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Non linear optics

(part I, II and III)

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RAMAN EFFECT

The Raman effect has its origin in **molecular transitions** which occur during the light scattering process. When a light quantum with any frequency ν_0 (wavelength λ_0) and energy $h\nu_0$ interacts with a molecule in its ground state n or in any of its excited stationary states k (fig.1) the energy of the system is increased to $h\nu_0 + E_n$ or $h\nu_0 + E_k$.

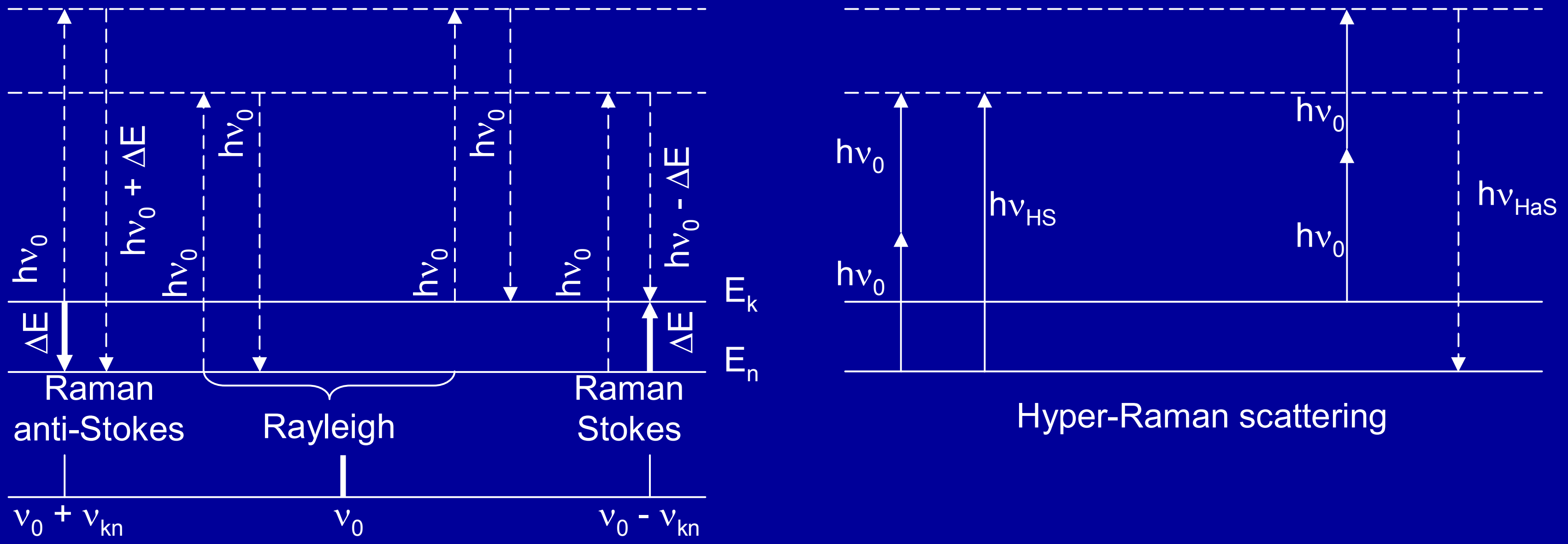
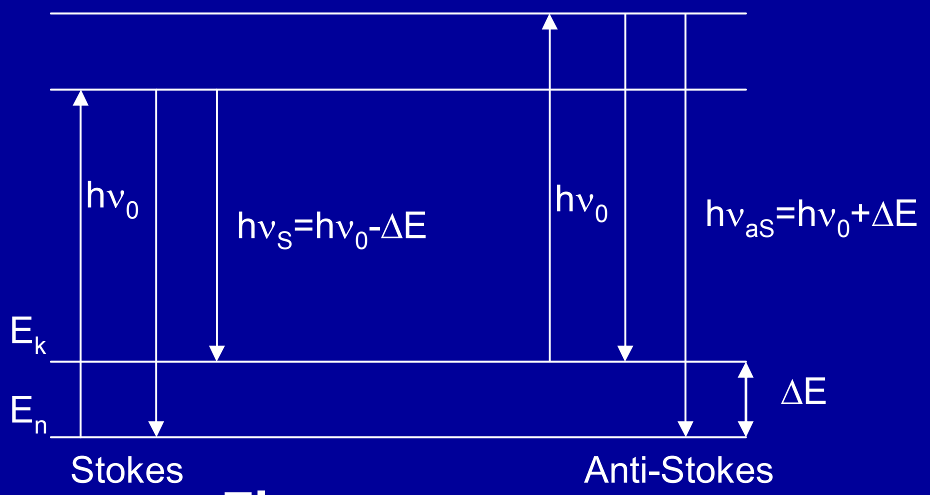


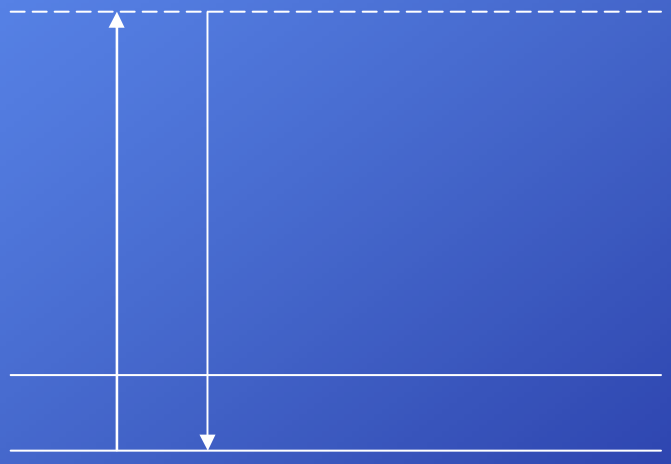
Fig.1. An energy level diagram representing the quantum theory of Raman and Reyleigh scattering. The solid arrows indicate the molecular transitions while the broken arrows represent virtual transitions. The resulting spectrum is shown at the bottom.

If the molecule possesses a stationary state with the energy $h\nu_0 + E_n$ or $h\nu_0 + E_k$, the incident light quantum is absorbed raising the molecule to this excited state. After a certain time, a quantum can be **re-emitted** with the same frequency ν_0 or a changed frequency, depending on whether the molecule returns to its original state or to a different state. This process is called **fluorescence**.



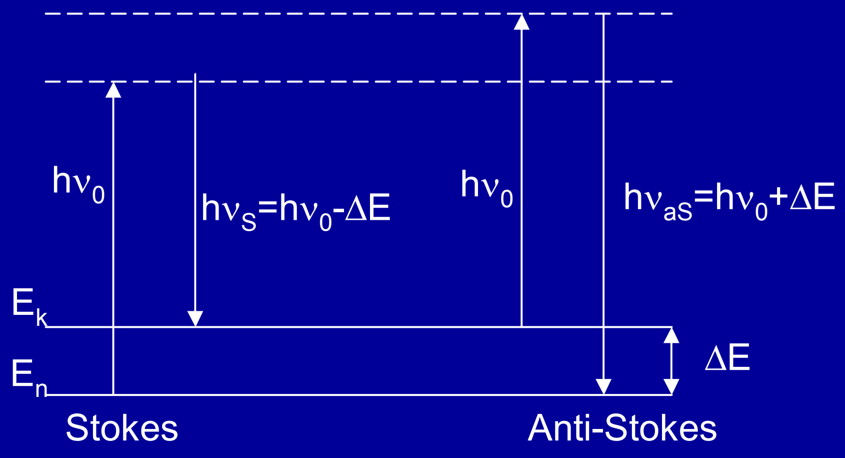
Fluorescence

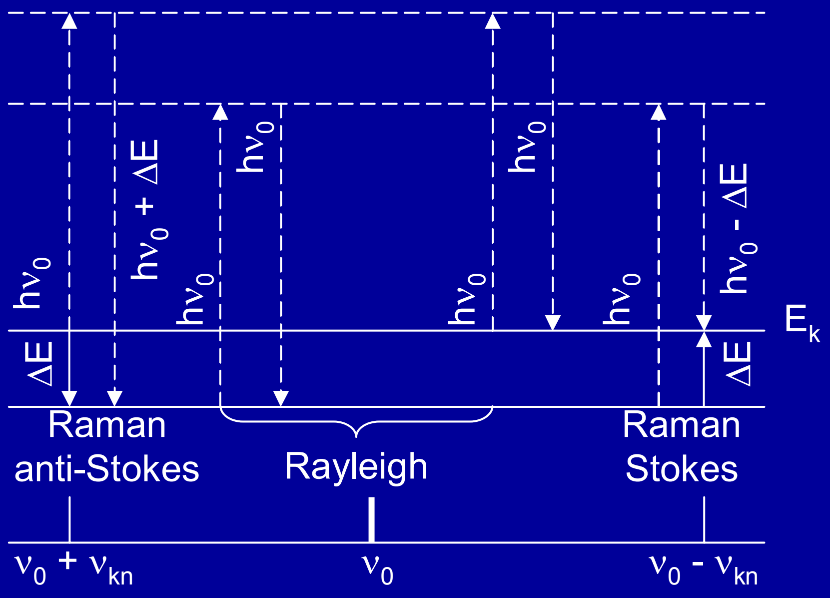
If the molecule returns to its original state, no energy has been taken from the light quantum nor has energy been given to it. Therefore, the frequency of the quantum remains unchanged and we have **Rayleigh scattering**.



Rayleigh

If the molecule goes over to another stationary state, it has either taken energy from the light quantum or given up part of its energy and the frequency of the light quantum is changed. As a consequence, the frequencies $\nu_0 - \nu_{nk}$ and $\nu_0 + \nu_{nk}$ appear in the scattered light and we have the **Raman effect**.





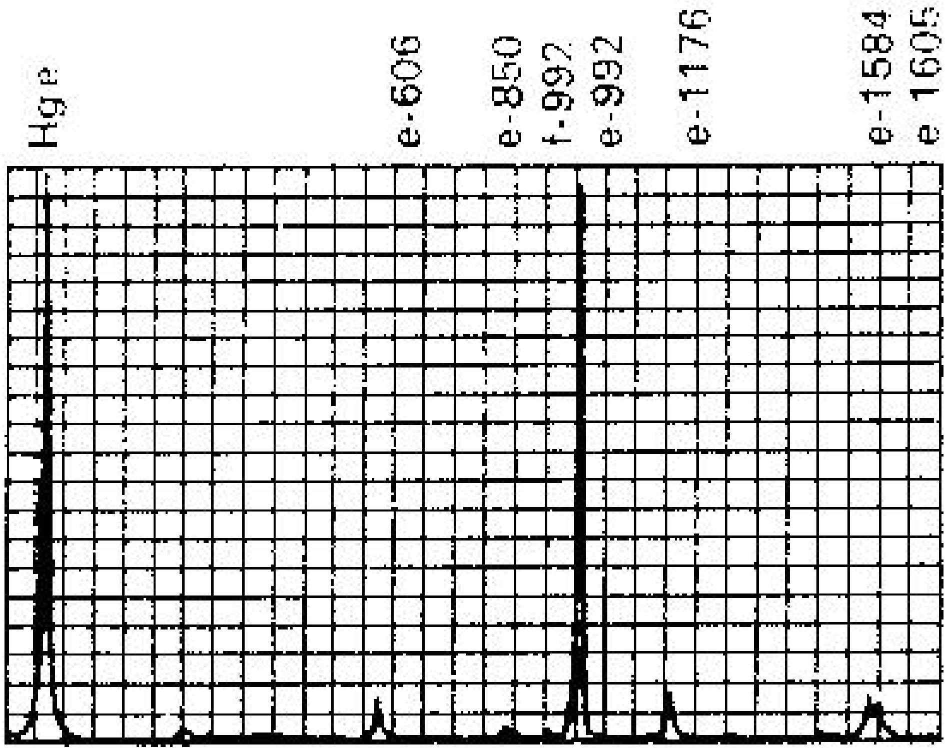


Figure 18.2 The spectrum of the Stokes radiation scattered by benzene. The line on the extreme left is the (greatly attenuated) exciting Hg *e* line at 22,938 cm^{-1} (4358 Å) which is the strongest line in the visible emission spectrum of Hg. The numbers on top give the downward shift in frequency (in cm^{-1}) thus corresponding to the vibrational frequencies. They are preceded by letters indicating the parent Hg line. The *f*-992 line is due to the *f* line of Hg at 22,995 cm^{-1}.

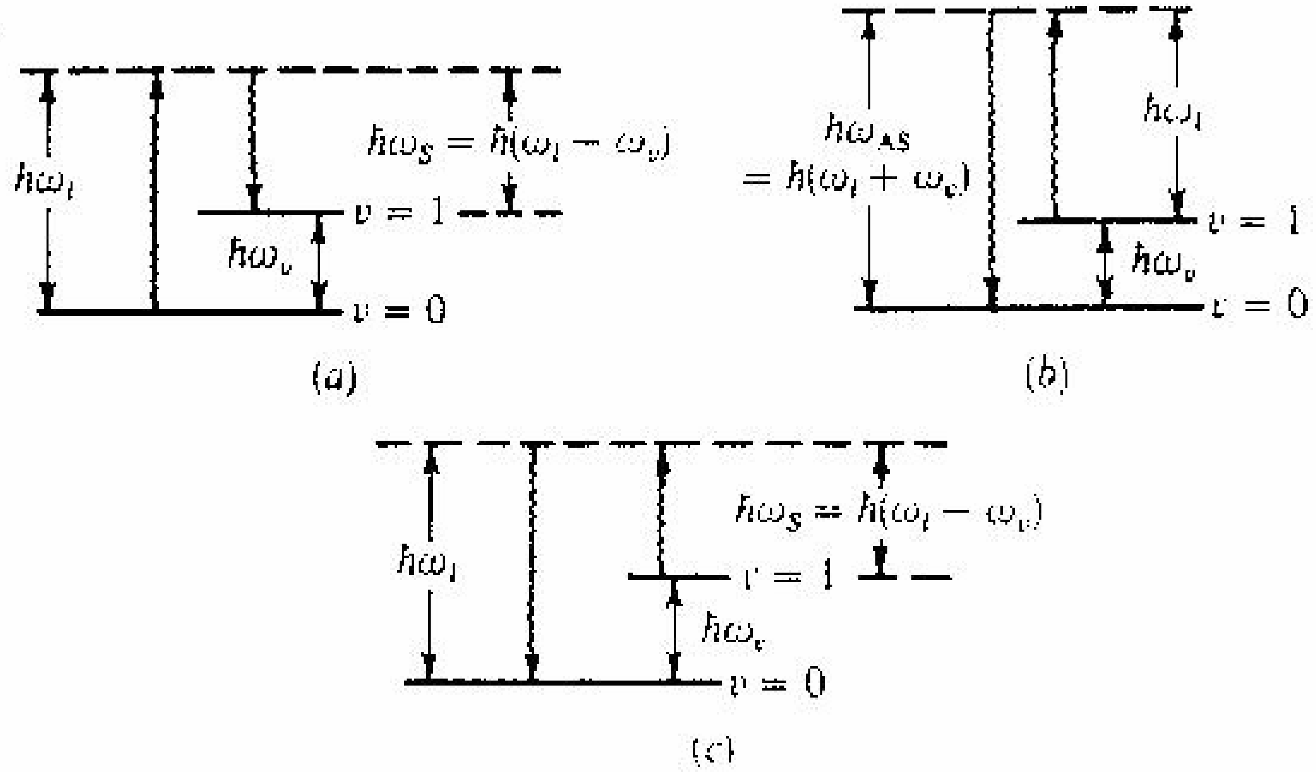


Figure 18.1 (*a*) A Stokes scattering in which a laser photon at ω_l is absorbed while a Stokes $(\omega_l - \omega_v)$ photon is created along with a vibrational $(v = 1)$ quantum. (*b*) An anti-Stokes scattering in which a laser photon at ω_l and a vibrational (ω_v) quantum are absorbed, while a photon at $\omega_l + \omega_v$ is created. (*c*) A process in which the presence of laser radiation at ω_l stimulates the absorption of Stokes photons at $\omega_l - \omega_v$, that is, the reverse of (*a*).

The intensity of scattered light at $\nu_0 \pm \nu_{nk}$ is given by

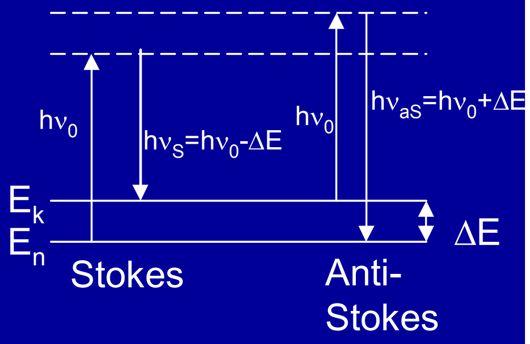
$$I(v_0 \pm v_{nk}) = NI(v_0)h(v_0 \pm v_{nk})A_{nk}, \qquad (1)$$

where the transition probability A_{nk} for a molecular transition n ↔ k during the scattering process is defined as

$$A_{nk} = \frac{64\pi^4}{3}\frac{h}{c^3}(\nu_0 \pm \nu_{nk})^3 \mu_{nk}^2, \qquad (2)$$

with

$$\mu_{nk} = \frac{1}{h}\sum_r \left[\frac{M_{nr}M_{rk}}{\nu_{rn} - \nu_0} + \frac{M_{nr}M_{rk}}{\nu_{rk} + \nu_0}\right]E. \qquad (3)$$



c is the velocity of light, h is Planck's constant, r represents any one level of a complete set of electronic levels, M_{nr} is the matrix element of the transition n ↔ r, E is the electric field of the light wave, N is the number of molecules in the initial state and $I(\nu_0)$ the intensity of the incident radiation.

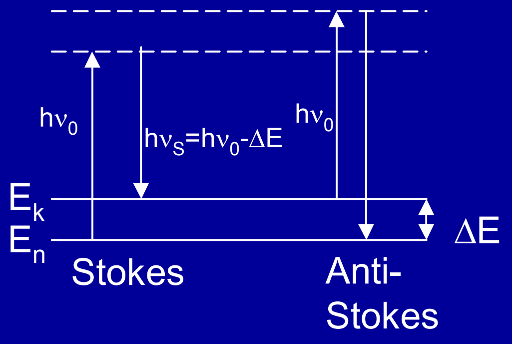
For k = n these equations apply to Rayleigh scattering.

The angular dependence of the scattered light intensity is given by $I(\theta) = I(\nu_0)(1+ \cos^2\theta)/2$ where θ is the angle between the incident and scattered light.

Equations (2) and (3) show that the probability for a Raman transition from a state n to a state k is determined by the sum over all states r of products of transition moments from the state n to some other state r and from the state r to the state k. Thus it can be seen that the Raman selection rules differ from the rules governing absorption and emission of dipole radiation: the former depend on the product of transition moments M_{nr} M_{rk}, and the latter depend only on the transition moments M_{nr} or M_{rk}.

$$A_{nk} = \frac{64\pi^4}{3}\frac{h}{c^3}(\nu_0 \pm \nu_{nk})^3 \mu_{nk}^2, \qquad (2)$$

$$\mu_{nk} = \frac{1}{h}\sum_r \left[\frac{M_{nr}M_{rk}}{\nu_{rn} - \nu_0} + \frac{M_{nr}M_{rk}}{\nu_{rk} + \nu_0} \right] E. \qquad (3)$$



The explicit Raman selection rule is that only levels having eigenfunctions of the same symmetry can combine with one another.

$$\mu_{nk} = \frac{1}{h}\sum_{r}\left[\frac{M_{nr}M_{rk}}{\nu_{rn}-\nu_0}+\frac{M_{nr}M_{rk}}{\nu_{rk}+\nu_0}\right]E. \qquad (3)$$

In the scattering formula for molecules in their ground electronic states under certain conditions (which are generally always fulfilled in experiments), the induced dipole moment μ_{kn} in eq.(3) can be replaced by

$$\mu = \alpha E$$

$$\mu_{nk} = \frac{1}{h}\sum_{r}\left[\frac{M_{nr}M_{rk}}{\nu_{rn} - \nu_0} + \frac{M_{nr}M_{rk}}{\nu_{rk} + \nu_0}\right]E. \qquad (3)$$

where E is the electric field vector of the light wave and α is the molecular polarizability tensor.

The transition probabilities and therefore intensity and selection rules are determined by integrals of the form

$$[\alpha_{XY}]^{kn} = \int \psi_n^* \alpha_{XY} \psi_k dt, \qquad (4)$$

where ψ_n and ψ_k are the time-dependent wave functions of the initial and the final states, α_{XY} is one of the components of the polarizability tensor of the molecule referred to space-fixed axes and the integration is over all space. The simplification introduced by the polarizability theory is that $[\alpha_{XY}]^{kn}$ in eq.(4), and hence μ_{kn}, depend on knowledge of the initial and final states only. According to eq.(4), it is necessary to know the form of the wave functions ψ_n, ψ_k and the dependence of the polarizability on the molecular structure.

The polarizability varies with the vibrational and rotational motions of a molecule. For vibrational motions of infinitesimal amplitudes, the polarizability can be represented by an expansion in terms of the 3N-6 normal coordinates q_i

$$\alpha_{xy} = \alpha_{xy} + \sum_{i=1}^{3N-6} \left(\frac{\partial \alpha_{xy}}{\partial q_i} \right) q_j + \text{higher terms} \qquad (5)$$

where the six components α_{xy} are expressed in a molecule-fixed system (xyz).

