

# CHEMISTRY 623- EXPERIMENTAL SPECTROSCOPY

## Spectroscopic units

Spectroscopic measurements rely on measuring the frequency of light. One difficulty confronting spectroscopists is the use of different energy, frequency, and wavelength units by different disciplines. The following chart relates these units.

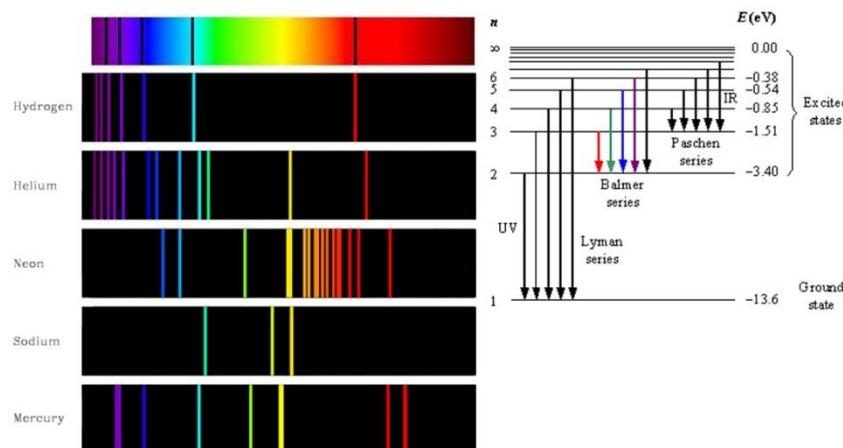
Energy Conversion Table								
	hartree	eV	cm <sup>-1</sup>	kcal/mol	kJ/mol	°K	J	Hz
hartree	1	27.2107	219 474.63	627.503	2 625.5	315 777.	43.60 x 10 <sup>-19</sup>	6.57966 x 10 <sup>+15</sup>
eV	0.0367502	1	8 065.73	23.060 9	96.486 9	11 604.9	1.602 10 x 10 <sup>-19</sup>	2.418 04 x 10 <sup>+14</sup>
cm <sup>-1</sup>	4.556 33 x 10 <sup>-6</sup>	1.239 81 x 10 <sup>-4</sup>	1	0.002 859 11	0.011 962 7	1.428 79	1.986 30 x 10 <sup>-23</sup>	2.997 93 x 10 <sup>+10</sup>
kcal/mol	0.001 593 62	0.043 363 4	349.757	1	4.18400	503.228	6.95 x 10 <sup>-21</sup>	1.048 54 x 10 <sup>+13</sup>
kJ/mol	0.000 380 88	0.010 364 10	83.593	0.239001	1	120.274	1.66 x 10 <sup>-21</sup>	2.506 07 x 10 <sup>+12</sup>
°K	0.000 003 166 78	0.000 086 170 5	0.695 028	0.001 987 17	0.008 314 35	1	1.380 54 x 10 <sup>-23</sup>	2.083 64 x 10 <sup>+10</sup>
J	2.294 x 10 <sup>+17</sup>	6.241 81 x 10 <sup>+18</sup>	5.034 45 x 10 <sup>+20</sup>	1.44 x 10 <sup>+20</sup>	6.02 x 10 <sup>+20</sup>	7.243 54 x 10 <sup>+22</sup>	1	1.509 30 x 10 <sup>+33</sup>
Hz	1.519 83 x 10 <sup>-16</sup>	4.135 58 x 10 <sup>-15</sup>	3.335 65 x 10 <sup>-11</sup>	9.537 02 x 10 <sup>-14</sup>		4.799 30 x 10 <sup>-11</sup>	6.625 61 x 10 <sup>-34</sup>	1

## Atomic Spectroscopy

Atoms have a series of electronic states that are sharp and well-defined. Absorption transitions occur from the lower states that are populated to upper states. The absorption strength depends on the population of the initial state. It is usually determined by the Boltzmann distribution.

Emission spectra occur from excited states that are

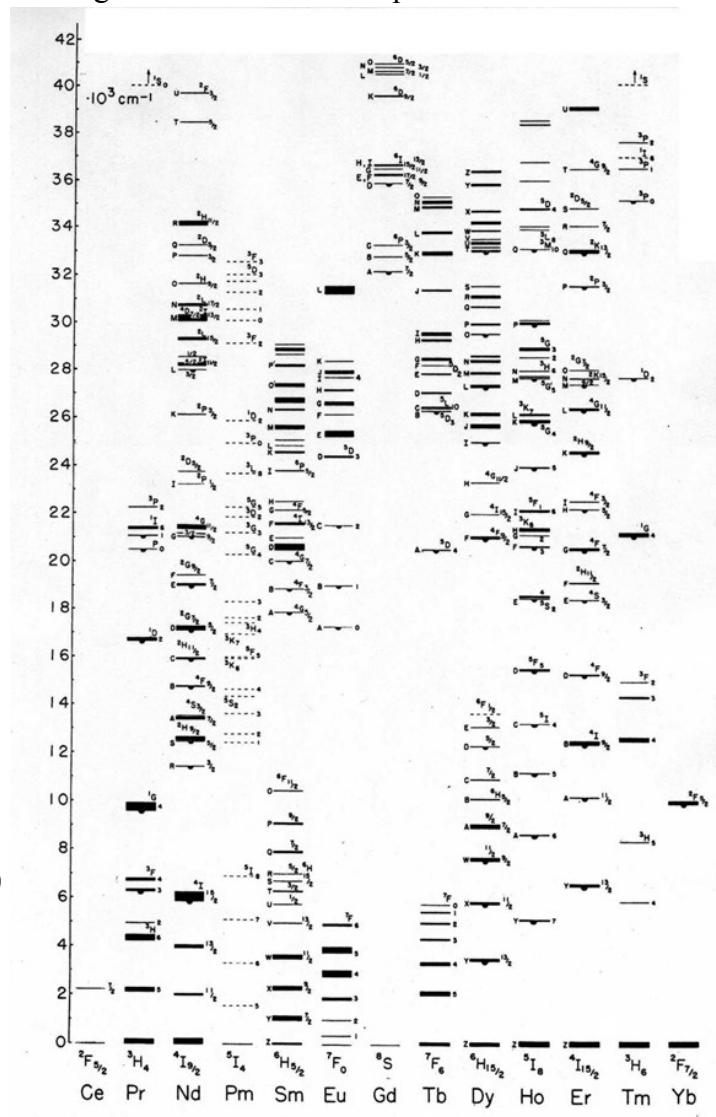
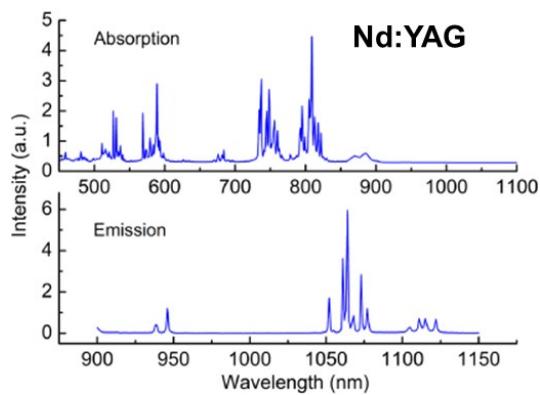
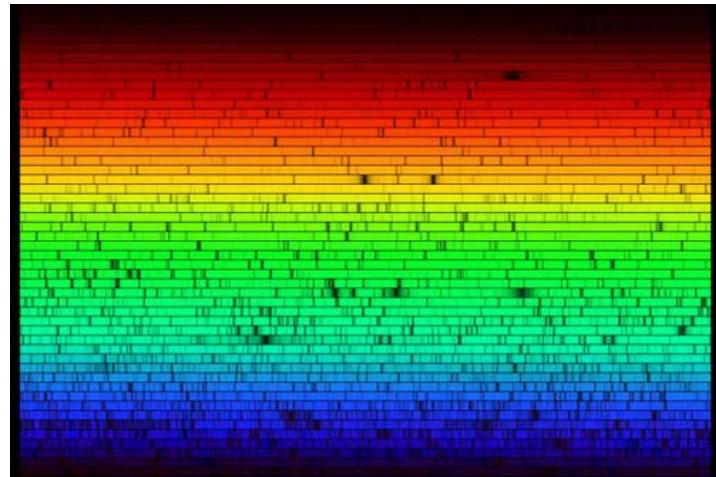
populated to lower states. The spectra shown below contain very sharp and bright lines because the transitions are allowed. The absorption strength is concentrated in the sharp lines so the absorption coefficients are enormous. Typical absorption cross-sections are 10<sup>-12</sup>-10<sup>-13</sup> cm<sup>2</sup>. The hydrogen spectra include an absorption spectrum and an emission spectrum. There is an energy level diagram that illustrates the transitions.



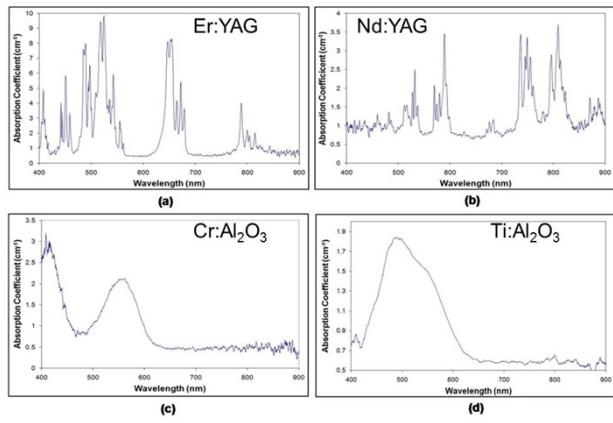
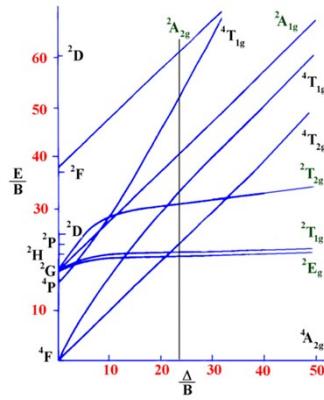
Astronomy makes heavy use of spectroscopy because the sharp atomic transitions define elemental compositions. The absorption spectrum of the sun is shown using cross-dispersion where the horizontal dispersion and resolution is very high and the vertical dispersion is low.

## Spectroscopy of Ions in Crystals and Complexes

Ions in crystals can have atomic like transitions when the transitions occur within unfilled inner orbitals like  $3d^n$  or  $4f^n$ . Although the transitions between unfilled are formally forbidden because of parity, the transitions become allowed in non-cubic environments because of perturbation by the crystal fields or ligands. The first set of spectra show the absorption and emission spectra of  $Nd^{3+}$  ions in Yttrium Aluminum Garnet (YAG), a well-known laser crystal. Notice the sharpness of the lines in the spectrum. They are sharp because they have long lifetimes and the transitions between inner electron orbitals are protected against seeing the thermal environment by outer orbitals. The Dieke diagram shown here has the energy levels of all the rare earth ions. You can identify the  $Nd^{3+}$  transitions in the diagram that corresponds to the transitions in the Nd:YAG spectra.



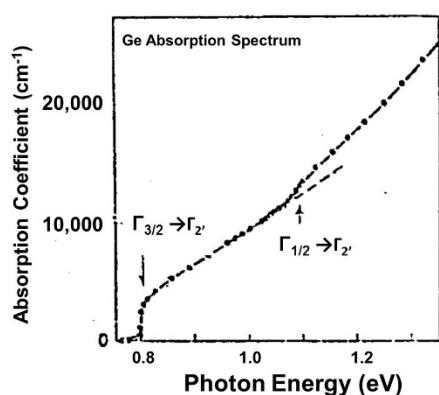
Transition metals also have unfilled d-shell orbitals but they are not as well protected from the environment show they are broader. The next set of spectra show the absorption spectra



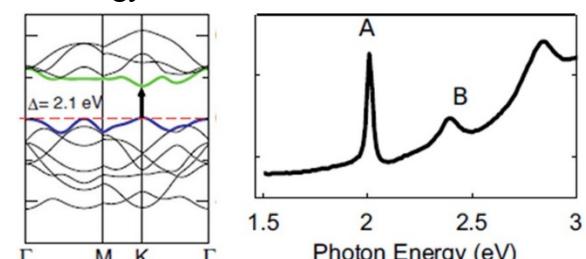
for other well-known laser crystals- a)  $\text{Er}^{3+}$ : Yttrium Aluminum Garnet (YAG), b)  $\text{Nd}^{3+}$ : YAG, c)  $\text{Cr}^{3+}$ :  $\text{Al}_2\text{O}_3$ , d)  $\text{Ti}^{3+}$ :  $\text{Al}_2\text{O}_3$ . The Cr and Ti spectra reflect typical transition metal spectra. The stronger interaction with the environment is shown most clearly by Tanabe-Sugano diagrams like the one shown for the crystal field splitting of  $\text{Cr}^{3+}$ :  $\text{Al}_2\text{O}_3$ , a  $3d^3$  ion. The abscissa is the strength of the crystal field and its effect on the energies of the  $\text{Cr}^{3+}$  quantum states.

## Semiconductors and Metals

The electronic states of the ions in crystals were representative of materials where the excitation of an electron remains localized on the ion. In semiconductors and metals, the excitation of electrons is not localized so the wave functions of individual atoms form bands as the atomic states are delocalized. The energies of these states depend on the wavelength of the delocalized states. In a particular crystal structure, the possible wavelengths depend on the direction of each wave. Wavelengths are related to the wave-vectors by the equation  $\vec{k} \equiv \frac{2\pi}{\lambda}$ .  $\vec{k}$  is proportional to the



momentum of the wave. A Fourier transform will transform the crystal lattice spatial dependence into a  $k$  space representation of the lattice called the Brillouin zone. It is the Fourier transform of the spatial positions of the atoms in the crystal. A plot of the energy of a particular state as a function of the direction describes how the energy of the state varies as a function of the momentum along different crystallographic directions. Letters are assigned to specify different directions in the Brillouin zone. For example,  $\Gamma$  specifies the center of the

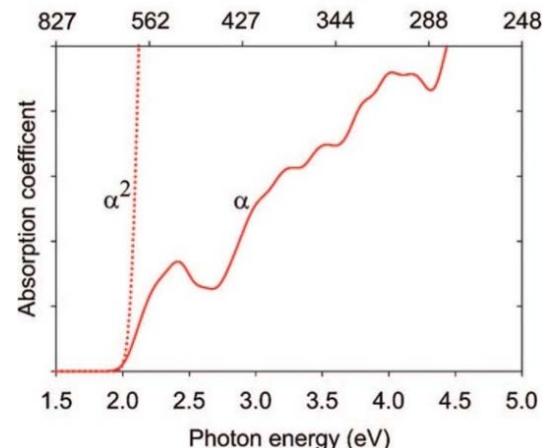
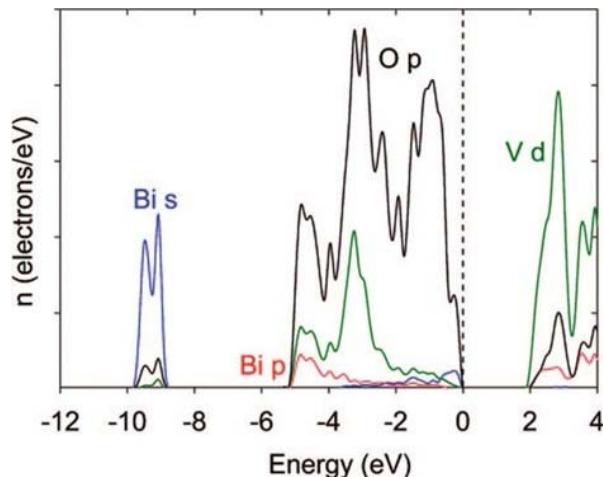
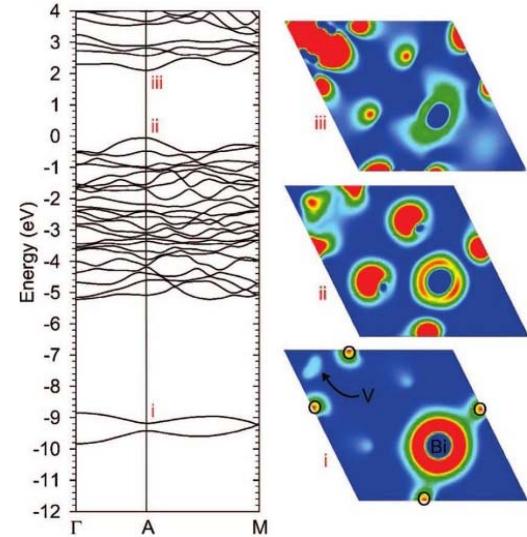


Brillouin zone that has no momentum (infinite wavelength), X specifies a direction perpendicular to the center of a cubic face, M is directed towards the center of an edge, etc. (see [http://en.wikipedia.org/wiki/Brillouin\\_zone](http://en.wikipedia.org/wiki/Brillouin_zone) for more details). The band diagram for germanium is shown above. Absorption transitions can occur from any point in the valence band to any point in the conduction band. The relative importance of the different transitions depends on the slope of the bands,  $\frac{dE}{dk}$ . Generally, the band absorption coefficient increases above the band gap as

$\sqrt{E - E_{gap}}$  if the transition results in free electron and hole carriers. If the carriers are bound by

Coulombic interactions that are larger than  $kT$ , they exist as Wannier or Frenkel excitons depending on whether they are delocalized (occurs when a large dielectric constant screens the charges) or localized (occurs when the dielectric constant is small), respectively. Exciton absorption appears as a sharper features in the absorption spectrum. The WS<sub>2</sub> thin film absorption spectrum appears above. The A and B excitons are strongly bound and correspond to transitions from two valence band states to the conduction band as shown by arrow in the band diagram. The two valence bands result from spin-orbit splitting that is not resolved in the band diagram.

BiVO<sub>4</sub> is an example of a more complicated semiconductor. It has a series of atomic levels that take on different energies depending on their direction in the lattice. The first graph shows the energy vs k-vector of a particular slice through the Brillouin zone. The top of the valence band corresponds to zero energy. The V<sup>5+</sup> states are therefore in the conduction band and are empty in BiVO<sub>4</sub> but the O<sup>2-</sup> 2p and Bi<sup>3+</sup> 6s states are filled. The second graph shows the spatial variation in the unit cell of the electron density contributed by the V, O, and Bi states that make up the top (largely V), middle (largely O), and bottom (largely Bi) bands. The third graph shows the density of states for the different Bi, V, and O ions. Absorption transitions can occur between all of these filled valence and vacant conduction band states as depicted in the absorption spectrum. The absorption spectrum contains contributions from free carrier and excitonic transitions.



