as a precursor in the synthesis of penicillin and other pharmaceuticals.

Synthesis

Single crystals of P-Bromo Acetanilide were grown by slow evaporation technique at 40°C. Recrystallized salt was used to prepare saturated solution of methanol at 40°C and the solution was kept in a constant temperature bath having an accuracy of $\pm 0.01^\circ\text{C}$. Seed crystals were obtained by controlled slow evaporation of the solvent.

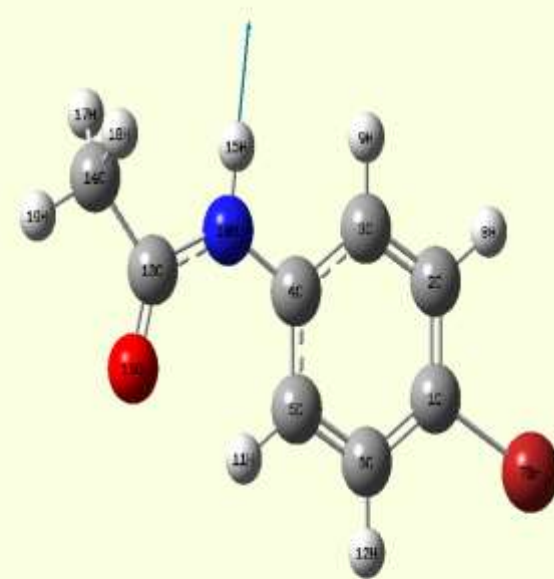
IR and Raman Spectra



Imino group Vibrations

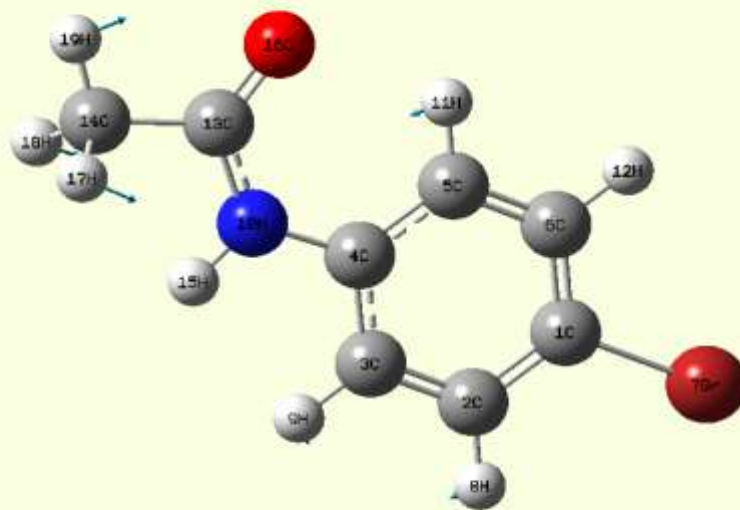
The N-H stretching wavenumber is red shifted by 174 cm^{-1} in IR with a strong intensity from the computed wavenumbers indicating strong intermolecular hydrogen bonding.

NBO analysis reveals the difference in stabilization energy $E^{(2)}$ associated with the hyperconjugative interaction $LP_1(O_{16}) \rightarrow \sigma^*(N_{31}-H_{33})$, \cdots and $LP_2(O_{16}) \rightarrow \sigma^*(N_{31}-H_{33})$, \cdots are 11.76 and $15.83\text{ kcal mol}^{-1}$ respectively, due to the accumulation of electron density in the N-H bond, leading to red shift of the N-H stretching wavenumber which results in ICT causing stabilization of H-bonded systems.



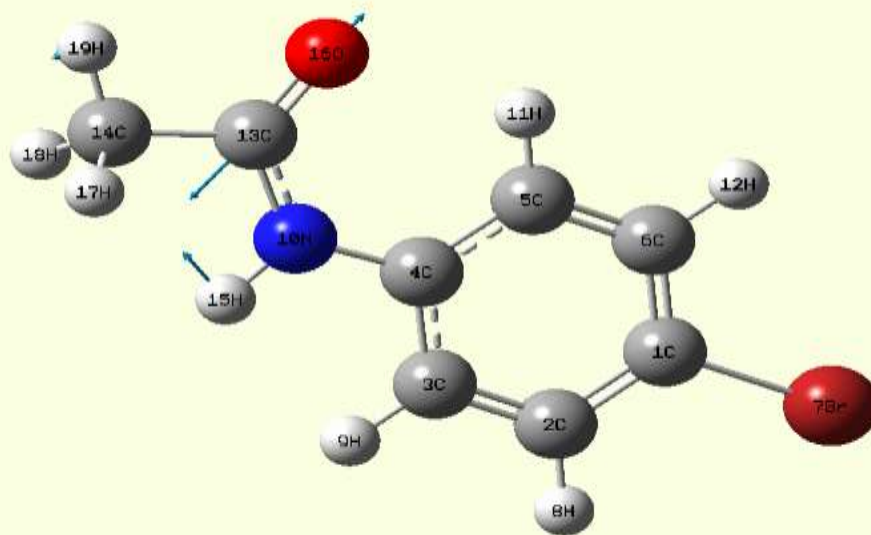
Methyl group Vibrations

The symmetric bending mode is observed with a relatively large value of IR intensity (1394 cm^{-1}) which suggests that a large positive charge is localized on the hydrogen, due to hyperconjugation.