Whether a particular vibration is Raman-active or inactive can be determined by considering the changes in the polarizability as the vibrating molecule goes through its equilibrium position. Also, an estimate can be made of whether the motion results in a change in the magnitude of the derivative of the polarizability (associated with totally symmetric vibrations) or in the anisotropy of the derivative of the polarizability (usually associated with antisymmetric vibrations).

If the higher-order terms in the polarizability (eq.5) or in the potential energy are considered, that is if anharmonicity is present, then overtone and combination frequencies can also occur (the second-order Raman spectrum).

$$\alpha_{xy} = \alpha_{xy} + \sum_{i=1}^{3N-6} \left(\frac{\partial \alpha_{xy}}{\partial q_i} \right) q_j + \text{higher terms} \quad (5)$$

But these are usually very much weaker than the fundamentals. On the other hand, in some crystals, f.e. the alkali halides, the fundamental vibration (the first-order Raman spectrum) is forbidden by symmetry and only the very weak second-order spectrum is observed.

Many types of vibrational bands can occur in the Raman effect (some of which may not occur in infra-red absorption) and their occurrence or nonoccurrence in the Raman spectrum may be used to determine the molecular symmetry or point group of molecules.

All totally symmetric vibrations are Raman-active. Since all molecules have at last one totally symmetric vibrations, all molecules will exhibit a vibrational Raman spectrum.

For rotational motions, the polarizability is expressed in a space-fixed coordinate system (XYZ) in terms of the polarizability components along the xyz axes fixed in the molecule. For example

$$\alpha_{XY} = \sum_{xy} \alpha_{xy} \cos(x, X) \cos(y, Y). \qquad (6)$$

The rotational selection rules are determined by the matrix elements $\int \psi_r^* \alpha_{xy} \psi_{r''} dt.$ For the special case of the rigid nonlinear molecule the selection rules are $\Delta J = 0, \pm 2$.

Moreover, transitions are only possible if the polarizability ellipsoid is anisotropic; this is a general condition for all molecules and holds for pure rotational transitions as well for vibration-rotational transitions.

A very simple explanation of the Raman effect can be given on a classical base.

Let us consider a simple diatomic molecule. If it is irradiated with monochromatic light of frequency ν, the electrons are periodically shifted and an electric moment is induced.

If

$$E = E_0 \cos 2\pi\nu t$$

the induced moment is

$$M = \alpha_0 E_0 \cos 2\pi\nu t$$

where α_0 is the polarizability that is a measure of the facility with which the charge distribution of the molecule can be deformed.

Let us suppose that the molecule vibrates along the line joining the nuclei, with a frequency ν_1. The polarizability will change as a function of the distance x between the nuclei and if x is small

$$\alpha \cong \alpha_0 + \alpha_1 x$$

If the induced motion is harmonic

$$x = x_0 \cos 2\pi\nu_1 t$$

The induced moment of the vibrating molecule is

$$\begin{aligned} M &= \alpha E = \left(\alpha_0 + \alpha_1 x_0 \cos 2\pi\nu_1 t\right) E_0 \cos 2\pi\nu t \\ &= \alpha_0 E_0 \cos 2\pi\nu t + \frac{1}{2}\alpha_1 x_0 E_0 \left\{\cos 2\pi(\nu+\nu_1)t + \cos 2\pi(\nu-\nu_1)t\right\} \end{aligned}$$

The diffused light now consists of the Rayleigh radiation and two new frequencies $\nu \pm \nu_1$ that are the Raman frequencies.

In order that these frequencies exist it must be

$$\alpha_1 \neq 0$$

In other words, the change of polarizability during a molecular vibration is responsible for the Raman effect.

This selection rule is very different from the one which governs an infrared absorption in which it is necessary that the vibration gives place to a change of the electric moment.

So the vibration of a mononuclear diatomic molecule as H_2 can be observed in the Raman effect but not in the absorption, because the vibration can produce a change in the polarizability but not in the electric moment.

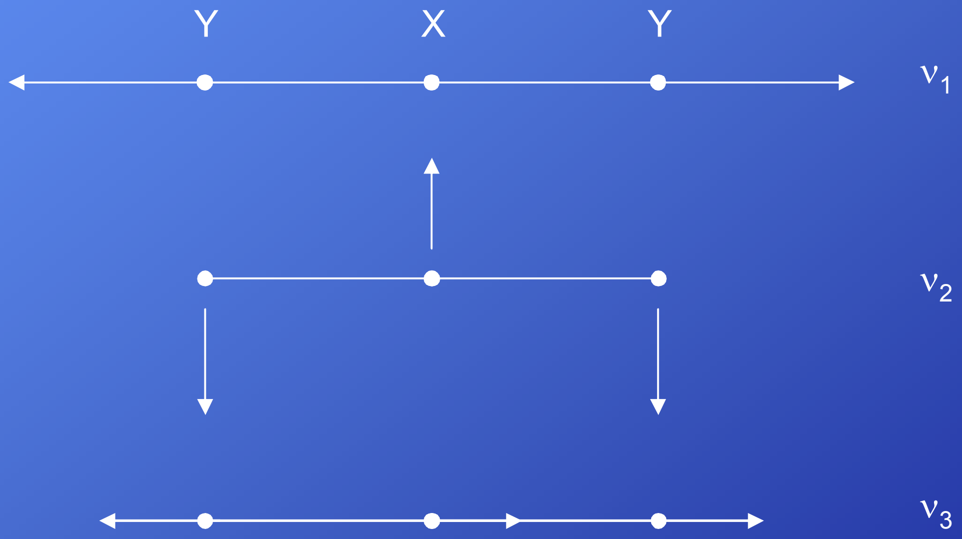
According to the classic electrodynamics, every motion in an atomic system which is connected with a change of its dipole moment brings to the emission or the absorption of radiation.

The motions connected with a change of the dipole moment, and therefore that appear in the infrared, are called **active**.

In the **asymmetric molecules** all the vibration modes are connected with a change of the dipole moment.

In the **symmetric molecules** there can be vibrations during which the change of the dipole moment is exactly zero and therefore they are inactive in the infrared.

For example in CO_2, during the totally symmetric vibration ν_1, the dipole moment remain zero as in the equilibrium position and therefore this vibration is inactive in the infrared. Instead the vibrations ν_2 and ν_3 are active.



GENERAL PROPERTIES OF RAMAN SCATTERING

The same pattern of lines if found for any given substance no matter what exciting line is used. That is, the frequency shifts of the Raman lines, or their displacements in units cm^{-1}, from any exciting line, are constant. These frequency shifts are found to equal the frequencies of rotational, vibrational and electronic transitions of the scattering molecules.

$$\nu = \frac{c}{\lambda} \therefore h\nu = \frac{hc}{\lambda} = (hc)\frac{1}{\lambda}$$

If $\frac{1}{\lambda}$ is in cm^{-1} and hc =12.5.10^{-5} eV.cm we have hν in eV (1eV = 1.6 × 10^{-19} joule).

Rotational transitions give rise to rotational lines in the spectra of gases close to the exciting line, usually within about 100 cm^{-1}.

At low resolution, these appear as a general broadening of the exciting line or as rotational wings.

At high resolution, the individual rotational lines may be observed.

These rotational wings sometimes persist with reduced intensity and extent even in liquids, where (excepting liquid hydrogen) free rotation is not found.

Vibrational transitions give rise to vibrational bands in the spectra of gases, liquids and solids, in the frequency range 100 to about 4000 cm^{-1}. For all molecules, in general, strong line-like Q branches ($\Delta J = 0$) are observed for those vibrations which produce changes in the magnitude of the polarizability derivative, i.e., for the totally symmetric vibrations (v_1). On the other hand, considerable broadening (in liquids, e.g., v_2, v_3, v_4) or strong rotational wings ($\Delta J = \pm1, \pm2$) are observed for those vibration which produce changes in the anisotropy of the polarizability derivative. In some liquids and solids the Raman bands may be modified in frequency, intensity or breadth from those in the gas phase because of intermolecular forces.

Much information is similar to that obtained by infrared spectroscopy and in part by microwave spectroscopy. However, according to the theory (and practice) the information obtained from Raman spectra complements that obtained from infra-red and microwave spectra. This valuable property arises from the basically different mechanisms which produce the spectra:

the Raman effect occurs because of a change in magnitude or direction of the electronic polarizability during the molecular motion,

while infra-red and microwave absorption occur because of a change in magnitude or direction of the electric dipole moment during the motion.

From measurements of the anti-Stokes lines the temperature distribution of samples can be determined. The intensity of these lines can, to a good approximation, be modeled via the occupation densities N_m of the vibronic states m with frequencies v_m which are given by the Boltzmann distribution:

$$N_m = N_0 e^{-h\nu_m / kT}$$

therefore

$$\frac{I(\nu_0 + \nu_m)}{I(\nu_0)} \propto e^{-h\nu_m / kT}. \qquad (1)$$

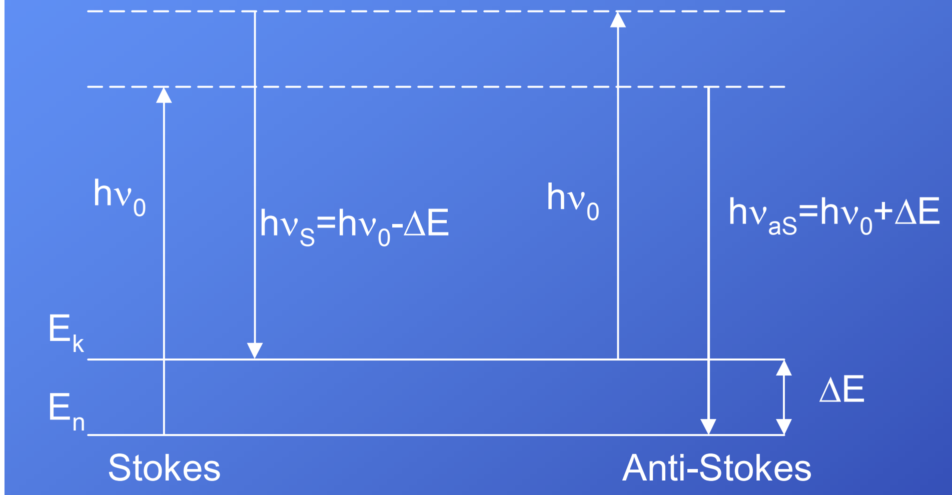
Raman scattering provides a rich variety of information on the structure and composition of matter, based on its vibrational fingerprints. The vibrational information, which usually occurs at IR frequencies, can be obtained by monitoring the frequency shifts between excitation and scattered light. As a scattering process, however, the Raman effect is exceedingly weak: Typical Raman cross sections per molecule range between 10^{-30} and 10^{-25} cm^2, with the larger values occurring during resonant Raman conditions, when the frequency of light happens to match an electronic transition in the molecule. By comparison, fluorescence spectroscopy, based on the absorption and emission light, exploits effective cross sections between 10^{-17} cm^2 and 10^{-16} cm^2.

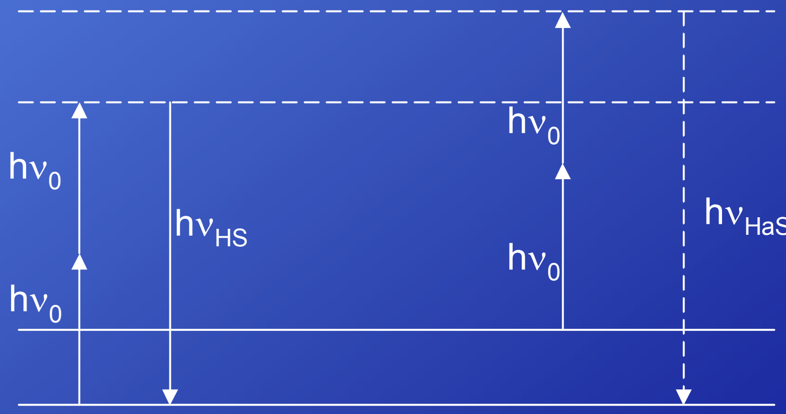
Other methods that are gaining interest among researchers include two-photon techniques.

By using two lower-energy photons during the scattering process, light can be shifted to longer wavelengths than is possible during one-photon scattering. The lower-energy incident photons penetrate many materials more deeply and simultaneously reduce the degradation of light-sensitive samples.

So far, most two-photon applications are based on fluorescence. Hyper-Raman scattering (HRS) is a potential tool for probing the chemistry of materials using two-photon scattering.

In **hyper-Raman scattering (HRS)**, two photons are simultaneously scattered from a molecule. The energies of the accompanying Raman signals are thus shifted relative to twice the energy of the excitation laser: $h\nu_{HS} = 2h\nu_L - h\nu_M$ and $h\nu_{HaS} = 2h\nu_L + h\nu_M$; the subscripts HS and HaS refer to hyper-Raman Stokes and anti-Stokes photons.





Hyper-Raman scattering

Because two photon HRS follows different symmetry selection rules than one-photon RS, the spectral information obtained in each can be complementary.

What’s more, the power of RS signals depends linearly on the laser’s excitation intensity, whereas HRS signals depend on the square of the intensity.

Another important application field is based on surface-enhanced Raman spectroscopy (SERS).

Enhancement factors for the Raman signal of up to 10^{20} were reported for molecules on cluster surfaces. This may enable single molecule detection via Raman spectroscopy with very high selectivity.

In 1974 Martin Fleischmann and co-workers reported an unexpectedly strong Raman signal from a monolayer of pyridine absorbed on an electrochemically roughened silver electrode.

The excitation of surface plasmons explains the enhanced Raman signals.

In the 30 years since its discovery and confirmation, surface-enhanced Raman scattering (SERS) has matured into a powerful spectroscopic method that exploits the interaction of light, molecules and metal nanostructures to boost Raman signals high enough – in some cases up to 14 orders of magnitude – that researchers can resolve the chemical structure of materials, even at the single-molecule level. Moreover, SERS has contributed to the development of plasmonics and the related field of near-field optics, which are revolutionizing optics and spectroscopy.

In the vicinity of metal nanoclusters, field enhancement occurs because of the resonant interaction between the optical fields and surface plasmons in the metal.

In essence, the light from a laser beam excites the surface plasmons, which are collective oscillations of conduction electrons. Those plasmons then radiate a dipolar field. The coherent interaction of the incoming electric field with the dipolar field leads to a redistribution of electric-field intensities in areas around the metal clusters.

A molecule nearby or absorbed on the metal feels an enhanced excitation intensity. So its Raman-scattered field is enhanced in the same way that the incident laser fields is. Indeed, one can liken the metallic clusters to tiny antennas that enhance and transmit the Raman-scattered light.

The enhancement depends on the type of metal, its degree of roughness – the sizes and shapes of the clusters that form – and the frequency of the incident light.

The original observation of SERS, in fact, was a fortunate accident that occurred because the laser frequency happened to fall in the plasmon resonance of nanometer-sized bumps on the rough silver electrodes.

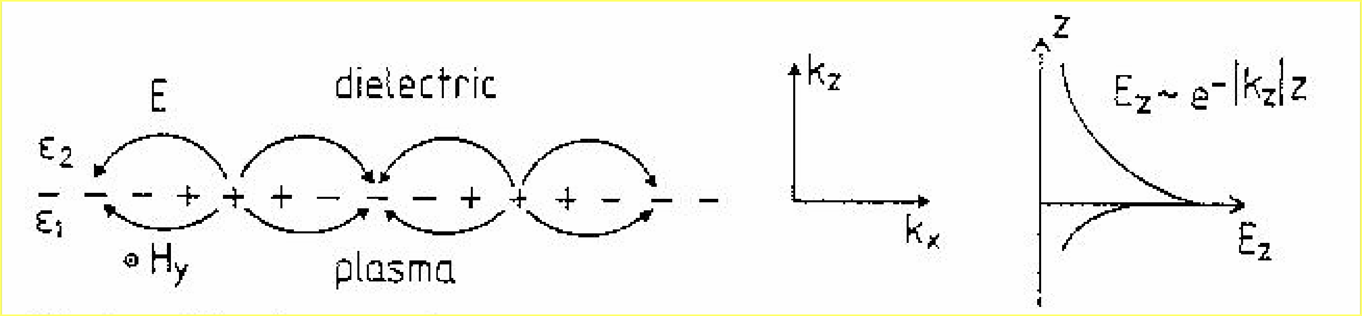
SERS enhancement is particularly strong when both laser and scattered fields are in resonance with the surface plasmons. The frequency shift between the laser and scattered light is usually small compared with the width of the plasmon resonance. Therefore, the laser and Raman-scattered fields increase by about the same amount, and the signal power scales roughly with the fourth power of the local optical-field enhancement.

For a Raman cross section of 10^{-29} cm^2, large numbers of molecules are required to convert enough laser photons to Raman photons to achieve a usable signal. From 100 mW laser light focused to 1 μm^2, a single molecule scatters only 10^{-4} photons per second. That means one would have to wait more than an hour for a single Raman photon. Before the advent of SERS, such estimates made single-molecule Raman spectroscopy science fiction.

By virtue of the extremely high enhancement factors obtainable in SERS, however, one can get insight into an individual molecule’s intrinsic vibrational properties and monitor its structural changes without resorting to ensemble averages. Indeed, the structure-sensitive detection of single molecules represents the ultimate limit in chemical analysis.

SURFACE PLASMONS ON SMOOTH SURFACES

The electron charges on a metal boundary can perform coherent fluctuations which are called surface plasma oscillations. The frequency ω of these longitudinal oscillations is tied to its wave vector k_x by a dispersion relation $\omega(k_z)$.



These charge fluctuations, which can be localized in the z direction within the Thomas-Fermi screening length of about 1 Å, are accompanied by a mixed transversal and longitudinal electromagnetic field which disappears at $|z| \to \infty$ (fig.1) and has its maximum in the surface z = 0, typical for surface waves. This explains their sensitivity to surface properties.

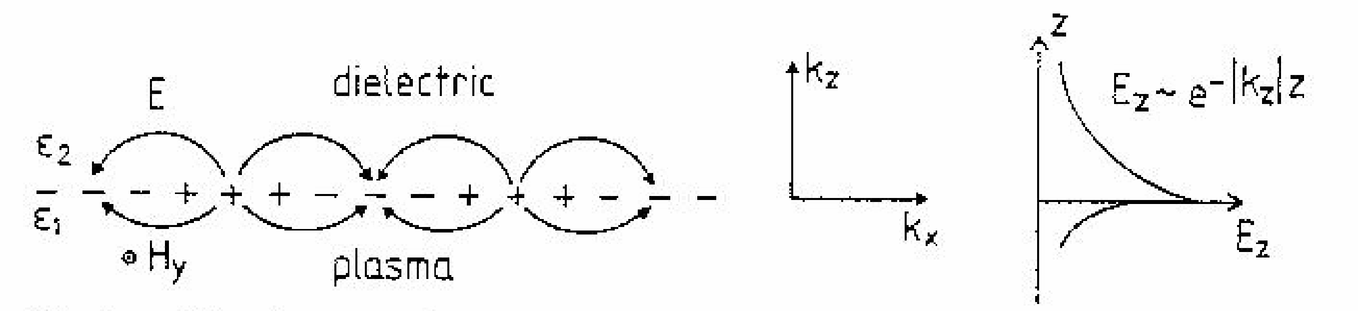


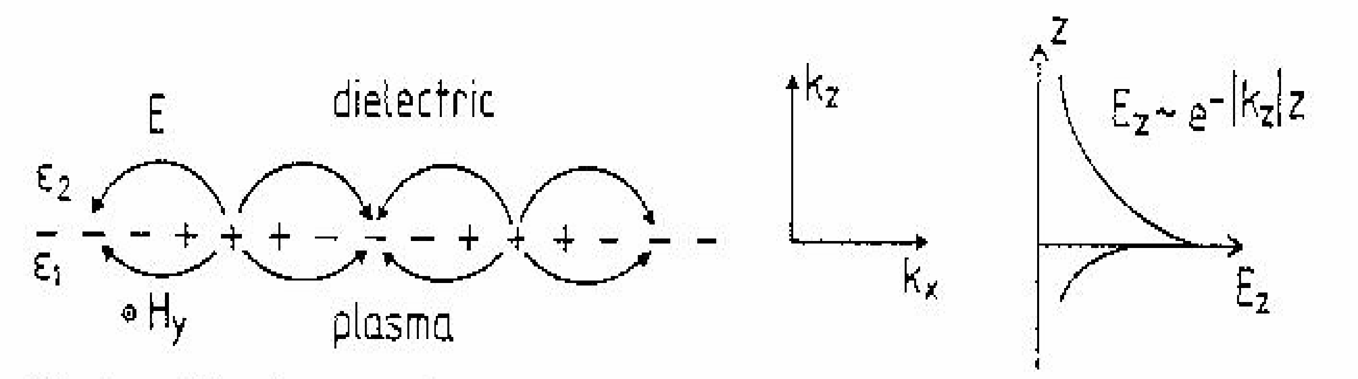
Fig.1 The charges and the electromagnetic field of SPs propagating on a surface in the x direction are shown schematically. The exponential dependence of the field E_z is seen on the right. H_y shows the magnetic field in the y direction of this p-polarized wave.

The field is described by

$$E = E_0^{\pm} \exp\left[+i\left(k_x x \pm k_z z - \omega t\right)\right] \qquad (1)$$

with + for z≥0, - for z≤0, and with imaginary k_z, which causes the exponential decay of the field E_z.

The wave vector k_x lies parallel to the x direction; $k_x = 2\pi/\lambda_p$, where λ_p is the wavelength of the plasma oscillation.