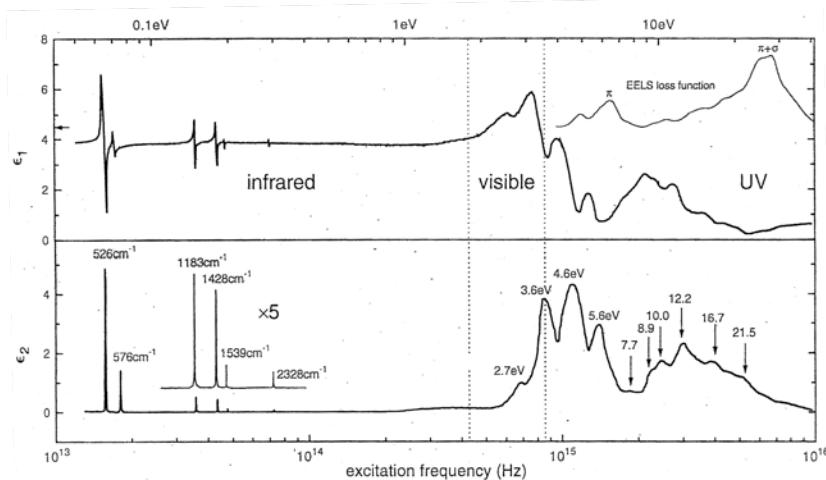
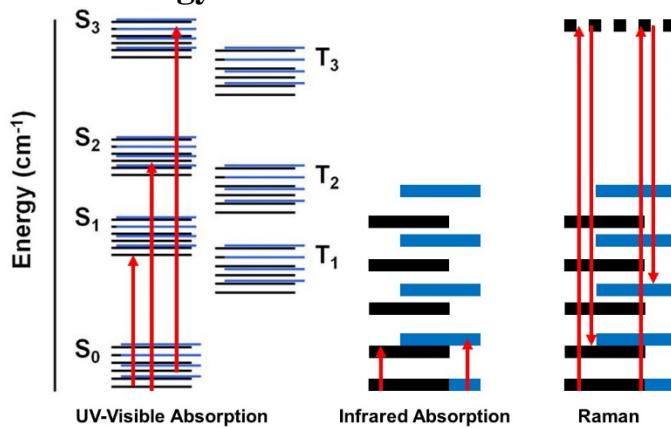
## Molecular Quantum States and Potential Energy Surfaces-Vibrational and Electronic Spectroscopy

When atoms bond together to form molecules, liquids, and solids, the atomic orbitals interact and create a series of new electronic states. In solids, the orbitals form bands and are typically classified as valence and conduction bands. In molecules, the orbitals form molecular orbitals. Molecular spectra result from transitions between the molecular electronic, vibrational, and rotational states. For condensed phase

spectroscopy, the rotational states do not play an important role. They do for gas phase spectroscopy, however. The simplest way to visualize the spectroscopy is an energy level diagram that shows the electronic states and their accompanying vibrational states. The vibrational states depend on the shape of the molecule and bond energies for each of the electronic states. Infrared and Raman spectroscopy depends on transitions between vibrational states while UV-visible and fluorescence spectroscopy depends on transitions between electronic states and their associated vibrational states. In typical organic molecules, the electrons are paired to form singlet spin states with no net spin. The electron excitation can occur to a state with the same spin or flipped to make either another singlet state or a triplet state where the spin  $M_s$  value can be 1, 0, or -1. The figure shows the simplest energy level diagram of a typical molecule. The  $S_n$  states are electronic singlet states where the electron spins are all paired and the subscript designates the relative energies. The  $T_n$  states are electronic triplet states where two electrons have the same spin. The diagram also has black and blue levels that represent two different vibrational modes with quantized energies given by  $E_v = \left( v + \frac{1}{2} \right) h\nu$ . The blue modes

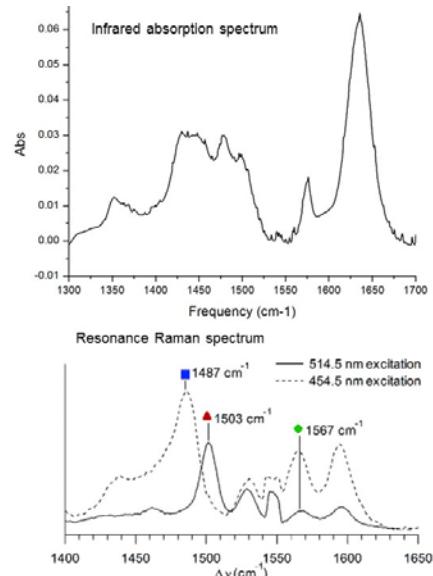
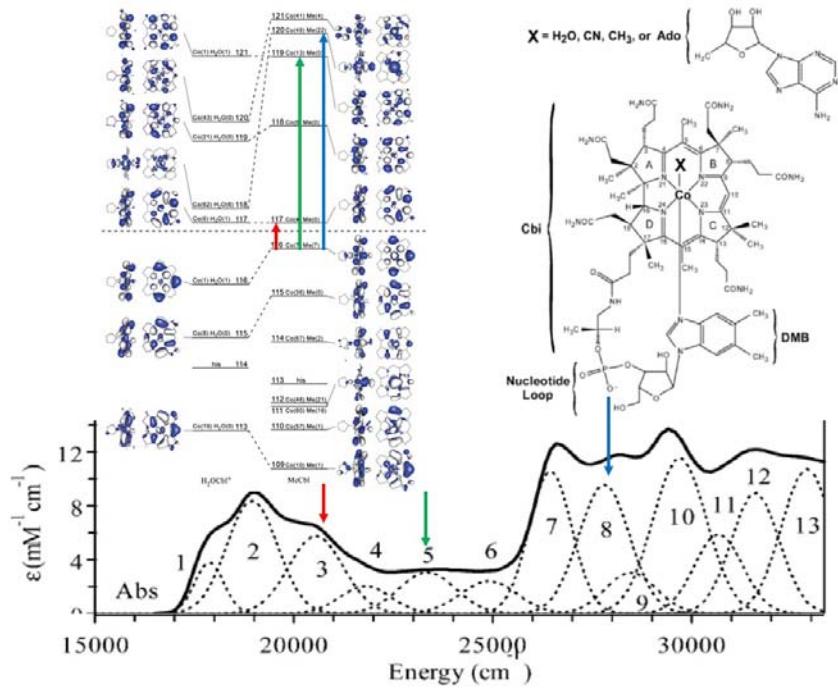
have an higher value of  $h\nu$ . The arrows show example transitions for UV-Visible, infrared, and Raman spectroscopy.

The UV-Visible-Infrared absorption and refractive index spectrum of  $C_{60}$  is shown below. The refractive index and the absorption spectra are related by a Kramers-Kronig transformation that we will learn about later. There are vibrational absorption lines in the infrared and electronic absorption bands in the visible and ultraviolet. The vibrational motions



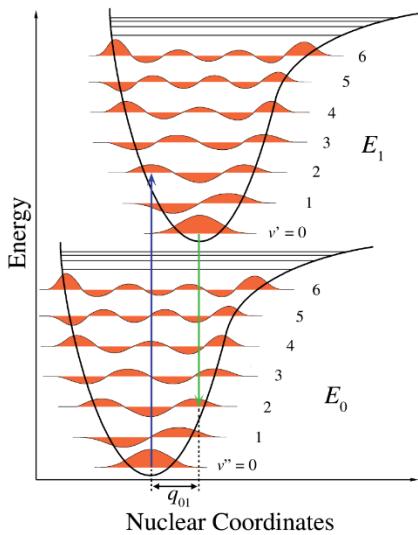
responsible for the infrared spectra can be seen at the web site in the footnote<sup>1</sup>. The visible absorption bands arise from transitions involving the aromatic  $\pi$  orbitals and the far UV transitions involve single bond electronic states. You can also see a series of peaks that are all associated with the same electronic excitation state. These peaks are vibronic features that arise from transitions to the C<sub>60</sub> breathing modes with different  $v$  quantum numbers. We will learn more about these features shortly.

A more informative picture is visualizing the transitions between the molecular orbitals. The figure shows the molecular orbitals, the absorption spectrum, and the structure of cobalamin (taken by Brunold's group). The transitions the molecular orbitals that are responsible for the absorption spectrum features labeled 3, 5, and 8 are shown. Each of the electronic states associated with each molecular orbital will have vibrational transitions. Vibrational transitions involving just the modes in the electronic ground state appear in the infrared and Raman transitions shown below. They involve ring breathing modes of the central corrin ring of the cobalamin.



<sup>1</sup> [http://www.public.asu.edu/~cosmen/C60\\_vibrations/mode\\_assignments.htm](http://www.public.asu.edu/~cosmen/C60_vibrations/mode_assignments.htm)

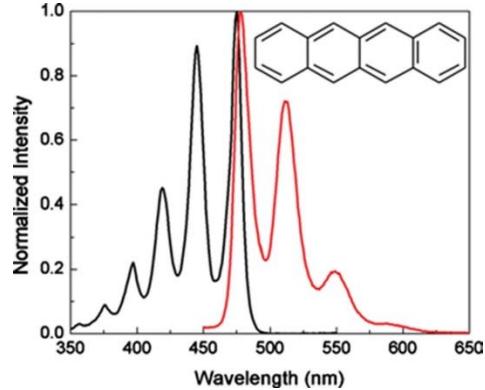
The C<sub>60</sub> spectrum had a series of vibronic features but the cobalamin spectrum did not have similar set of features. In order to understand these features more completely, we need to understand how the intensity of transitions involving changes in a vibrational mode depend upon how tightly that vibrational mode is coupled to the electronic state. That means the vibration changes the electronic state. The best example is an aromatic molecule where breathing modes change the conjugation of the molecule. The tetracene spectrum is an excellent example because it shows a vibronic progression where the breathing mode changes amplitude by  $v = 0 \dots 4$  in both the absorption and fluorescence spectrum. The relative intensities of vibronic features are defined by Franck Condon factors that measure the overlap between the wave functions of the initial and final states of the transitions.



consequence of the Born-Oppenheimer approximation that states that electronic state wave functions can be calculated without worrying whether the nuclear coordinate is changing (i.e. static nuclear coordinates. The intensity depends upon how much overlap occurs between the wave functions (shown in orange) of  $v''$  and  $v'$ . The Franck-Condon factors describe the amount of overlap. The blue and green arrows have the most overlap.

The wave functions for a vibrational mode depend on Hermite polynomials. The wave function for a simple harmonic oscillator is  $\psi_v(\xi) = \frac{1}{\sqrt{2^v v! \sqrt{\pi}}} H_v(\xi) e^{-\xi^2/2}$  where  $v$  is the

vibrational quantum number and  $\xi$  is a normalized vibrational displacement and  $H_v(\xi)$  is a Hermite polynomial defined in the table. The Hermite polynomials are a complete, orthonormal set of basis functions that are analogous to the sine and cosine functions in that linear combinations of them can represent any arbitrary function, just as in Fourier transforms. The table defines a series of Hermite polynomials and the figure visualizes the wave functions. The  $x$  is the displacement of the configuration coordinate from equilibrium. The optical cross-



### Configuration coordinate diagrams

Configuration coordinate diagrams help visualize how the energy of states changes as a function of the vibrational excitation. The diagram shown below depicts the potential energy of the bottom two electronic states, E<sub>1</sub> and E<sub>0</sub>, as a function of the internuclear distance. The minimum is the equilibrium bond distance. E<sub>1</sub> has a lower bond energy so its minimum is displaced. Vibrational states form when the internuclear distance changes. They are quantized ( $v=0, 1, 2, \dots$ ) and are roughly equally spaced. The  $v''=0$  has the highest population at room temperature and has transitions to all the  $v'$  states. The  $v''=1$  and  $2$  have lower populations given by the Boltzmann distribution. Transitions between  $v''$  and  $v'$  occur much faster than changes in the nuclear coordinate so they appear vertically on this diagram (a

$v$	$H_v(x)$
<b>0</b>	1
<b>1</b>	$2x$
<b>2</b>	$4x^2 - 2$
<b>3</b>	$8x^3 - 12x$
<b>4</b>	$16x^4 - 48x^2 + 12$
<b>5</b>	$32x^5 - 160x^3 + 120x$

section for a transition between two vibronic states is proportional to the overlap of the two vibrational states is

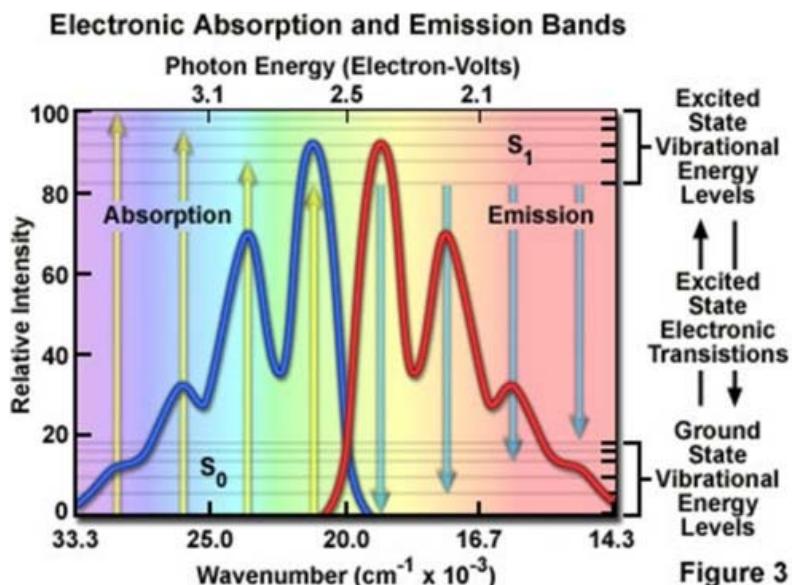
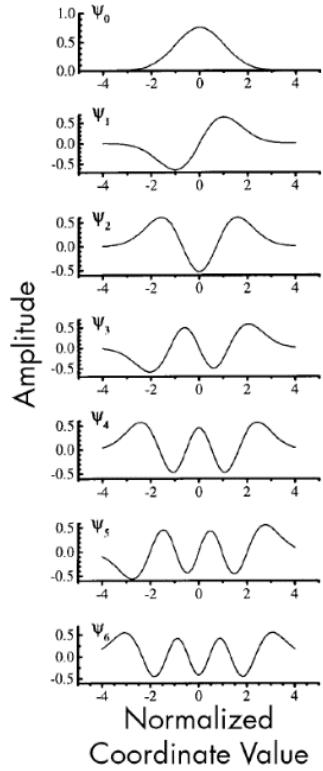
$$\sigma_{v'v''} = \frac{4\pi f_{v''}\omega\mu^2}{3hc} \left| \int_{-\infty}^{\infty} \psi_v \psi_{v''}^* d\tau \right|^2 \left( \frac{\Gamma}{(\omega_o - \omega)^2 + \Gamma^2} \right) \text{ where } v' \text{ and } v''$$

designate the vibrational state of the ground and excited electronic states, respectively,  $f_{v''}$  is the fraction of molecules in the ground state,  $\omega$  is the incident light frequency,  $\omega_o$  is the transition frequency,  $\mu$  is the electronic transition moment,  $c$  is the speed of light,  $\Gamma$  is the transition line width, and  $\psi$  is the vibrational wave function for vibrational state  $v$ . If there are multiple transitions, the cross sections for each are additive. The last factor describes the Lorentzian line shape of an absorption transition. For this work, it is important to recognize the middle factor as the integral that describes the overlap between the two vibrational states—that is, the probability that the molecular states have common coordinate values. The square of the integral is the Franck–Condon factor.  $\int H_i(x) \sum_v H_v(x) dx$  where  $H_i$  is

the initial vibrational mode and the  $H_v$  are the Hermite polynomials of the final vibrational mode that has been displaced. If it hasn't been displaced, the summation simplifies to a specific  $H_v$ .

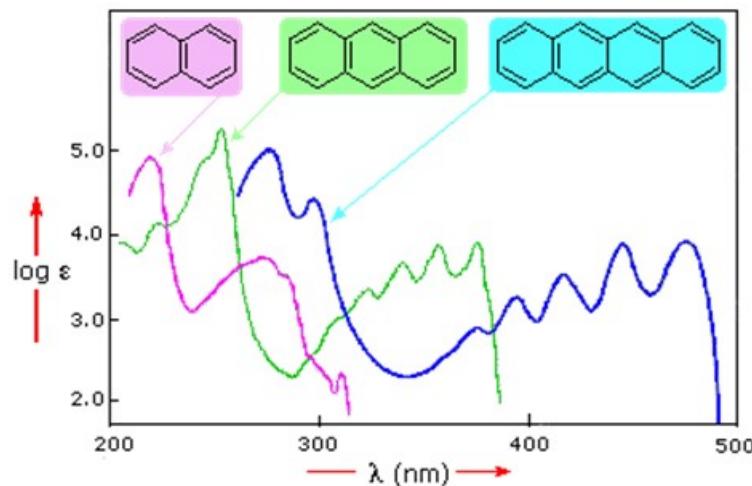
One can also have emission transitions between the electronic states. The  $v'=0$  state will have the highest population and the higher states will have exponentially lower populations (Maxwell-Boltzmann populations). The transitions from  $v'=0$  to  $v''=2$  will have lower frequencies than  $v''=0$  to  $v'=2$ . If the Franck-Condon factors are the same, the spectra absorption and emission spectra will have mirror symmetry.

The following figure shows these same characteristics for a fictional molecule. Note the mirror symmetry between the absorption and emission spectra. Also note the shift between the  $v''=0$  to  $v'=0$  peak and the  $v'=0$  to  $v''=0$  peak. The shift is caused by changes in the solvation shell of the molecule when the molecule's structure changes in the excited electronic state. It is called the Stokes shift. figure shows these same characteristics for a fictional molecule. Note the mirror symmetry between the absorption and emission spectra. Also note the shift between the  $v''=0$  to  $v'=0$  peak and the  $v'=0$  to  $v''=0$  peak. The shift is caused by changes in the solvation shell of the molecule when the molecule's structure changes in the excited electronic state. It is called the Stokes shift.



### Example UV-visible absorption and emission spectra\*

The following fluorescence spectra of naphthalene, anthracene, and tetracene illustrate the progression of vibronic states from ground state to the excited electronic state. The reddest transition is  $v''=0$  to  $v'=0$  and the bluer states go from  $v''=0$  to  $v'=1, 2, 3, 4$ , etc. Tetracene is the clearest example. It has the first electronic state at 480 nm and a second one at  $\sim 300$  nm. Notice how the absorption spectra shift to higher energies when the aromatic system becomes smaller.



Notice also that naphthalene's spectrum does not show the same behavior. Its electronic state is distorted relative to its ground state. The lower figure shows these same characteristics for a fictional molecule. Note the mirror symmetry between the absorption and emission spectra. Also note the shift between the  $v''=0$  to  $v'=0$  peak and the  $v'=0$  to  $v''=0$  peak. The shift is caused by changes in the solvation shell of the molecule when the molecule's structure changes in the excited electronic state. It is called the Stokes shift.

Spectra provide the most powerful way for extracting the energies of a molecule's quantum states since the transitions between states must have the same energies as the photons inducing the transitions. The simple relationship is  $E = h\nu$ . Spectroscopists however use many different units for energy that can refer to the actual energies or to the photons. The actual energies are ergs or joules but it is common in materials science to use electron volts- 1 electron volt or  $eV$  is  $1.6 \times 10^{-19}$  joules, the energy of an electron in a 1 volt potential. Light is characterized by wavelength ( $\lambda$ ), frequency ( $\nu$ ), and speed ( $c = 3 \times 10^{10}$  cm/sec). These quantities are related by

$c = \nu\lambda$ . In addition, light has a period ( $T = \frac{1}{\nu}$ ), angular frequency ( $\omega = 2\pi\nu$ ), wavenumber ( $\bar{\nu} = \frac{1}{\lambda}$  in  $\text{cm}^{-1}$ ), wave-vector ( $\vec{k} \equiv \frac{2\pi}{\lambda} = 2\pi\bar{\nu}$ ), and energy ( $E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$ ). Also note

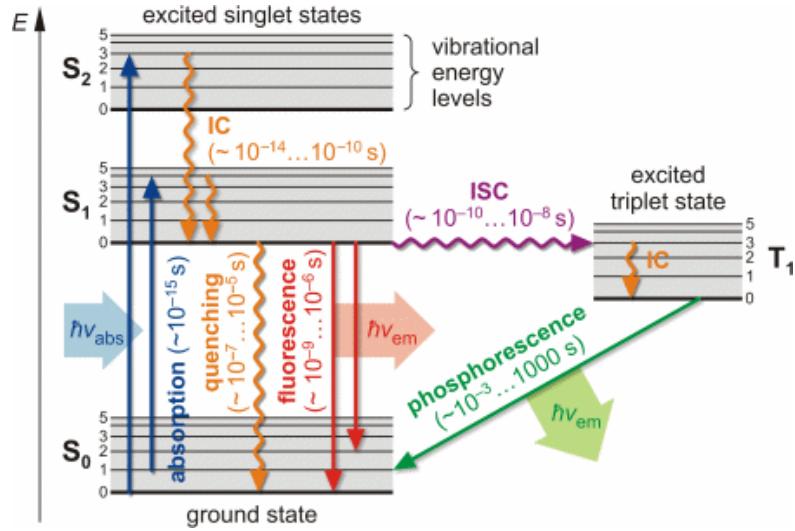
that  $\nu = \bar{\nu}c$ . You will use these relationships often. Spectroscopy often uses  $\bar{\nu}$  as an energy unit (eg. 500 nm is  $20,000 \text{ cm}^{-1}$ ). There are  $\frac{hc}{e} = 8065.73 \frac{\text{cm}^{-1}}{\text{eV}}$ .

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\*A good reference is the web site <http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/UV-Vis/spectrum.htm#uv1>

## Dynamics

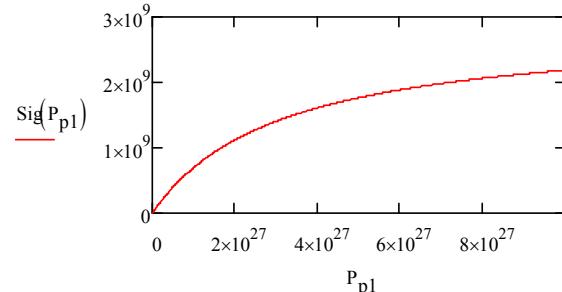
- **Relaxation processes-** vibrational relaxation ( $\sim 10^{12} \text{ sec}^{-1}$ ), radiative decay ( $\sim 10^8 \text{ sec}^{-1}$  for fluorescence and  $10^{-3}\text{-}10^3 \text{ sec}^{-1}$  for phosphorescence), internal conversion (IC,  $\sim 10^4\text{-}10^{14} \text{ sec}^{-1}$ ), intersystem crossing (ISC $\sim 10^6\text{-}10^{10} \text{ sec}^{-1}$ ), absorption and stimulated emission (rates depend on excitation intensity).
- **Rate equations-** photonic transitions, intramolecular relaxation, intermolecular relaxation. Each is defined by a rate constant. For transitions between levels m and n, we define the rate constant  $w_{mn}$ . We will write any radiative rate as  $w_{rad}$ .
- The total relaxation rate of a level is the inverse of its lifetime. Let's consider a system that has 3 energy levels, a ground state, an excited electronic state, and a state in between that can either be a vibrational state or a triplet state. Then,  $\tau_2^{-1} = w_{21} + w_{20}$  and  $\tau_1^{-1} = w_{10}$ .
- Let's next assume that we have  $n_p$  photons  $\text{sec}^{-1} \text{ cm}^{-2}$  impinging on the system and that the absorption coefficient at the frequency of the photons is  $\sigma$ . Then the rate of absorption and stimulated emission will be  $\sigma n_p$ . We can now write rate equations that describe the rate of change of the state populations as follows (the dot above the  $N$  indicates a time derivative)
  - $\dot{N}_0 = -\sigma n_p (N_0 - N_2) + w_{10} N_1$  (1)
  - $\dot{N}_1 = -\tau_1^{-1} N_1 + w_{21} N_2$  (2)
  - $\dot{N}_2 = -\tau_2^{-1} N_2 + \sigma n_p (N_0 - N_2)$  (3)
  - These equations are actually over-determined, i.e. they are not independent since one of them can be derived from the other three. We need one more equation (population conservation) to constrain the populations-  $N_{Total} = N_0 + N_1 + N_2$
  - in the steady state approximation where  $\dot{N} = 0$ ,
    - From the eqn. 3,  $N_2 = \frac{\sigma n_p N_0}{(\tau_2^{-1} + \sigma n_p)}$  (4)
    - Can now write the *fluor intensity* =  $h\nu w_{rad} N_2 = \frac{h\nu w_{rad} \sigma n_p N_0}{(\sigma n_p + \tau_2^{-1})}$  (5)
    - From eqns. 2 and 4, find  $N_1 = \frac{w_{21} \sigma n_p N_0}{\tau_1^{-1} (\tau_2^{-1} + \sigma n_p)}$  (5)



- Low light limit  $\text{fluor intensity} = \frac{h\nu w_{rad} \sigma n_p N_0}{\tau_2^{-1}} = h\nu \eta \sigma n_p N_0$  where  $\eta$  is the fluorescence quantum efficiency, the fraction of the total relaxation rate from level 2 that is fluorescence.
- Note that for high light intensities,  $N_2=N_0$  (condition for saturation). If level 1 relaxes very quickly to the ground state (vibrational levels will often do exactly that), then level 1 has negligible population and  $N_{Total} \approx N_0 + N_2$ . Now, we can get a simple expression for the fluorescence intensity if we substitute the population conservation condition into equation (1) & solve for  $N_2$ .

$$N_2 = \frac{\sigma n_p N_{Total}}{(\tau_2^{-1} + 2\sigma n_p)}$$

This equation shows how the fluorescence saturates for high excitation intensities ( $n_p \gg \tau_2^{-1}$ ).