Carbonyl group Vibrations

Simultaneous IR and Raman activation of $C_{13}=O_{16}$ stretching modes, explains the charge-transfer interaction between donor and acceptor through the π -conjugated path.



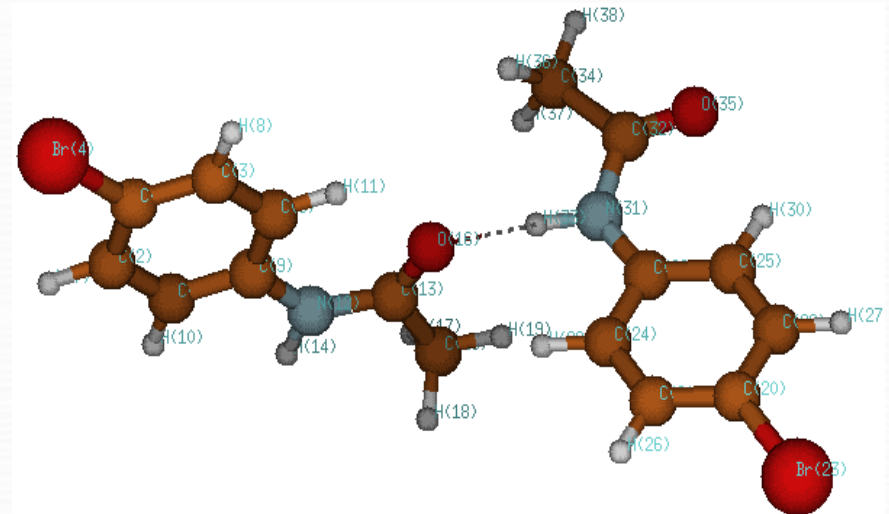
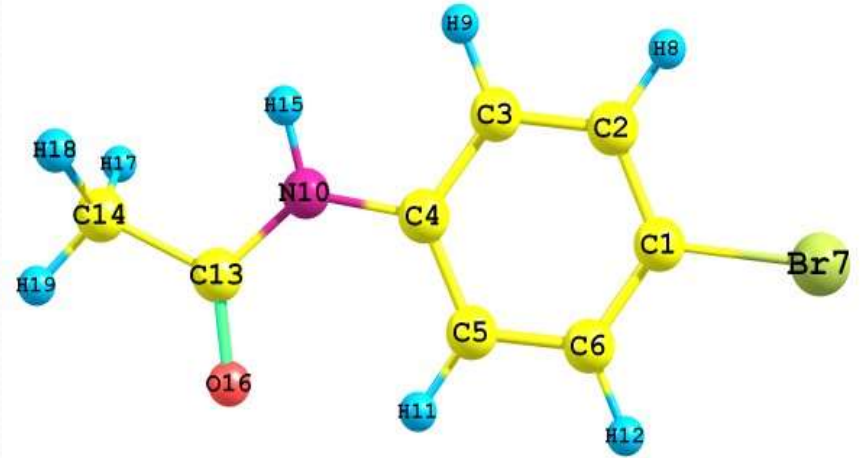
Low Wavenumber Hydrogen Bond Vibrations

Occurrence of an intense Raman band in the low wavenumber region *ca* 111 cm⁻¹ corresponds to the N-H···O stretching H-bond vibrations through which the charge transfer can take place inside the crystal making the molecule NLO active.