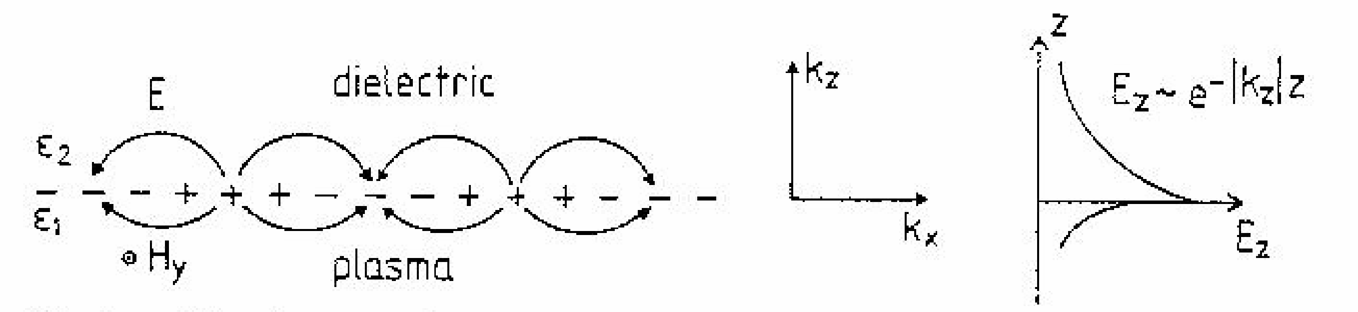


Maxwell's equations yield the retarded dispersion relation for the plane surface of a semi-infinite metal with the dielectric function $(\varepsilon_1 = \varepsilon_1' + i\varepsilon_1'')$, adjacent to a medium ε_2 as air or vacuum:

$$D_0 = \frac{k_{z1}}{\varepsilon_1} + \frac{k_{z2}}{\varepsilon_2} = 0 \quad \text{together with} \qquad (2)$$

$$\varepsilon_1 \left(\frac{\omega}{c}\right)^2 = k_x^2 + k_{zi}^2 \quad \text{or} \qquad (3)$$

$$k_{zi} = \left[\varepsilon_i \left(\frac{\omega}{c}\right)^2 - k_z^2\right]^{1/2}, \quad i = 1, 2.$$



The wave vector k_x is continuous through the interface. The dispersion relation (2) can be written as

$$k_x = \frac{\omega}{c}\left(\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{1/2}. \qquad (4)$$

If we assume besides a real ω and ε_2 that $\varepsilon_1'' < \left|\varepsilon_1'\right|,$ we obtain a complex $k_x = k_x' + ik_x''$ with

$$k_x' = \frac{\omega}{c}\left(\frac{\varepsilon_1'\varepsilon_2}{\varepsilon_1'+\varepsilon_2}\right)^{1/2} \qquad (5)$$

$$k_x'' = \frac{\omega}{c}\left(\frac{\varepsilon_1'\varepsilon_2}{\varepsilon_1'+\varepsilon_2}\right)^{3/2}\frac{\varepsilon_1''}{2(\varepsilon_1')^2}. \qquad (6)$$

For real k'_x one needs $\varepsilon'_1 < 0$ and $\left|\varepsilon_1'\right| > \varepsilon_2,$ which can be fulfilled in a metal also in a doped semiconductor near the eigen frequency; k_2'' determined the internal absorption. In the following we write k_x in general instead of k'_z.

The dispersion relation (see fig.2) approaches the light line $\sqrt{\varepsilon_2}\omega/c$ at small k_x, but remains larger than $\sqrt{\varepsilon_2}\omega/c$ so that the SPs cannot transform into light: it is a “nonradiative” SP.

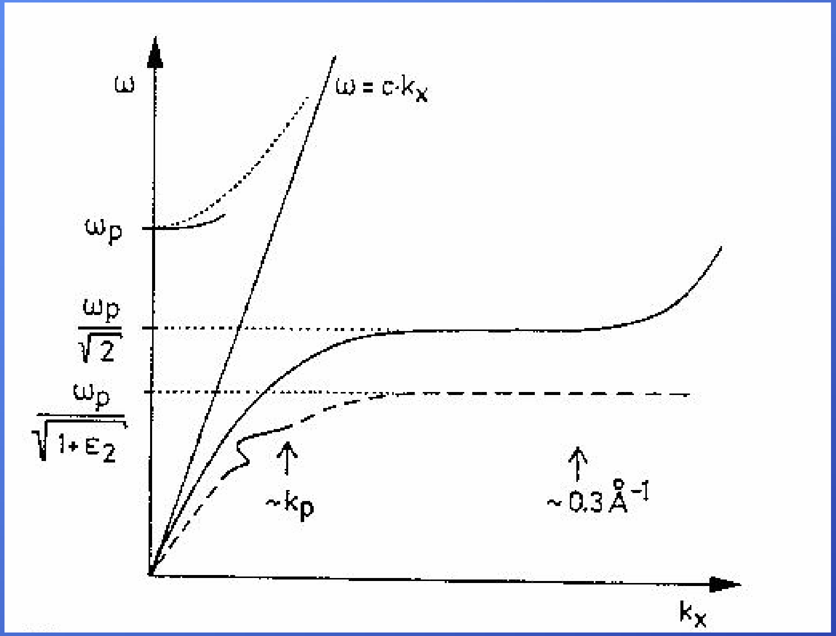


Fig.2. The dispersion relation of nonradiative SPs (—), right of the light line $\omega = ck_x$; the retardation region extends from $k_x = 0$ up to about $k_p = 2\pi/\lambda_p$ (λ_p plasma wavelength). The dashed line, right of $\omega = ck_x$, represents SPs on a metal surface coated with a dielectric film (ε_2). Left of the light line, $\omega(k_x)$ of the radiative SPs starts at ω_p (—). The slight modulation in the dashed dispersion curve comes from an eigen frequency in a monomolecular dye dilm deposited on a Langmuir-Blodgett film (ε_2).

At large k_x or

$$\varepsilon_1' \to -\varepsilon_2 \qquad (7)$$

the value of ω approaches

$$\omega_{sp} = \left[\frac{\omega_p}{1+\varepsilon_2}\right]^{1/2} \qquad (8)$$

for a free electron gas where ω_p is the plasma frequency $\sqrt{4\pi ne^2/m}$, with n the bulk electron density.

With increasing ε_2, the value of ω_{sp} is reduced.

At large k_x the group velocity goes to zero as well as the phase velocity, so that the SP resembles a localized fluctuation of the electron plasma.

STIMULATED RAMAN SCATTERING

The model used in the analysis is as follows: the Raman medium is taken as consisting of N harmonic oscillators per unit volume, each oscillator representing one molecule. The oscillators are independent of each other so that the ensemble of oscillators cannot support a wavemotion with a nonvanishing group velocity. Each oscillator is characterized by its position z (the analysis is one-dimensional so that $\partial/\partial x = \partial/\partial y = 0$) and normal vibrational coordinate $X(z,t)$.

The equation of motion for a single oscillator is then

$$\frac{d^2X(z,t)}{dt^2} + \gamma\frac{dX}{dt} + \omega_v^2 X = \frac{F(z,t)}{m} \qquad (1)$$

where γ is the damping constant chosen so that the observed spontaneous Raman scattering linewidth is $\Delta\nu = \gamma/2\pi$, ω_v is the (undamped) resonance frequency, m is the mass and F(z,t) is the driving force.

The driving term can be derived by considering the electromagnetic energy in the presence of the molecules. The electrostatic stored energy density is

$$E = \frac{1}{2}\varepsilon \mathrm{E}^2$$

that, using

$$\varepsilon = \varepsilon_0 (1 + N\alpha) = \varepsilon_0 \left\{ 1 + N \left[\alpha_0 + \left(\frac{\partial \alpha}{\partial X} \right)_0 X \right] \right\} \qquad (2)$$

can be written as

$$E = \frac{1}{2}\varepsilon_0 \left\{ 1 + N \left[\alpha_0 + \left(\frac{\partial \alpha}{\partial X} \right)_0 \right] \right\} \mathrm{E}^2 \qquad (3)$$

The force per unit volume of polarizable material is $\partial E/\partial X$ that after dividing by N, gives the force per oscillator as

$$F(z,t) = \frac{1}{2}\varepsilon_0 \left(\frac{\partial\alpha}{\partial X}\right)_0 \overline{E}^2(z,t) \qquad (4)$$

where the bar indicates averaging over a few optical periods since the molecules cannot respond to optical frequencies.

This shows that because of the nonvanishing differential polarizability, $(\partial\alpha/\partial X)_0$, the molecular vibration can be driven by the electric field.

Our next problem is to show how the field induced excitation of molecular vibration X(z,t) reacts back on the electromagnetic fields.

The molecular vibration at ω_v causes, according to (2), a modulation of the dielectric constant ε at ω_v. This leads to phase modulation of any radiation field present thus creating sidebands separated by ω_v.

Stated differently, a modulation of ε at ω_v, caused by molecular vibrations, can lead to energy exchange between electromagnetic fields separated in frequency by multiples of ω_v, such as, for example, the laser (ω_l) and the

Stokes ($\omega_s = \omega_l - \omega_v$) fields.

$$\varepsilon = \varepsilon_0 (1 + N\alpha) = \varepsilon_0 \left\{ 1 + N \left[\alpha_0 + \left(\frac{\partial \alpha}{\partial X} \right)_0 X \right] \right\} \qquad (2)$$

The total field is taken as the sum of the Stokes (ω_1) and the laser field (ω_2)

$$\mathrm{E}(z,t) = \frac{1}{2}\mathrm{E}_1(z)e^{i\omega_1 t} + \frac{1}{2}\mathrm{E}_2(z)e^{i\omega_2 t} + c.c. \qquad (5)$$

so that

$$\overline{\mathrm{E}}^2(z,t) = \frac{1}{4}\mathrm{E}_2(z)\mathrm{E}_1^*(z)e^{i(\omega_2-\omega_1)t} + c.c. \qquad (6)$$

Substituting (6) in (4) and then in the molecular equation of motion, (1) gives

$$F(z,t) = \frac{1}{2}\varepsilon_0\left(\frac{\partial\alpha}{\partial X}\right)_0 \overline{\mathrm{E}}^2(z,t) \qquad (4)$$

$$\frac{1}{2}\left(\omega_v^2 - \omega^2 + i\omega\gamma\right)X(z)e^{i\omega t} = \frac{\varepsilon_0}{8m}\left(\frac{\partial\alpha}{\partial X}\right)_0 \mathrm{E}_2\mathrm{E}_1^* e^{i(\omega_2-\omega_1)t} \qquad (7)$$

where

$$X(z,t) = \frac{1}{2}X(z)e^{i\omega t} + c.c. \qquad (8)$$

It follows from (7) that the molecular vibration is driven at a frequency $\omega = \omega_2 - \omega_1$ with a complex amplitude

$$X(z) = \frac{\varepsilon_0 \left(\frac{\partial \alpha}{\partial X} \right) E_2(z) E_1^*(z)}{4m\left[\omega_v^2 - (\omega_2 - \omega_1)^2 + i(\omega_2 - \omega_1)\gamma \right]} \qquad (9)$$

The polarization induced in the molecules by the field at ω_1 is

$$P = \varepsilon_0 N \alpha(z,t) E(z,t) = \varepsilon_0 N \left[\alpha_0 + \left(\frac{\partial \alpha}{\partial X} \right)_0 X(z,t) \right] E(z,t) \qquad (10)$$

Our concern here is with the nonlinear polarization term which is proportional to the product XE. Using (5) and (9) in (10) it becomes

$$P_{NL}(z,t) = \frac{1}{4}\varepsilon_0 N\left(\frac{\partial\alpha}{\partial X}\right)_0 \left\{ \frac{\varepsilon_0\left(\frac{\partial\alpha}{\partial X}\right)E_2E_1^* e^{i(\omega_2-\omega_1)t}}{4m\left[\omega_v^2-(\omega_2-\omega_1)^2+i(\omega_2-\omega_1)\gamma\right]} + c.c. \right\}$$

$$\times (E_1(z)e^{i\omega_1 t} + E_2(z)e^{i\omega_2 t} + c.c. \qquad (11)$$

If we multiply the two terms in (11) we get polarizations oscillating at

ω_1, ω_2, $2\omega_1 - \omega_2$ and $2\omega_2 - \omega_1$.

Let us concentrate first on the ω_1 term.

$$P_{NL}^{(\omega_1)}(z,t)=\frac{1}{2}P_{NL}^{(\omega_1)}(z)e^{i\omega_1 t}+c.c. \qquad (12)$$

where

$$P_{NL}^{(\omega_1)}(z)=\frac{\varepsilon_0^2 N\left(\frac{\partial\alpha}{\partial X}\right)_0^2 \left|E_2\right|^2}{8m\left[\omega_v^2-(\omega_2-\omega_1)^2-i(\omega_2-\omega_1)\gamma\right]}E_1(z) \qquad (13)$$

The coefficient relating an induced polarization to the inducing field is the susceptibility. From (13) we can define a complex Raman nonlinear susceptibility through the relation

$$P_{NL}^{(\omega_1)}(z)=\varepsilon_0\chi_{Raman}(\omega_1)\left|E_2(z)\right|^2 E_1(z) \qquad (14)$$

so that

$$\chi_{Raman}(\omega_1)=\frac{\varepsilon_0 N\left(\frac{\partial\alpha}{\partial X}\right)_0^2}{8m\left[\omega_v^2-(\omega_2-\omega_1)^2-i(\omega_2-\omega_1)\gamma\right]} \qquad (15)$$

More generally we can characterize the effect of induced molecular vibration by means of a fourth-rank tensor

$$P_i^{(\omega_i=\omega_j-\omega_k+\omega_l)} = \chi_{ijkl}^{(\omega_i=\omega_j-\omega_k+\omega_l)} E_j^{(\omega_j)} E_k^{(\omega_k)} E_l^{(\omega_l)} \qquad (16)$$

so that (14) is but a special case where $\omega_j = \omega_k = \omega_2$, $\omega_l = \omega_l = \omega_1$.

Returning to (15) we define

$$\chi_{Raman}(\omega_1) = \chi'_{Raman}(\omega_1) - i\chi''_{Raman}(\omega_1) \qquad (17)$$

where

$$\chi'_{Raman}(\omega_1) \simeq \frac{\varepsilon_0 N \left(\dfrac{\partial\alpha}{\partial X}\right)_0^2 \left[\omega_v - (\omega_2 - \omega_1)\right]}{16 m\omega_v \left\{\left[\omega_v - (\omega_2 - \omega_1)\right]^2 + \gamma^2/4\right\}} \qquad (18)$$

and

$$\chi''_{Raman}(\omega_1) \simeq \frac{-\varepsilon_0 N \left(\dfrac{\partial\alpha}{\partial X}\right)_0^2 (\gamma/2)}{16 m \omega_v \left\{\left[\omega_v - (\omega_2 - \omega_1)\right]^2 + \gamma^2/4\right\}} \qquad (19)$$

where the approximation applies to the high Q case $\gamma \ll \omega_v$ that is usually the case (typically $\gamma \le 10^{-2}\omega_v$).

The nonlinear Raman susceptibility is thus Lorentzian as its linear counterpart. It is plotted in fig.1.

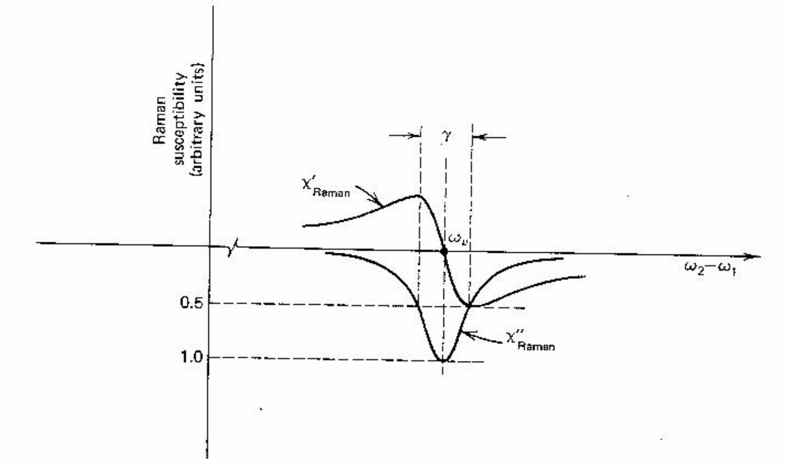


Fig.1. The in-phase (χ'_{Raman}) and quadrature (χ''_{Raman}) components of the Raman nonlinear susceptibility as a function of the Stokes frequency, ω_1. (ω_1 increases from right to left).

The presence of a Raman polarization (14) at ω_1 can be accounted for by modifying the propagation constant as in (4) from k_1 to

$$k_1' = k_1\left[1+\frac{\chi_{Raman}(\omega_1)}{2n_1^2}|E_2|^2\right] = = k_1\left[1+\frac{|E_2|^2}{2n_1^2}(\chi'_{Raman}(\omega_1)-i\chi''_{Raman}(\omega_1))\right] \quad (20)$$

so that

$$E^{(\omega_1)}(z) = E^{(\omega_1)}(0)\exp\left[-ik_1 z\left(1+\frac{|E_2|^2\chi'_{Raman}(\omega_1)}{2n_1^2}\right)-k_1 z\frac{|E_2|^2\chi''_{Raman}(\omega_1)}{2n_1^2}\right] \quad (21)$$

The exponential gain coefficient is thus

$$g(\omega_1) = -\frac{k_1}{2n_1^2}\left|E_2\right|^2 \chi''_{Raman}(\omega_1) \qquad (22)$$

and is positive since $\chi''_{\mathrm{Raman}}(\omega_1)<0$. Using (19) $g(\omega_1)$ is given as

$$\chi''_{Raman}(\omega_1) \simeq \frac{-\varepsilon_0 N \left(\frac{\partial \alpha}{\partial X}\right)_0^2 (\gamma/2)}{16 m \omega_\mathrm{v} \left\{[\omega_\mathrm{v} - (\omega_2 - \omega_1)]^2 + \gamma^2/4\right\}} \qquad (19)$$

$$g(\omega_1) = \frac{k_1 \varepsilon_0 \left(\frac{\partial \alpha}{\partial X}\right)_0^2 N \gamma \left|E_2\right|^2}{32 n_1^2 m \omega_\mathrm{v} \left\{[\omega_\mathrm{v} - (\omega_2 - \omega_1]^2 + \gamma^2/4\right\}} \qquad (23)$$

By comparing (23) to (5) we can identify the normalized Raman lineshape as

$$S(v_1) = \frac{\gamma/2\pi}{[v_\mathrm{v} - (v_2 - v_1)]^2 + \left(\frac{\gamma}{4\pi}\right)^2} \qquad (24)$$

ANTI-STOKES SCATTERING

The anti-Stokes radiation at $\omega_3 \simeq \omega_2 + \omega_v$ can be generated by Raman transitions originating in the excited (v = 1) vibrational state. To treat the problem electromagnetically, let us consider the ω_3 polarization induced in the Raman medium due to an electric field

$$E(z,t) = \frac{1}{2}\left[E_1(z)e^{i\omega_1 t} + E_2(z)e^{i\omega_2 t} + E_3(z)e^{i\omega_3 t} + c.c. \right] \quad (1)$$

where $\omega_3 - \omega_2 = \omega_2 - \omega_1$.

First we obtain a term due to the driving of the molecular vibration by the product $E_3E_2^*$. This term is analogous to (11) and is derived in an identical manner. We can thus obtain the polarization by modifying (13) recalling that now E_3 is the high frequency field and E_2 the low one.

$$P_{NL}^{(\omega_1)}(z) = \frac{\varepsilon_0^2 N \left(\frac{\partial \alpha}{\partial X}\right)_0^2 |E_2|^2}{8m\left[\omega_v^2 - (\omega_2 - \omega_1)^2 - i(\omega_2 - \omega_1)\gamma\right]} E_1(z) \qquad (13)$$

We thus replace E_2 by E_3 and E_1 by E_2, ω_2 - ω_1 by ω_3 - ω_2. The result is

$$P_{NL}^{(\omega_3)}(z) = \frac{\varepsilon_0^2 N \left(\frac{\partial \alpha}{\partial X}\right)_0^2 |E_2|^2}{8m\left[\omega_v^2 - (\omega_3 - \omega_2)^2 + i(\omega_3 - \omega_2)\gamma\right]} E_3(z) \qquad (2)$$

The important difference between (2) and (13) is the opposite sign of the imaginary term. This difference translates into an opposite sign of $\chi''(\omega_3)$ relative to $\chi''(\omega_1)$

$$P_{NL}^{(\omega_1)}(z) = \frac{\varepsilon_0^2 N \left(\frac{\partial\alpha}{\partial X}\right)_0^2 |E_2|^2}{8m\left[\omega_v^2 - (\omega_2-\omega_1)^2 - i(\omega_2-\omega_1)\gamma\right]} E_1(z) \qquad (13)$$

$$\chi''_{Raman}(\omega_3) = \frac{\varepsilon_0 N \left(\frac{\partial\alpha}{\partial X}\right)_0^2 (\gamma/2)}{16m\omega_\mathrm{v}\left\{\left[\omega_\mathrm{v} - (\omega_3-\omega_2)\right]^2 + \gamma^2/4\right\}} \qquad (3)$$

so that the gain constant exercised by the anti-Stokes wave (ω_3) is

$$g(\omega_3) = -\frac{k_1}{2n_3^2}|E_2|^2 \chi''_{Raman}(\omega_3) < 0 \qquad (4)$$

and the wave attenuates.

We thus reach the conclusion that if one were to introduce anti-Stokes ($\omega_3 = \omega_2 + \omega_v$) radiation into a Raman active medium in the presence of an ω_2 wave and in the absence of Stokes ($\omega_1 = \omega_2 - \omega_v$) radiation, it would attenuate.