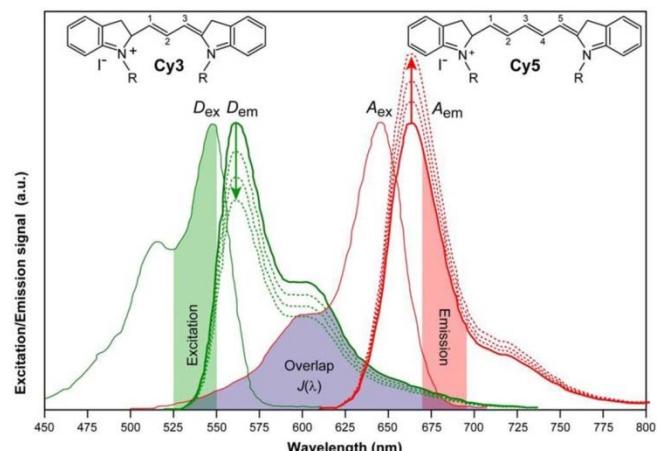


- **FRET- Forster Resonant Energy Transfer-** Energy transfer can also occur between molecules or chromophores within a molecule. It usually occurs through coupling between the transition dipole moments of the pair. Dipole-dipole coupling depends inversely on the 6<sup>th</sup> power of the distance between the pair and directly as the amount of overlap between the absorption and fluorescence spectra. The efficiency of energy transfer depends on the distance between the two molecules exchanging energy, r.

$$E = \frac{1}{1 + \left( \frac{r}{R_o} \right)^6}$$

$R_o$  is the Forster distance where the efficiency becomes 50%.  $\kappa$  describes the orientational dependence of the dipole coupling. They are given by the equations

$$R_o^6 = \frac{0.9 \ln 10}{128\pi^5 N_A} \frac{\kappa^2 Q_D}{n^4} \int f_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda \quad \text{and} \quad \kappa = \vec{\mu}_A \cdot \vec{\mu}_B - 3(\vec{\mu}_A \cdot \vec{R})(\vec{\mu}_B \cdot \vec{R})$$



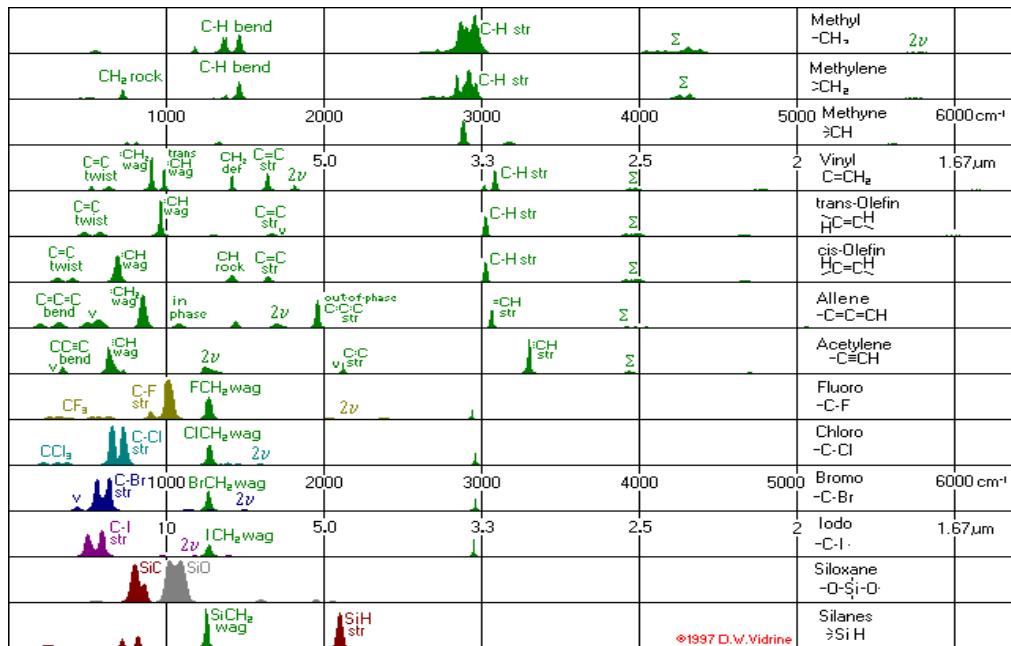
where  $N_A$  and  $\epsilon_A$  are the acceptor concentration and molar absorptivity,  $f_D(\lambda)$  and  $Q_D$  are the normalized donor fluorescence spectrum and quantum efficiency,  $n$  is the refractive index,  $\mu$  is the dipole moment of the donor and acceptor, and  $R$  is the vector between them. The diagram shows the spectra of Cy3 and Cy5 fluorescence labels that are commonly used for measuring distances between biologically active sites on a molecule.

## Vibrational Spectroscopy

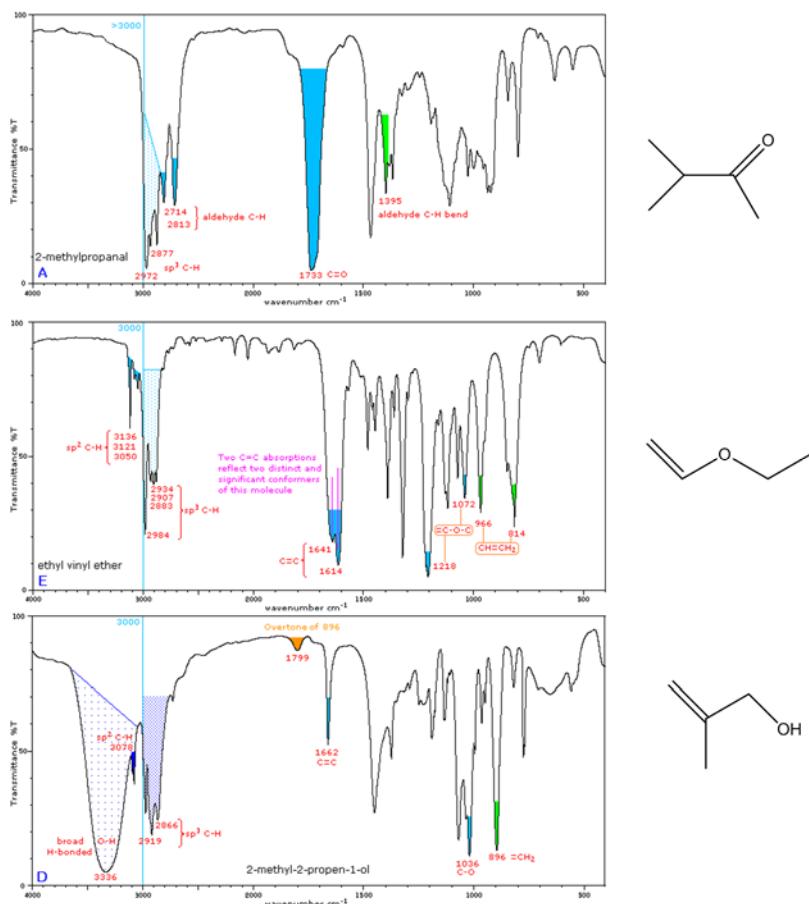
- **Number of modes for a molecule-**  $3N-6$  modes for a  $N$ -atom molecule or  $3N-5$  for linear molecule- modes include stretches, bends, wags, torsions
- **Symmetry selection rules-** change in dipole moment required to observe IR absorption (eg. asymmetric vibrations) and change in polarizability to observe Raman transitions (eg. symmetric vibrations).
- **Energy of a mode-** Quantum mechanically, the amplitude of a vibration is quantized. For a given mode, there are a series of energy states that depend on the quantized amplitude for the vibration-  $E = (\nu + 1/2)hv$  where  $\nu = 0, 1, \dots$  is the vibrational quantum number.
- **Selection rule for transitions between two  $\nu$  quantum numbers-**  $\Delta\nu = \pm 1$  for fundamental modes. Combination bands and overtones involve larger changes and are much weaker.
- **Vibrational Frequencies-**  $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$  where  $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$  for a diatomic molecule- table below assumes  $\nu \sim \sqrt{\frac{k}{\mu}}$ ,  $k$  ~ number of bonds, and the reduced mass,  $\mu$ , can be represented by a diatomic (not particularly good approximations)

Stretch Mode	reduced mass	predicted freq. ( $\text{cm}^{-1}$ )	observed freq. ( $\text{cm}^{-1}$ )
C-H	0.92	assume 3,000	2900-3100
C-C	6	1174	900-1100
C=C	6	1661	1550-1650
C≡C	6	2034	2120
C=O	6.86	1553	1600-1700
C-N	6.46	1132	1250
C-O	6.86	1098	1250
O-H	0.94	2967	3400-3600
N-H	0.93	2983	3300-3500

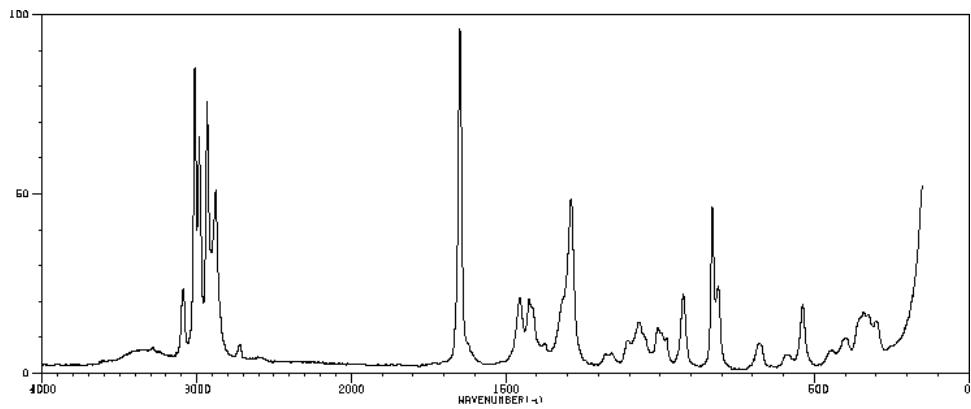
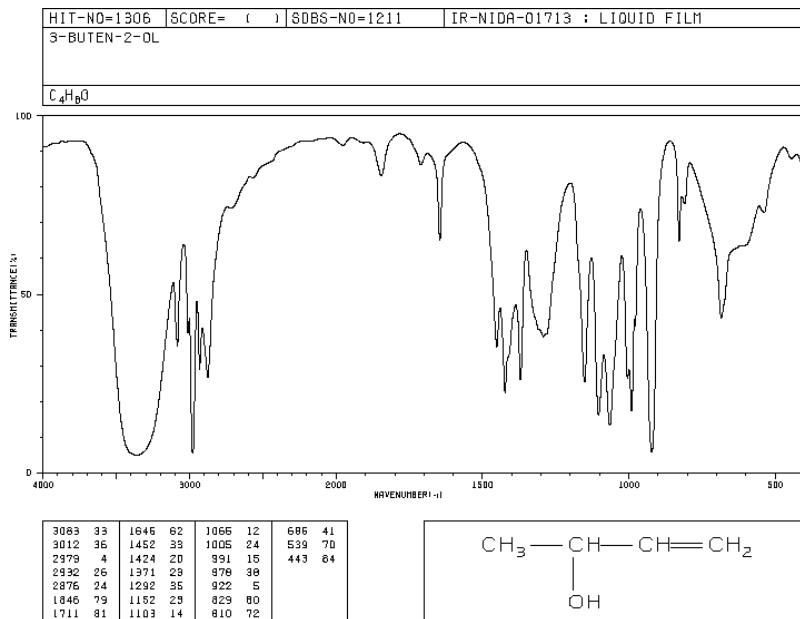
- Correlation diagrams**- divided into 3 regions - stretch region ( $2000\text{-}3600\text{ cm}^{-1}$ ), finger-print region ( $300\text{-}2000\text{ cm}^{-1}$ ), Far IR ( $40\text{-}300\text{ cm}^{-1}$ ) (Thz spectroscopy)



- Three example spectra of  $\text{C}_4\text{H}_8\text{O}$  isomers along with vibrational assignments. Data from <http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/InfraRed/infrared.htm>



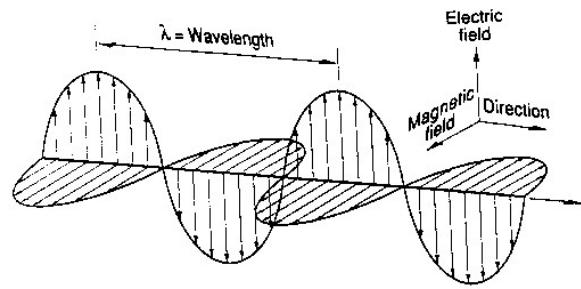
## I Raman and IR Spectroscopy comparison example



3-BUTEN-2-OL      SDBSNO = 1211       $C_4H_6O$       RM-01-00987 : 4880A.200H.LIQUID

3015	86	813	24
2987	86	540	18
2934	75		
2879	51		
1649	95		
1466	21		
1426	20		
1289	48		
927	22		
833	46		

**Light-** Light is an oscillating electric field that carries an orthogonal magnetic field. The light's polarization is defined by the direction of the electric field. When light interacts with matter, the electric field induces a polarization (notice the two different uses of the word polarization) in the material. All of optical spectroscopy is based upon these polarizations and we will need to understand these polarizations to understand all optical spectroscopies. We will not treat cases where the magnetic field interacts with a magnetic dipole moment. This case is important for NMR spectroscopy and follows very similar ideas.



Light is a wave that has a spatial and temporal behavior. We will describe it in two ways:

$$E = \vec{\sigma} E^o \cos(\vec{k} \cdot \vec{z} - \omega t) \quad (1)$$

which is real or

$$E = \vec{\sigma} E^o e^{i(\vec{k} \cdot \vec{z} - \omega t)} \quad (2)$$

which is complex but does contain both the sine and cosine information. The  $\vec{\sigma}$  vector is called the Jones vector and it describes the polarization of the light in the x-y plane. By convention, the Jones vectors for vertical, horizontal, right circular, and left circular polarizations are:

$\sigma = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ ,  $\begin{pmatrix} 1 \\ 0 \end{pmatrix}$ ,  $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix}$ , and  $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix}$ , respectively. The imaginary  $i$  in the equations denotes the  $\pi/2$  phase shift between the horizontal and vertical electromagnetic fields. The  $k$  vector is defined as  $\vec{k} \equiv \frac{2\pi}{\lambda} \hat{z}$  and is the wave vector describing the wavelength and propagation in the  $z$

direction ( $\text{cm}^{-1}$ ).  $\omega$  is the angular frequency (radians/sec). Note the form of eqn. (2) has important implications. When  $z$  increases with  $t$  constant, the function will describe a complete cycle of  $2\pi$  when  $z$  changes by  $\lambda$ . When  $t$  increases with  $z$  constant, the function will describe a

complete cycle of  $2\pi$  when  $t$  changes by  $\frac{2\pi}{\omega} = \frac{1}{\nu}$  or one period. If  $(kz - \omega t)$  is a constant (i.e. the phase of the electric field is constant), then  $z$  will advance by  $\lambda$  when  $t$  advances by one period,  $T = \frac{1}{\nu}$ , so the velocity of constant phase is  $\frac{\Delta z}{\Delta t} = c = \lambda \nu$ .

When light is quantized, the quantization introduces an uncertainty in the amplitude and phase of the wave such that the product is  $\frac{1}{2}$ . A quantized wave is described by the number of photons in a mode and the phase of the wave. The uncertainty product is  $\Delta n \Delta \phi = 1/2$ . If light is in a single mode number state where the number of photons is exactly  $n$ , then there is infinite uncertainty in the phase. If light is in a coherent photon state where the phase is exactly known, the number of photons in that mode is infinite. The latter is a state that can't be reached. More commonly, if light is in a single mode coherent state, there is uncertainty in both the phase and photon number. For states with  $n \gg 1$  photons on average, the uncertainty in the number is  $\sqrt{n}$  and the minimum phase uncertainty is  $1/2\sqrt{n}$ .

The intensity of light is related to the cycle averaged value of the electric field. Using the definitions given by equations (1) and (2), the intensity is related to the electric field by the equations

$$I = \frac{cn_{\text{index}}\xi}{8\pi} E^o{}^2 \text{ (cgs units) and} \quad (3)$$

$$I = \frac{c\varepsilon_o n_{\text{index}}\xi}{2\eta} E^o{}^2 = \frac{n_{\text{index}}\xi}{2\eta} E^o{}^2 = 1.33 \times 10^{-3} n_{\text{index}}\xi E^o{}^2 \text{ (mks units)} \quad (4)$$

where  $\varepsilon_o$  is the permittivity of free space,  $\eta = \sqrt{\frac{\mu_o}{\varepsilon_o}}$  is the impedance of the vacuum, and  $\mu_o$  is the magnetic permeability of free space. They relate the electric and magnetic field magnitudes and define the speed of light:  $E^o = cB^o$  and  $c = \frac{1}{\sqrt{\varepsilon_o\mu_o}}$ . Some authors define the electric field as  $E = E^o e^{i(kz - \omega t)} + c.c.$ . With that convention, eqns. 3 and 4 will be multiplied by 4.

## Time dependence of Quantum Mechanical Wave Functions

Quantum mechanics is based on the idea that everything is a wave that is described by a wave function that is complex. The real and imaginary parts of the wave function oscillate between each other. These oscillations are hidden from us for reasons we don't understand but the magnitude of the wave function is a quantity that we can measure. If there is no time dependent perturbation, the time dependent Schrodinger equation states

$$\frac{\delta\Psi(x,t)}{\delta t} = -\frac{i}{\hbar} H_o \Psi(x,t).$$

where  $H_o$  is a time independent differential equation. Note that the equation states that the rate of change of the real part of the wave function is proportional to the imaginary part of the wave function and vice versa. That means the real and imaginary parts oscillate sinusoidally at the frequency defined by

$$\frac{H_o\Psi}{\hbar} = \frac{E_o\Psi}{\hbar} = \omega_o$$

where  $\Psi$  is an eigenfunction of  $H_o$ . So we now know the time dependence of the wave function,  $\Psi(x,t) = \psi(x)e^{-i\omega_o t}$ . It is a frequency that we cannot measure directly because we can only measure the magnitude. The magnitude is given by  $|\Psi|^2 = \psi e^{-i\omega_o t} \psi^* e^{i\omega_o t} = \psi \psi^*$  which has no time dependence. So unfortunately, we are not allowed to look directly at the real and imaginary parts of the wave function.

Next we find the spatial dependence of  $\Psi$  by solving the Schrodinger time independent equation,

$$H_o\psi(x) = E\psi(x).$$

The solution is an infinite number of wave functions like the hydrogenic wave functions that describe the atomic and molecular orbitals' spatial dependence of each wave function. We will write these wave functions as  $\psi_n(x)$ .

Spectroscopy is based on perturbing wave functions using light, i.e. an electric field that oscillates. The Schrodinger equation then becomes

$$\frac{\partial \Psi(x,t)}{\partial t} = -\frac{i}{\hbar} (H_o + V(t)) \Psi(x,t)$$

$$\text{where } V(t) = -\vec{\mu} \cdot \vec{E} = -\vec{\mu} \cdot \vec{\sigma} \frac{E^o}{2} \left( e^{i(\vec{k} \cdot \vec{z} - \omega_o t)} + e^{-i(\vec{k} \cdot \vec{z} - \omega_o t)} \right). \quad (5)$$

Notice that the electric field has an amplitude,  $E^o$ , and frequency and  $k$ -vector describing the spatial and temporal oscillations, and the overall form is a cosine wave. The  $\vec{\mu}$  is the dipole moment associated with the two states that are coupled by the electromagnetic field. It is called the **transition dipole**. The perturbation causes the wave function to change in time, i.e. the wave function must now oscillate. Quantum mechanically, that means that the perturbed wave function is a time dependent mixture of  $\psi_n$  states called a superposition state.