Computational Details

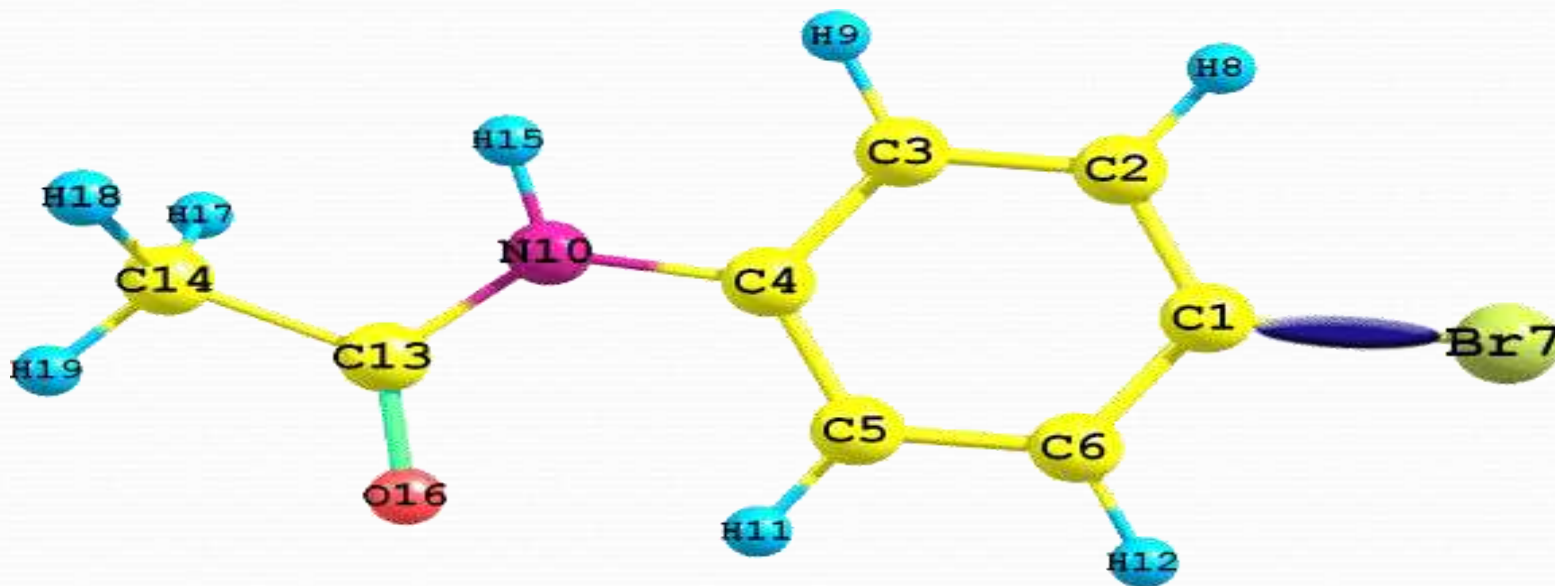
➔ *DFT* computations were performed using Gaussian'98 program package to derive the optimized geometry and vibrational wavenumbers.

➔ NBO analysis - using NBO 3.1 package.