There exists, however, another source of polarization at ω_3. It is obtained by taking the term in (11).

$$P_{NL}^{(\omega_3)} \propto E_2 E_2 E_1^* \exp\left[i\left(2\omega_2 - \omega_1\right)t\right] \quad (5)$$

This term does not involve E_3 and can be viewed as the upper sideband [(ω_2 + (ω_2 + ω_1))] due to a modulation of the dielectric constant “seen” by ω_2 at the driven molecular frequency (ω_2 - ω_1). This term acts as a source radiation at ω_3.

If we insert the spatial dependence into the polarization of (5) we find that

$$P_{NL}^{(\omega_3)}(z) \propto E_2 E_2 E_1^* \, \mathrm{e}^{-i(2k_2 - k_1)\cdot r} \qquad (6)$$

This term will generate a field at ω_3 with a spatial dependence $E_3 e^{-ik_3 \cdot r}$ such that

$$k_3 = 2k_2 - k_1 \qquad (7)$$

Anti-Stokes radiation will thus be emitted in any direction k_3, that satisfies (7).

$$k_3 = 2k_2 - k_1 \qquad (7)$$

The resulting direction, k_3, of the emitted anti-Stokes beam is shown in fig.2. (It should be recalled that in an isotropic medium the magnitudes of k_1, k_2 and k_3 are determined by their respective frequencies and are $|k_i| = \omega_i n_i / c$, where n_i is the index of refraction at ω_l and is determined by the intersection of the k_1 locus and that of k_3.

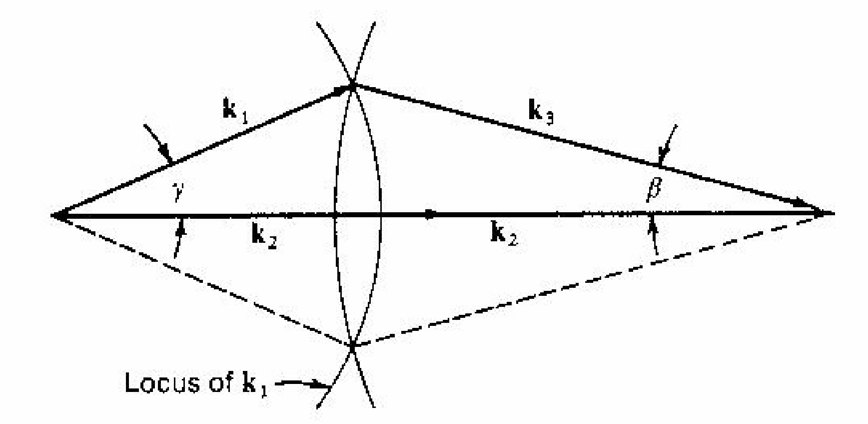


Fig.2. A construction for finding the direction of propagation, k_3, of the anti-Stokes radiation.

This is the reason why anti-Stokes radiation is emitted in the form of a conical shell with a half-apex angle β about the laser propagation direction.

The “real-life” situation in stimulated Raman emission is considerably more complicated than that portrayed above.

In addition to the existence of higher-order Stokes and anti-Stokes radiation that was mentioned earlier, it is found that, as an example, the direction of the emitted anti-Stokes radiation derivates because of “trapping” from that predicted by (7).

OTHER TYPES OF RAMAN SCATTERING

Inverse Raman spectroscopy (IRS) is obtained if the depletion of a weak probe light signal in the linear intensity range at the frequency of the SRS pump transition is measured while a strong laser is tuned across the Stokes frequency of the matter as schematically shown in fig.3.

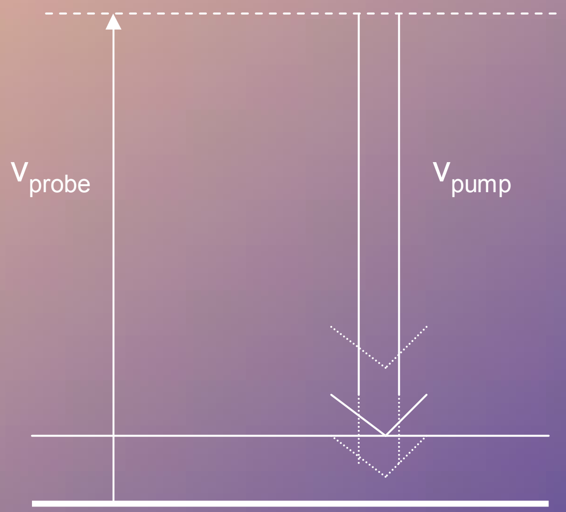


Fig.3. Inverse Raman spectroscopy (IRS) with measurement of the depletion of a weak probe signal at the frequency of the SRS pump as a function of the frequency of a strong and tunable laser at the Stokes wavelength.

Another spectroscopy possibility is the measurement of the amplification via the gain coefficient g_{probe} of a week tunable probe signal with the light frequency around the Raman Stokes signal while strong laser pumping with a suitable frequency for this Stokes signal (see fig.4). This method is called stimulated gain spectroscopy (SRGS).

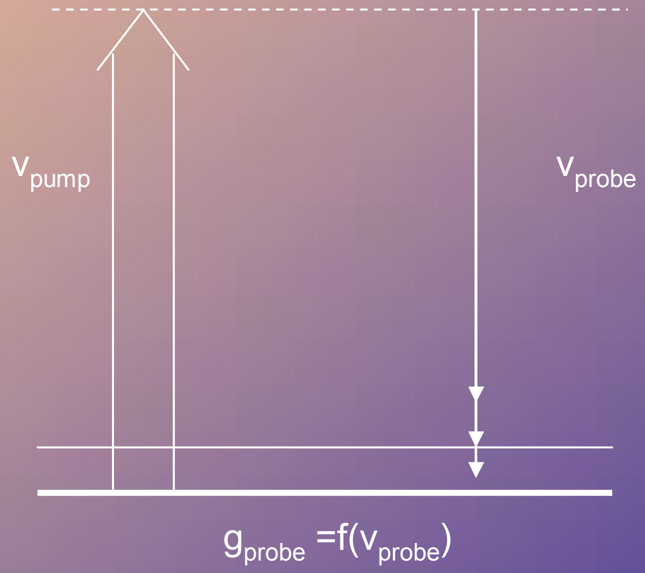


Fig.4. Stimulated Raman gain spectroscopy (SRGS) measuring the amplification for determining the gain g_{probe} of a weak tunable probe signal around the SRS Stokes frequency under strong pumping.

CARS

The combination of simultaneous stimulated Stokes and anti-Stokes Raman scattering leads to the interaction of four photons in the matter. In coherent anti-Stokes Raman scattering (CARS) two strong laser beams with frequencies v_{inc} and $v_{SRS,S}$ are applied (see fig.5) and the Raman anti-Stokes signal is studied.

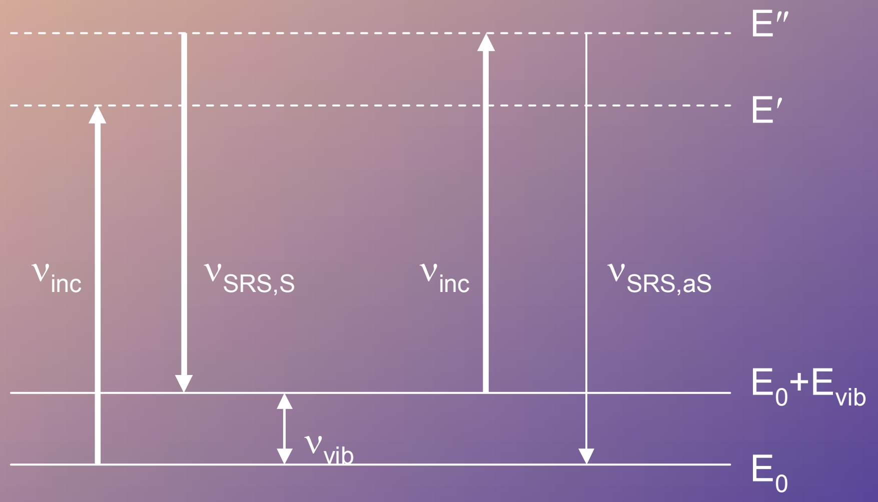


Fig.5. Coherent anti-Stokes Raman scattering (CARS) pumping with two laser beams with frequencies v_{inc} and $v_{SRS,S}$, obtaining the anti-Stokes Raman light with $v_{SRS,aS}$. For strong signals phase matching has to be achieved.

Phase matching is achieved if the momenta of the four involved photons are conserved and thus the wave vectors of the incident laser light k_{inc} and of the Raman Stokes light $k_{SRS,s}$ and the anti-Stokes light $k_{SRS,as}$ have to fulfill the angle condition of fig. 6.

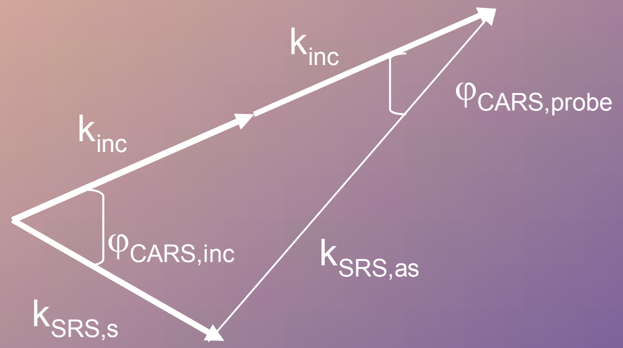
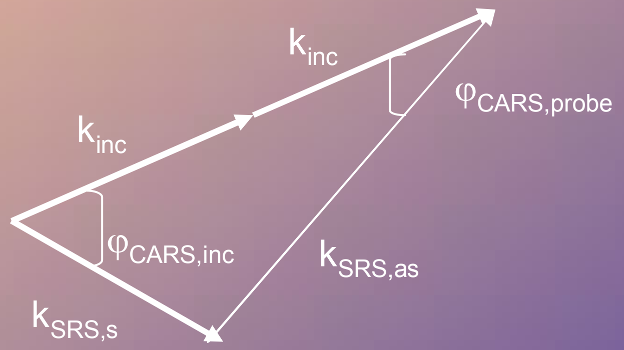


Fig.6. Phase matching of the incident laser light and the generated Stokes and anti-Stokes Raman light in CARS experiments.

Therefore, the two incident laser beams have to be enclosed in the angle $\varphi_{CARS,inc}$ and the anti-Stokes Raman light beam can be observed at the angle $\varphi_{CARS,probe}$ to the laser with k_{inc} in the forward direction.



Thus CARS allows highly sensitive measurements of the anti-Stokes Raman signal in a spatial direction with no background light. The two strong pump lasers will populate the excited anti-Stokes Raman scattering will occur. The scattering intensity $I_{CARS,aS}$ is proportional to:

$$I_{CARS,As} \propto I_{inc}^2 I_{SRS,S} N_{mat}^2 \qquad (2)$$

with the pump laser intensities I_{inc} of the incident and $I_{SRS,S}$ of the light and particle density N_{mat}. Even continuously operating (cw) laser can be used and then very high spectral resolution is possible.

The scattering efficiency can be increased by many orders of magnitude if the pump laser energy matches the electronic transitions of the material (resonant CARS). In this case, the virtual Raman levels of the energy schemes above will be real energy states of the matter.

Absorption will take place and thus the interaction length and/or concentration are limited by the maximum optical absorption of approximately $\sigma_{pump}NL<1$.

If the CARS scattering angles are too small for safe splitting of the different signals the BOX CARS technique can be used. The incident laser beam is therefore split into two beams which are applied at the single $\varphi_{\text{BOX CARS}}$ as shown in fig.7.

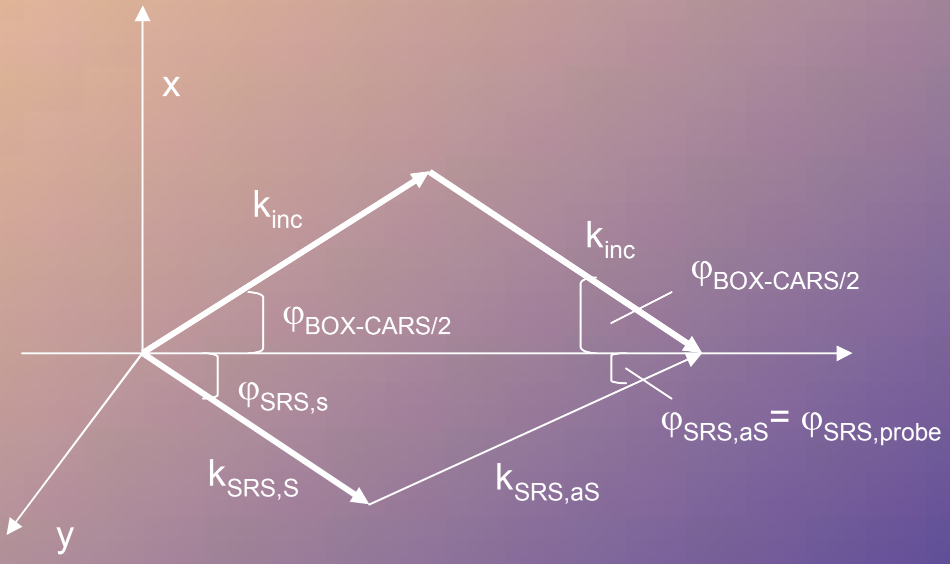


Fig.7. BOX CARS angle conditions for phase matching allowing good spatial separation of the different signals.

Assuming as in fig.7 the two pump laser beams with frequency ν_{inc} are applied at the angle $\varphi_{BOX\ CARS}$ symmetrically in the xz plane each making the angle $\varphi_{BOX\ CARS}/2$ each with the z axis the third laser beam with frequency $\nu_{SRS,S} = \nu_{inc} - \nu_{vib}$ can be applied in the yz plane at the angle $\varphi_{SRS,S}$ with the z axis. The resulting angle $\varphi_{SRS,aS}$ for detecting the newly generated anti-Stokes Raman light with frequency $\nu_{SRS,aS}$ can be calculated from:

$$\varphi_{SRS,aS} = \arccos\left\{ \frac{1}{1+\left(\nu_{vib}\lambda_{inc/c}\right)} \cdot \left[2\cos\left(\frac{\varphi_{BOX\,CARS}}{2}\right) - \left(1+\frac{\nu_{vib}\lambda_{inc}}{c}\right)\cos\varphi_{SRS} \right] \right\}. \quad (3)$$

The three beams with their different directions have to overlap in the sample. Other geometrical arrangements as in fig.7 are possible. Therefore, this technique allows a wide range of different experimental setups for analytical and spectroscopic investigations.

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Nonlinear Optical Interactions

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OUTLINE

Linear and Nonlinear Systems
Propagation in Anisotropic Media
Nonlinear Susceptibility
Nonlinear Optical Interactions
Second harmonic
Other nonlinear processes
Raman scattering

Linear and Nonlinear Systems

A **linear system** is defined as one which has a response proportional to external influence and has a well-known property, i.e. if influences, F1, F2 …., Fn are applied simultaneously, the response produced is the sum of the responses that would be produced if the influence were applied separately.

A **nonlinear system** is one in which the response is not strictly proportional to the influence and the transfer of energy from one influence to another can occur.

If the **influences** are periodic in time, the response of a nonlinear system can contain frequencies different from those present in the influences. However, the point to emphasize here is that, as well as the generation of new frequencies, nonlinear optics provides the ability to control light with light and so to transfer information directly from one beam to another without the need to resort to electronics.

Traditionally, nonlinear optics has been described phenomenologically in terms of **the effect of an electric field on the polarization within a material**.

MAXWELL EQUATIONS

Electromagnetic processes are described by Maxwell's equations which constitute a set of linear equations. In SI units:

$$\nabla\cdot\mathbf{D}=\rho \qquad \operatorname{div}\mathbf{D}=\rho$$

$$\nabla\times\mathbf{E}=-\frac{\partial\mathbf{B}}{\partial t} \qquad \operatorname{rot}\mathbf{E}=-\frac{\partial\mathbf{B}}{\partial t}$$

$$\nabla\cdot\mathbf{B}=0 \qquad \operatorname{div}\mathbf{B}=0$$

$$\nabla\times\mathbf{H}=\frac{\partial\mathbf{D}}{\partial t}+\mathbf{J} \qquad \operatorname{rot}\mathbf{H}=\frac{\partial\mathbf{D}}{\partial t}+\mathbf{J}$$

where **E** and **B** are the electric and magnetic fields. The displacement fields **D** and **H** arise from the external charge and conduction current densities ρ and **J**. In most cases of interest in nonlinear optics, $\rho = 0$ and $J = 0$.

‘Constitutive relations’ connect the charge and current distributions within the medium and the displacement fields to the electric and magnetic fields.

$$\mathbf{D} = \mathbf{P} + \varepsilon_0 \mathbf{E} = \varepsilon \mathbf{E} \qquad\qquad \mathbf{B} = \mu \mathbf{H}$$

where **P** is the induced polarization in the medium resulting from the field E, ε is defined as a dielectric constant and ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1} in MKS units). Optical materials are mostly **non magnetic** $\mu = \mu_r \mu_0 = \mu_0$.

LINEAR THEORY

Usually one assumes a linear response of a dielectric material to an external field

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

Where **P** is the vector representing the electric dipole moment per unit volume induced by the external electric field **E**, ε_0 is vacuum permittivity and χ is a quantity characteristics of the considered material with no dimensions, called **electric susceptibility**.

In general χ is a tensor

$$\begin{vmatrix} P_x \\ P_y \\ P_z \end{vmatrix} = \varepsilon_0 \begin{vmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{vmatrix} \begin{vmatrix} E_x \\ E_y \\ E_z \end{vmatrix}$$

The symmetry properties of the material indicate which ones of the χ_{ij} coefficients are zero.

Alternatively

$$\begin{vmatrix} D_x \\ D_y \\ D_z \end{vmatrix} = \begin{vmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{vmatrix} \begin{vmatrix} E_x \\ E_y \\ E_z \end{vmatrix}$$

HOMOGENEOUS MATERIALS

ε not depending on space

$$\begin{array}{lcl} \mathrm{div}\,\varepsilon\mathbf{E} = \rho & & \mathrm{div}\,\mathbf{E} = \dfrac{\rho}{\varepsilon} \\ \mathrm{rot}\,\mathbf{E} = -\dfrac{\partial \mathrm{B}}{\partial t} & \Rightarrow & \mathrm{rot}\,\mathbf{E} = -\dfrac{\partial \mathbf{B}}{\partial t} \\ \mathrm{div}\,\mathbf{B} = 0 & & \mathrm{div}\,\mathbf{B} = 0 \\ \mathrm{rot}\left(\dfrac{\mathbf{B}}{\mu}\right) = \left(\mathbf{j} + \dfrac{\partial \varepsilon \mathbf{E}}{\varepsilon t}\right) & & \mathrm{rot}\,\mathbf{B} = \mu\left(\mathbf{j} + \dfrac{\partial \varepsilon \mathbf{E}}{\partial t}\right) \end{array}$$

If $\rho = 0$ $\mathbf{j} = 0$

$$\begin{array}{ll} \mathrm{div}\,\mathbf{E} = 0 & \mathrm{div}\,\mathbf{B} = 0 \\ \mathrm{rot}\,\mathbf{E} = -\dfrac{\partial \mathbf{B}}{\partial t} & \mathrm{rot}\,\mathbf{B} = \mu\varepsilon\dfrac{\partial \mathbf{E}}{\partial t} \end{array}$$

WAVE EQUATION

Starting from Maxwell's Eqs

$$\left\{\mathrm{div}\,\vec{E} = 0\right.$$

$$\left\{\mathrm{rot}\,\vec{E} = -\frac{\partial \vec{B}}{\partial t}\right.$$

$$\left\{\mathrm{div}\,\vec{B} = 0\,\mathrm{div}\,\vec{B} = 0\right.$$

$$\left\{\mathrm{rot}\,\vec{B} = \mu_0 \frac{\partial \vec{D}}{\partial t}\right.$$

$$\mathrm{rot}\,\mathrm{rot}\,\mathbf{E} = -\nabla^2 \mathbf{E} + \mathrm{grad}\,\mathrm{div}\,\mathbf{E}$$

$$= -\frac{\partial}{\partial t}\mathrm{rot}\,\mathbf{B}$$

$$-\nabla^2 \mathbf{E} + \mathrm{grad}\,\mathrm{div}\,\mathbf{E} = -\mu_0 \frac{\partial}{\partial t}\frac{\partial \mathbf{D}}{\partial t} = -\mu_0 \frac{\partial^2 \mathbf{D}}{\partial t^2}$$

$$\nabla^2 \mathbf{E} = \left(\frac{\partial^2 \mathbf{E}_x}{\partial x^2} + \frac{\partial^2 \mathbf{E}_x}{\partial y^2} + \frac{\partial^2 \mathbf{E}_x}{\partial z^2}\right)\mathbf{i} + \left(\frac{\partial^2 \mathbf{E}_y}{\partial x^2} + \frac{\partial^2 \mathbf{E}_y}{\partial y^2} + \frac{\partial^2 \mathbf{E}_y}{\partial z^2}\right)\mathbf{j} + \left(\frac{\partial^2 \mathbf{E}_z}{\partial x^2} + \frac{\partial^2 \mathbf{E}_z}{\partial y^2} + \frac{\partial^2 \mathbf{E}_z}{\partial z^2}\right)\mathbf{k}$$

⇒

$$\nabla^2 \mathbf{E} = -\mu_0 \varepsilon \frac{\partial^2 \mathbf{E}}{\partial t^2} = \frac{1}{v^2}\frac{\partial^2 \mathbf{E}}{\partial t^2}$$

$$v = \frac{c}{\sqrt{\varepsilon_r}} = \frac{c}{n} \qquad c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}$$

refractive index

$$n = \sqrt{\varepsilon_r}$$

DISPERSION

Experimentally the refractive index is a function of wavelength (frequency)

$$n(\lambda) = \sqrt{\varepsilon_r(\lambda)} \qquad \varepsilon_r(\lambda) = 1 + \chi(\lambda)$$

This phenomenon is called DISPERSION.