### Coherences- Quantum Mechanical Superposition States

Before discovering how the superposition state is formed, let's look at its properties. If the system contains just two states, the superposition state becomes

$$\Psi(x,t) = a\psi_a(x)e^{-i\omega_o t} + b\psi_b(x)e^{-i\omega_b t}. \text{ The magnitude of the superposition state is}$$

$$\begin{aligned} \Psi\Psi^* &= (a\psi_a e^{-i\omega_o t} + b\psi_b e^{-i\omega_b t})(a^*\psi_a^* e^{i\omega_o t} + b^*\psi_b^* e^{i\omega_b t}) \\ &= aa^*\psi_a\psi_a^* + bb^*\psi_b\psi_b^* + ba^*\psi_b\psi_a^* e^{-i\omega_{bo}t} + ab^*\psi_a\psi_b^* e^{i\omega_{bo}t} \end{aligned}$$

The superposition state oscillates in time at the frequency difference between the two states. We call the superposition state a quantum mechanical coherence because there is a well-defined phase relationship between the two states. This oscillation can be directly measured. Coherences form the heart of all spectroscopy because they are the first result of light interacting with matter.

The next step is to see quantitatively how coherences are formed when light perturbs a stationary state. If we start in state  $\psi_a$  and apply a perturbation, the perturbation will mix in other states like  $\psi_b$ . To simplify our work, let us consider a two state system with wave functions  $\psi_a$ , and  $\psi_b$  that depend only on the spatial coordinates,  $\psi_a(x)$ ,  $\psi_b(x)$ . Then,  $c_a$  and  $c_b$  now carry the **entire** time dependence including the Bohr frequency dependence. So we can write

$$\psi = c_a \psi_a + c_b \psi_b \quad (6)$$

We assume a Hamiltonian,  $H$ , that has a time independent part,  $H_o$ , and a time dependent part,  $V$ , such that

$$H = H_o + V, \text{ where} \quad (7)$$

$$H_o \psi_a = E_a \psi_a \text{ (time independent Schrödinger equation), and} \quad (8)$$

The evolution of the system's wave function is defined by the time dependent Schrödinger equation:

$$\frac{\partial \psi}{\partial t} = \dot{\psi} = -\frac{i}{\hbar} H \psi \quad (9)$$

To keep our treatment simple, we will assume the transition moment,  $\vec{\mu}$ , is aligned with the electric field,  $\vec{E}$ . In reality, one would need to perform the ensemble average over all relative orientations of the molecules and the exciting field. We are also going to ignore the spatial part of the electric field,  $e^{i\vec{k} \cdot \vec{z}}$ , since the time dependent Schrödinger equation is primarily connected with the temporal dynamics. We will add it in later to the temporal part to make  $e^{i(\vec{k} \cdot \vec{z} - \omega t)}$ .

Notice the important relationship between the rate of change in  $\psi$  and  $\psi$  itself. For example, the real part of the rate of change depends on the imaginary part of  $H\psi$  and vice-versa. Since  $H\psi$  is  $\sim E\psi$ , the real and imaginary parts of  $\psi$  feed each other at the Bohr frequency. The Bohr frequency for state  $a$  will be  $\omega_{ag} = E/\hbar$  relative to the ground state,  $g$ . The Bohr frequency is the frequency at which the system oscillates. If a transition occurs between states  $a$  and  $b$ , the Bohr frequency is then the difference between the frequencies of the two states,  $\omega_{ba}$ . More quantitatively, we substitute (6) into (9) and find

$$\frac{\partial}{\partial t}(c_a\psi_a + c_b\psi_b) = -\frac{i}{\hbar}(H_o + V)(c_a\psi_a + c_b\psi_b) \quad (10)$$

$$(\dot{c}_a\psi_a + \dot{c}_b\psi_b) = -\frac{i}{\hbar}(E_a c_a\psi_a + E_b c_b\psi_b) - \frac{i}{\hbar}(c_a V\psi_a + c_b V\psi_b)^\dagger \quad (11)$$

The wave functions are found in the usual way from the time independent Schoedinger equation. We will concentrate on finding the  $c$  coefficients that control the temporal dependence. To find the  $c$  coefficients, multiply both sides by  $\psi_a^*$  and integrate over all space

$$\dot{c}_a = -\frac{i}{\hbar}c_a E_a - \frac{i}{\hbar}(c_a V_{aa} + c_b V_{ab}) \quad (12)$$

where the expectation value for the perturbation is  $V_{ab} = \int \psi_a^* V \psi_b d\tau$  and

$V_{aa} = \int \psi_a^* V \psi_a d\tau = -\bar{E} \int \psi_a^* \vec{\mu} \psi_a d\tau = 0$  by symmetry. The product of the wave functions creates a symmetric function and together with the antisymmetric vector, the integral becomes zero. Therefore, we must have

$$\dot{c}_a = -i\omega_{ag}c_a - \frac{i}{\hbar}V_{ab}c_b \quad (13)$$

Similarly,

$$\dot{c}_b = -i\omega_{bg}c_b - \frac{i}{\hbar}V_{ba}c_a \quad (14)$$

and

$$\dot{c}_a^* = i\omega_{ag}c_a^* + \frac{i}{\hbar}V_{ab}c_b^* \quad (15)$$

$$\dot{c}_b^* = i\omega_{bg}c_b^* + \frac{i}{\hbar}V_{ba}c_a^* \quad (16)$$

### Dissipation Dynamics, Dephasing, Population Relaxation

Optical nutation is rarely seen in experiments because the quantum system is never isolated for a long enough time period and interactions of the surroundings destroy the phase relationships between the light and the quantum system so one rarely proceeds very far into a Rabi cycle. This process of destroying the phase information is called **decoherence** or **dephasing**.

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<sup>†</sup> Note, we defined the  $c$  coefficients as containing the entire time dependence so we just differentiate the  $c_{a,b}$ 's.

In order to treat the dephasing and relaxation effects, one must phenomenologically add an exponential decay rate,  $\Gamma$ , to the time-dependent terms in (13)-(16). (More rigorous treatments define the decay with Redfield theory, which explicitly treats the effects of chaotic thermal fields of the bath.)

$$\dot{c}_a = -i\omega_{ag}c_a - \frac{i}{\hbar}V_{ab}c_b - \Gamma_a c_a \quad (17)$$

$$\dot{c}_b = -i\omega_{bg}c_b - \frac{i}{\hbar}V_{ba}c_a - \Gamma_b c_b \quad (18)$$

$$\dot{c}_a^* = i\omega_{ag}c_a^* + \frac{i}{\hbar}V_{ab}c_b^* - \Gamma_a c_a^* \quad (19)$$

$$\dot{c}_b^* = i\omega_{bg}c_b^* + \frac{i}{\hbar}V_{ba}c_a^* - \Gamma_b c_b^* \quad (20)$$

With this change, the amplitudes decay exponentially so if V is zero, then  $c_a = \exp(-i\omega_{ag}t)^*\exp(-\Gamma_a t)$ . Note also that the  $\omega$ 's have units of radians/sec. and the  $\Gamma$ 's are rate constants with units of 1/sec. The equations do not include terms that define the states that gain amplitude because of the loss defined by the  $\Gamma$  rate constant. Thus, the loss does not conserve the total population from all states but it does describe population decay.

It is also interesting to note that the feeding of one population involves interactions with the amplitude and its complex conjugate. The imaginary part of one amplitude feeds the real part of the other. The same is true for the complex conjugates of the feeding and receiving amplitudes but they have the opposite signs. The consequence of these two changes is that only the imaginary part of an amplitude is responsible for feeding a population. For example, the changes in  $c_b$  depend on  $c_a$  equation 26 and 28. The changes in the real part of  $c_b$  caused by each equation cancel each other so only the imaginary part ends up changing  $c_b$ . This behavior is identical to the simple harmonic oscillator where the driving force and the response are out of phase by 90°.

There are two interesting cases for these equations, free induction decay and the steady state limit. Both involving solving equation (18). Free induction decay is the most important limit for ultrafast spectroscopy when the laser excitation is so fast relative to the dephasing rate that it can be considered a delta function. The steady state is the most important limit when the light source is on for a much longer time than the dephasing time.

## Density Matrices

There is a problem with using the amplitude of a state to describe spectroscopic problems because we need to know the amplitudes and phases between states involved in spectroscopic transitions. For this reason, we need to define density matrices because density matrices contain both the amplitude and the quantum mechanical phases. To describe a superposition state,

$\Psi(x,t) = a\psi_a(x)e^{-i\omega_a t} + b\psi_b(x)e^{-i\omega_b t}$ , we define a density matrix element for this wave function as  $\rho_{ba} \equiv c_b c_a^*$ . Dirac introduced bra-ket notation as a quantum mechanical shorthand for integrals so  $\int \psi_a^* V \psi_b d\tau$  could be abbreviated as  $\langle \psi_a | V | \psi_b \rangle$  in his bracket notation. So the  $\langle \psi_a |$  is the bra and  $| \psi_b \rangle$  is the ket. The quantum mechanical phase is contained in the relative size of the real and imaginary parts. Density matrices allow us to define not only how a state can decay in time with a rate constant given by  $\Gamma$ , we can also incorporate pure dephasing. Pure dephasing occurs when the environment causes stochastic changes in the state frequency and phase

relationship to the electromagnetic fields but it doesn't create a loss of state amplitude. This frequency modulation destroys the temporal phase relationship and interference effects change evolution of any state. Since the process is stochastic, it must be modeled by performing an ensemble average over a large number of different stochastic trajectories. Density matrices provide a cleaner way to treat environmental effects that change the relative phase of different states because they consider the relationships between state amplitudes. In addition, experimental observations do not measure the  $c$  coefficients directly. They measure populations given by  $c_a c_a^*$  and  $c_b c_b^*$  and transition dipole moments that are proportional to the coherences given by  $c_a c_b^*$  and  $c_b c_a^*$ . For these reasons, it is important to define density matrices that contain not only the amplitude of a state but also the phase of that state relative to other states. The phase is encoded by making the coefficients complex so the relative size of the real and imaginary parts define the quantum mechanical phase. For a two state system of  $a$  and  $b$ , we define a 2x2 matrix with the 4 elements

$$\rho_{ba} = c_b c_a^* \quad \rho_{aa} = c_a c_a^* \quad \rho_{bb} = c_b c_b^* \quad \rho_{ab} = c_a c_b^* \quad (21)$$

In order to provide the most general description of spectroscopy, we will consider how an electromagnetic field will induce transitions between two superposition states, an initial one,  $\Psi = c_k \psi_k + c_l \psi_l$ , and a final one,  $\Psi' = c_i \psi_i + c_j \psi_j$ . The density matrices for these two superposition states are  $\rho_{kl}$  and  $\rho_{ij}$ . The transitions we will consider are  $\psi_k \rightarrow \psi_i$  or  $\psi_l \rightarrow \psi_j$ . We first rewrite our equations relating the amplitudes for being in a particular state:

$$\dot{c}_i = -i\omega_i c_i - \frac{i}{\hbar} V_{ik} c_k - \Gamma_i c_i \quad (22)$$

$$\dot{c}_j = -i\omega_j c_j - \frac{i}{\hbar} V_{jl} c_l - \Gamma_j c_j \text{ or its complex conjugate} \quad (23)$$

$$\dot{c}_j^* = i\omega_j c_j^* + \frac{i}{\hbar} V_{jl} c_l^* - \Gamma_j c_j^* \quad (24)$$

We also rewrite the temporal evolution of the density matrix, equation:

$$\dot{\rho}_{ij} = \dot{c}_i c_j^* + c_i \dot{c}_j \quad (25)$$

and we substitute

$$\dot{\rho}_{ij} = \left( -i\omega_i c_i - \frac{i}{\hbar} V_{ik} c_k - \Gamma_i c_i \right) c_j^* + c_i \left( i\omega_j c_j^* + \frac{i}{\hbar} V_{jl} c_l^* - \Gamma_j c_j^* \right) \quad (26)$$

and simplify,

$$\dot{\rho}_{ij} = -i\omega_i \rho_{ij} - \frac{i}{\hbar} V_{ik} \rho_{kj} + i\omega_j \rho_{ij} + \frac{i}{\hbar} V_{jl} \rho_{il} - \Gamma_{ij} \rho_{ij} \quad (27)$$

Defining  $\omega_{ij} \equiv \omega_i - \omega_j$  and  $\Gamma_{ij} \equiv \Gamma_i + \Gamma_j$ , this becomes:

$$\dot{\rho}_{ij} = -i\omega_{ij} \rho_{ij} - \frac{i}{\hbar} (V_{ik} \rho_{kj} - V_{jl} \rho_{il}) - \Gamma_{ij} \rho_{ij} \quad (28)$$

The next step is writing the actual expression for the electromagnetic perturbation,  $V$ . The equation now becomes

$$\dot{\rho}_{ij} = -i\delta_{ij} \rho_{ij} + \frac{i}{2} (e^{-i\omega t} + e^{i\omega t}) (\Omega_{ik} \rho_{kj} - \Omega_{jk} \rho_{ik}) \quad (29)$$

where  $\delta_{ij} = \omega_{ij} - i\Gamma_{ij}$ . This equation is general because it describes how a transition on the bra or ket transition of an initial wave function can create a new wave function. Now we just need to know how to solve it.

### The Rotating Wave Approximation

It is most common to numerically integrate this expression. The problem arises that the frequencies like  $\omega$  or  $\omega_{ij}$  are very high so the integration requires a large number of small steps in time. Computationally, that is a problem. To solve the problem, we make the rotating wave approximation. If it is not, one simply uses the equation given above. Let  $\rho_{ij} = \tilde{\rho}_{ij}e^{-i\omega_{RW}t}$  (The actual choice doesn't make a lot of difference. Good choices might be  $\omega_{RW} \sim \omega_{ij}$  or  $\omega$  or the center of an inhomogeneous distribution,  $\omega_j^0$ ). This transformation into the rotating frame makes numerical integration of the equations easier since rapidly oscillating terms require very small time increments. Then,

$$\dot{\tilde{\rho}}_{ij}e^{-i\omega_{RW}t} - i\omega_{RW}\tilde{\rho}_{ij}e^{-i\omega_{RW}t} = -i\delta_{ij}\tilde{\rho}_{ij}e^{-i\omega_{RW}t} + \frac{i}{2}(e^{-i\omega t} + e^{i\omega t})(\Omega_{ik}\rho_{kj} - \Omega_{jk}\rho_{ik}) \quad (30)$$

**Note that the frequencies for the kj and ik coherences can be either the free induction decay frequency and/or the driven frequency.** We are going to assume the initial coherences are oscillating at their free induction decay frequencies and that they are not themselves being driven by laser fields. If they are being driven, then the  $\omega_{kj}$  and  $\omega_{ik}$  frequencies should be chosen to be the laser excitation frequencies.

$$\dot{\tilde{\rho}}_{ij} = i\omega_{RW}\tilde{\rho}_{ij} - i\delta_{ij}\tilde{\rho}_{ij} + \frac{i}{2}(e^{-i(\omega-\omega_{RW})t} + e^{i(\omega+\omega_{RW})t})(\Omega_{ik}\tilde{\rho}_{kj}e^{-i\omega_{kj}t} - \Omega_{jk}\tilde{\rho}_{ik}e^{-i\omega_{ik}t}) \quad (31)$$

The rotating wave approximation neglects one of the two terms oscillating at  $(\omega - \omega_{RW})$  or  $(\omega + \omega_{RW})$  because it will average to zero in comparison with the term that has a similar frequency to either  $\rho_{kj}$  or  $\rho_{ik}$ . Then, the net phase associated with the exponentials will be  $e^{-i(\pm\omega-\omega_{ij})t-i\omega_{kj}t} = e^{-i(\pm\omega-\omega_{ik})t}$  or  $e^{-i(\pm\omega-\omega_{ij})t-i\omega_{ik}t} = e^{-i(\pm\omega-\omega_{kj})t}$  where  $\omega_{ik}$  or  $\omega_{kj}$  is the frequency of the transition initiated by  $\omega$ . One chooses the sign on  $\omega$  according to which makes the smallest exponent, ideally zero. Equation (10) can then be written:

$$\dot{\tilde{\rho}}_{ij} = i(\omega_{RW} - \delta_{ij})\tilde{\rho}_{ij} + \frac{i}{2}(\Omega_{ik}\tilde{\rho}_{kj}e^{-i(\pm\omega-\omega_{RW}+\omega_{kj})t} - \Omega_{jk}\tilde{\rho}_{ik}e^{-i(\pm\omega-\omega_{RW}+\omega_{ik})t}) \quad (32)$$

### This is the equation we want! It can describe all of spectroscopy!

We will actually use only one of the terms in this equation. In order to have the slowest rate of change for  $\tilde{\rho}_{ij}$ , we want  $\omega_{RW} = \pm\omega + \omega_{kj}$  for the ket side transition or  $\omega_{RW} = \pm\omega + \omega_{ik}$  for the bra side transition. (As an example, a common choice for  $\omega_{RW}$  is to have the excitation frequency,  $\omega$ , resonant with the  $k \rightarrow i$  or  $k \rightarrow j$  transitions. Then,  $\omega_{RW} = \omega_{ij}$ .)

There are two cases to consider for the evaluating the equation:

Ket side transition-  $\dot{\tilde{\rho}}_{ij} = i(\pm\omega + \omega_{kj} - \delta_{ij})\tilde{\rho}_{ij} + \frac{i\Omega_{ik}}{2}\tilde{\rho}_{kj}$  and  $\rho_{ij} = \tilde{\rho}_{ij}e^{-i(\pm\omega + \omega_{kj})t}$ . (12)

Bra side transition-  $\dot{\tilde{\rho}}_{ij} = i(\pm\omega + \omega_{ik} - \delta_{ij})\tilde{\rho}_{ij} - \frac{i\Omega_{jk}}{2}\tilde{\rho}_{ik}$  and  $\rho_{ij} = \tilde{\rho}_{ij}e^{-i(\pm\omega + \omega_{ik})t}$ .

These equations form the basis for a numerical integration to find the temporal dependence of the density matrix. The time dependence of the amplitude is typically defined by the time dependence of the electric field amplitude contained within the Rabi frequency,  $\Omega = \frac{\mu E^o(t)}{\hbar}$ .

It is also interesting to note that the equation for the bra side transition could be obtained by simply taking the complex conjugate of the ket side transition.

### Steady State Expressions

In the steady state, equations (12) become:

$$\tilde{\rho}_{ij} = -\frac{i\Omega_{ik}}{2i(\pm\omega + \omega_{kj} - \delta_{ij})}\tilde{\rho}_{kj} \quad \text{and} \quad \tilde{\rho}_{ij} = \frac{i\Omega_{jk}}{2i(\pm\omega + \omega_{ik} - \delta_{ij})}\tilde{\rho}_{ik}$$

which in turn become:

Ket side-  $\tilde{\rho}_{ij} = -\frac{i\Omega_{ik}}{2i(\pm\omega + \omega_{kj} - (\omega_{ij} - i\Gamma_{ij}))}\tilde{\rho}_{kj} = \frac{\Omega_{ik}}{2(\omega_{ik} \mp \omega - i\Gamma_{ij})}\tilde{\rho}_{kj}$

Bra side-  $\tilde{\rho}_{ij} = \frac{i\Omega_{jk}}{2i(\pm\omega + \omega_{ik} - (\omega_{ij} - i\Gamma_{ij}))}\tilde{\rho}_{ik} = -\frac{\Omega_{jk}}{2(\omega_{kj} \mp \omega - i\Gamma_{ij})}\tilde{\rho}_{ik}$

We have assumed that the initial coherence was not being driven but was undergoing free induction decay. If it was driven at some  $\omega_1$  frequency and now it is being driven at  $\omega_2$ , these equations become:

Ket side-  $\tilde{\rho}_{ij} = -\frac{i\Omega_{ik}}{2i(\pm\omega_2 \pm \omega_1 - (\omega_{ij} - i\Gamma_{ij}))}\tilde{\rho}_{kj} = \frac{\Omega_{ik}}{2(\omega_{ij} \mp \omega_1 \mp \omega_2 - i\Gamma_{ij})}\tilde{\rho}_{kj}$

Bra side-  $\tilde{\rho}_{ij} = \frac{i\Omega_{jk}}{2i(\pm\omega_2 \pm \omega_1 - (\omega_{ij} - i\Gamma_{ij}))}\tilde{\rho}_{ik} = -\frac{\Omega_{jk}}{2(\omega_{ij} \mp \omega_1 \mp \omega_2 - i\Gamma_{ij})}\tilde{\rho}_{ik}$

where the signs are defined by the resonance conditions for the initial and final coherences.

### Population Relaxation and Pure Dephasing

There are two ways for a superposition state to decay- losing amplitude and losing the phase between the two states. Losing phase is something that an ensemble of states will do since phase requires comparing two or more molecules. For a two state system, we know that  $\Gamma_{ba} = \Gamma_a + \Gamma_b$ ,

$\Gamma_{aa} = 2\Gamma_a$ , and  $\Gamma_{bb} = \Gamma_b + \Gamma_b$ . Therefore,  $\Gamma_{ba} = \frac{\Gamma_{aa} + \Gamma_{bb}}{2}$ .  $\Gamma_{aa}$  and  $\Gamma_{bb}$  are rates of loosing

population so  $\Gamma_{ba}$  is the rate that the ba coherence is lost because of population decay of states a and b. If we now add the dephasing rate onto it, we have a description of how the ba coherence

decays from loosing both population and phase,  $\Gamma_{ba} = \frac{\Gamma_{aa} + \Gamma_{bb}}{2} + \Gamma_{ba}^*$ . This expression is also

commonly written as  $\frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$  where  $T_2$  is the total dephasing time,  $T_1$  is the population decay time and  $T_2^*$  is the pure dephasing time.