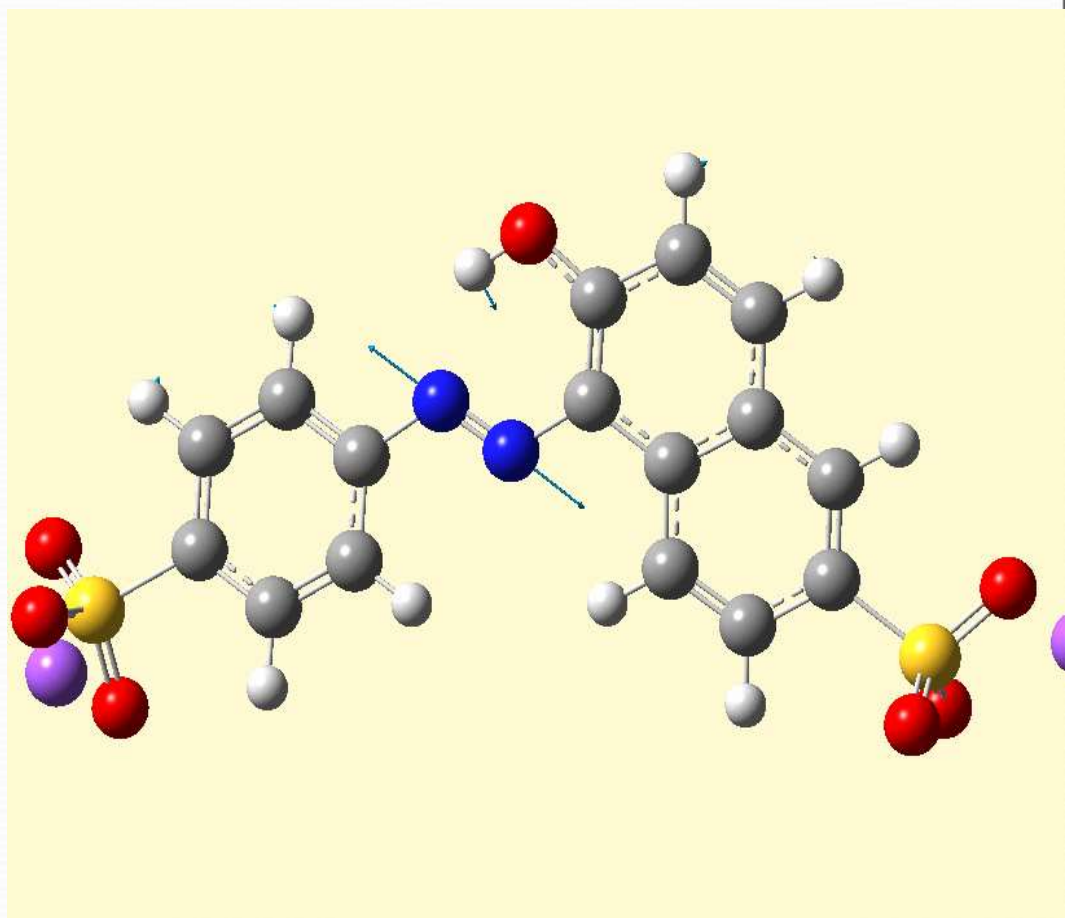
NLO Properties

The computed first hyperpolarizability β_{tot} of PBA is 9.403069×10^{-31} e.s.u., which is 6.6 times that of urea.



Disodium 2-hydroxy-1(4 sulfonate phenylazo)naphthalene-6-sulfonate (Sunset Yellow E110)

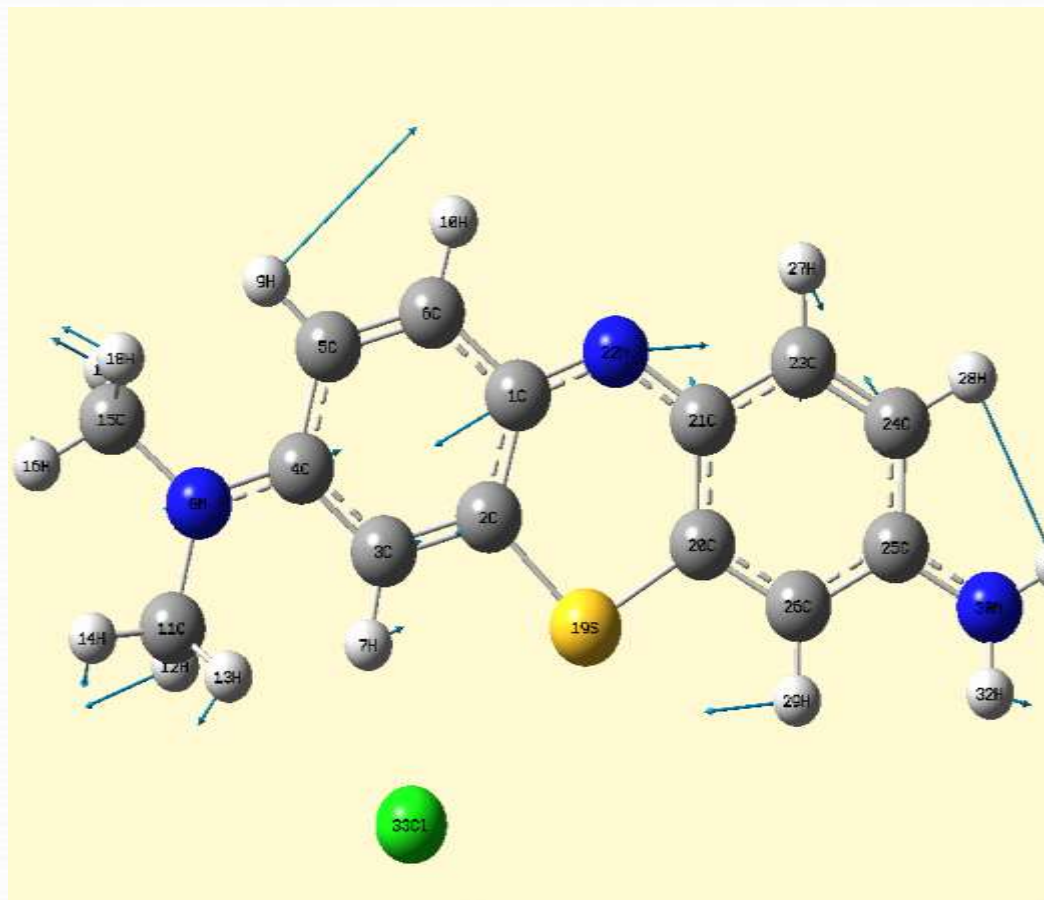
- ($\nu_{\text{Cal}} = 1387\text{cm}^{-1}$, $\nu_{\text{IR}} = 1386\text{cm}^{-1}$ and $\nu_{\text{Raman}} = 1384\text{ cm}^{-1}$).
- N=N stretching wavenumber is lowered due to conjugation, π -electron delocalization and intra molecular hydrogen bonding and cause optical nonlinearity in the molecule.
- The calculated first hyperpolarizability is $3.367 \times 10^{-30}\text{e.s.u}$ (26 times that of Urea).