The polarization in a material medium can be explained considering the electrons tied to the atoms as harmonic oscillators.

Nucleus: ~2000 electron mass, i.e., infinite mass

DISPERSION

$$m\ddot{x} + \beta\dot{x} + kx = -eE_0e^{i\omega t}$$ (one-dimensional model)

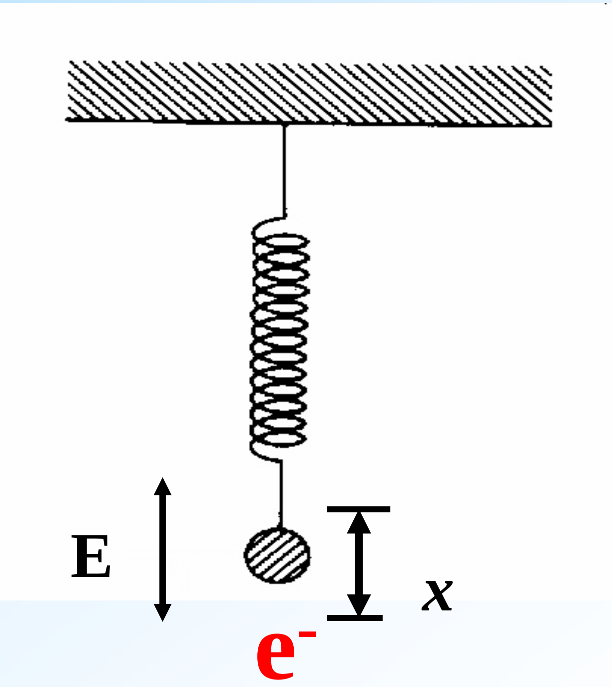
Damping **Restoring Force** **Driving Force**

From the solution:

$$x = \frac{-eE_0e^{i\omega t}}{m(\omega_0^2 - \omega^2 + i\omega\gamma)}$$

$$\gamma = \frac{\beta}{m}$$

$$\omega_0^2 = \frac{k}{m}$$



the induced moment is calculated:

$$p = -ex = \frac{e^2}{m\left(\omega_0^2 - \omega^2 + i\omega\gamma\right)} \cdot E_0e^{i\omega t}$$

For N oscillators per volume unit, the polarization is:

$$P = N \cdot p = \frac{N \cdot e^2}{m\left(\omega_0^2 - \omega^2 + i\omega\gamma\right)} E_0 e^{i\omega t}$$

Calling

$$\alpha = \frac{\mathrm{e}^2}{\mathrm{m}(\omega_0^2 - \omega^2 + \mathrm{i}\gamma\omega)} \equiv \text{ atomic polarizability}$$

➔ $\mathrm{P} = \mathrm{N}\alpha\mathrm{E} = \varepsilon_0 \chi \mathrm{E}$ $\qquad \mathrm{E} = \mathrm{E}_0 \mathrm{e}^{\mathrm{i}\omega t}$ $\qquad \chi = \frac{\mathrm{N}\alpha}{\varepsilon_0}$

where χ is the electric susceptibility.

➡

$$\varepsilon_0 \varepsilon_\mathrm{r} = \varepsilon_0 (1 + \chi) = \varepsilon_0 \left(1 + \frac{\mathrm{N}\alpha}{\varepsilon_0} \right)$$

$$\mathrm{n}^2 = 1 + \chi = 1 + \frac{\mathrm{N}\alpha}{\varepsilon_0} \qquad \mathrm{n} = \sqrt{\varepsilon_\mathrm{r}}$$

$$n^2 = 1 + \frac{Ne^2}{\varepsilon_0 m(\omega_0^2 - \omega^2 + i\gamma\omega)}$$

If the second term is lower than 1 (as it happens in gases):

$$\boxed{n \cong 1 + \frac{Ne^2}{2\varepsilon_0 m(\omega_0^2 - \omega^2 + i\gamma\omega)}}$$

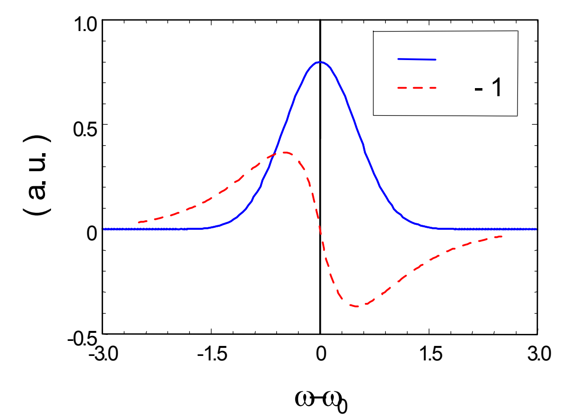
In the expression n comes out to be a complex number.

ABSORPTION

The term $i\gamma\omega$ is responsible for absorption. The complex index can be written as

$$n = \tilde{n} - i\tilde{k} = 1 + \frac{Ne^2(\omega_0^2 - \omega^2)}{2\varepsilon_0 m\left[\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2\right]} - i\frac{Ne^2\gamma\omega}{2\varepsilon_0 m\left[\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2\right]}$$

If we consider a plane wave



where

$$E = A\exp\left[i(\omega t - kz)\right]$$

$$k = \omega\sqrt{\mu\varepsilon} = \frac{\omega}{c}n = \frac{2\pi}{\lambda}n$$

we see that, substituting the complex refractive index, one has

$$k = \frac{2\pi}{\lambda}(\tilde{n} - i\tilde{k})$$

which gives

$$E = A\exp\left[i\left(\omega t - \frac{2\pi\tilde{n}}{\lambda}z\right)\right]\exp\left(-\frac{2\pi\tilde{k}}{\lambda}z\right)$$

The last exponential represents a term of attenuation. The attenuation coefficient may be defined from:

$$-\alpha = \frac{1}{I}\frac{dI}{dz} \qquad I(z) = |E|^2 = I_{(0)}e^{-\alpha z}$$

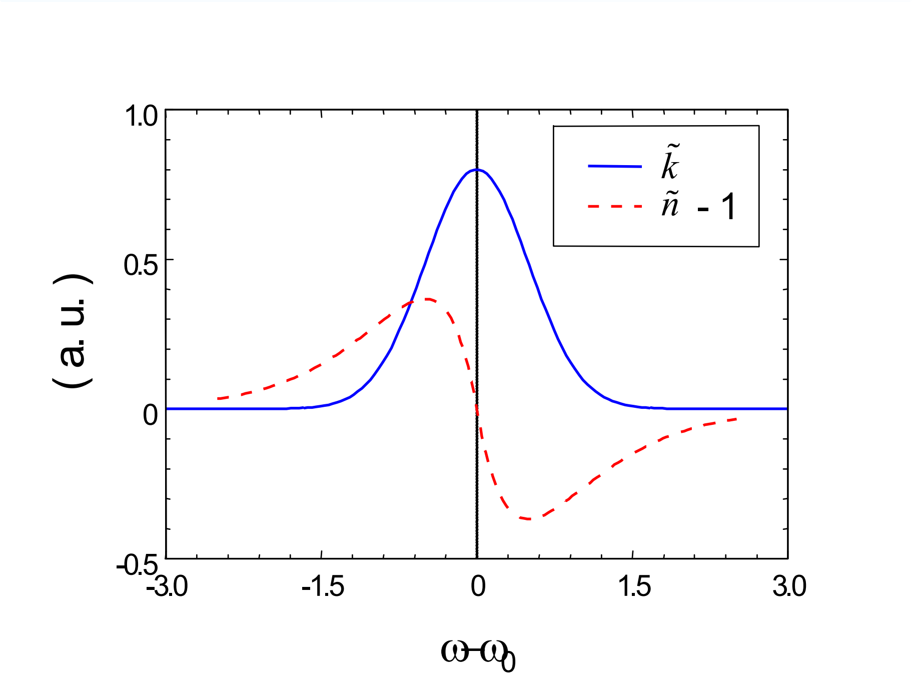
By comparison with the previous equation

$$E = A\exp\left[i\left(\omega t - \frac{2\pi\tilde{n}}{\lambda}z\right)\right]\exp\left(-\frac{2\pi\tilde{k}}{\lambda}z\right)$$

$$\alpha = \frac{4\pi}{\lambda}\tilde{k}$$

It can be noticed that a small value of $\tilde{k}$ leads to an elevated attenuation.

$\tilde{k} = 0.0001$ and $\lambda = 0.5\mu m$ gives $\alpha = 25\ \mathrm{cm}^{-1}$.



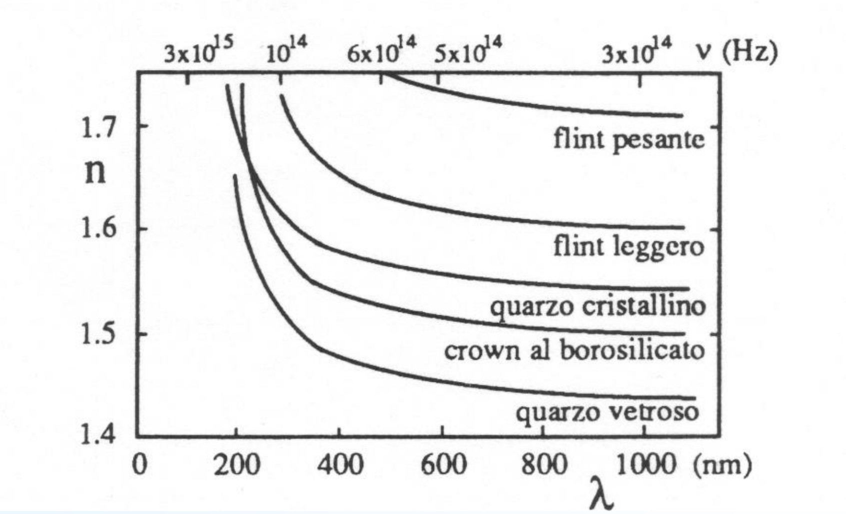
Both $\tilde{n}$ and $\tilde{k}$ are functions of the frequency.

Substance	n (for yellow light)	$\sqrt{\varepsilon_r}$ (static value)
Air (1 atm)	1.0002926	1.0002925
CO (1 atm)	1.00045	1.0005
Polistyren	1.59	1.6
Glass	1.5 ÷ 1.7	2 ÷ 3
Fused quartz	1.46	1.94
Water	1.33	9
Ethanol	1.36	5

Table I

Values of n and ε_r for some materials

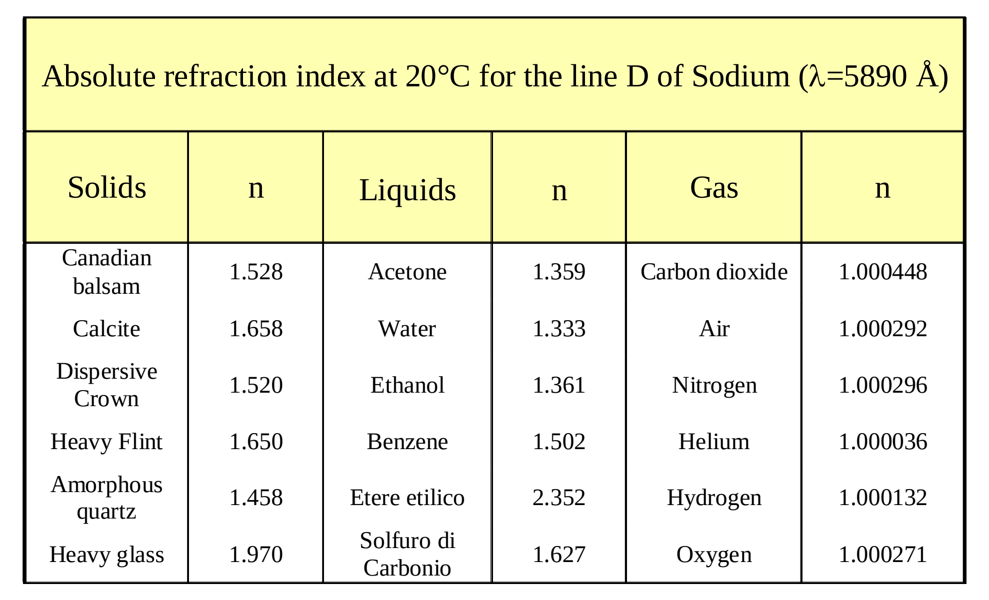
n as a function of λ for some materials



$\tilde{n} > 1$ for $\omega < \omega_0$ **normal dispersion**

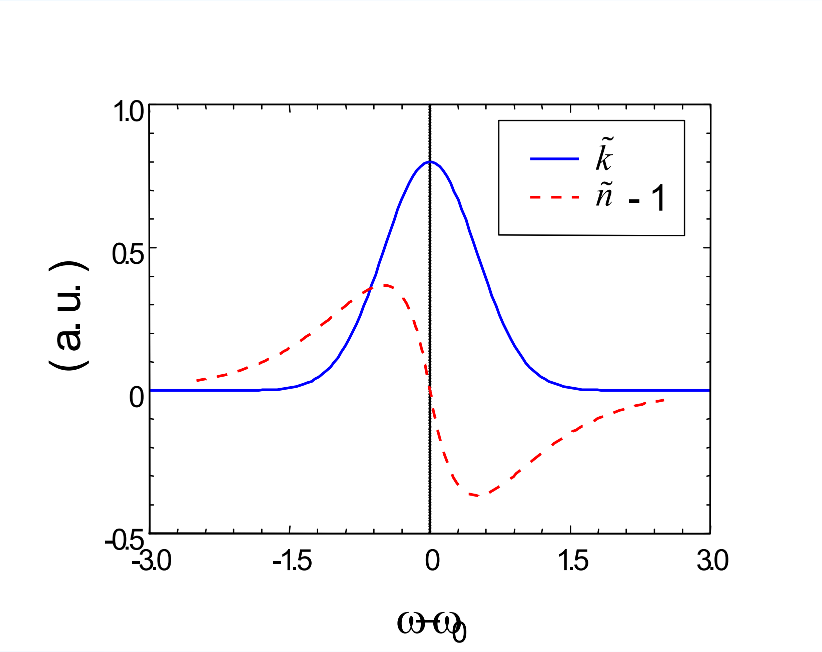
At resonance ($\omega = \omega_0$)

the slope of $\tilde{n}$ is negative **anomalous dispersion**



Absolute refraction index at 20°C for the line D of Sodium (λ=5890 Å)

Solids	n	Liquids	n	Gas	n
Canadian balsam	1.528	Acetone	1.359	Carbon dioxide	1.000448
Calcite	1.658	Water	1.333	Air	1.000292
Dispersive Crown	1.520	Ethanol	1.361	Nitrogen	1.000296
Heavy Flint	1.650	Benzene	1.502	Helium	1.000036
Amorphous quartz	1.458	Etere etilico	2.352	Hydrogen	1.000132
Heavy glass	1.970	Solfuro di Carbonio	1.627	Oxygen	1.000271



METALS

In a metal the electrons are free and they do not oscillate around the atoms. **Therefore k = 0 and ω_0 = 0.**

In the equation for n^2 it is sufficient to put $\omega_0 = 0$.

$$n^2 = 1 - \frac{Ne^2}{\varepsilon_0 m(\omega^2 - i\gamma\omega)} \qquad N \equiv \text{density of electrons}$$

If $\gamma << \omega$

$$n^2 \approx 1 - \frac{\omega_p^2}{\omega^2}$$

$$\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m}$$

Frequency of plasma

For Al, Cu, Au, Ag $N \sim 10^{23}$ cm^{-3} and $\omega_P \sim 2.10^{16}$ s^{-1}.

For $\omega > \omega_P$ n is real and the waves propagate freely.

For $\omega < \omega_P$ n is pure imaginary and the field is exponentially attenuated with the distance from the surface. Therefore the radiation is reflected from the surface.

Therefore, for visible radiation and infrared $\omega < \omega_P$ and n is imaginary. In general, n is complex because there is γ:

$$1-n^2 = \frac{Ne^2}{\omega\varepsilon_0 m(\omega - i\gamma)}\frac{(\omega+i\gamma)}{(\omega+i\gamma)} = \frac{Ne^2}{\omega\varepsilon_0 m\left(\omega^2+\gamma^2\right)} + i\gamma\frac{Ne^2}{\omega\varepsilon_0 m\left(\omega^2+\gamma^2\right)} =$$

$$\frac{\omega_p}{\left(\omega^2+\gamma^2\right)} + i\frac{\omega_p}{\left(\omega^2+\gamma^2\right)}\frac{\gamma}{\omega}$$

PROPAGATION IN ANISOTROPIC MEDIA

An anisotropic medium is characterized by a dielectric tensor

$$\begin{vmatrix} D_x \\ D_y \\ D_z \end{vmatrix} = \begin{vmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{vmatrix} \begin{vmatrix} E_x \\ E_y \\ E_z \end{vmatrix}$$

The dielectric tensor is symmetric $\varepsilon_{ij} = \varepsilon_{ji}$

It is possible to rotate the axis to find a system of axis (<u>main axis</u>) for which

$$\begin{vmatrix} D_x \\ D_y \\ D_z \end{vmatrix} = \begin{vmatrix} \varepsilon_x & 0 & 0 \\ 0 & \varepsilon_y & 0 \\ 0 & 0 & \varepsilon_z \end{vmatrix} \begin{vmatrix} E_x \\ E_y \\ E_z \end{vmatrix} = \varepsilon_0 \begin{vmatrix} n_x^2 & 0 & 0 \\ 0 & n_y^2 & 0 \\ 0 & 0 & n_z^2 \end{vmatrix} \begin{vmatrix} E_x \\ E_y \\ E_z \end{vmatrix}$$

A plane wave propagating along f.e. the direction z (E_z = 0) can have two phase velocities depending on its polarization.

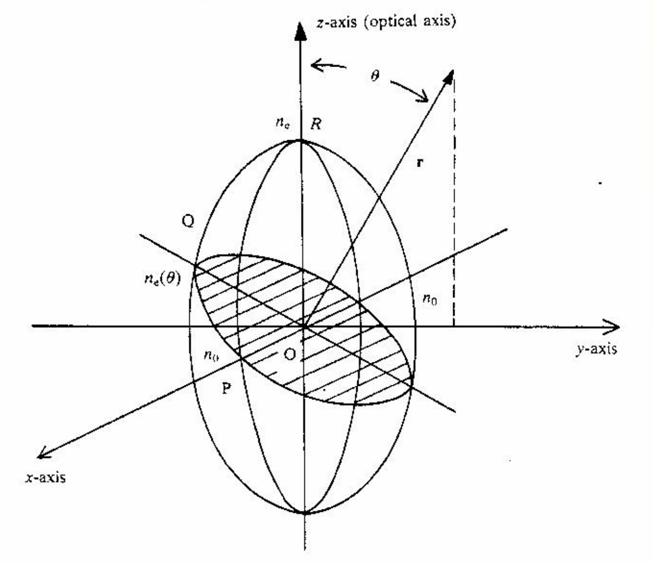
Therefore, in any propagating direction there are two refractive indices n_1 and n_2 that correspond to two different phase and group velocities.

The displacement vectors D_1 and D_2 are orthogonal between them. To obtain n_1, n_2, D_1, D_2, E_1, E_2, H_1 and H_2 the method of the ellipsoid of indices is used.

ELLIPSOID OF INDICES

The ellipsoid of indices is

$$\frac{x^2}{\varepsilon_{rx}}+\frac{y^2}{\varepsilon_{ry}}+\frac{z^2}{\varepsilon_{rz}}=1=\frac{x^2}{n_x^2}+\frac{y^2}{n_y^2}+\frac{z^2}{n_z^2}$$



To obtain the values of n_1 and n_2 for a particular direction of propagation r the plane passing through the origin of the ellipsoid perpendicular to r is considered. The intersection of this plane with the ellipsoid of indices gives an ellipse. The two main axis of the ellipse correspond to $2n_1$ and $2n_2$ respectively.

The corresponding D_1 and D_2 are parallel to the main axis of the ellipse. The vector $\mathbf{E}$ is given by

$$\mathbf{D} = n^2 \varepsilon_0 \left[\mathbf{E} - \mathbf{s}(\mathbf{s} \cdot \mathbf{E}) \right]$$

To see this, let us consider a monochromatic plane wave

$$(1) \quad \mathbf{E} = \mathbf{E}_0\, e^{i(n\mathbf{k} \bullet \mathbf{r} - \omega t)} \qquad \mathbf{D} = \mathbf{D}_0\, e^{i(n\mathbf{k} \bullet \mathbf{r} - \omega t)} \quad (3)$$

$$(2) \quad \mathbf{H} = \mathbf{H}_0\, e^{i(n\mathbf{k} \bullet \mathbf{r} - \omega t)} \qquad \mathbf{B} = \mathbf{B}_0\, e^{i(n\mathbf{k} \bullet \mathbf{r} - \omega t)} \quad (4)$$

and the Maxwell equations for an homogeneous dielectric magnetically isotropic ($B = \mu_0$ H)

$$(5) \quad \operatorname{div} \mathbf{D} = 0 \qquad \operatorname{rot} \mathbf{E} = -\mu \frac{\partial \mathbf{H}}{\partial t} \quad (7)$$

$$(6) \quad \operatorname{div} \mathbf{H} = 0 \qquad \operatorname{rot} \mathbf{H} = -\frac{\partial \mathbf{D}}{\partial t} \quad (8)$$

Substituting (3) into (5)

$$\frac{\partial}{\partial x} e^{i\left[n(k_x x + k_y y + k_z z)\right]} = i\,n\,k_x e^{i(n\mathbf{k}\bullet\mathbf{r})} \quad \text{etc.} \quad \text{therefore}$$

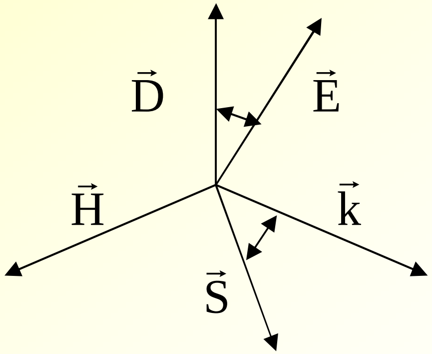
$$\text{div}\,\mathbf{D} = 0 = in\mathbf{k}\cdot\mathbf{D}$$

And, similarly, substituting (2) into (6) ➔ $\boxed{in\mathbf{k}\cdot\mathbf{H} = 0}$

Therefore **D** and **H** must be orthogonal to **k**.