### Generalized Liouville Equation

The equations for  $\dot{\rho}$  can be written in compressed form with the notation

$$\dot{\rho} = -\frac{i}{\hbar} [H, \rho] - \rho^R \quad (\text{Liouville equation}) \quad (33)$$

where  $\rho^R$  is a relaxation matrix. For our two level system, the variables are:

$$\rho = \begin{pmatrix} \rho_{aa} & \rho_{ba} \\ \rho_{ab} & \rho_{bb} \end{pmatrix} \quad (34)$$

$$H = \begin{pmatrix} H_{aa} & H_{ba} \\ H_{ab} & H_{bb} \end{pmatrix} \text{ and} \quad (35)$$

More explicitly, one sees after matrix multiplication:

$$\begin{pmatrix} \dot{\rho}_{aa} & \dot{\rho}_{ba} \\ \dot{\rho}_{ab} & \dot{\rho}_{bb} \end{pmatrix} = -\frac{i}{\hbar} \begin{pmatrix} H_{aa}\rho_{aa} + H_{ba}\rho_{ab} & H_{aa}\rho_{ba} + H_{ba}\rho_{bb} \\ H_{ab}\rho_{aa} + H_{bb}\rho_{ab} & H_{ab}\rho_{ba} + H_{bb}\rho_{bb} \end{pmatrix} + \frac{i}{\hbar} \begin{pmatrix} H_{aa}\rho_{aa} + H_{ab}\rho_{ba} & H_{ba}\rho_{aa} + H_{bb}\rho_{ba} \\ H_{aa}\rho_{ab} + H_{ab}\rho_{bb} & H_{ba}\rho_{ab} + H_{bb}\rho_{bb} \end{pmatrix} - \rho^R \quad (36)$$

This equation is equivalent to equations **Error! Reference source not found.**, **Error! Reference source not found.**, **Error! Reference source not found.**, and **Error! Reference source not found.**. Here,  $H_{aa}$  and  $H_{ba}$  are numbers from evaluating the matrix elements of the Hamiltonian with the indicated wave functions:  $H_{aa} = E_a$  and

$$H_{ba} = \frac{\mu_{ba} E^o}{2} (e^{i\omega t} + e^{-i\omega t}).$$

### Impulsive Limit of Liouville Equation- Two States

There are two limits where the Liouville equations are easily solved: the impulsive and steady state limits. We will do the impulsive limit first where we assume the electromagnetic field excitation is an instantaneous pulse occur at time  $t = \tau$ . It is written as  $\delta(t-\tau)$  and is infinite when the argument of the function is zero and zero at any other time. It is normalized so its integral is 1. The best approach is to obtain an exact differential that can be easily integrated. To do that, we multiply both sides of equation **Error! Reference source not found.** and rewriting the resulting equation to obtain

$$\dot{\rho}_{ba} e^{(i\omega_{ba} + \Gamma_{ab})t} + (i\omega_{ba} + \Gamma_{ab}) \rho_{ba} e^{(i\omega_{ba} + \Gamma_{ab})t} = (-i\delta(t - \tau)(\rho_{aa} - \rho_{bb})) e^{(i\omega_{ba} + \Gamma_{ab})t} \quad (37)$$

Now the left side is an exact differential as is easily seen by differentiating the following:

$$\frac{d\left(\rho_{ba}e^{(i\omega_{ba}+\Gamma_{ab})t}\right)}{dt} = -i\delta(t-\tau)(\rho_{aa}-\rho_{bb})e^{(i\omega_{ba}+\Gamma_{ab})t} \quad (38)$$

We can now integrate both sides,

$$\int d\left(\rho_{ba}e^{(i\omega_{ba}+\Gamma_{ab})t}\right) = -i \int_{-\infty}^t \delta(t'-\tau)(\rho_{aa}-\rho_{bb})e^{(i\omega_{ba}+\Gamma_{ab})t'} dt' \text{ or} \quad (39)$$

$$\rho_{ba}e^{(i\omega_{ba}+\Gamma_{ab})t} = -i(\rho_{aa}(\tau)-\rho_{bb}(\tau))e^{(i\omega_{ba}+\Gamma_{ab})\tau} \text{ or} \quad (40)$$

$$\rho_{ba} = -i(\rho_{aa}(\tau)-\rho_{bb}(\tau))e^{-(i\omega_{ba}+\Gamma_{ab})(t-\tau)} = -i(\rho_{aa}(\tau)-\rho_{bb}(\tau))e^{-i\delta_{ba}(t-\tau)} \quad (41)$$

### Steady State Limit of Liouville Equation- Two States

The steady state limit is reached when the electromagnetic field excitation continues for times that are much longer than  $\frac{1}{\Gamma}$ . For this case, the coherence will be oscillating at the excitation frequency rather than its natural free induction decay frequency. We assume

$$\rho_{ba} = \tilde{\rho}_{ba}e^{i(kz-\omega t)} \quad (42)$$

(One could assume the same functionality with the opposite sign for the exponential but you would find it was anti-resonant.) This function explicitly incorporates the fast temporal dependence of the Bohr frequency and any slower temporal dependence associated with the amplitude,  $\tilde{\rho}_{ba}$ .

Substituting (5) and (42) into **Error! Reference source not found.**,

$$\begin{aligned} \dot{\tilde{\rho}}_{ba}e^{i(kz-\omega t)} - i\omega\tilde{\rho}_{ba}e^{i(kz-\omega t)} &= -i\omega_{ba}\tilde{\rho}_{ba}e^{i(kz-\omega t)} \\ + \frac{i}{2\hbar}\mu_{ba}E^o &\left[ e^{i(kz-\omega t)} + e^{-i(kz-\omega t)} \right] (\rho_{aa}-\rho_{bb}) - \Gamma_{ab}\tilde{\rho}_{ba}e^{i(kz-\omega t)} \end{aligned} \quad (43)$$

Once again, we invoke the rotating wave approximation where we neglect the  $e^{i\omega t}$  term because it oscillates at  $2\omega$  relative to the terms involving  $e^{-i\omega t}$ . This approximation is called the rotating wave approximation. Then,  $\dot{\tilde{\rho}}_{ba} = -i(\omega_{ba}-\omega-i\Gamma_{ab})\tilde{\rho}_{ba} + \frac{i}{2\hbar}\mu_{ba}E^o(\rho_{aa}-\rho_{bb})$

or

$$\dot{\tilde{\rho}}_{ba} = -i\Delta_{ba}\tilde{\rho}_{ba} + \frac{i\Omega_{ba}}{2}(\rho_{aa}-\rho_{bb}) \quad (45)$$

$$\text{where } \Omega_{ba} = \frac{\mu_{ba}E^o}{\hbar} \quad (\text{Rabi frequency}) \quad (46)$$

$$\text{and } \Delta_{ba} = \omega_{ba} - \omega - i\Gamma_{ba}. \quad (47)$$

Note that  $E^o$  is the local electric field inside the material. There are three time scales represented in equation (45)- the fast time scale of the Bohr oscillations, the slower time scale of the dephasing times, and the Rabi frequency time scale which depends on the excitation intensity and the transition strength. Optical spectroscopy has short coherence dephasing times, especially

when compared with NMR where the dephasing times are quite long. Equation (45) can be solved for excitations that are very short compared to  $\Gamma_{ba}$  to find the transient polarization, excitations that are very long compared to  $\Gamma_{ba}$  to find the steady state polarization, or shaped excitations to match particular pulses. We will concentrate on the steady state solutions.

In steady state,  $\dot{\tilde{\rho}}_{ba} = 0$  so

$$\tilde{\rho}_{ba} = \frac{\Omega_{ba}}{2\Delta_{ba}}(\rho_{aa} - \rho_{bb}) \quad \text{and} \quad \rho_{ba} = \tilde{\rho}_{ba} e^{i(kz - \omega t)} = \frac{\Omega_{ba}}{2\Delta_{ba}}(\rho_{aa} - \rho_{bb}) e^{i(kz - \omega t)} \quad (48)$$

Similarly,

$$\rho_{ab} = \tilde{\rho}_{ab} e^{-i(k'z - \omega t)} \quad \text{and} \quad \rho_{ab} = \frac{\Omega_{ba}}{2\Delta_{ba}^*}(\rho_{aa} - \rho_{bb}) e^{-i(kz - \omega t)} \quad (49)$$

We can use these relationships to generalize the way to relate a transition to a state to the initially populated state to all possible cases of transitions. These cases include bra (right hand state changing) or ket side (left hand state changing) absorption and stimulated emission transitions.

	Absorption	Stimulated Emission
<b>Ket side transition</b>	$\rho_{ba} = \frac{\Omega_{ba}}{2\Delta_{ba}} \rho_{aa} e^{i(kz - \omega t)}$	$\rho_{ab} = -\frac{\Omega_{ba}}{2\Delta_{ba}^*} \rho_{bb} e^{-i(kz - \omega t)} = \frac{\Omega_{ba}}{2\Delta_{ab}} \rho_{bb} e^{-i(kz - \omega t)}$
<b>Bra side transition</b>	$\rho_{ab} = \frac{\Omega_{ba}}{2\Delta_{ba}^*} \rho_{aa} e^{-i(kz - \omega t)} = -\frac{\Omega_{ba}}{2\Delta_{ab}} \rho_{aa} e^{-i(kz - \omega t)}$	$\rho_{ba} = -\frac{\Omega_{ba}}{2\Delta_{ba}} \rho_{bb} e^{i(kz - \omega t)}$

Each coherence represented by  $\rho_{ij}$  will correspond to a macroscopic polarization that will launch an electromagnetic wave.

### Relationship Between Coherences and Polarization

Now that we have found the coherences, we need to find the polarizations that correspond to these coherences. There is a subtlety that arises because the Rabi frequency is defined by the local electric field which contains both the contributions from the internal macroscopic electric field and the polarization of the medium. Since the electric field that we measure is usually the macroscopic internal field, we need a correction factor so the polarization defined by the ensemble average of the molecular transition dipole moment is:

$$\vec{P} = NF \langle \vec{\mu} \rangle \quad (50)$$

where  $N$  = concentration of chromophores ( $\text{cm}^{-3}$ ) and  $F$  = local field enhancement factor

$= \frac{E_{local}}{E_{MacroscopicInternalField}}$ . The local field enhancement is necessary because the macroscopic internal

electric field is augmented by the local polarization induced in the material by the electric field of the light. If the electric field in our definition of the Rabi frequency is the macroscopic field but the actual field acting on the molecule is the local electric field that is enhanced, we need the local field enhancement factor.

Let's first find the expectation value for the molecular transition dipole moment:

$$\langle \vec{\mu} \rangle = \int \psi^* \vec{\mu} \psi \, d\tau . \quad (51)$$

Since the wavefunction is a linear combination of two states, we can rewrite this equation as

$$\langle \vec{\mu} \rangle = \int (c_a^* \psi_a^* + c_b^* \psi_b^*) \vec{\mu} (c_a \psi_a + c_b \psi_b) d\tau = \left[ c_a^* c_b \int \psi_a^* \vec{\mu} \psi_b d\tau + c_b^* c_a \int \psi_b^* \vec{\mu} \psi_a d\tau \right] \quad (52)$$

$$\text{or as } \langle \vec{\mu} \rangle = (\rho_{ba} \vec{\mu}_{ab} + \rho_{ab} \vec{\mu}_{ba}) = \vec{\mu}_{ba} (\rho_{ba} + \rho_{ab}) . \quad (53)$$

(We have used the fact that  $\vec{\mu}_{aa} = \vec{\mu}_{bb} = 0$  from symmetry.) The isotropic macroscopic polarization of the ensemble will then be

$$\vec{P} = NF \vec{\mu}_{ba} (\rho_{ba} + \rho_{ab}) = NF \vec{\mu}_{ba} \left( \tilde{\rho}_{ba} e^{i(kz-\omega t)} + \tilde{\rho}_{ab} e^{-i(kz-\omega t)} \right) \quad (54)$$

We know the values of  $\rho_{ba}$  and  $\rho_{ab}$  from equations (48) and (49) so the polarization becomes

$$\begin{aligned} P &= NF \left( \mu_{ba} \frac{\Omega_{ab}}{2\Delta_{ab}} e^{-i(kz-\omega t)} + \mu_{ab} \frac{\Omega_{ba}}{2\Delta_{ba}} e^{i(kz-\omega t)} \right) (\rho_{aa} - \rho_{bb}) \\ &= \frac{NF \mu_{ba} \Omega_{ba}}{2} \left( \frac{e^{i(kz-\omega t)}}{\Delta_{ba}} + \frac{e^{-i(kz-\omega t)}}{\Delta_{ab}} \right) (\rho_{aa} - \rho_{bb}) \end{aligned} \quad (55)$$

We can also relate the polarization to the electric field responsible for it by explicitly writing out the Rabi frequency in equation (55).

$$\begin{aligned} P &= \frac{NF \mu_{ba} \mu_{ba} E^o (\rho_{aa} - \rho_{bb})}{2\hbar} \left( \frac{e^{i(kz-\omega t)}}{\Delta_{ba}} + \frac{e^{-i(kz-\omega t)}}{\Delta_{ab}} \right) \\ &= \frac{NF \mu_{ba}^2 E^o (\rho_{aa} - \rho_{bb})}{2\hbar} \left( \frac{e^{i(kz-\omega t)}}{\Delta_{ba}} + \frac{e^{-i(kz-\omega t)}}{\Delta_{ab}} \right) \end{aligned} \quad (56)$$

In the theory of electricity and magnetism, the proportionality constant between the macroscopic polarization and the macroscopic electric field in a material is the susceptibility,  $\chi^{(1)}$ . Equation (56) is interesting because it gives an explicit expression for the electrical susceptibility, i.e. the proportionality constant between the polarization and the electric field:

$$\vec{P} = \chi^{(1)} \vec{E} \quad (57)$$

so comparing (57) and (56) and remembering the form of  $E$  shows us

$$\chi^{(1)} = \frac{NF \mu_{ba}^2}{\hbar \Delta_{ba}} (\rho_{aa} - \rho_{bb})^* \quad (58)$$

Now let's define the local field enhancement. The electric field on the outside of a material differs from the macroscopic field on the inside through the transmission coefficient. If  $n_1$  and  $n_2$  are the refractive indices on the outside and inside, respectively, then

$$E_{macrointernal}^o = \frac{2n_1}{n_1 + n_2} E_{external}^o . \text{ A standard treatment (that neglects excited state populations) shows}$$

\* Note that we have neglected the difference between  $\Delta_{ba}$  and  $\Delta_{ab}$  in eqn. (56). They are related by  $\Delta_{ba} = -\Delta_{ab}^*$  and a correct treatment shows that there should be a phase shift introduced in the polarization relative to the electromagnetic field. Note also that a factor of 3 is often put into the denominator because in a real sample, only 1/3 of the molecules have their dipole moment oriented along the polarization of the light field. We are also neglecting non-resonant pathways that will give another antiresonant term,  $\omega_{ba} + \omega$ .

that the local field at a molecule is influenced by the polarization and the macroscopic electric field. Thus,

$$P = N\alpha E_{local} = N\alpha \left( E_{macro} + \frac{4\pi P}{3} \right) \quad (59)$$

where  $\alpha$  is the polarizability of the material. If we define  $\chi$  by

$$\chi = \frac{N\alpha}{E_{macro}} \quad (60)$$

and compare this with the previous equation, we see that

$$\chi = \frac{N\alpha F}{E_{macro}} \quad (61)$$

$$\text{where } F = \frac{1}{1 - 4\pi N\alpha / 3}. \quad (62)$$

We can also compare (60) with equation (56) and find that

$$\chi = \frac{NF\mu_{ba}^2}{\hbar\Delta_{ba}} \quad (63)$$

One can show that this results finally in

$$F = \frac{n^2 + 2}{3}. \quad (64)$$

One can understand the field enhancement intuitively by realizing that the speed of light is slower when  $n > 1$  so the energy is concentrated over a shorter distance. The slower speed is caused because the electric field launched by the polarization is adding to the electric field that created the polarization.

## Index of Refraction and Absorption

We now need to bring the Maxwell equations into the picture in order to make the connection between the polarization that is induced by the excitation fields and the electric fields that the polarization launches. **We will use cgs (esu) units for all the electromagnetic equations.** The fundamental relationship relates the spatial and temporal curvature and polarization:

$$\nabla^2 E - \frac{1}{c^2} \ddot{E} = \frac{4\pi}{c^2} \ddot{P} \quad \text{in cgs or esu units} \quad (65)$$

$$\text{(or } \nabla^2 E - \frac{1}{c^2} \ddot{E} = \frac{1}{\epsilon_0 c^2} \ddot{P} \text{ in mks units)}$$

If the field propagates in a vacuum,  $P = 0$  and the equation now relates the curvature of the spatial variation of  $E$  to the temporal curvature of  $E$ . We will assume infinite plane wave traveling in z direction so

$$E = \frac{1}{2} \left[ E^o e^{i(kz - \omega t)} + E^{o*} e^{-i(kz - \omega t)} \right] \quad (66)$$

Substituting into equation (65),

$$-k^2 \left( \frac{E^o e^{i(kz - \omega t)}}{2} + \frac{E^{o*} e^{-i(kz - \omega t)}}{2} \right) + \frac{1}{c^2} \omega^2 \left( \frac{E^o e^{i(kz - \omega t)}}{2} + \frac{E^{o*} e^{-i(kz - \omega t)}}{2} \right) = 0 \quad (67)$$

so,  $k = \frac{\omega}{c}$  or  $kc = \omega$  which is simply the relationship between the angular frequency and the wave-vector of an electromagnetic field propagating at a velocity,  $c$ .

If the field propagates inside a material,  $P \neq 0$ . The electric fields are the macroscopic internal electric fields, not the local electric fields. One can define the first order susceptibility as the proportionality constant between the polarization and the macroscopic internal electric field.

$$P = \chi^{(1)} E. \quad (68)$$

Now the relationship of the spatial and temporal curvatures has been modified and the speed of light is changed. To find out how, substitute (68) into (65) so

$$\nabla^2 E - \frac{1}{c^2} \ddot{E} = \frac{4\pi}{c^2} \chi^{(1)} \ddot{E} \quad (69)$$

$$\text{or } \nabla^2 E - \frac{1+4\pi\chi^{(1)}}{c^2} \ddot{E} = 0 \quad (70)$$

Carrying out the same procedure that produced equation (67), we find that equation (66) is a solution to equation (70) if

$$k = \frac{\omega\sqrt{1+4\pi\chi^{(1)}}}{c} \quad (71)$$

so the index of refraction must be:

$$n = \sqrt{1+4\pi\chi^{(1)}}. \quad (72)$$

and it must be complex since  $\chi^{(1)}$  is complex. The electric field is then

$$E = \frac{1}{2} \left[ E^o e^{i\left(\frac{\omega\sqrt{1+4\pi\chi^{(1)}}}{c} z - \omega t\right)} + E^{o*} e^{-i\left(\frac{\omega\sqrt{1+4\pi\chi^{(1)}}}{c} z - \omega t\right)} \right] = \frac{1}{2} \left[ E^o e^{i\left(\frac{\omega n}{c} z - \omega t\right)} + E^{o*} e^{-i\left(\frac{\omega n}{c} z - \omega t\right)} \right] \quad (73)$$

Note that the exponential in (73) has a dependence on  $z$  with real parts that cause the amplitude of the wave to change and imaginary parts that represent the oscillation. If we define the real ( $n'$ ) and imaginary ( $n''$ ) parts of  $n$  by the expression  $n \equiv n' + i n''$ , then (73) becomes

$$E = \frac{E^o e^{-\omega n'' z / c}}{2} \left[ e^{i\left(\frac{\omega n'}{c} z - \omega t\right)} + e^{-i\left(\frac{\omega n'}{c} z - \omega t\right)} \right] \quad (74)$$

so  $n'$  must be the normal index of refraction and  $\frac{\omega n''}{c}$  must be related to the absorption

coefficient. So, the index of refraction is the real part of the complex index of refraction so

$$n = \operatorname{Re} \left( \sqrt{1+4\pi\chi^{(1)}} \right) \quad (75)$$

If  $4\pi\chi^{(1)} \ll 1$ , then

$$n \approx 1 + 2\pi \operatorname{Re}(\chi^{(1)}) = 1 + \operatorname{Re} \left( \frac{2\pi NF \mu_{ba}^2}{\hbar \Delta_{ba}} \right) = 1 + \frac{2\pi NF \mu_{ba}^2 \operatorname{Re}(\delta_{ba} + i\Gamma_{ba})}{\hbar |\Delta_{ba}|^2} \quad (76)$$

$$\text{or, } n \approx 1 + \frac{2\pi NF \mu_{ba}^2 \delta_{ba}}{\hbar |\Delta_{ba}|^2} \quad (77)$$

Next, we need to find the absorption coefficient which is defined by the intensity decay:

$$I(z) = I(z=0)e^{-\alpha z} \quad (78)$$

We must convert the electric field in (74) to intensity. The cycle averaged intensity of light that corresponds to an electric field is given by

$$I = \frac{cn_{index}\xi}{8\pi} E^o{}^2 \quad (\text{esu units}) \quad \text{or} \quad I = \frac{c\varepsilon_o n_{index}\xi}{2} E^o{}^2 \quad (\text{mks units}) \quad (79)$$

where  $E^o$  is the electric field amplitude,  $n$  is the refractive index characteristic of the field's macroscopic electric field within the material,  $\xi$  is a constant that is 1 if  $E$  is a classical electromagnetic field but can take on other values for nonclassical fields, and  $c\varepsilon_o$  is  $2.66 \times 10^{-3}$ . The amplitude in equation (74) is  $E^o e^{-\omega n'' z/c}$  so the intensity becomes

$$I = \frac{cn_{index}\xi}{8\pi} (E^o e^{-\omega n'' z/c})^2 = I_o e^{-2\omega n'' z/c}, \quad (80)$$

so comparing this with (78), the absorption coefficient is

$$\alpha = \frac{2\omega n''}{c} \quad (81)$$

and we just have to find how  $n''$  depends on the transition moment and frequencies. That can't be done conveniently since equation (72) involves the square root but it can be done by approximating (72) since the second term is usually small compared with one. In that case,

$$\alpha = \frac{2\omega}{c} \text{Im} \left( \sqrt{1 + 4\pi\chi^{(1)}} \right) \approx \frac{2\omega}{c} \text{Im} \left( 1 + \frac{4\pi\chi^{(1)}}{2} \right) \quad (82)$$

Substituting (63),

$$\begin{aligned} \alpha &\approx \frac{2\omega}{c} \text{Im} \left( 1 + \frac{4\pi \frac{NF\mu_{ba}^2}{\hbar\Delta_{ba}} (\rho_{aa} - \rho_{bb})}{2} \right) = \frac{2\omega}{c} \text{Im} \left( 1 + \frac{4\pi \frac{NF\mu_{ba}^2 (\delta_{ba} + i\Gamma_{ba})}{\hbar|\Delta_{ba}|^2} (\rho_{aa} - \rho_{bb})}{2} \right) \\ &= \frac{2\omega}{c} \frac{4\pi NF\mu_{ba}^2 \Gamma_{ba} (\rho_{aa} - \rho_{bb})}{2\hbar|\Delta_{ba}|^2} \end{aligned} \quad (83)$$

so,

$$\alpha \approx \frac{4\pi\omega NF\mu_{ba}^2 \Gamma_{ba} (\rho_{aa} - \rho_{bb})}{\hbar c |\Delta_{ba}|^2} \quad (84)$$

This last expression usually is reduced by 1/3 to take into account that only 1/3 of the dipole moments are aligned with the polarized light field.