3-amino -7-(dimethyl amino) phenothiazin-5- ium chloride

(Azure A Chloride)

- The C-N stretching wavenumber is observed as very strong band both in IR and Raman at 1396 cm^{-1} is blue shifted by 19 cm^{-1} due to strong π conjugation.
- The conjugative effect through the heterocyclic center bridge provides a pathway for the redistribution of electric charges under the influence of electric field.
- The intramolecular charge transfer interaction ($n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$,) around the rings must be responsible for the bioactivity and NLO properties of the dye.
- The calculated first hyperpolarizability is 1.92×10^{-30} e.s.u, (13 times that of Urea).



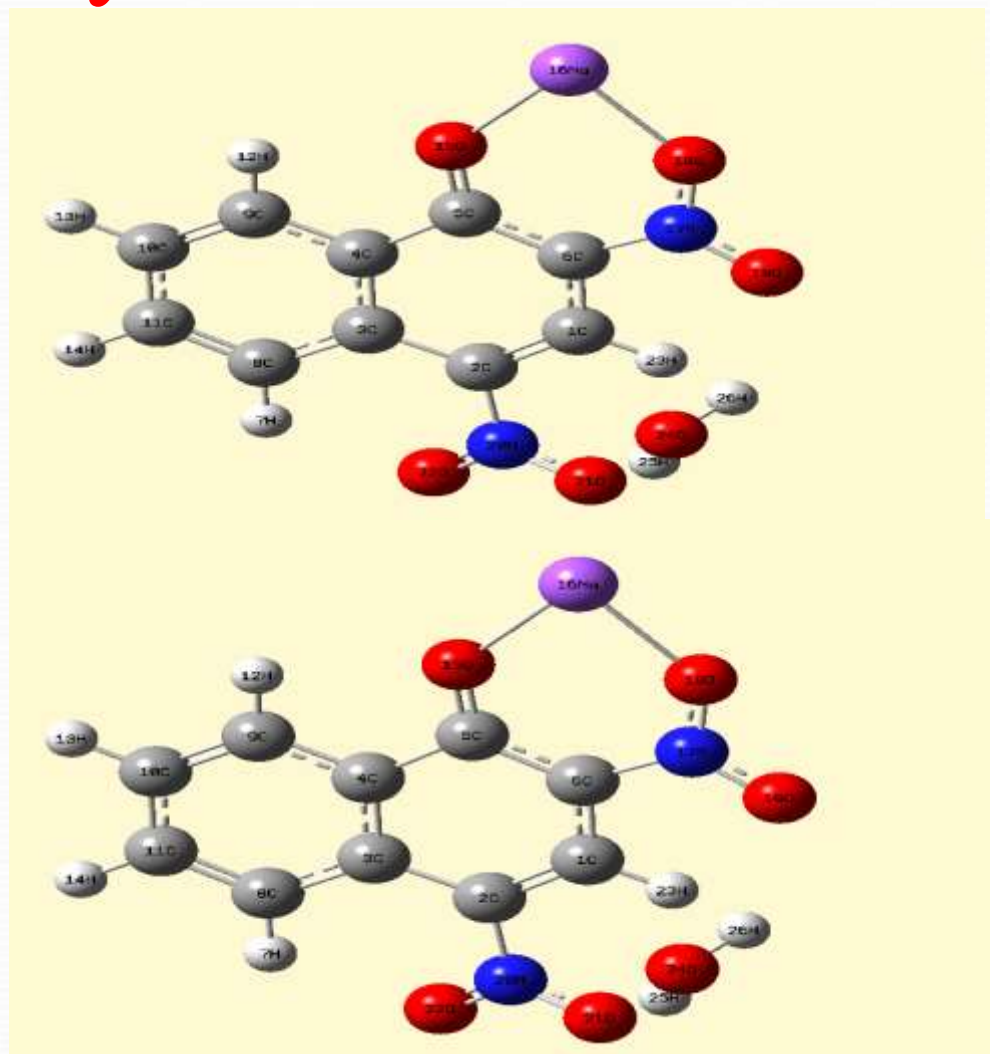
Martius yellow Sodium Salt Monohydrate

- Asymmetric stretching vibrations of the NO_2 group are strong in IR and weak in Raman.