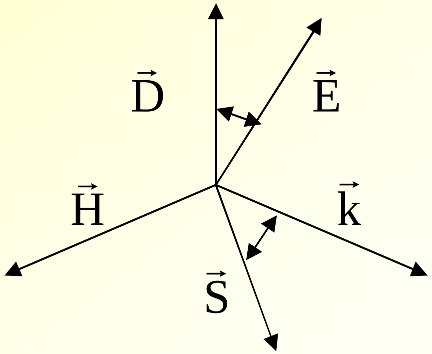
Inserting (2) and (3) in (8) ➔ $\boxed{in\mathbf{k}\times\mathbf{H} = -i\omega\mathbf{D}}$

Therefore $\mathbf{D},\mathbf{H},\mathbf{k}$ form the term indicated in the figure.



Inserting (1) and (2) in (7) → $\mathrm{i}\,n\,\mathbf{k}\times\mathbf{E}=\mathrm{i}\,\omega\,\mu_0\mathbf{H}$

therefore **H** must be orthogonal to the plane **E, k** and **E** must stay in the plane **D, k**. Also the Poynting vector $\mathbf{S}=\mathbf{E}\times\mathbf{H}$ lies in the plane **D, k**. If the medium is electrically isotropic **D** and **E** would be parallel and also **k** and **S** would be parallel. In the anisotropic medium **D** and **E** form an angle and the wave propagation and the direction of the energy propagation are not in the same direction.



From $\mathrm{i}\,n\,\mathbf{k}\times\mathbf{H} = -\mathrm{i}\,\omega\mathbf{D}$

one may see that the modulus of **H** is:

$$H = \frac{\omega D}{n\,k} \qquad (1)$$

If $E_\perp$ is the component of **E** orthogonal to **k**, from

$$\mathrm{i}\,n\,\mathbf{k}\times\mathbf{E} = \mathrm{i}\,\omega\,\mu_0\mathbf{H}$$

we have $E_\perp = \dfrac{\omega\,\mu_0}{n\,k}H$

That, taking into account (1), gives $E_\perp = \dfrac{\omega^2\mu_0}{n^2k^2}\mathbf{D} = \dfrac{1}{\varepsilon_0 n^2}\mathbf{D}$

If s is the unit vector of **k** we can write

$$\mathbf{E} - (\mathbf{s} \cdot \mathbf{E})\mathbf{s} = \frac{1}{\varepsilon_0 n^2}\mathbf{D}$$

where $\mathrm{s} \cdot \mathbf{E}$ is the component of **E** parallel to **k**.

Therefore

$$\mathbf{E} - (\mathbf{s} \cdot \mathbf{E})\mathbf{s} = \mathrm{E}_{\perp} \;.$$

DETERMINATION OF THE POLARIZATION

Let us consider a wave propagating f.e. in the direction z. If its electric field is parallel to the direction x, it induces only a polarization P_x

$$P_x = \varepsilon_0 \chi_{xx} E_x = D_x - \varepsilon_0 E_x = (\varepsilon_{xx} - 1)\varepsilon_0 E_x$$

which is determined by ε_{xx}, that is a refraction index n_x.

On the contrary, if the wave is polarized with the electric field that vibrates along y, it finds a refractive index n_y.

Every non polarized wave propagating in the direction z can be decomposed into two components with polarization parallel to directions x and y. These two components travel in the crystal with different velocities (different n).

The uniaxial crystals are characterized by a main axis (conventionally the axis z) along which the dielectric constant is ε_{zz}, but perpendicularly to which the dielectric constant does not depend on the direction (that is $\varepsilon_{xx} = \varepsilon_{yy}$). Therefore these crystals have only two main refractive indices.

The direction z is unique because the propagation velocity is independent from the polarization. It is called optical axis. The difference between n_x(=n_y) and n_z is a measure of the birefringence which is called positive or negative depending on $n_z – n_x > 0$ or lower than 0.

Crystals with lower symmetry have two optical axis and they are called bi-axial. For them $n_x \neq n_y \neq n_z$.

UNIAXIAL CRYSTALS

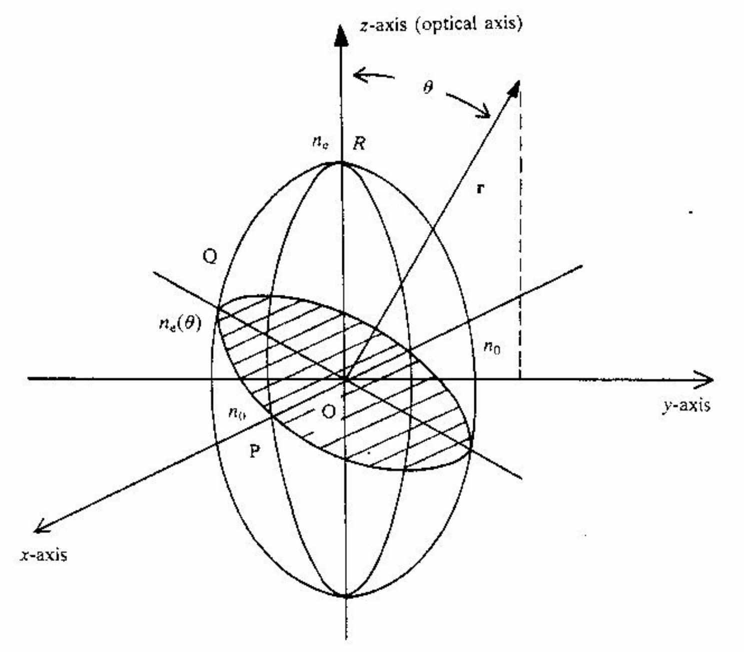
$$\frac{x^2}{n_x^2}+\frac{y^2}{n_y^2}+\frac{z^2}{n_z^2}=1$$

This equation represents an ellipsoid with semi axis n_x, n_y, n_z. For a uniaxial crystal $n_x = n_y \neq n_z$ and the ellipsoid has circular symmetry around the axis z, as shown in the figure.

The index $n_x(=n_y)$ is indicated as the ordinary refractive index n_0 and n_z is called extraordinary index n_e. The ellipsoid is rewritten

$$\frac{x^2}{n_0^2}+\frac{y^2}{n_0^2}+\frac{z^2}{n_e^2}=1$$

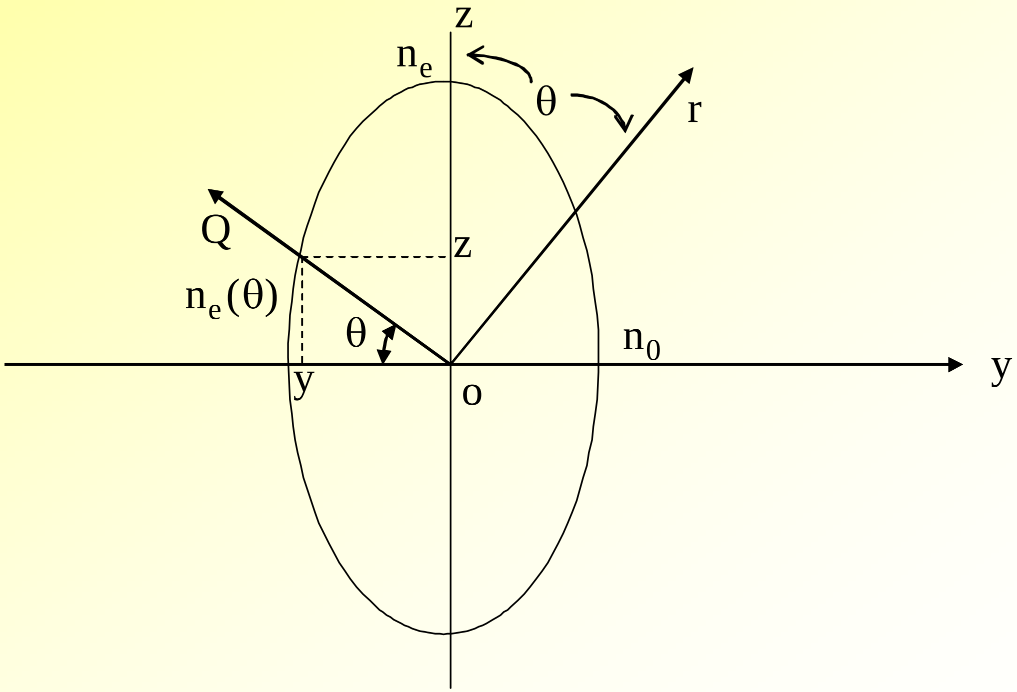
If a light beam propagates in a direction r that forms an angle ϑ with the optical axis (z), because of the circular symmetry we can choose the axis y coincident with the projection of r on the plane xy.

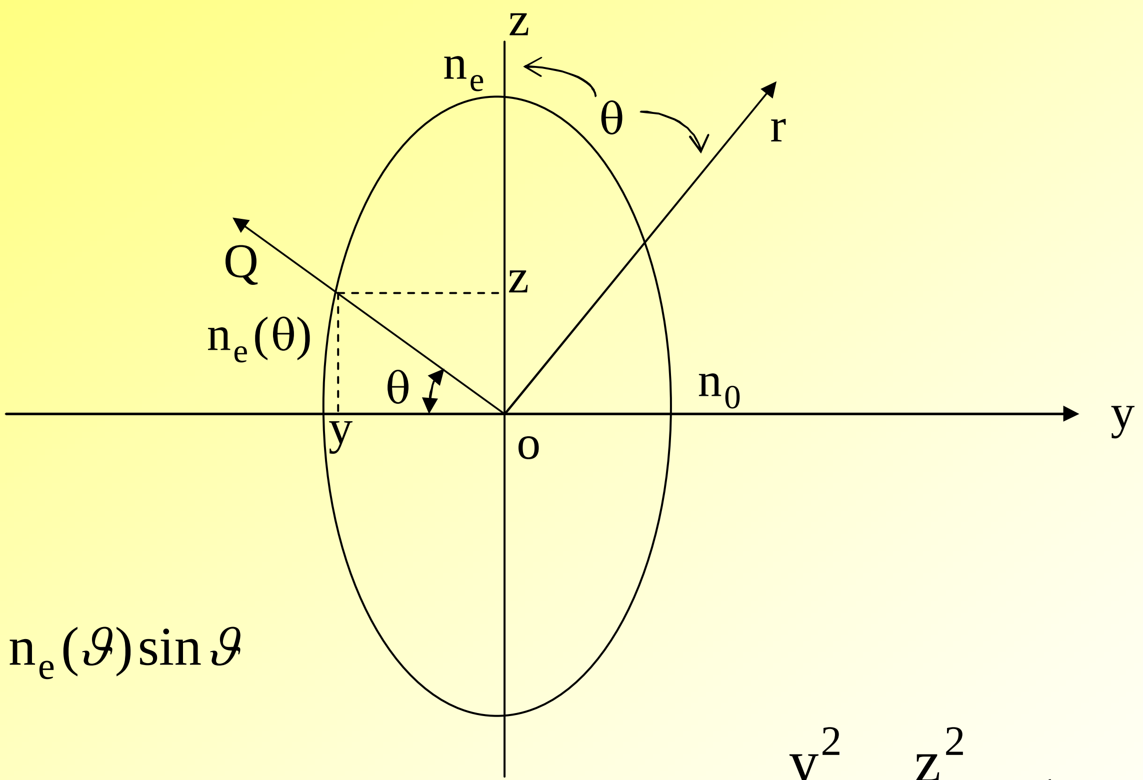


The normal plane to r intercepts the ellipsoid in an ellipse (outlined in the figure). The two permitted directions of polarization are parallel to the axis of this ellipse and therefore they correspond to OP and OQ.

The two polarized waves along these directions have refractive indices given by OP = n_0 and OQ = $n_e(\vartheta)$. In the case of the extraordinary wave, the plane of polarization varies with ϑ and so does the refractive index.

With reference to the figure which shows the intersection of the ellipsoid of the indices with the plane yz





$$n_e^2(\vartheta) = z^2 + y^2 \quad \text{and} \quad z = n_e(\vartheta)\sin\vartheta$$

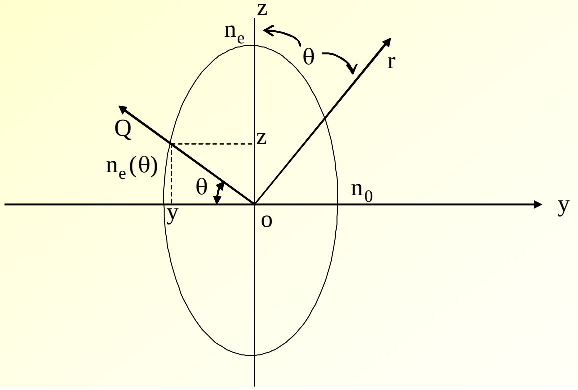
Substituting in the equation of the ellipse $\frac{y^2}{n_0^2} + \frac{z^2}{n_e^2} = 1$

we have $\boxed{\frac{1}{n_e^2(\vartheta)} = \frac{\cos^2\vartheta}{n_0^2} + \frac{\sin^2\vartheta}{n_e^2}}$

Therefore for ϑ = 0°, that is for propagation along the optical axis, $n_e(0°) = n_0$, while for ϑ = 90°, $n_e(90°) = n_e$.

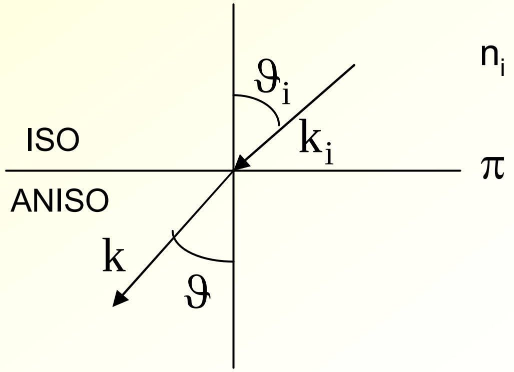
The two polarizations which can be propagated correspond to the maximum and minimum refractive index given by the ellipsoid of indices (for positive crystals $n_e > n_0$, for negative crystals $n_e < n_0$). For the propagation **parallel** to the optical axis (direction z) there is no birefringence, because the section of the ellipsoid perpendicular to the direction z is a circle.

For a propagation **perpendicular** to the optical axis, i.e. in the direction x, the birefringence will be maximum and the allowed polarization will be parallel to the axis y with index n_0 and parallel to axis z with index n_e.



REFLECTION AND REFRACTION OF PLANE WAVES

We now study the phenomenon of the refraction of a monochromatic plane wave at the plane surface of separation between an isotropic medium and an anisotropic one. Let us indicate with k_i the wave vector of the incident field, with ϑ_i the corresponding angle of incidence and with n_i the refractive index of the isotropic medium. Let us call π the pane of separation between the two media. The situation is shown in the figure, in which the figure plane coincides with the incidence plane.



To find the refracted wave, the boundary conditions on π have to be imposed. Because these conditions must be satisfied in every point of π and at every time, it is necessary that the phase distributions produced by the incident and the refracted wave be equal, that is

$$n_i \mathbf{k}_i \cdot \mathbf{r} - \omega t = n\mathbf{k} \cdot \mathbf{r} - \omega t \qquad (1)$$

for every point r belonging to π. We have indicated with **k** and n the wave vector and the refractive index for the refracted wave, respectively. Since the phase distribution of the incident wave is, at every time, independent from the coordinate orthogonal to the plane in fig. 1, the same must be true for the refracted wave.

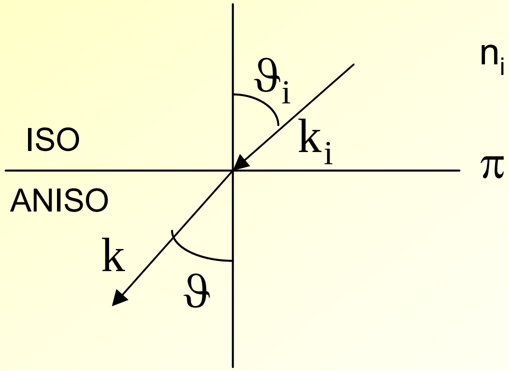
Therefore k must stay in the incidence plane. If ϑ is the angle between k and the normal to π and taking an abscissa ξ along p, eq.(1) becomes

$$n_i k_i \xi \sin\vartheta_i - \omega t = nk\xi \sin\vartheta - \omega t \qquad (2)$$

that is

$$n_i \sin\vartheta_i = n \sin\vartheta \qquad (3)$$

having taken into account that k_i and k have the same length. As we can see, relation (3) is the same law of Snell-Cartesio valid for the refraction between two isotropic media.



However there are two great differences. The first is that in the second member of (3) both n and ϑ are incognita. In fact we know that n depends on the direction of **k**, indeed for every direction of **k** in general two values of n exist to which two possible directions for **D** (orthogonal to **k**) are associated. Therefore (3) alone, it is not sufficient to find the refracted waves.

The second difference is that, as we saw before, the Poynting vector **S** can be non collinear to **k**. Therefore if, according to the concepts of geometric optics, we associate the directions of the light rays to those in which the energy propagates, that is to the directions of **S**, the law of Snell-Cartesio, which is true for the wave vectors, cannot be valid for the rays.

The disagreement with the law of Snell-Cartesio can regard another aspect too. We know that S must be found in the plane of k and D. In general, this plane does not coincide with the incidence plane. Therefore, the rays may not belong to the incidence plane, in contrast with what is predicted by the law of Snell-Cartesio.

Since (3), alone, does not characterize the refracted waves, we must add to it the law that expresses the relation between n and ϑ. A possible procedure is the following. We draw in the incidence plane the vector $n_i\chi_i$, where χ_i is the unit vector of the incidence wave, so that it ends in a point, we say O, of the surface of separation between two media (see fig.2).

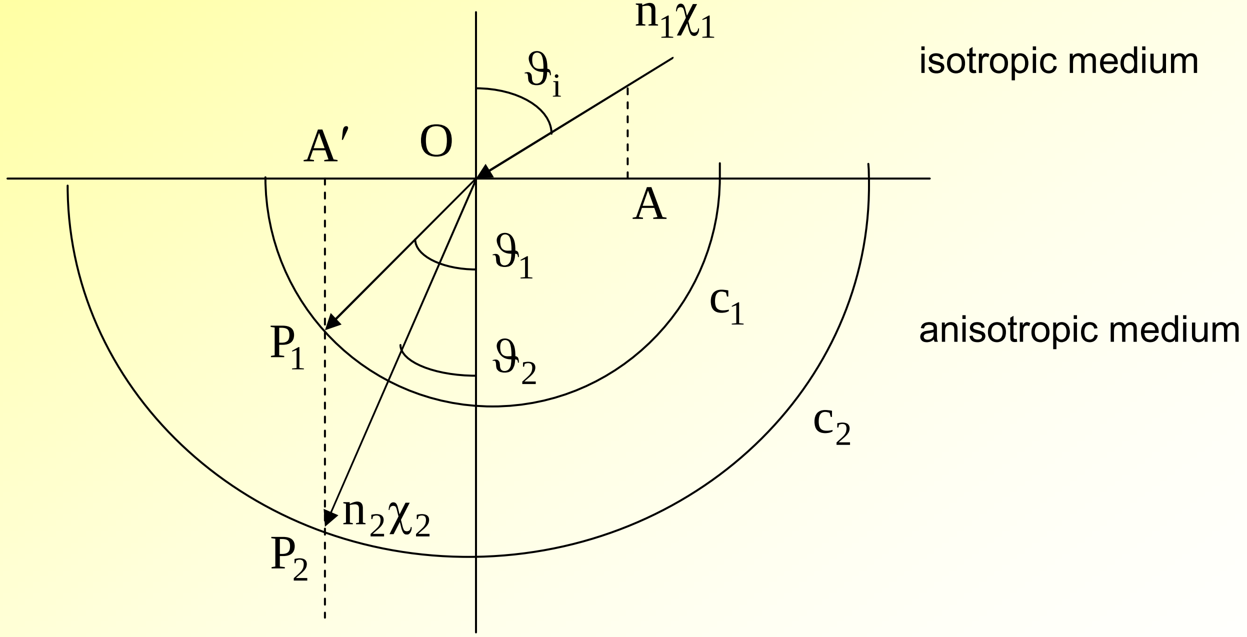
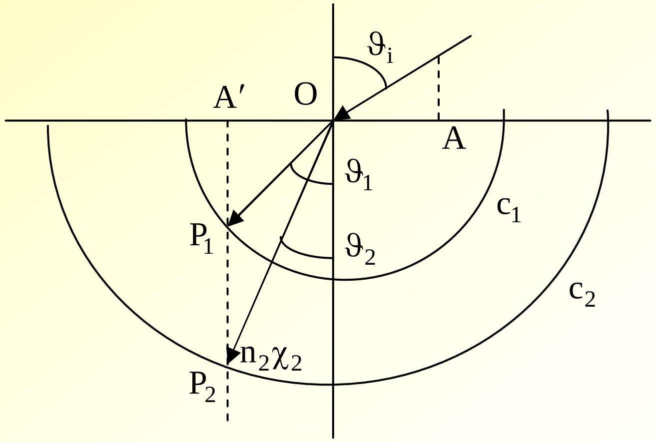
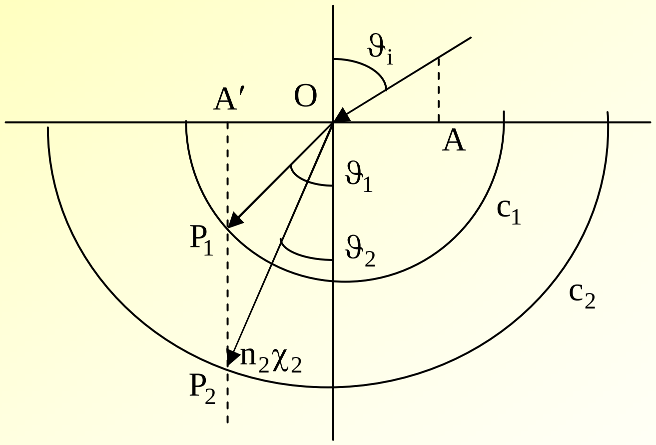


Fig. 2

The projection OA of $n_i\chi_I$ on this surface, has the length **$n_i\sin\vartheta_I$** and therefore it equals the first member of (3). Let us consider now, in the semi space of the anisotropic medium, the surface built as follows. Along every direction outgoing from O we mark the two points whose distance from O equals the possible values for the refractive index met by a plane wave having the wave vector along the direction line. We call surface of indices (not to be confused with the ellipsoid of indices) the two surfaces so obtained.