The index of refraction and the absorption coefficient are necessarily linked because they both come from the coherence,  $\rho_{ba} \sim \frac{1}{\delta - i\Gamma} = \frac{\delta + i\Gamma}{\delta^2 + \Gamma^2}$ . A Kramers-Kronig transformation in fact transforms the index of refraction into the absorption coefficient and vice versa. There are therefore the following relationships between  $\alpha$  and  $\Delta n$ :

$$\alpha = \frac{2\omega\Gamma\Delta n}{\delta c} \quad \text{and} \quad \Delta n = \frac{\delta c\alpha}{2\omega\Gamma}. \quad (85)$$

The derivation of  $\alpha$  explicitly assumed that the sample was pure and the index of refraction and the absorption were caused by the same material. If the absorption is caused by a solute in a solvent, the derivation is changed. Now the polarization has two contributions so there will be a  $\chi$  for each one. Equation (82) must now be written as

$$\alpha = \frac{2\omega}{c} \operatorname{Im} \left( \sqrt{1 + 4\pi\chi_{\text{solvent}}^{(1)} + 4\pi\chi_{\text{solute}}^{(1)}} \right) = \frac{2\omega}{c} \operatorname{Im} \left( \sqrt{\left(1 + 4\pi\chi_{\text{solvent}}^{(1)}\right) \left(1 + \frac{4\pi\chi_{\text{solute}}^{(1)}}{1 + 4\pi\chi_{\text{solvent}}^{(1)}}\right)} \right) \quad (86)$$

$$= \frac{2\omega}{c} \operatorname{Im} \left( \sqrt{\left(1 + 4\pi\chi_{\text{solvent}}^{(1)}\right)} \sqrt{\left(1 + \frac{4\pi\chi_{\text{solute}}^{(1)}}{1 + 4\pi\chi_{\text{solvent}}^{(1)}}\right)} \right) = \frac{2\omega}{c} \operatorname{Im} \left( n_{\text{solvent}}^o \sqrt{\left(1 + \frac{4\pi\chi_{\text{solute}}^{(1)}}{n_{\text{solvent}}^o{}^2}\right)} \right) \quad (87)$$

$$\approx \frac{2\omega}{c} \operatorname{Im} \left( n_{\text{solvent}}^o \left( 1 + \frac{2\pi\chi_{\text{solute}}^{(1)}}{n_{\text{solvent}}^o{}^2} \right) \right) \approx \frac{2\omega}{c} \operatorname{Im} \left( n_{\text{solvent}}^o + 2\pi \frac{NF\mu_{ba}^2(\delta_{ba} + i\Gamma_{ba})}{\hbar|\Delta_{ba}|^2 n_{\text{solvent}}^o} (\rho_{aa} - \rho_{bb}) \right) \quad (88)$$

$$\approx \frac{4\pi\omega NF\mu_{ba}^2\Gamma_{ba}}{\hbar c|\Delta_{ba}|^2 n_{\text{solvent}}^o} (\rho_{aa} - \rho_{bb}) \quad (89)$$

There are many other measures of absorption. The absorption coefficient is defined by the exponential spatial decay of the light intensity over the pathlength  $l$  so

$$I = I_o e^{-\alpha l}. \quad (90)$$

The molar absorptivity is defined by the Beer's law relationship which can be stated in several ways:

$$A = \log \frac{I_o}{I} = \varepsilon l C, \quad I = I_o 10^{-\varepsilon l C}, \quad I = I_o e^{-\varepsilon l C \ln(10)}. \quad (91)$$

The optical cross-section,  $\sigma$  (measured in  $\text{cm}^2$ ), is defined by the differential relationship

$$\frac{dI}{I} = -\sigma N dx \quad (92)$$

where  $N$  is the concentration in molecules/ $\text{cm}^3$ . This equation integrates to

$$I = I_o e^{-\sigma N l}. \quad (93)$$

These equations show the following relationships

$$\alpha = \sigma N = \varepsilon C \ln(10). \quad (94)$$

The oscillator strength of a transition is often used to characterize a transition. It is defined by the equation

$$f_{ba} = \frac{2m\omega_{ba}\mu_{ba}^2}{3\hbar e^2}$$

where  $m$  and  $e$  are the mass and charge of the electron, respectively. It is useful because one can show that the sum of the oscillator strengths of the transitions from a state to all others is one,

$$\sum_b f_{ba} = 1. \quad \text{It is the oscillator sum rule.}$$

The Einstein B coefficient defines the rate of a transition induced by an energy density per unit angular frequency,  $\rho_\omega$ ,  $W_{ba} = B_{ba}\rho_\omega N$ . It has units of volume, angular frequency, energy<sup>-1</sup> time<sup>-1</sup>. The optical cross section is related to the Einstein B coefficient by the equation:

$\sigma(\omega) = \frac{\hbar\omega B_{ba}g(\omega)}{c}$  where  $g(\omega)$  is a line shape function normalized to one. The Einstein A coefficient is the inverse of the radiative lifetime and it is related to the Einstein B coefficient by

$$B_{ba} = \frac{\pi^2 c^3}{\hbar\omega_{ba}^3} A_{ba} = \frac{\pi^2 c^3}{\hbar\omega_{ba}^3 \tau_{radiative}}$$

The Einstein A coefficient can also be written as  $A_{ba} = \frac{4\omega_{ba}^3 \mu_{ba}^2}{3\hbar c^3}$  where the factor of 3 in the denominator occurs because the ensemble average over the relative dipole moment directions and the light fields.

## Nonlinear Polarizations

The previous section dealt with the effects of an external electromagnetic field on a quantum system. We now want to deal with how the quantum system itself can produce an electromagnetic field through the oscillating dipole moment of its quantum states, i.e. its coherence. The oscillating dipole moment itself may have been produced by other electromagnetic fields so those must also be included in our description. For example, nonlinear processes involve two or more fields that together create polarizations with different frequencies and/or directions from the fields that produced them. Our description must therefore include the nonlinear polarization, the new electromagnetic field it produces, and the linear polarization created by the new field. We assume the nonlinear polarization is small. We remember equation (59)

$$P = N\alpha E_{local} = N\alpha \left( E_{macro} + \frac{4\pi P}{3} \right) \quad (95)$$

but now we have the additional polarization,  $P_{NL}$ , that is creating the macroscopic electric field so that must be incorporated as well. Now,

$$P = N\alpha \left( E + \frac{4\pi P}{3} \right) + P_{NL} \quad (96)$$

where  $\alpha$  is the polarizability of the material. Note that the electric field in this equation is the result of the polarization,  $P_{NL}$ . That electric field then creates the polarization that we saw becomes the index of refraction as well as describing absorption. We solve for the polarization,

$$P = \frac{N\alpha E}{1 - \frac{4\pi N\alpha}{3}} + \frac{P_{NL}}{1 - \frac{4\pi N\alpha}{3}} = \chi^{(1)} E + F P_{NL} \quad (97)$$

$$\text{where } \chi^{(1)} = \frac{N\alpha}{1 - \frac{4\pi N\alpha}{3}} \text{ or equivalently } N\alpha = \frac{\chi^{(1)}}{1 + \frac{4\pi\chi^{(1)}}{3}}. \quad (98)$$

We also used the relationship for  $F$ , equation (62). We could also write equation (97) in terms of  $\chi^{(1)}$  as

$$P = \chi^{(1)} E + \left( 1 + \frac{4\pi\chi^{(1)}}{3} \right) P_{NL} \quad (99)$$

We will assume the polarization is an infinite plane wave that has been created by previous fields. To be general, we will also permit its direction can differ from the electromagnetic field that it creates. However, its frequency cannot differ from the field it creates. We therefore assume

$$P = \frac{1}{2} \left[ P^o e^{i(k'z - \omega t)} + P^{o*} e^{-i(k'z - \omega t)} \right] \quad (100)$$

The electric field is then also infinite plane wave<sup>†</sup> that is traveling in z direction so

---

<sup>†</sup> Later we will see that an infinite plane wave polarization is required to create the electromagnetic plane wave. We will also see how we can modify the equations to account for waves with any shape.

$$E = \frac{1}{2} [E^o e^{i(kz - \omega t)} + E^{o*} e^{-i(kz - \omega t)}]. \quad (101)$$

but now it has a direction given by  $\vec{k}$  rather than  $\vec{k}'$ . If we now compare equation (100) with equation (54),  $P = NF \left[ \mu_{ab} \tilde{\rho}_{ba} e^{i(k'z - \omega t)} + \mu_{ab} \tilde{\rho}_{ab} e^{-i(k'z - \omega t)} \right]$ , we can see

$$P^o = 2NF \mu_{ba} \tilde{\rho}_{ba} \quad (102)$$

We are now ready to find the electric field that is created by an oscillating polarization. Substituting (99) into (65), we obtain

$$\nabla^2 E - \frac{1}{c^2} \ddot{E} = \frac{4\pi}{c^2} (\chi^{(1)} \ddot{E} + F \dot{P}_{NL}) \quad (103)$$

Rearranging,

$$\nabla^2 E - \frac{(1+4\pi\chi^{(1)})}{c^2} \ddot{E} = \frac{4\pi F}{c^2} \dot{P}_{NL} \text{ or,} \quad (104)$$

$$\nabla^2 E - \frac{\epsilon}{c^2} \ddot{E} = \frac{4\pi F}{c^2} \dot{P}_{NL} \quad (105)$$

where we have defined a new constant called the dielectric constant,

$$\epsilon \equiv 1 + 4\pi\chi^{(1)} \quad (106)$$

With this new definition, we could also write

$$F = \frac{\epsilon + 2}{3}. \quad (107)$$

We will show that  $n^2 = \epsilon\mu$  where the refractive index is  $n$  and the magnetic permittivity,  $\mu$ , is 1 for nonmagnetic materials. Thus,

$$F = \frac{n^2 + 2}{3}. \quad (108)$$

Substituting (101) and (102) into (84),

$$\begin{aligned} & \frac{1}{2} \left\{ -E^o k^2 e^{i(kz - \omega t)} + 2ik \frac{\partial E^o}{\partial z} e^{i(kz - \omega t)} + \frac{\partial^2 E^o}{\partial z^2} e^{i(kz - \omega t)} + c.c. \right\} \\ & - \frac{\epsilon}{2c^2} \left\{ -E^o \omega^2 e^{i(kz - \omega t)} - 2i\omega \frac{\partial E^o}{\partial t} e^{i(kz - \omega t)} + \frac{\partial^2 E^o}{\partial t^2} e^{i(kz - \omega t)} + c.c. \right\} = . \\ & \frac{4\pi F}{2c^2} \left\{ -P_{NL}^o \omega^2 e^{i(k'z - \omega t)} - 2i\omega \frac{\partial P_{NL}^o}{\partial t} e^{i(k'z - \omega t)} + \frac{\partial^2 P_{NL}^o}{\partial t^2} e^{i(k'z - \omega t)} + c.c. \right\} \end{aligned} \quad (109)$$

In the slowly varying amplitude approximation, we neglect  $\frac{\partial^2 P^o}{\partial t^2}$ ,  $\frac{\partial^2 E^o}{\partial t^2}$ ,  $\frac{\partial^2 E^o}{\partial z^2}$ ,  $\frac{\partial P^o}{\partial t}$  and keep the other first derivatives. Equating common factors containing  $e^{-i\omega t}$ , we get:

$$-E^o k^2 + 2ik \frac{\partial E^o}{\partial z} + \frac{E^o \epsilon \omega^2}{c^2} + \frac{2i\epsilon\omega}{c^2} \frac{\partial E^o}{\partial t} = -\frac{4\pi F P_{NL}^o \omega^2}{c^2} e^{i(k' - k)z} \quad (110)$$

$$\text{where } k^2 = \frac{\epsilon\omega^2}{c^2} = \frac{n^2\omega^2}{c^2} \text{ (if } \mu = 1)$$

We can then write

$$\frac{\partial E^o}{\partial z} + \frac{\epsilon\omega}{kc^2} \frac{\partial E^o}{\partial t} = \frac{2\pi i F \omega^2 P_{NL}^o}{kc^2} e^{i\Delta kz} \quad (111)$$

$$\frac{\partial E^o}{\partial z} + \frac{n}{c} \frac{\partial E^o}{\partial t} = \frac{2\pi i F \omega P_{NL}^o}{nc} e^{i\Delta kz} \quad (112)$$

This equation controls the electromagnetic radiation generated by a nonlinear polarization.

There are two important cases for equation (112). The first is where the amplitude of the nonlinear polarization depends on the same electric field that it creates,  $E^o$ , and the other where it does not. In each case, we will assume the electric field amplitude changes slowly compared with the period so we can neglect the second term. Let's solve equation (112) for each case.

### **Case 1- Nonlinear polarization depends on the same field that it creates.**

$$\frac{\partial E^o}{\partial z} = \chi E^o e^{i\Delta kz} \quad (113)$$

where  $\chi \equiv \frac{2\pi i F \omega P_{NL}^o}{nc E^o}$ . Solving (113),

$$\ln \frac{E^o(z)}{E^o(z=0)} = \frac{\chi}{i\Delta k} (e^{i\Delta kz} - 1). \quad (114)$$

For this case,  $\Delta k$  is usually zero so we need to use L'Hospital's rule and find

$$E^o(z) = E^o(z=0) e^{\chi z} \quad (115)$$

### **Case 2- Nonlinear polarization is independent of the field that it creates.**

$$E^o(z) - E^o(z=0) = \frac{2\pi i F \omega P_{NL}^o}{nc E^o} \frac{(e^{i\Delta kz} - 1)}{i\Delta k} \quad (116)$$

## **Multiple Interactions- Nonlinear Problems**

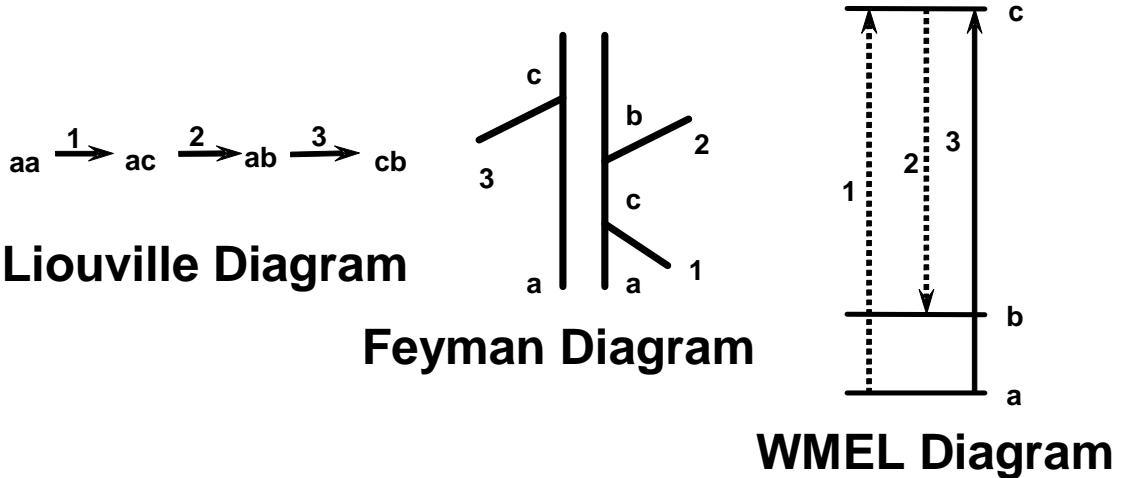
Thus far, we have concentrated on simple linear interactions where the electric field acts once to perturb the system. The linear interactions created refraction, absorption, and stimulated emission. The next step is to include several interactions or nonlinear interactions. In order to create some simple ways of visualizing how each interactions changes the states, we will introduce three ways of keeping track of the states- Liouville diagrams, Feynman diagrams, and wave mixing energy level diagrams (WMEL diagrams). The three diagrams below show three transitions induced by excitation fields 1, 2, and 3. The first two are bra-side transitions that change state a into state c and then state c into state b. The last interaction changes state a into state c.

**Liouville diagram-** the states are labeled by letters and the excitation fields are labeled by numbers. The two letters represent and ket and bra of the coherences or populations.

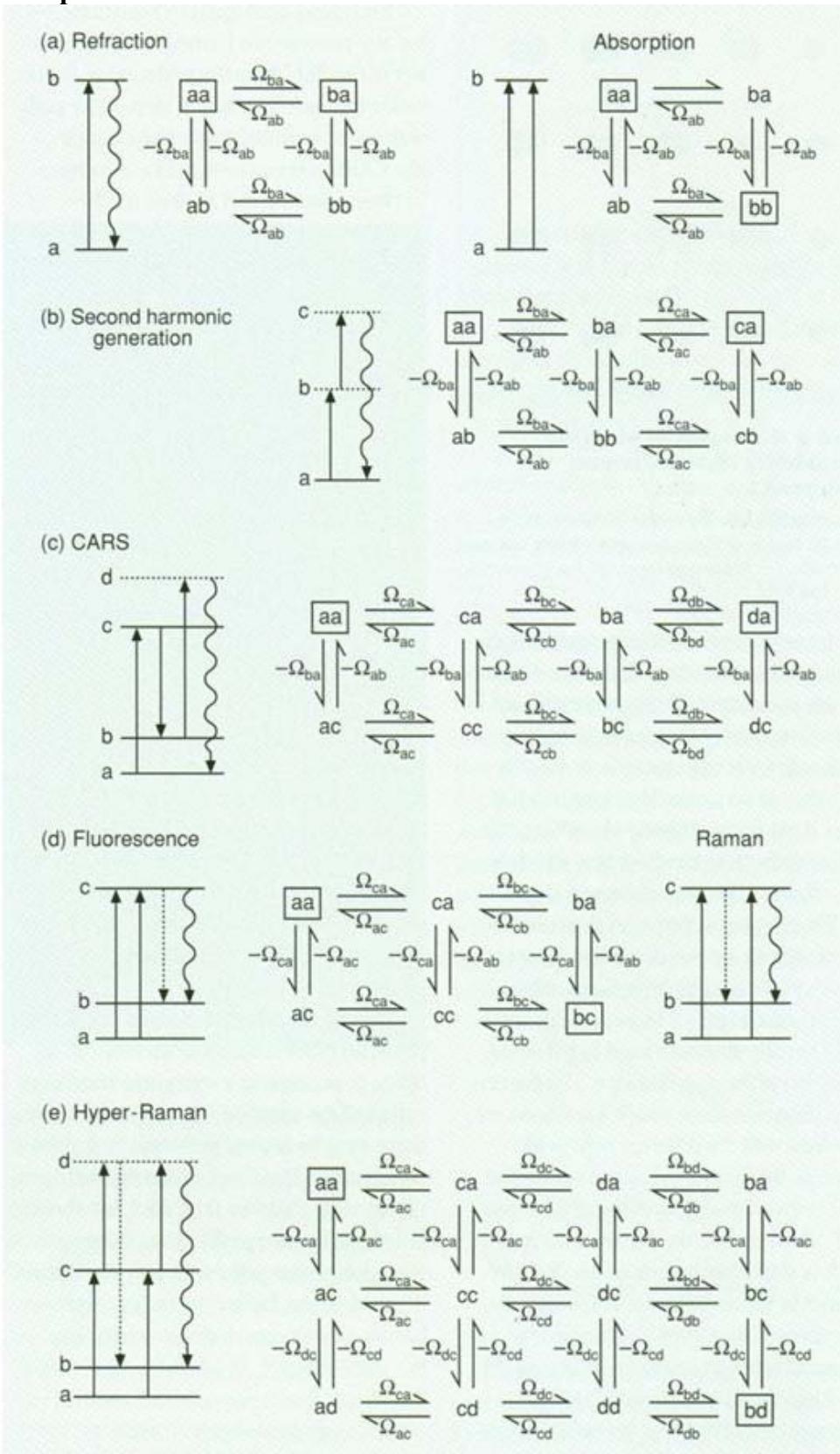
**Feynman diagram-** the two vertical lines represent the time evolution of the ket and bra. The ket is the left line and the bra is the right line. Time evolves from the bottom to the top. The

states at any given time are indicated by the letters. The interaction occurs at the intersection of the vertical and sloped lines. Absorption interactions appear as sloped lines as they approach the vertical lines and emission interactions as lines that increase as they leave the vertical lines.