$$\nu_{\text{IR}} = 1576, 1541 \text{ cm}^{-1}$$

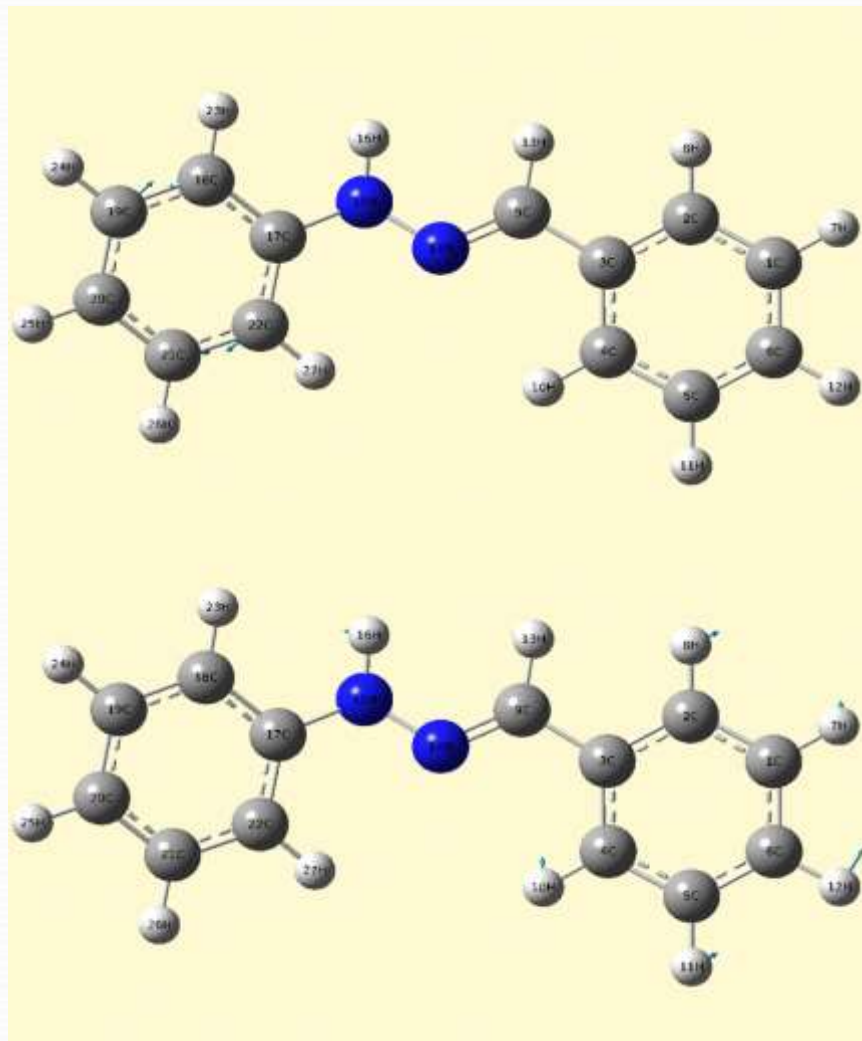
$$\nu_{\text{Raman}} = 1577, 1540 \text{ cm}^{-1}$$

- Symmetric stretching mode of the NO_2 groups mixed with ring stretching vibrations appear as very intense bands in IR (1394, 1332 cm^{-1}) and Raman (1396, 1332 cm^{-1}).
- The intensity enhancement of these wavenumbers is due to conjugation with the aromatic ring
- The calculated first hyperpolarizability is found to be 6.92×10^{-30} e.s.u (36 times that of urea).



Benzaldehyde phenylhydrazone

- The normal mode 8a has been observed in IR at 1606 and in Raman at 1604 cm^{-1} . The 19b mode is observed as at 1454 cm^{-1} IR and the counterpart in Raman appear at 1450 cm^{-1} .
- The simultaneous occurrence of 8a and 19b provide evidences for the charge transfer interactions