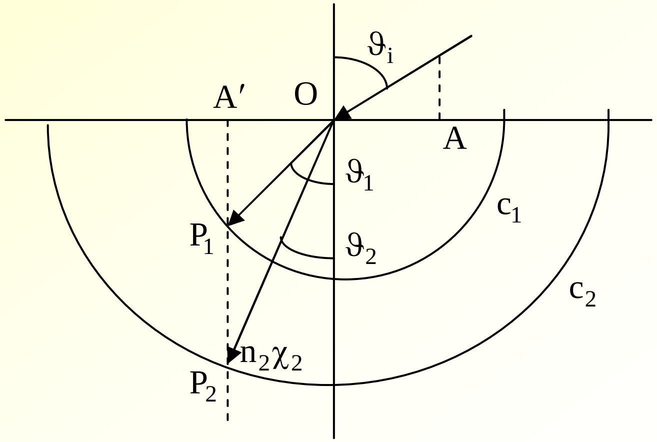


Let us suppose that c_1 and c_2, in fig.2, are the intersection curves between this surface and the incidence plane. Now we take the point A′, symmetric of A compared with O and we trace the perpendicular to A′ to the plane of separation between the two media. This straight line meets the surface of indices in two points P_1 and P_2. The segments OP_1 and OP_2 give the directions of the two refracted plane waves.



To see this, let us call n_1 and n_2 the refractive indices given by the lengths OP_1 and OP_2 and call ϑ_1 and ϑ_2 the angles formed by OP_1 and OP_2 with the normal to the plane of separation. We observe that the projections of OP_1 and OP_2 on the plane, which are $n_1\sin\vartheta_1$ and $n_2\sin\vartheta_2$, both are equal to OA' whose length is, for construction, equal to $n_1\sin\vartheta_1$. Therefore, the waves that in the isotropic medium proceed along the unit vectors χ_1 and χ_2 of OP_1 and OP_2 satisfy eq.(3).

$$n_i \sin\vartheta_i = n \sin\vartheta. \qquad (3)$$



NONLINEAR SUSCEPTIBILITY

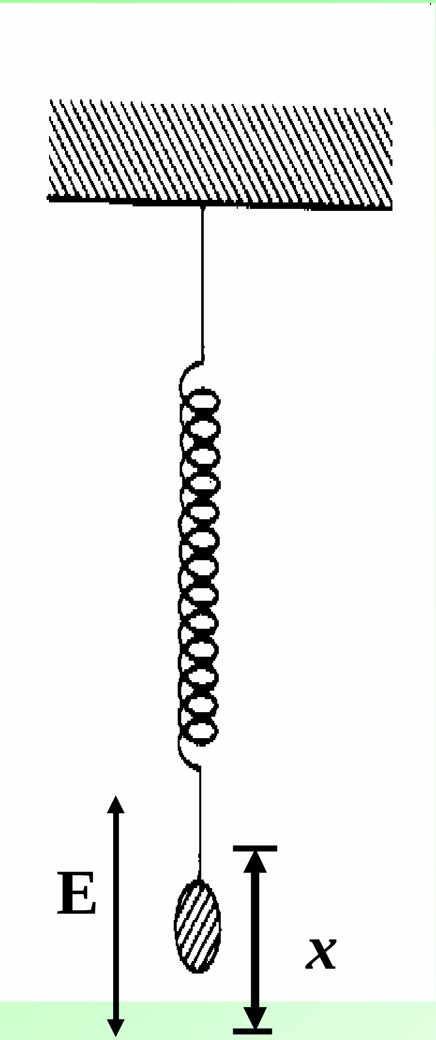
Dipole moment per unit volume or polarization in the linear case

$$P_i = P_i^0 + \chi_{ij} E_j$$

The general form of polarization in a nonlinear medium is

$$P_i = P_i^0 + \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \cdots$$

JUSTIFICATION OF THE PRESENCE OF A NONLINEAR RESPONSE



If the force exercised by the electric field of the wave becomes comparable with the Coulomb’s force between the electron and the nucleus, the oscillator is perturbed (**anharmonic oscillator**) and, at the lower level of the perturbation, we can write:

$$\ddot{x}(t) + \sigma\dot{x}(t) + \omega_0^2 x(t) + Dx^2(t) = -(e/m)E(t) \qquad (4)$$

The solution of eq.(4) can express as the sum of two terms

$$x(t) = x^{(1)}(t) + x^{(2)}(t) \qquad (5)$$

in which $x^{(1)}(t)$ is obtained solving eq.(4) without the anharmonic term, whereas $x^{(2)}(t)$ is considered a small correction of the solution at the first order $x^{(1)}(t)$ and is obtained utilizing $x^{(1)}(t)$ in the anharmonic term

$$\ddot{x}^{(2)}(t) + \sigma\dot{x}^{(2)}(t) + \omega_0^2 x^{(2)}(t) = -\frac{eE(t)}{m} - D\left[x^{(1)}(t)\right]^2. \qquad (6)$$

In this way, considering the case in which the forcing electric field is formed by the sum of two fields at different frequencies

$$E(t) = E_1 \cos\omega_1 t + E_2 \cos\omega_2 t = \frac{1}{2}\left[E_1 e^{-j\omega_1 t} + E_2 e^{-j\omega_2 t} + c.c.\right] \qquad (7)$$

We have the solution at the **first order**

$$x^{(1)}(t)=\frac{1}{2}\left[x^{(1)}(\omega_1)e^{-j\omega_1 t}+x^{(1)}(\omega_2)e^{-j\omega_2 t}+\text{c.c.}\right] \qquad (8)$$

and subsequently the solution at the **second order**, solving eq.(6) with the use of (8) is

$$x^{(2)}(t)=\frac{1}{2}[x^{(2)}(\omega_1+\omega_2)e^{-j(\omega_1+\omega_2)t}+x^{(2)}(\omega_1-\omega_2)e^{-j(\omega_1-\omega_2)t}+$$
$$+x^{(2)}(2\omega_1)e^{-j2\omega_1 t}+x^{(2)}(2\omega_2)e^{-j2\omega_2 t}+\text{c.c}] \qquad (9)$$

in which

$$x^{(2)}(\omega_1\pm\omega_2)=-\frac{1}{2}\frac{D(e/m)^2}{\left(\omega_0^2-\omega_1^2+j\sigma\omega_1\right)\left(\omega_0^2-\omega_2^2+j\sigma\omega_2\right)}\cdot\frac{E_1E_2}{\left[\omega_0^2-(\omega_1\pm\omega_2)^2+j\sigma(\omega_1\pm\omega_2)\right]}$$

$$x^{(2)}(2\omega_k)=-\frac{1}{2}\frac{D(e/m)^2\cdot E_k^2}{\left(\omega_0^2-\omega_k^2+j\sigma\omega_k\right)^2\left(\omega_0^2-4\omega_k^2+j\sigma\omega_k\right)};\quad k=1,2. \qquad (10)$$

Therefore the solution of the second order brings to the generation of **oscillations at a frequency different from the ones of the forcing field**. In particular, it is possible to have frequencies equal to the **sum** or to the **difference** of the field frequencies or to the double (second harmonic). Moreover, we emphasize that the previous formulas remain valid also if just a single forcing field ω is present. In this case $x^{(2)}(t)$ will be the sum of a second harmonic term (2ω) with a null pulsation term (term of optical rectification).

Now, remembering the expression for the medium polarization, we can write

$$P(t) = -Ne\left[x^{(1)}(t) + x^{(2)}(t)\right] \qquad (11)$$

where N is the number of dipoles for volume unit; that is

$$P(t) = P_L(t) + P_{NL}(t) \qquad (12)$$

Which, compared with (10)

$$x^{(2)}(\omega_1 \pm \omega_2) = -\frac{1}{2}\frac{D(e/m)^2}{\left(\omega_0^2 - \omega_1^2 + j\sigma\omega_1\right)\left(\omega_0^2 - \omega_2^2 + j\sigma\omega_2\right)} \cdot \frac{E_1E_2}{\left[\omega_0^2 - (\omega_1 \pm \omega_2)^2 + j\sigma(\omega_1 \pm \omega_2)\right]}$$

$$x^{(2)}(2\omega_k) = -\frac{1}{2}\frac{D(e/m)^2 \cdot E_k^2}{\left(\omega_0^2 - \omega_k^2 + j\sigma\omega_k\right)^2\left(\omega_0^2 - 4\omega_k^2 + j\sigma\omega_k\right)}; \quad k = 1,2. \qquad (10)$$

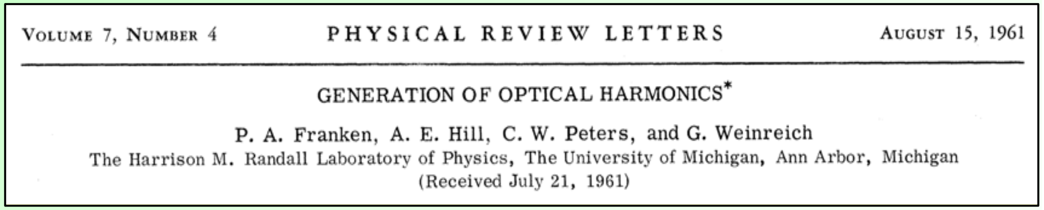
permits to write

$$P_L = \varepsilon_0 \chi^{(1)} E$$

$$P_{NL} = \chi^{(2)} E \cdot E. \qquad (13)$$

SECOND HARMONIC PRODUCTION

The nonlinear properties in the optical region have been demonstrated for the first time in **1961** by Franken et al. during an experiment of **second harmonic generation**. Sending red light of a ruby laser (λ = 6.943 Å) onto a crystal of quartz, they observed ultraviolet light.



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GENERATION OF OPTICAL HARMONICS*

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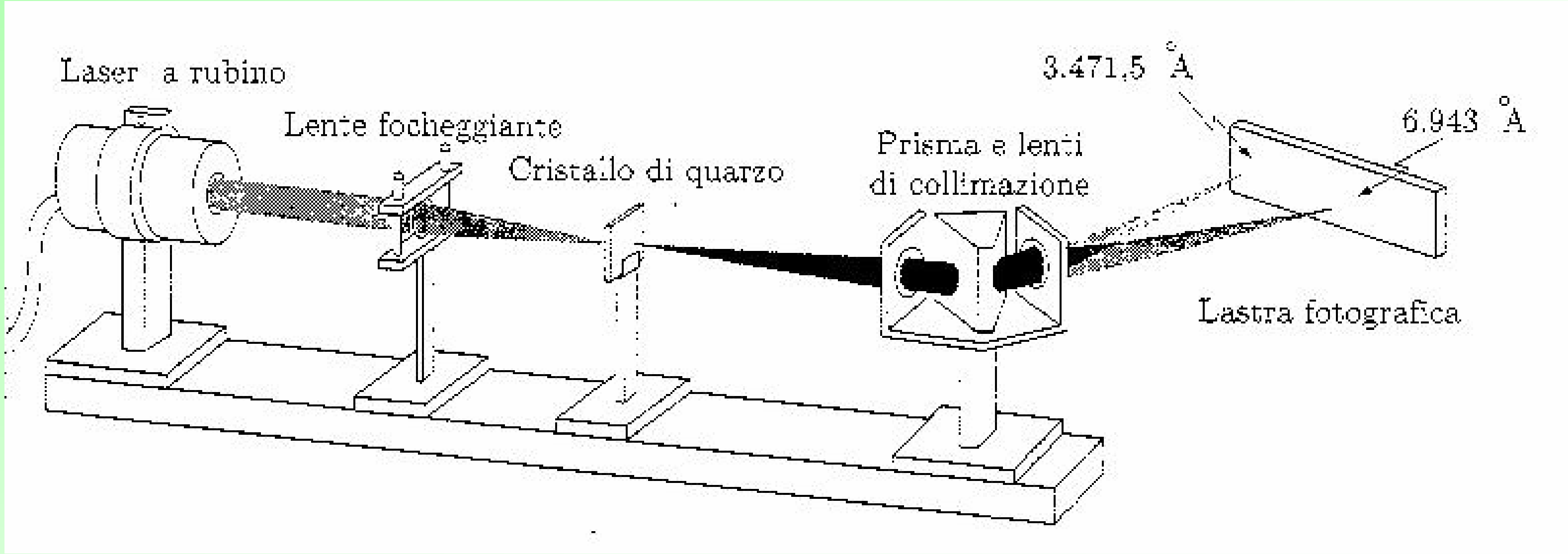


To describe the phenomenon, it is necessary to observe that in many crystal materials the nonlinear polarization depends on the **direction of propagation**, on the polarization of the electric field and on the orientation of the optical axis of the crystal. Since in such materials the vectors **P** and **E** are not necessarily parallel, the coefficient χ is a tensor. The second order polarization can be written as

$$P_i^{(2)} = \sum_{j,k} d_{ijk} E_j E_k \qquad (14)$$

where i, j, k represent the coordinates x, y, z. The main part of the coefficients d_{ijk}, however, are usually zero and so only a few of them must be considered.

Only the **non-centrosymmetric crystals** can have a non null tensor d_{ijk}. In facts, let us consider an isotropic crystal. In this case d_{ijk} is independent from the direction and therefore it is constant. If now we invert the direction of the electric field, also the polarization must change sign, that is

$$-P_i^{(2)} = \sum d_{ijk}(-E_j)(-E_k) = \sum d_{ijk} E_j E_k = +P_i^{(2)}.$$

It is clear that, not being able to be $-P_i^{(2)} = +P_i^{(2)}$, d_{ijk} must be null.

Moreover, in materials for which $d \neq 0$, since no physical meaning cannot be assigned to an exchange of E_j with E_k, it must be $d_{ijk} = d_{ikj}$.

Now if we consider the Maxwell equations writing

$$D = \varepsilon_0 E + P \qquad (15)$$

we have

$$\mathrm{rot}\, B = \mu j + \mu \frac{\partial D}{\partial t} = \mu j + \mu \varepsilon_0 \frac{\partial E}{\partial t} + \mu \frac{\partial P}{\partial t}$$

$$\mathrm{rot}\, E = -\frac{\partial B}{\partial t}. \qquad (16)$$

The polarization can be written as the sum of a linear term plus a nonlinear one

$$P = \varepsilon_0 \chi_L E + P_{NL} \qquad (17)$$

where, in case of materials with second order nonlinearity is, f.e.

$$\left(P_{NL}\right)_i = \sum d_{ijk} E_j E_k. \qquad (18)$$

So eq.(16) can be written, assuming j = 0

$$\mathrm{rot}\,B = \mu\frac{\partial \varepsilon E}{\partial t} + \mu\frac{\partial P_{NL}}{\partial t} \qquad (19)$$

from which

$$\nabla^2 E = \mu\varepsilon\frac{\partial^2 E}{\partial t^2} + \mu\frac{\partial^2 P_{NL}}{\partial t^2}. \qquad (20)$$

If we consider the unidimensional case of propagation along a direction z, we have

$$\frac{\partial^2 E_i}{\partial z^2} = \mu\varepsilon\frac{\partial^2 E_i}{\partial t^2} + \mu\frac{\partial^2 (P_{NL})_i}{\partial t^2}. \qquad (21)$$

Let us consider now three monochromatic fields with frequencies $\omega_1, \omega_2, \omega_3$ using the complex notation

$$E_i^{(\omega_1)}(z,t) = \frac{1}{2}\left[E_{1i}(z)e^{j(\omega_1 t - k_{1z})} + c.c.\right]$$

$$E_k^{(\omega_2)}(z,t) = \frac{1}{2}\left[E_{2k}(z)e^{j(\omega_2 t - k_{2z})} + c.c.\right]$$

$$E_j^{(\omega_3)}(z,t) = \frac{1}{2}\left[E_{3j}(z)e^{j(\omega_3 t - k_{3z})} + c.c.\right] \qquad (22)$$

where the indices i, j, k represent the components x or y.

The polarization at frequency $\omega_1 = \omega_3 - \omega_2$, for example, from (18) and from (22) results

$$P_i^{(\omega_1)} = \frac{1}{2}\sum_{j,k} d_{ijk} E_{3j}(z) E_{2k}^*(z) e^{j[(\omega_3 - \omega_2)t - (k_3 - k_2)z]} + c.c. \qquad (23)$$

Substituting eqs.(22) into (21) for the component E_{1i}, it is necessary to calculate

$$\frac{\partial^2 E^{(\omega_1)}}{\partial z^2} = \frac{1}{2}\frac{\partial^2}{\partial z^2}\left[E_{1i}(z)e\left(\omega_1 t - k_1 z\right) + \text{c.c.}\right]. \quad (24)$$

If we assume

$$\frac{dE_{1i}}{dz}k_1 \gg \frac{d^2E_{1i}}{dz^2} \qquad (25)$$

we have

$$\frac{\partial^2 E_i^{(\omega_1)}}{\partial z^2} = -\frac{1}{2}\left[k_1^2 E_{1i}(z) + 2jk_1\frac{dE_{1i}(z)}{dz}\right]e^{j(\omega_1 t - k_1 z)} + \text{c.c.} \qquad (26)$$

with similar expressions for

$$\frac{\partial^2 E_j^{(\omega_2)}}{\partial z^2} \quad \text{and} \quad \frac{\partial^2 E_k^{(\omega_3)}}{\partial z^2}.$$

Finally, substituting (26) and (23) into (21) we have

$$\frac{dE_{1i}(z)}{dz} = -j\frac{\omega_1}{2}\sqrt{\frac{\mu_0}{\varepsilon_1}}\sum d_{ijk}E_{3j}E_{2k}^{*}e^{-j(k_3-k_2-k_1)z} + \text{c.c.} \qquad (27)$$

and in analogous way

$$\frac{dE_{2k}^{*}}{dz} = \frac{j\omega_2}{2}\sqrt{\frac{\mu_0}{\varepsilon_2}}\sum d_{ijk}E_{1i}E_{3j}^{*}e^{-j(k_1-k_3+k_2)z} + \text{c.c.}$$

$$\frac{dE_{3j}}{dz} = -j\frac{\omega_3}{2}\sqrt{\frac{\mu_0}{\varepsilon_3}}\sum d_{ijk}E_{1i}E_{2k}e^{-j(k_1+k_2-k_3)z} + \text{c.c.}. \qquad (28)$$

The **second harmonic generation** is obtained immediately from (27) and (28) for the case of $\omega_1 = \omega_2$ and $\omega_3 = 2\omega_1$. Therefore it is enough consider only, f.e., (27) and the last one of (28).