**WMEL diagram-** the states are represented by horizontal lines that are labeled with the state. The ket- and bra-side interactions are indicated by solid and dotted vertical lines, respectively. Time evolves from left to right.



## **Examples-**



## Raman and Fluorescence

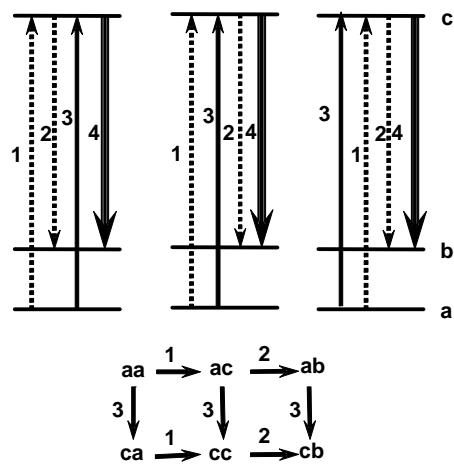
We are now ready to study the quantum mechanics of fluorescence and Raman spectroscopy. The figure uses both WMEL and Liouville diagrams to show the interactions. There are three equivalent ways to create the final coherence between states  $c$  and  $b$ . The upper state,  $c$ , represents an excited electronic state of the molecule and the lower state  $b$  represents a vibrational state of the ground electronic state. The diagram has three transitions at the amplitude level for a fluorescence or Raman transition. The fourth arrow represents the output field created by the last coherence between states  $c$  and  $b$ .

Let's examine the first WMEL diagram in more detail. The first and second arrows represent resonances where a transition occurs for the bra part of the wave function. The original ground state population described by  $\rho_{aa}$  evolves to the coherence,  $\rho_{ac}$ , and then to the coherence,  $\rho_{ab}$ . The third arrow (dashed) causes a transition for the ket part of the wave function where state "a" changes to state "c". The  $\rho_{ab}$  coherence therefore changes to a  $\rho_{cb}$  coherence. Since the interactions with these three photons can occur with any time ordering, there are several pathways that the original ground state population can evolve from  $\rho_{aa}$  to  $\rho_{cb}$  and all three pathways are shown in the right side of the drawing. The  $\rho_{cb}$  coherence launches the electromagnetic field that is detected. It can either correspond to **fluorescence** or **Raman** depending upon whether or not the pathway involves the excited state population ( $\rho_{cc}$ ). Thus, the pathway  $aa \rightarrow ac \rightarrow ab \rightarrow cb$  is the **Raman** pathway (although it is not solely the Raman pathway, as we will see) and pathways  $aa \rightarrow ca \rightarrow cc \rightarrow cb$  and  $aa \rightarrow ac \rightarrow cc \rightarrow cb$  are the **fluorescence** pathways. We can write the relationship between the  $\rho_{cb}$  coherence and the experimental parameters using our rules for finding  $\rho$ 's and obtain the following relationship:

$$\rho_{cb} = \left( \frac{\Omega_{ac}}{2\Delta_{ac}} \frac{\Omega_{cb}}{2\Delta_{ab}} \frac{\Omega_{ac}}{2\Delta_{cb}} + \frac{\Omega_{ac}}{2\Delta_{ca}} \frac{\Omega_{ac}}{2\Delta_{cc}} \frac{\Omega_{bc}}{2\Delta_{cb}} + \frac{\Omega_{ac}}{2\Delta_{ac}} \frac{\Omega_{ac}}{2\Delta_{cc}} \frac{\Omega_{cb}}{2\Delta_{cb}} \right) \rho_{aa} \quad (117)$$

$$\rho_{cb} = \frac{\Omega_{ac}^2 \Omega_{cb}}{8\Delta_{cb}} \left( \frac{1}{\Delta_{ac}\Delta_{ab}} + \frac{1}{\Delta_{ca}\Delta_{cc}} + \frac{1}{\Delta_{ac}\Delta_{cc}} \right) \rho_{aa} \quad (118)$$

$$\begin{aligned} \Delta_{ca} &= \omega_{ca} - \omega_3 - i\Gamma_{ca} \\ \Delta_{ab} &= \omega_{ab} + \omega_1 - \omega_2 - i\Gamma_{ab} \\ \Delta_{ac} &= \omega_{ac} + \omega_1 - i\Gamma_{ca} = -(\omega_{ca} - \omega_1 + i\Gamma_{ca}) = -\Delta_{ca}^* \\ \Delta_{cb} &= \omega_{cb} + \omega_1 - \omega_2 - \omega_3 - i\Gamma_{cb} \\ \Delta_{cc} &= -i\Gamma_{cc} \end{aligned} \quad (119)$$



Some terms like  $\omega_{ca}$  in (118) are positive and others like  $\omega_{ab}$  are negative. Many involve the same states so it is not clear how the terms interact to produce the observed resonances. We need to combine terms in a way that makes the predictions of (118) clear.

Combine the last two terms in (118),

$$\rho_{cb} = \frac{\Omega_{ac}^2 \Omega_{cb} \rho_{aa}}{8\Delta_{cb}} \left( \frac{1}{\Delta_{ac}\Delta_{ab}} + \frac{\Delta_{ac} + \Delta_{ca}}{\Delta_{ca}\Delta_{ac}\Delta_{cc}} \right) \quad (120)$$

Simplifying and remembering that  $\omega_1 = \omega_3$ ,

$$\rho_{cb} = \frac{\Omega_{ac}^2 \Omega_{cb} \rho_{aa}}{8\Delta_{cb}\Delta_{ac}} \left( \frac{1}{\Delta_{ab}} - \frac{2i\Gamma_{ca}}{\Delta_{ca}\Delta_{cc}} \right) \quad (121)$$

Adding and subtracting  $1/\Delta_{ca}$

$$\rho_{cb} = \frac{\Omega_{ac}^2 \Omega_{cb} \rho_{aa}}{8\Delta_{cb}\Delta_{ac}} \left( \frac{1}{\Delta_{ab}} + \frac{1}{\Delta_{ca}} - \frac{1}{\Delta_{ca}} - \frac{2i\Gamma_{ca}}{\Delta_{ca}\Delta_{cc}} \right) \quad (122)$$

Combining the first two terms in (122) gives

$$\rho_{cb} = \frac{\Omega_{ac}^2 \Omega_{cb} \rho_{aa}}{8\Delta_{cb}\Delta_{ac}} \left( \frac{\Delta_{ca} + \Delta_{ab}}{\Delta_{ab}\Delta_{ca}} - \frac{1}{\Delta_{ca}} - \frac{2i\Gamma_{ca}}{\Delta_{ca}\Delta_{cc}} \right) \quad (123)$$

$$\rho_{cb} = \frac{\Omega_{ac}^2 \Omega_{cb} \rho_{aa}}{8\Delta_{cb}\Delta_{ac}} \left( \frac{\Delta_{cb} + i\Gamma_{cb}^a}{\Delta_{ab}\Delta_{ca}} - \frac{1}{\Delta_{ca}} - \frac{2i\Gamma_{ca}}{\Delta_{ca}\Delta_{cc}} \right) \quad (124)$$

where we have used the relationships

$$\Delta_{ab} + \Delta_{ca} = \Delta_{cb} + i\Gamma_{cb}^a, \quad (125)$$

$$\Gamma_{cb}^a = \Gamma_{cb} - \Gamma_{ba} - \Gamma_{ca} = \Gamma_{cb}^* - \Gamma_{ba}^* - \Gamma_{ca}^* - \Gamma_{aa} \quad (126)$$

and  $\Gamma_{aa}$  is zero. This relationship can be verified by just writing out  $\Delta_{ab}$ ,  $\Delta_{ca}$ , and  $\Delta_{cb}$  and using algebra.

Simplifying (124) and remembering that  $\Delta_{cc} = \omega_{cc} - \omega_1 + \omega_3 - i\Gamma_{cc}$ , we can see  $\Delta_{cc} = -i\Gamma_{cc}$  since  $\omega_1 - \omega_3 = 0$ :

$$\rho_{cb} = -\frac{\Omega_{ac}^2 \Omega_{cb} \rho_{aa}}{8|\Delta_{ca}|^2} \left( \frac{1}{\Delta_{ba}^*} + \frac{1}{\Delta_{cb}} \left( \frac{i\Gamma_{cb}^a}{\Delta_{ba}^*} + 1 - \frac{2\Gamma_{ca}}{\Gamma_{cc}} \right) \right) \quad (127)$$

This form has terms that depend on dephasing.

Consider typical values for (127).

$$1 - \frac{2\Gamma_{ca}}{\Gamma_{cc}} = 1 - \frac{2 \left( \frac{\Gamma_{aa} + \Gamma_{cc}}{2} + \Gamma_{ca}^* \right)}{\Gamma_{cc}} = 1 - \frac{\Gamma_{aa} + \Gamma_{cc} + 2\Gamma_{ca}^*}{\Gamma_{cc}} = \frac{\Gamma_{aa}}{\Gamma_{cc}} + \frac{2\Gamma_{ca}^*}{\Gamma_{cc}} \quad (128)$$

In many cases, the pure dephasing effects are small and it is common to assume that

$$\Gamma_{bc}^a = \Gamma_{bc}^* - \Gamma_{ba}^* - \Gamma_{ac}^* - \Gamma_{aa} \approx 0 \quad (129)$$

$$\text{so } \rho_{cb} \approx \frac{\Omega_{ac}^2 \Omega_{cb} \rho_{aa}}{8|\Delta_{ca}|^2} \left( \frac{1}{\Delta_{ba}^*} + \frac{i\Gamma_{cb}^a}{\Delta_{ba}^* \Delta_{cb}} - \frac{1}{\Delta_{cb}} \frac{(\Gamma_{aa} + 2\Gamma_{ca}^*)}{\Gamma_{cc}} \right) \quad (130)$$

The first term corresponds to Raman scattering (depends on  $\Delta_{aa}$ ), the second term has both a fluorescence and Raman component, and the third term describes only fluorescence (depends only on  $\Delta_{cb}$ ). The second and thirds term vanish if there is no pure dephasing and relaxation of the ground state is slow ( $\Gamma_{aa} = 0$ ).

The polarization that is generated can be written as

$$P_{NL} = NF \mu_{cb} (\tilde{\rho}_{cb} \exp[i(kz - \omega t)] + \tilde{\rho}_{cb} \exp[-i(kz - \omega t)]) \quad \text{so} \quad (131)$$

$$P_{NL}^o = 2NF_{net} \mu_{cb} \tilde{\rho}_{cb}.$$

Here,

$$F_{net} = \frac{(n_1^2 + 2)}{3} \frac{(n_2^2 + 2)}{3} \frac{(n_3^2 + 2)}{3} \quad (132)$$

We can substitute (102) into (112) to find the resulting field:

$$\frac{\partial E_{cb}^o}{\partial z} + \frac{1}{c} \frac{\partial E_{cb}^o}{\partial t} = \frac{2\pi i F_{cb} \omega_{cb}}{n_{cb} c} NF_{net} \mu_{cb} 2\tilde{\rho}_{cb} \quad (133)$$

Assume steady state where  $\partial E^o / \partial t = 0$  and substitute (130) for  $\tilde{\rho}_{cb}$

$$\frac{\partial E_{cb}^o}{\partial z} = \frac{4\pi i \omega_{cb}}{n_{cb} c} NF \mu_{cb} \frac{\Omega_{ac}^2 \Omega_{bc} \rho_{aa}}{8|\Delta_{ca}|^2} \left( \frac{1}{\Delta_{ba}^*} + \frac{i\Gamma_{cb}^a}{\Delta_{ba}^* \Delta_{cb}} - \frac{2\Gamma_{ca}^*}{\Gamma_{cc} \Delta_{ba}} \right) \quad (134)$$

Substituting for  $\Omega_{cb}$  and rearranging in preparation for integrating,

$$\frac{\partial E_{cb}^o}{E_{cb}^o} = \frac{4\pi i \omega_{cb}}{n_{cb} c} NF \mu_{cb} \frac{\Omega_{ac}^2 \mu_{cb} \rho_{aa}}{8\hbar |\Delta_{ca}|^2} \left( \frac{1}{\Delta_{ba}^*} + \frac{i\Gamma_{cb}^a}{\Delta_{ba}^* \Delta_{cb}} - \frac{2\Gamma_{ca}^*}{\Gamma_{cc} \Delta_{cb}} \right) dz \quad (135)$$

Integrating,

$$E_{cb}^o(z) = E_{cb}^o(0) \exp \left( \frac{4\pi i \omega_{cb} NF \mu_{cb}^2 \Omega_{ac}^2 \rho_{aa}}{8n_{cb} \hbar c |\Delta_{ca}|^2} \left( \frac{1}{\Delta_{ba}^*} + \frac{i\Gamma_{cb}^a}{\Delta_{ba}^* \Delta_{cb}} - \frac{2\Gamma_{ca}^*}{\Gamma_{cc} \Delta_{cb}} \right) z \right) \quad (136)$$

Changing  $\Omega_{ac}^2$  into an intensity

$$I_{ac} = \frac{cn_{ac}}{8\pi} E_{ac}^{o,2} = \frac{cn_{ac}}{8\pi} \frac{\Omega_{ac}^2 \hbar^2}{\mu_{ac}^2} \quad (137)$$

$$\Omega_{ac}^2 = \frac{8\pi\mu_{ac}^2 I_{ac}}{c\hbar^2 n_{ac}} \quad (138)$$

so equation (138) relates the Rabi frequency to the intensity.

Substituting into (136),

$$E_{cb}^o(z) = E_{cb}^o(0) \exp \left( \frac{4\pi i \omega_{cb} NF \mu_{cb}^2 \rho_{aa}}{8n_{cb} \hbar c |\Delta_{ca}|^2} \frac{8\pi\mu_{ac}^2 I_{ac}}{c\hbar^2 n_{ac}} \left( \frac{1}{\Delta_{ba}^*} + \frac{i\Gamma_{cb}^a}{\Delta_{ba}^* \Delta_{cb}} - \frac{2\Gamma_{ca}^*}{\Gamma_{cc} \Delta_{cb}} \right) z \right) \quad (139)$$

Converting (139) into an intensity, (the imaginary part disappears)

$$I_{cb}(z) = I_{cb}(0) \exp \left( \frac{4\pi^2 \omega_{cb} NF \mu_{ac}^2 \mu_{cb}^2 I_{ac} \rho_{aa}}{\hbar^3 c^2 n_{cb} n_{ac} |\Delta_{ca}|^2} \left( \frac{2\Gamma_{ba}}{|\Delta_{ba}^*|^2} - \frac{2\Gamma_{cb}^a (\delta_{cb} \delta_{ba} + \Gamma_{cb} \Gamma_{ba})}{|\Delta_{ba}^*|^2 |\Delta_{cb}|^2} + \frac{4\Gamma_{ca}^* \Gamma_{cb}}{\Gamma_{cc} |\Delta_{cb}|^2} \right) z \right) \quad (140)$$

This equation has the form

$$I = I_o e^{Gz}$$

where G is a gain or amplification coefficient. The signal grows exponentially with path length. We can divide (140) into different terms. For the pure Raman component (the first term),

$$I_{cb}^{Raman}(z) = I_{cb}(0) \exp \left( \frac{8\pi^2 \omega_{cb} NF \mu_{ac}^2 \mu_{cb}^2 I_{ac} \Gamma_{ba} \rho_{aa}}{\hbar^3 c^2 n_{cb} n_{ac} |\Delta_{ca}|^2 |\Delta_{ba}|^2} z \right) \quad (141)$$

$$G_{Raman} = Ramangain = \frac{8\pi^2 \omega_{cb} NF \mu_{ac}^2 \mu_{cb}^2 I_{ac} \Gamma_{ba} \rho_{aa}}{\hbar^3 c^2 n_{cb} n_{ac} |\Delta_{ca}|^2 |\Delta_{ba}|^2} \quad (142)$$

For the stimulated emission component (the third term in (140)),

$$I_{cb}^{Fluor}(z) = I_{cb}(0) \exp \left( \frac{16\pi^2 \omega_{cb} NF \mu_{ac}^2 \mu_{cb}^2 I_{ac} \Gamma_{ca}^* \Gamma_{cb} \rho_{aa}}{\hbar^3 c^2 n_{cb} n_{ac} |\Delta_{ca}|^2 |\Delta_{cb}|^2 \Gamma_{cc}} z \right) \quad (143)$$

$$G_{Stim.Emission} = \frac{16\pi^2 \omega_{cb} NF \mu_{ac}^2 \mu_{cb}^2 I_{ac} \Gamma_{ca}^* \Gamma_{cb} \rho_{aa}}{\hbar^3 c^2 n_{cb} n_{ac} |\Delta_{ca}|^2 |\Delta_{cb}|^2 \Gamma_{cc}} \quad (144)$$

The intensity gets exponentially larger as it goes through the sample.

### Stimulated Emission Cross-Section

It is interesting to approach this problem from the viewpoint that absorption of light with intensity  $I_{ac}$  creates an excited population with an absorption cross-section of  $\sigma_{ac}$  and that population is stimulated to emit with a stimulated emission cross-section of  $\sigma_{cb}$ . The rate equations for this process are:

$$\dot{N}_c = P_p (N_a - N_c) - P_s (N_c - N_b) - \tau_c^{-1} N_c \quad (145)$$

where  $P_p$  and  $P_s$  are the excitation pumping rate and the stimulated emission rate, respectively, and  $\tau_c^{-1}$  is the state  $c$  relaxation rate. The pumping rate and stimulated emission rate depend on the light intensities at the  $a \rightarrow c$  and  $c \rightarrow b$  transition frequencies. If  $N_a \gg N_c \gg N_b$  and  $P_s \ll \tau_c^{-1}$ , we can easily find the population of state  $c$  in the steady state limit.

$$N_c = \frac{P_p}{\tau_c^{-1}} N_a = \frac{P_p}{\Gamma_{cc}} N_a. \quad (146)$$

Let's first look at the excitation pumping rate. If we look at a single molecule with an optical cross-section of  $\sigma_{ca}$  and the excitation intensity is  $n_p$  photons/sec cm<sup>2</sup>, the pumping rate will be

$$P_p = \sigma_{ca} n_p.$$

The intensity and  $n_p$  are directly related by

$$I = \hbar \omega n_p. \quad (147)$$

so

$$P_p = \frac{\sigma_{ca} I_{ca}}{\hbar \omega_{ca}} \quad (148)$$

The excited state population in equation (146) is therefore

$$N_c = \frac{\sigma_{ca} I_{ca}}{\hbar \omega_{ca} \Gamma_{cc}} N_a \quad (149)$$

The output intensity resulting from stimulated emission can be written as a Beer's Law expression except now stimulated emission is occurring instead of absorption.

$$I_s = I_s^o e^{\sigma_s N_c l} \text{ or} \quad (150)$$

$$I_s = I_s^o e^{\frac{\sigma_{cb} \sigma_{ca} I_{ca} N_a l}{\hbar \omega_{ca} \Gamma_{cc}}}. \quad (151)$$

Comparing this expression with equation (143), we can see

$$\sigma_{ac} = \frac{4\pi \omega_{ca} F_1 \mu_{ac}^2 \Gamma_{ca}^*}{\hbar c n_{ac} |\Delta_{ca}|^2} \quad (152)$$

which is just the absorption coefficient for the  $a \rightarrow c$  transition, (see equation (84)) and

$$\sigma_{cb} = \frac{4\pi \omega_{cb} F_1 \mu_{cb}^2 \Gamma_{cb}}{\hbar c n_{cb} |\Delta_{cb}|^2} \quad (153)$$

which is the stimulated emission coefficient for the  $c \rightarrow b$  transition. So equation (151) is completely equivalent to equation (143).

### Spontaneous Raman and Fluorescence

One can also find the spontaneous rates for fluorescence and Raman scattering if you use the zero point fields of the vacuum to stimulate the processes. If there are  $m$  photons in a mode, the energy is  $\hbar \omega \left( m + \frac{1}{2} \right)$  for the mode where the  $\frac{1}{2}$  comes from the contribution of the vacuum fluctuations. To define the vacuum fluctuations and the quantum mechanical

representation of the electromagnetic field, one defines a cavity, in our case a rectangular box. The modes are the standing waves that can be created in the box. The intensity of a light beam will be

$$I = \frac{\hbar\omega(m + \frac{1}{2})}{A\Delta t} \quad (\text{watts/cm}^2) \quad (154)$$

If we release  $m$  photons traveling in the  $z$  direction over an area,  $A$ , of our cavity, then after  $\Delta t$  seconds the photons will occupy a volume of  $V = A \frac{c}{n} \Delta t$  in volume where  $n$  is the index of refraction. So,  $A\Delta t = \frac{nV}{c}$ . We can now write (154) as

$$I = \frac{\hbar\omega(m + \frac{1}{2})}{V \frac{n}{c}} = \frac{\hbar c\omega(m + \frac{1}{2})}{nV}. \quad (155)$$

We will use this relationship between intensity and photons.