Acetoacetanilide

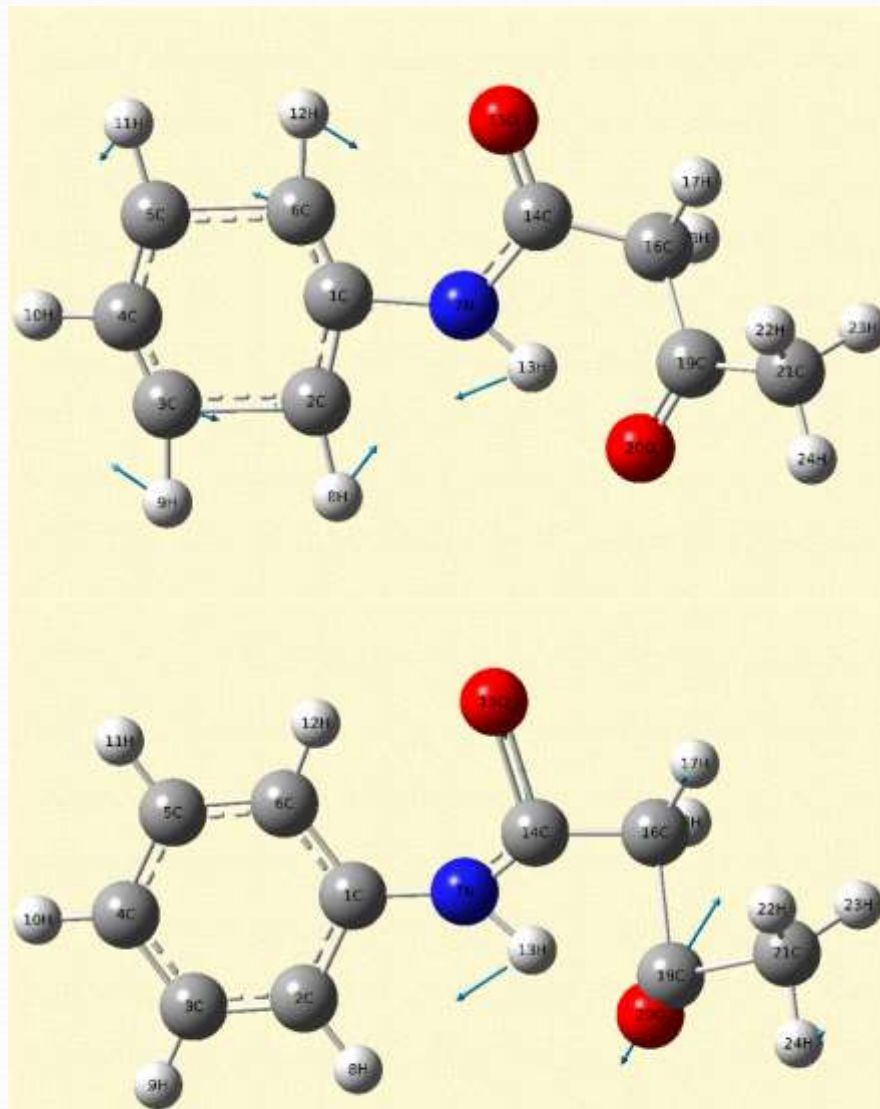
✓ 8a mode:

IR @ 1659 cm^{-1} and Raman @ 1661 cm^{-1} . The blue shifting of C-C stretching 8a wavenumber and the intensity enhancement clearly exhibits the higher degree of conjugation in the side chain.

✓ C=O stretching:

IR @ 1713 cm^{-1} and Raman @ 1715 cm^{-1} . The lowering of C=O stretching wavenumbers is due to the conjugation between carbonyl C=O groups and the aromatic ring.

✓ The calculated first hyperpolarizability is 7.43×10^{-31} esu which is 5 times that of urea.