To further simplify the analysis we can assume that the power lost by the frequency ω_1 (fundamental) is negligible, and therefore

$$\frac{dE_{1i}}{dz} \simeq 0. \qquad (29)$$

So it is sufficient to consider just the last one of (28)

$$\frac{dE_{2k}^*}{dz} = \frac{j\omega_2}{2}\sqrt{\frac{\mu_0}{\varepsilon_2}}\sum d_{ijk}E_{1i}E_{3j}^* e^{-j(k_1-k_3+k_2)z} + c.c.$$

$$\frac{dE_{3j}}{dz} = -j\frac{\omega_3}{2}\sqrt{\frac{\mu_0}{\varepsilon_3}}\sum d_{ijk}E_{1i}E_{2k} e^{-j(k_1+k_2-k_3)z} + c.c.. \qquad (28)$$

$$\frac{dE_{3j}}{dz} = -j\omega\sqrt{\frac{\mu_0}{\varepsilon}}\sum d_{jik}E_{1i}E_{1k} e^{j\Delta k\cdot z} \qquad (30)$$

where

$$\omega = \omega_1 = \frac{\omega_3}{2}$$

and

$$\Delta k = k_3^{(j)} - k_1^{(i)} - k_1^{(k)}. \qquad (31)$$

In eq.(31) $k_1^{(i)}$ is the constant of propagation of the beam at ω_1 polarized in the direction i. The solution of (30) for $E_{3j}(0) = 0$ for a crystal of length L is

$$E_{3j}(L) = -j\omega\sqrt{\frac{\mu_0}{\varepsilon}}\sum d_{jik}E_{1i}E_{1k}\frac{e^{j\Delta k\cdot L}-1}{j\Delta k}$$

or

$$I(L) = \left|E_{3j}(L)\right|^2 = \frac{\mu_0}{\varepsilon}\omega^2\left|\sum d_{jik}E_{1i}E_{1k}\right|^2 L^2\frac{\mathrm{sen}^2(\Delta k\cdot L/2)}{(\Delta k\cdot L/2)^2}. \qquad (32)$$

According to (32) a requirement for an efficient second harmonic generation is that $\Delta k = 0$, that is from (31) with $\omega_3 = 2\omega$, $\omega_1 = \omega_2 = \omega$

$$\Delta k = k_3^{(j)} - k_1^{(i)} - k_1^{(k)}. \qquad (31)$$

$$k^{(2\omega)} = 2k^{(\omega)}. \qquad (33)$$

If $\Delta k \neq 0$, the second harmonic wave generated at a generic plane z_1 which propagates until another plane z_2 is not in phase with that generated in z_2. This generates an interference described by the factor

$$\frac{\operatorname{sen}^2(\Delta k \cdot L/2)}{(\Delta k \cdot L/2)^2}$$

in (32).

$$I(L) = \left|E_{3j}(L)\right|^2 = \frac{\mu_0}{\varepsilon}\omega^2 \left|\sum d_{jik} E_{1i} E_{1k}\right|^2 L^2 \frac{\operatorname{sen}^2(\Delta k \cdot L/2)}{(\Delta k \cdot L/2)^2}. \qquad (32)$$

The condition (33) is never practically satisfied because, due to dispersion, the refractive index depends on ω.

$$k^{(2\omega)} = 2k^{(\omega)}. \qquad (33)$$

Therefore, we have

$$\Delta k = k^{(2\omega)} - 2k^{(\omega)} = \frac{2\omega}{c}\left(n^{(2\omega)} - n^{(\omega)}\right) \qquad (34)$$

being

$$k^{(\omega)} = \frac{\omega n^{(\omega)}}{c} \qquad (35)$$

and therefore

$$\Delta k \neq 0.$$

However, it is possible to make $\Delta k = 0$ (**phase-matching condition**) using various skills; the most used of which takes advantage from the natural birefringence of the anisotropic crystals. From (34) we can see that $\Delta k = 0$ implies

$$n^{(2\omega)} \simeq n^{(\omega)} \qquad (36)$$

$$\Delta k = k^{(2\omega)} - 2k^{(\omega)} = \frac{2\omega}{c}\left(n^{(2\omega)} - n^{(\omega)}\right) \qquad (34)$$

so that the refractive indices of second harmonic and of fundamental frequency have to be equal.

In the materials with normal dispersion, the index of the ordinary and extraordinary wave along a direction increase with ω, as it is shown in the table.

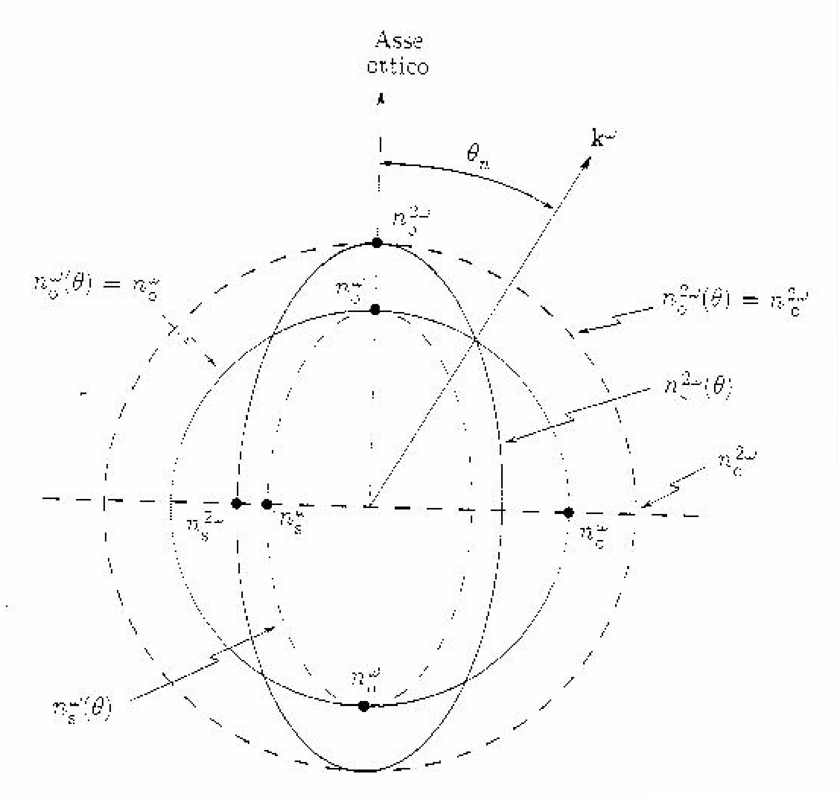
λ, µm	Index	
	n_o (ordinary beam)	n_s (extraordinary beam)
0,2000	1,622630	1,563913
0,3000	1,545570	1,498153
0,4000	1,524481	1,480244
0,5000	1,5144928	1,472486
0,6000	1,509274	1,468267
0,7000	1,505235	1,465601
0,8000	1,501924	1,463708
0,9000	1,498930	1,462234
1,0000	1,496044	1,460993
1,1000	1,493147	1,459884
1,2000	1,490169	1,458845
1,3000	1,487064	1,457838
1,4000	1,483803	1,456838
1,5000	1,480363	1,455829
1,6000	1,476729	1,454797
1,7000	1,472890	1,453735
1,8000	1,468834	1,452636
1,9000	1,464555	1,451495
2,0000	1,460044	1,450308

This makes it possible to satisfy eq.(36) when both the beams are of the same kind (that is both extraordinary or ordinary). Or (36) can be satisfied, in some cases, using an ordinary and an extraordinary wave.

In order to illustrate this point we can consider the dependence of the refractive index of the extraordinary wave in a uniaxial crystal, from the angle ϑ between the direction of propagation and the optical axis (z) of the crystal.

$$\frac{1}{n_s^2(\vartheta)} = \frac{\cos^2\vartheta}{n_0^2} + \frac{\mathrm{sen}^2\vartheta}{n_s^2}. \qquad (37)$$

If $n_s^{(2\omega)} < n_0^{(\omega)}$ an angle ϑ_n exists for which $n_s^{(2\omega)}(\vartheta_n) = n_0^{(\omega)}$. In this case if the fundamental beam (frequency ω) is propagated along ϑ_n as a ordinary beam, the second harmonic beam will be generated along the same direction as an extraordinary beam. This situation is shown in the figure.



The angle ϑ_n is determined by the intersection between the sphere (shown as a circle in the figure) which corresponds to the index surface of the ordinary beam to ω with the index ellipsoid of the extraordinary beam. The angle ϑ_n, for negative uniaxial crystals (that is for crystals for which $n_s^{(2\omega)} < n_0^{(\omega)}$ is given by

$$\frac{\cos^2\vartheta_n}{\left[n_0^{(2\omega)}\right]^2} + \frac{\operatorname{sen}^2\vartheta_n}{\left[n_s^{(2\omega)}\right]^2} = \frac{1}{\left[n_0^{(\omega)}\right]^2} \qquad (38)$$

that is

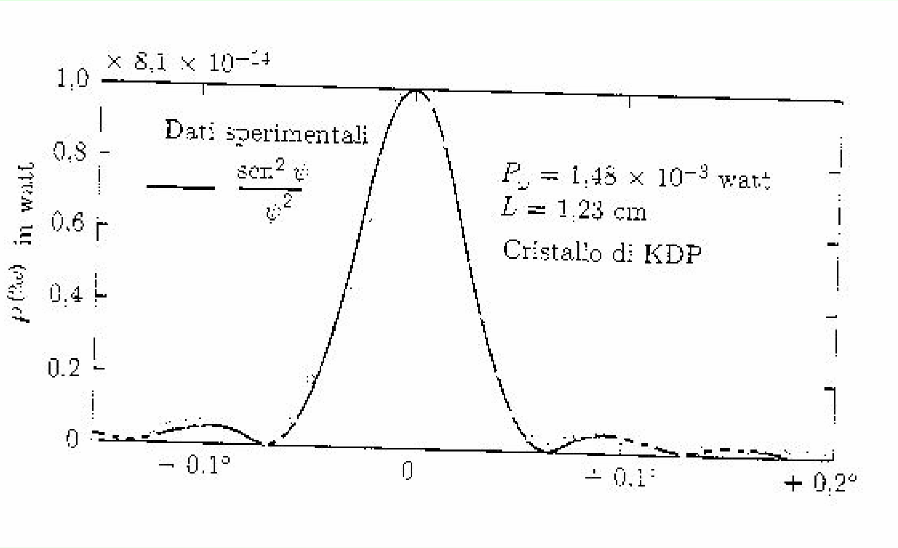
$$\operatorname{sen}^2\vartheta = \frac{\left[n_0^{(\omega)}\right]^{-2} - \left[n_0^{(2\omega)}\right]^{-2}}{\left[n_s^{(2\omega)}\right]^{-2} - \left[n_0^{(2\omega)}\right]^{-2}}. \qquad (39)$$

According to (32), if we deviate from the matching condition, for a fixed length L of the nonlinear crystal, we have a reduction of the second harmonic power generated by the factor

$$\frac{P^{(2\omega)}}{P_{\max}^{(2\omega)}} = \frac{\mathrm{sen}^2\left(\Delta k \cdot L/2\right)}{\left(\Delta k \cdot L/2\right)^2}. \qquad (40)$$

This relation can be easily verified varying the angle $\sigma = \vartheta - \vartheta_n$ between the direction of index matching and the propagation direction.

A diagram of the second harmonic power according to σ is shown in the figure (where the theoretical curve $\mathrm{sen}^2 x / x^2$ is also shown).



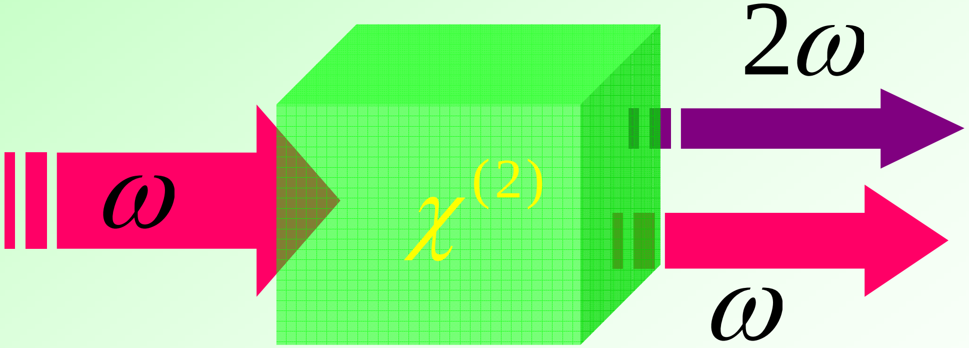
Nonlinear Optical Interactions

- The E-field of a laser beam

$$\tilde{E}(t) = Ee^{-i\omega t} + \text{C.C.}$$

- 2nd order nonlinear polarization

$$\tilde{P}^{(2)}(t) = 2\chi^{(2)}EE^{*} + (\chi^{(2)}E^{2}e^{-2i\omega t} + \text{C.C.})$$



2^{nd} Order Nonlinearities

- The incident optical field

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + C.C.$$

- Nonlinear polarization contains the following terms

$P(2\omega_1) = \chi^{(2)} E_1^2$ (SHG)

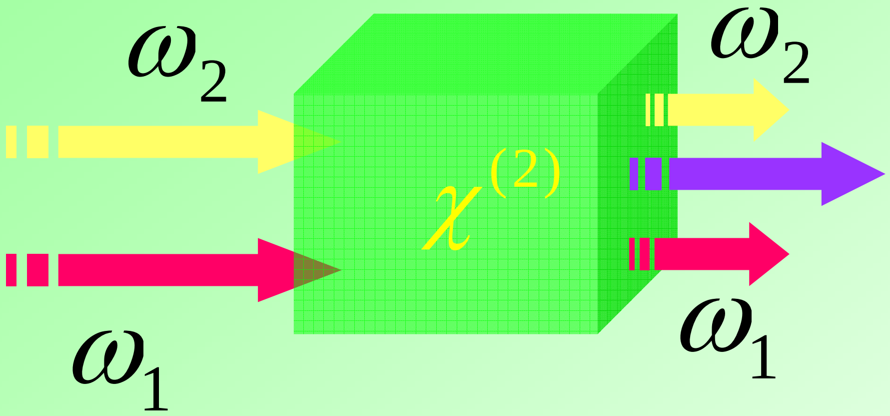
$P(2\omega_2) = \chi^{(2)} E_2^2$ (SHG)

$P(\omega_1 + \omega_2) = 2\chi^{(2)} E_1 E_2$ (SFG) summ frequency generation

$P(\omega_1 - \omega_2) = 2\chi^{(2)} E_1 E_2^*$ (DFG) difference frequency generation

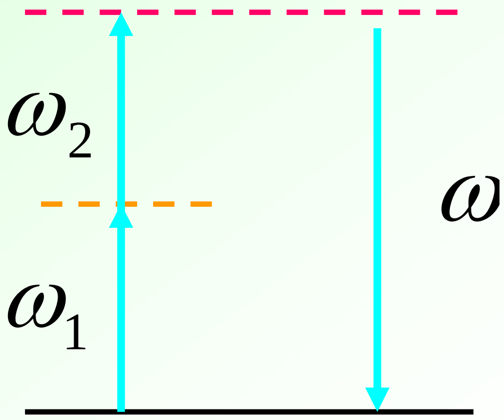
$P(0) = 2\chi^{(2)} (E_1 E_1^* + E_2 E_2^*)$ (OR)

Sum Frequency Generation

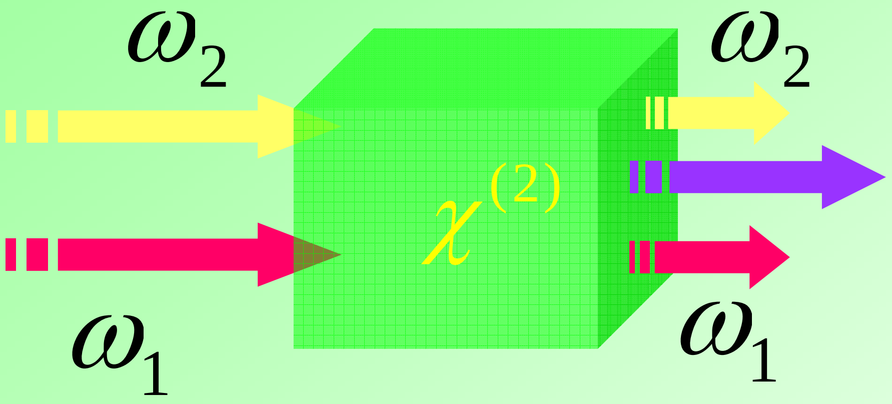


$$\omega_3 = \omega_1 + \omega_2$$

Application:
Tunable radiation in the UV Spectral region.



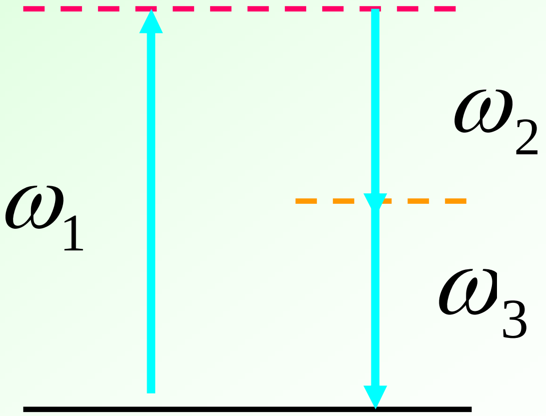
Difference Frequency Generation



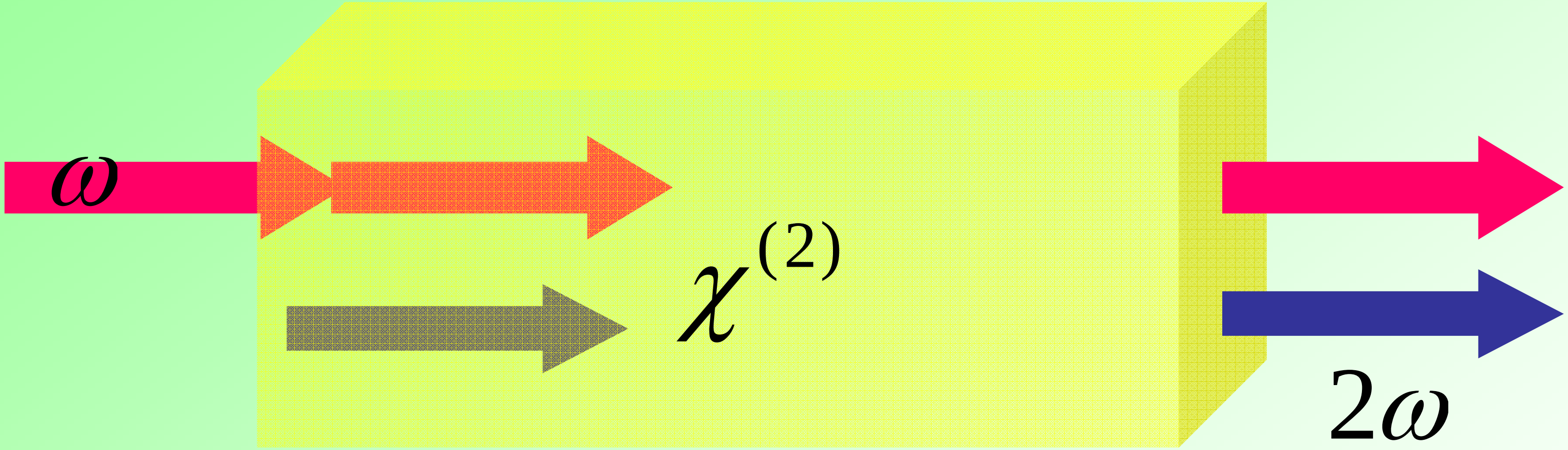
$$\omega_3 = \omega_1 - \omega_2$$

Application:

The low frequency photon, ω_2 amplifies in the presence of high frequency beam ω_1. This is known as parametric amplification.



Phase Matching



- Since the optical (NLO) media are dispersive, The fundamental and the harmonic signals have different propagation speeds inside the media.

- The harmonic signals generated at different points interfere destructively with each other.

Third Order Nonlinearities

When the general form of the incident electric field is in the following form,

$$\tilde{E}(t) = E_1 e^{-i\omega_1 t} + E_2 e^{-i\omega_2 t} + E_3 e^{-i\omega_3 t}$$

The third order polarization will have 22 components

$$\omega_i, 3\omega_i, (\omega_i + \omega_j + \omega_k), (\omega_i + \omega_j - \omega_k)$$
$$(2\omega_i + \omega_j), (2\omega_i - \omega_j), i, j, k = 1,2,3$$

The Intensity Dependent Refractive Index

- The incident optical field

$$\tilde{E}(t) = E(\omega)e^{-i\omega t} + \mathrm{C.C.}$$

- Third order nonlinear polarization

$$P^{(3)}(\omega) = 3\chi^{(3)}(\omega = \omega + \omega - \omega)\,|E(\omega)|^2\,E(\omega)$$

The total polarization can be written as

$$P^{\mathrm{TOT}}(\omega) = \chi^{(1)} E(\omega) + 3\chi^{(3)}(\omega = \omega + \omega - \omega) \, | E(\omega) |^2 \, E(\omega)$$

One can define an effective susceptibility

$$\chi_{\mathrm{eff}} = \chi^{(1)} + 4\pi \, | E(\omega) |^2 \, \chi^{(3)}$$

The refractive index can be defined as usual

$$n^2 = 1 + 4\pi\chi_{\mathrm{eff}}$$

By definition

$$\boxed{n = n_0 + n_2 I}$$

where

$$I = \frac{n_0 c}{2\pi} |E(\omega)|^2$$

$$\boxed{n_2 = \frac{12\pi^2}{n_0^2 c} \chi^{(3)}}$$

Typical values of nonlinear refractive index

Mechanism	n_2 (cm^2/W)	$\chi^{(3)}_{1111}$ (esu)	Response time (sec)
Electronic Polarization	10^{-16}	10^{-14}	10^{-15}
Molecular Orientation	10^{-14}	10^{-12}	10^{-12}
Electrostriction	10^{-14}	10^{-12}	10^{-9}
Saturated Atomic Absorption	10^{-10}	10^{-8}	10^{-8}
Thermal effects	10^{-6}	10^{-4}	10^{-3}
Photorefractive Effect	large	large	Intensity dependent

Third order nonlinear susceptibility of some material

Material	$\chi^{(3)}$	Response time
Air	1.2×10^{-17}	
CO_2	1.9×10^{-12}	2 Ps
GaAs (bulk room temperature)	6.5×10^{-4}	20 ns
CdS_xSe_{1-x} doped glass	10^{-8}	30 ps
GaAs/GaAlAs (MQW)	0.04	20 ns
Optical glass	$(1\text{-}100)\times10^{-14}$	Very fast