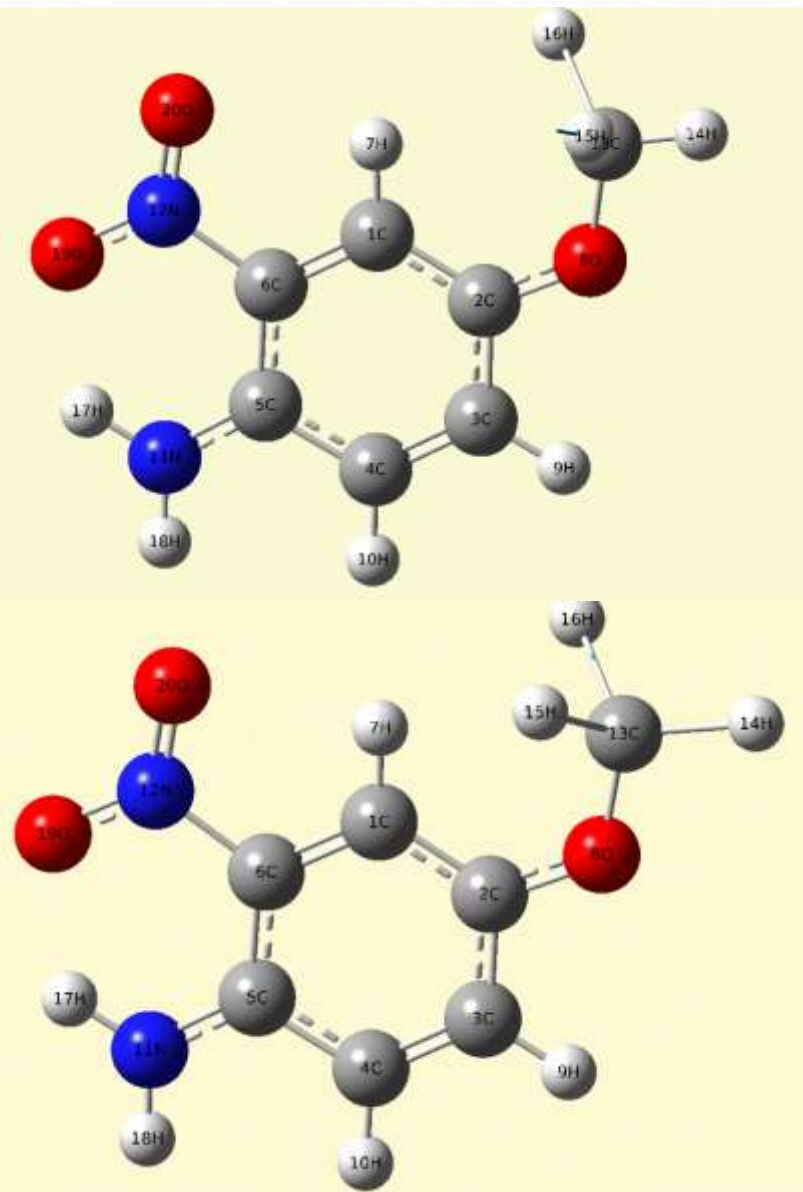


4-Methoxy-2-nitroaniline

Methyl stretching

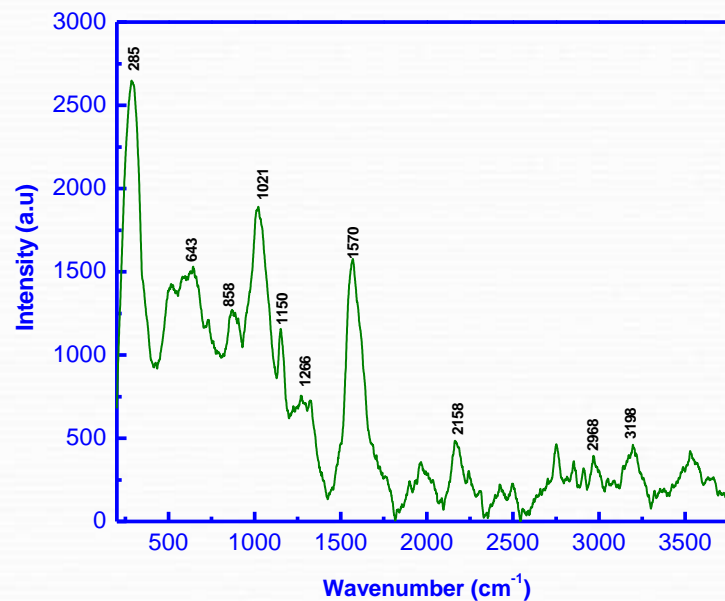
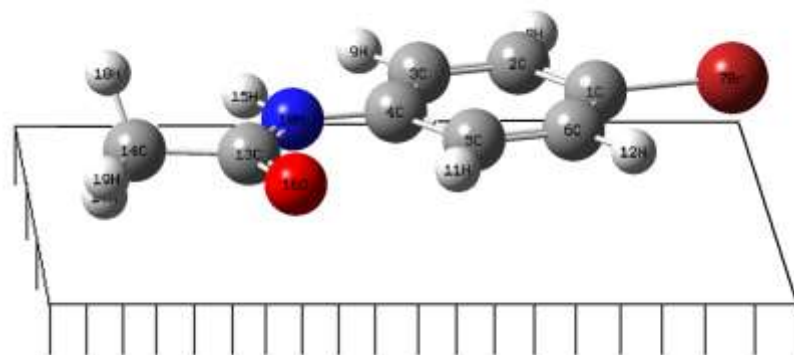
Raman @ 3080 cm^{-1} (asym str) and IR @ 2958 cm^{-1} (sym str) . The blue shifting of methyl stretching modes is due to back-donation of charge from lone pair oxygen atom to the antibonding $\sigma^*(\text{C}-\text{H})$ bonds.

The calculated first hyperpolarizability is 2.38×10^{30} esu, which is 12 times that of urea.



SERS Spectral Investigations

Observed aromatic out-of-plane bending mode at 643, 728 and 858 cm^{-1} are much more intense with respect to the in-plane bending mode at 1150 cm^{-1} . Therefore, the molecule is adsorbed flat on to the silver surface.



Summary

- ① Resemblance between IR and Raman spectra reveals the existence of intramolecular charge transfer (ICT), thus the molecule behaves as an effective push-pull NLO system.
- ② Charge-transfer interaction between the NH-CO-CH₃ group and Br through phenyl ring is responsible for simultaneous strong IR and Raman activation of the ring mode 8a.
- ③ Lowering of the imino stretching wavenumber confirms the existence of strong intermolecular N-H···O hydrogen bonding, substantiated by the natural bond orbital (NBO) analysis.
- ④ Lowering of stretching wavenumbers of methyl group due to electronic effects simultaneously caused by induction and hyperconjugation is due to the presence of the oxygen atom.
- ⑤ SERS spectra predict that the PBA molecule is adsorbed flat on the silver surface.



Thank You