If there are  $\frac{n^3\omega^2 d\omega}{2\pi^2 c^3}$  modes per unit volume (see Appendix for derivation), the number of modes within the volume with two polarizations will be:

$$\frac{n^3\omega^2 V d\omega}{\pi^2 c^3}. \quad (156)$$

Here, we are assuming a single oriented molecule where the transition moment and the driving electric field are aligned so  $\vec{\mu} \cdot \vec{E}$  is a maximum. To get a better expression, one should perform an ensemble average over all the orientations in the sample so one gets both the isotropic and anisotropic response.

If  $m$  (the number of photons in mode) = 0, the intensity associated with all modes and polarizations in the volume will be

$$I_{cb}^o = \frac{\hbar c\omega n_{cb}^3 \omega^2 V d\omega}{2Vn \pi^2 c^3} = \frac{n_{cb}^2 \hbar \omega^3 d\omega}{2\pi^2 c^2}. \quad (157)$$

Substituting into (141),

$$I_{cb}^{Raman}(z) = \frac{n_{cb}^2 \hbar \omega_{cb}^3 d\omega_{cb}}{2\pi^2 c^2} \exp\left(\frac{8\pi^2 \omega_{cb} NF \mu_{ac}^2 \mu_{cb}^2 I_{ac} \Gamma_{ba} \rho_{aa}}{\hbar^3 c^2 n_{cb} n_{ac} |\Delta_{ca}|^2 |\Delta_{ba}|^2} z\right). \quad (158)$$

If the exponent is small, one can use a Taylor series expansion and obtain

$$I_{cb}^{Raman}(z) - I_{cb}(0) \approx \frac{n_{cb}^2 \hbar \omega_{cb}^3 d\omega_{cb}}{2\pi^2 c^2} \left( \frac{8\pi^2 \omega_{cb} NF \mu_{ac}^2 \mu_{cb}^2 I_{ac} \Gamma_{ba} \rho_{aa}}{\hbar^3 c^2 n_{cb} n_{ac} |\Delta_{ca}|^2 |\Delta_{ba}|^2} z \right) \quad (159)$$

Note that the Raman intensity is the output at  $\omega_s$  and  $I_{ac}$  is the excitation intensity.

$$\frac{\Delta I_{cb}}{I_{ac}} \approx \frac{8\pi^2 n_{cb} \hbar \omega_{cb}^4 NF \mu_{ac}^2 \mu_{cb}^2 \Gamma_{ba} \rho_{aa} z}{2\pi^2 \hbar^3 c^4 n_{ac} |\Delta_{ca}|^2 |\Delta_{ba}|^2} d\omega_{cb} \quad (160)$$

This expression is very similar to Beer's law which can be written as  $dI/I = \sigma N l$  except now  $dI$  and  $I$  are at different frequencies. This difference presents a problem because we can get a cross-section that is different depending upon whether we define the intensities in terms of joules/sec. cm<sup>2</sup> or photons/sec. cm<sup>2</sup>. The two approaches differ by factors of  $\omega_s/\omega_p$ . We will define the intensity in terms of watts/cm<sup>2</sup>. The differential spectral Raman cross-section is therefore

$$\frac{d\sigma}{d\omega_{cb}} = \frac{4F n_{cb} \omega_{cb}^4 \mu_{ac}^2 \mu_{cb}^2 \Gamma_{ba} \rho_{aa}}{\hbar^2 c^4 n_{ac} |\Delta_{ca}|^2 |\Delta_{ba}|^2}. \quad (161)$$

If only a fraction,  $d\Omega/4\pi$  is scattered into the solid angle actually detected, then we can write a differential Raman cross-section

$$\frac{d\sigma}{d\omega_{cb} d\Omega} = \frac{F n_{cb} \omega_{cb}^4 \mu_{ac}^2 \mu_{cb}^2 \Gamma_{ba} \rho_{aa}}{\pi \hbar^2 c^4 n_{ac} |\Delta_{ca}|^2 |\Delta_{ba}|^2}. \quad (162)$$

(If this expression was rewritten assuming the intensities were measured in photons/sec. cm<sup>2</sup>, it would have  $\omega_{cb}^3 \omega_{ac}$  instead of  $\omega_{cb}^4$ .) This equation assumed that the Raman signal was emitted isotropically in  $4\pi$  steradians but typically, it is emitted anisotropically with a  $\sin^2\theta$  dependence typical of an emitting dipole. The  $d\sigma/d\omega$  is the spectral cross-section for all angles at the peak of the Raman line and is independent of how the Raman scattering is distributed. If we integrate  $d^2\sigma/d\omega d\Omega$  over the  $\sin^2\theta$  distribution, we must get the total cross-section so,

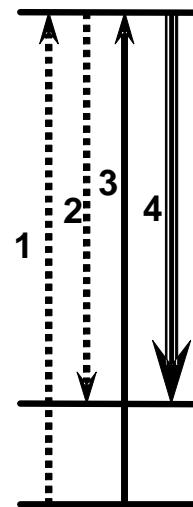
$$\frac{d\sigma}{d\omega} = \int_0^{2\pi} d\phi \int_0^\pi d\theta \frac{d^2\sigma}{d\omega_{cb} d\Omega} \sin^2 \theta \sin \theta = \frac{8\pi}{3} \frac{d^2\sigma}{d\omega d\Omega} \quad (163)$$

(The extra  $\sin \theta$  dependence comes from integration over angles.) This expression assumes that emission occurs into all the angles available. If we are interested in one particular value of the solid angle,  $\Omega$ , we integrate over only that solid angle,

$$\left( \frac{d\sigma}{d\omega} \right)_{measured} = \int d\phi \int d\theta \frac{d^2\sigma}{d\omega_{cb} d\Omega} \sin^3 \theta \quad (164)$$

## Stimulated Raman, Inverse Raman, Raman Gain, and Raman Loss

These coherent Raman processes all involve the same Raman pathway shown in the figure. Stimulated Raman occurs from a combination of an extremely intense light beam with frequency  $\omega_1 = \omega_3$ , and the vacuum fluctuations at  $\omega_2$ , creates stimulated emission at  $\omega_4$  which in turn acts as a real beam at  $\omega_2$  to create still more stimulated emission at  $\omega_4$ . The process grows exponentially to create a very strong output. Stimulated Raman has a threshold intensity. When a molecule has many different vibrational modes, stimulated Raman will usually only occur for the strongest Raman scattering mode because it reaches threshold first and depletes the excitation source intensity so the other modes cannot reach threshold.



Inverse Raman spectroscopy is performed by using a broad band laser at  $\omega_1 = \omega_3$  along with a strong narrow band light source for  $\omega_2$ . A Raman process will create more light at  $\omega_2 = \omega_4$  and deplete the excitation intensity at  $\omega_1 = \omega_3$ . The broad band light source is measured with a monochromator and one sees a sharp absorption feature at the frequencies where  $\omega_2 = \omega_1 - \omega_{ba}$ .

Raman gain and Raman loss spectroscopy use two strong narrow band lasers, one for  $\omega_1 = \omega_3$  and the other for  $\omega_2$ . Raman gain or loss spectroscopy monitors the beams as they leave the sample and measures either the gain in intensity of the  $\omega_2$  beam or the loss in intensity of the  $\omega_1 = \omega_3$  beam, respectively.

## Raman and Fluorescence Spectroscopy

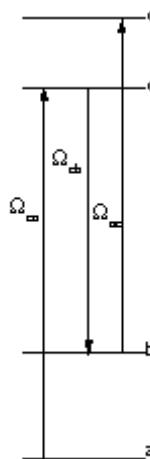
Fluorescence spectroscopy usually uses a broad band incoherent light to excite the sample because the absorption transitions of molecules are usually very broad so absorption occurs over a large band of wavelengths. It results in high excited state populations. Raman spectroscopy uses a narrow band coherent light source that is not usually resonant with any electronic state. One often states that the excitation occurs to a virtual state. The virtual state is actually all of the real electronic states. They simply are not resonant. In both spectroscopies, the Raman and fluorescence is measured perpendicular to the direction of the excitation light. Fluorescence spectra are usually broad because the excited electronic state is broad ( $\Gamma_{ca}$  is fast). Raman spectra are very sharp because they originate from a driven coherence at the frequency of the excitation and the vibrational coherence is narrow ( $\Gamma_{ba}$ ).

## Coherent Anti-Stokes Raman Spectroscopy (CARS)

If three lasers are simultaneously focused into a material, new coherent beams will be generated at frequency combinations of the lasers as shown in the diagram. The sequence of coherences is

$aa \rightarrow ca \rightarrow ba \rightarrow da$

The relationships between the coherences is:



$$\begin{aligned}
\rho_{ca} &= \frac{\Omega_{ac}}{2\Delta_{ca}} \rho_{aa} e^{i(k_1 z - \omega_1 t)} \\
\rho_{ba} &= \frac{\Omega_{cb}}{2\Delta_{ba}} \rho_{ca} e^{-i(k_2 z - \omega_2 t)} \\
&= \frac{\Omega_{ac}\Omega_{cb}}{4\Delta_{ca}\Delta_{ba}} \rho_{aa} e^{i[(k_1 - k_2)z - [(\omega_1 - \omega_2)t]]} \\
\rho_{da} &= \frac{\Omega_{bd}}{2\Delta_{da}} \rho_{ba} e^{i(k_3 z - \omega_3 t)} \\
&= \frac{\Omega_{ac}\Omega_{cb}\Omega_{bd}}{8\Delta_{ca}\Delta_{ba}\Delta_{da}} \rho_{aa} e^{i[(k_1 - k_2 + k_3)z - [(\omega_1 - \omega_2 + \omega_3)t]]}
\end{aligned}$$

We can find the polarization associated with  $\rho_{da}$  which produces the output signal:

$$\tilde{\rho}_{da} = \frac{\Omega_{ca}}{2\Delta_{ca}} \frac{\Omega_{cb}}{2\Delta_{ba}} \frac{\Omega_{bd}}{2\Delta_{da}} \rho_{aa} \quad (165)$$

This produces a polarization given by the analog of (102)

$$P = NF_{net} \mu_{da} \left( \tilde{\rho}_{da} e^{i(k'_4 z - \omega_4 t)} + \tilde{\rho}_{ad} e^{-i(k'_4 z - \omega_4 t)} \right) \quad (166)$$

where

$$F_{net} = \left( \frac{n_1^2 + 2}{3} \right) \left( \frac{n_2^2 + 2}{3} \right) \left( \frac{n_3^2 + 2}{3} \right) \left( \frac{2n_1}{n_1 + n_{external}} \right) \left( \frac{2n_2}{n_2 + n_{external}} \right) \left( \frac{2n_3}{n_3 + n_{external}} \right) \quad (167)$$

corrects for the factors relating the local field to the macroscopic internal field and for the transmission of the external field into the macroscopic internal field. We can now use (112) to predict the CARS electric field:

$$\frac{\partial E_4^o}{\partial z} + \frac{n_4}{c} \frac{\partial E_4^o}{\partial t} = \frac{2\pi i \omega_4}{n_4 c} 2NF_4 \mu_{da} \tilde{\rho}_{da} e^{i(k'_4 - k_4)z} \quad (168)$$

where  $E_4^o$  is the macroscopic internal field. For this case, the nonlinear input polarization and the output signal have different wavelengths so  $k_4' \neq k_4$ . To find  $k'_4$ , we assume the beams are parallel to each other and then perform the vector sum,  $\vec{k}'_4 = \vec{k}_1 - \vec{k}_2 + \vec{k}_3$ . Since  $|k| = n\omega/c$ ,

$$k'_4 = \frac{n_1 \omega_1}{c} - \frac{n_2 \omega_2}{c} + \frac{n_3 \omega_3}{c} \quad \text{and} \quad k_4 = \frac{n_4 \omega_4}{c}. \quad (169)$$

If  $n_1 = n_2 = n_3 = n_4$ , then  $k_4 = k'_4$ . If the refractive indices are different,  $k'_4 \neq k_4$ . If the beams are traveling in different directions, the equation (169) must be modified to account for the different angles. We assume steady state ( $\partial E^o / \partial t = 0$ ) and integrate equation (168).

$$E_4^o = \frac{4\pi\omega_4 NF_4 \mu_{da} \tilde{\rho}_{da}}{n_4 c (k'_4 - k_4)} \left( e^{i(k'_4 - k_4)z} - 1 \right) \quad (170)$$

Converting to an intensity using equation (79):

$$I = \frac{cn}{8\pi} \frac{16\pi^2 \omega_4^2 N^2 F_4^2 \mu_{da}^2 |\tilde{\rho}_{da}|^2}{n_4^2 c^2 (k'_4 - k_4)^2} \left( 2 - e^{i(k'_4 - k_4)z} - e^{-i(k'_4 - k_4)z} \right) \quad (171)$$

$$= \frac{2\pi\omega_4^2 N^2 F_4^2 \mu_{da}^2 |\tilde{\rho}_{da}|^2}{n_4 c (k'_4 - k_4)^2} 2 \left( 1 - \cos(k'_4 - k_4)z \right) \quad (172)$$

We know  $\sin\frac{\theta}{2} = \sqrt{\frac{1 - \cos\theta}{2}}$  so

$$I = \frac{8\pi\omega_4^2 N^2 F_4^2 \mu_{da}^2 |\tilde{\rho}_{da}|^2}{n_4 c (k'_4 - k_4)^2} \sin^2 \frac{(k'_4 - k_4)z}{2} \quad (173)$$

It is convenient to convert  $\sin^2 x$  into  $\text{sinc}^2 x = \frac{\sin^2 x}{x^2}$  and using equation (173)

$$I = \frac{2\pi\omega_4^2 N^2 F_4^2 F_{net}^2 \mu_{da}^2 \Omega_{ca}^2 \Omega_{cb}^2 \Omega_{bd}^2 \rho_{aa}^2 z^2}{32n_4 c |\Delta_{ca}|^2 |\Delta_{ba}|^2 |\Delta_{da}|^2} \text{sinc}^2 \frac{(k'_4 - k_4)z}{2} \quad (174)$$

At this point, we have found the intensity within the sample in terms of external electric fields that are contained within the Rabi frequencies. We can convert to an external output intensity using the transmission coefficient.

$$I_{output} = \frac{4n_4 n_{external}}{(n_4 + n_{external})^2} I. \quad (175)$$

It is interesting to get expressions that use  $\chi^{(3)}$  as well. In the Maker-Terhune convention,  $\chi^{(3)}$  is defined by

$$P^o = D \chi^{(3)} E_1^o E_2^o E_3^o \quad (176)$$

where the E's are macroscopic internal fields, and D takes care of the different permutations of the electric fields that occur if the original expression  $P = \chi^{(3)} E^3$  is expanded by substituting  $E = E_1 + E_2 + E_3$ . Thus,  $D = 6$  if  $\omega_1 \neq \omega_2 \neq \omega_3$ , 3 if  $\omega_1 = \omega_2 \neq \omega_3$ , and 1 if  $\omega_1 = \omega_2 = \omega_3$ . If one of the fields is a dc field, the field should be doubled since it appears as  $E = E^o$  instead of

$\frac{1}{2} E^o (e^{i(kz - \omega t)} + e^{-i(kz - \omega t)})$ . We also know that

$$\frac{1}{2} P^o = NF_{net} \mu_{da} \rho_{da} \quad (177)$$

so now we substitute eqns. (165) and (166),

$$P^o = \frac{NF_{net} \omega_4 \mu_{da} \mu_{ac} \mu_{cb} \mu_{bd} \rho_{aa}}{4\hbar^3 \Delta_{ca} \Delta_{ba} \Delta_{da}} E_1^o E_2^o E_3^o \quad (178)$$

Comparing eqns. (176) and (178), we can see that  $\chi^{(3)}$  must then be

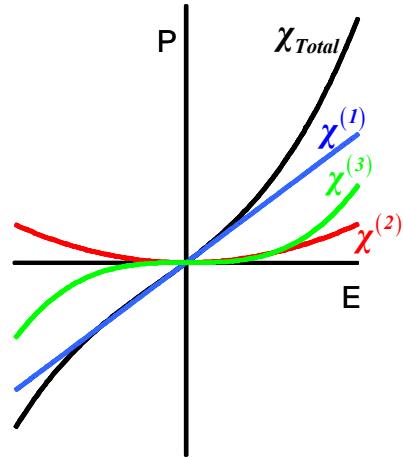
$$\chi^{(3)} = \frac{NF_{net} \mu_{da} \mu_{ac} \mu_{cb} \mu_{bd} \rho_{aa}}{4D\hbar^3 \Delta_{ca} \Delta_{ba} \Delta_{da}} \quad (179)$$

Now that we have an expression for the  $\chi^{(3)}$ , we can rewrite our expression for the intensity (see eqn. (174)) in terms of  $\chi^{(3)}$ . To do so, we need to convert Rabi frequencies and electric fields into intensities using eqn. 46. We also must remember that the excitation fields are external so the refractive indices required in the electric field-intensity conversion correspond to the external material. We then obtain,

$$I = \frac{256\pi^4 \omega_4^2 D^2 F_4^2 |\chi^{(3)}|^2 z^2}{n_4 c^4} \text{sinc}^2 \frac{(k'_4 - k_4)z}{2} I_1 I_2 I_3 \quad (180)$$

where all of the input intensities are external but the CARS intensity is an internal intensity. Again, conversion to an external output intensity uses eqn. (175).

**Other Nonlinear Methods-** When several light beams are focused into a sample, the electric fields can be comparable to the fields within molecules. The figure shows a schematic relationship between the electric field and the induced polarization. The induced polarization can be distorted because the response to one of the fields can be influenced by another field that changes the sample's polarizability. The result is that new light beams are formed at new frequencies that correspond to all the sums and differences that can be created from the initial excitation frequencies. In addition, the excitation beams leaving the sample at their original frequencies will still have altered intensities and/or phases. We will examine three wave mixing and four wave mixing where two or three excitation waves create a third or fourth output wave. The output beams are coherent because the coherent excitation beams create a phased array of oscillators, i.e. a coherent polarization, which re-emit directional beams. Their directions are defined by momentum conservation. Momentum conservation is defined by the same phase matching relationships between excitation and output  $k$ -vectors. The oscillators have a coherent spatial modulation defined by wave vector addition (i.e. a grating) and a coherent temporal modulation.



### Taylor's Series Expansion of Polarization

It is common to use a Taylor's series expansion of the polarization in order to have a qualitative description of the relationship. The graph shows the individual contributions in the Taylor's series expansion to the total polarization.

$$\vec{P} = \tilde{\chi}_{i,j}^{(1)} \vec{E} + \tilde{\chi}_{i,j,k}^{(2)} \vec{E}^2 + \tilde{\chi}_{i,j,k,l}^{(3)} \vec{E}^3 + \dots \quad (181)$$

$$\text{where } \vec{E} = \sum_i \vec{E}_i. \quad (182)$$

**Two cases for the relationship between the polarization and the field it creates:**

$$\frac{\partial E^o}{\partial z} + \frac{n}{c} \frac{\partial E^o}{\partial t} = \frac{2\pi i F \omega P_{NL}^o}{nc} e^{i\Delta k z} \quad (183)$$

- a)  $P_{NL}^o$  depends on  $E^o$  - output frequency is same as an excitation frequency- see equation (115).
- b)  $P_{NL}^o$  does not depend on  $E^o$  - output frequency is different from any of the excitation frequencies- see equation (116).

### Three Wave Mixing

This method is based on the  $\chi_{i,j,k}^{(2)}$  term in (181). Two excitation fields create the output field. It requires an anisotropy in order to obtain a measurable output signal. The importance of anisotropy is most clear when considering that the polarization changes sign if the electric field changes sign in an isotropic material. However, the quadratic term does not change sign if the electric field reverses so it cannot contribute in an isotropic sample. In three wave mixing,

$$\vec{E} = \vec{E}_1 + \vec{E}_2$$

$\vec{k}_1 + \vec{k}_1 -$	second harmonic generation (SHG)
$\vec{k}_1 + \vec{k}_2 -$	sum frequency generation (SFG)
$\vec{k}_1 - \vec{k}_2 -$	difference frequency generation (DFG)
$\vec{k}_1 - \vec{k}_1 -$	optical rectification

### Four Wave Mixing

This method is based on the  $\chi_{i,j,k,l}^{(3)}$  term in (181). Three excitation fields create the output field.

In four wave mixing,

$$\vec{E} = \vec{E}_1 + \vec{E}_2 + \vec{E}_3$$

$\vec{k}_1 - \vec{k}_1 + \vec{k}_1 -$  pulse propagation effects- index of refraction is intensity dependent (optical Kerr effect)-  $n = n_o + n_2 I$

- self-phase modulation or chirp (the most intense temporal part of the pulse has a larger refractive index so it slows while the leading and trailing edges travel faster. This effect scrambles the frequencies in a complex way. One finds that the red frequencies occur at leading edge if the pulse and blue frequencies at trailing edge so there is a linear change of frequency in time, i.e. a chirp)
- self focusing (the most intense spatial part of the pulse has a larger refractive index so a Gaussian pulse shape creates its own lens and the beam focuses)
- white light generation

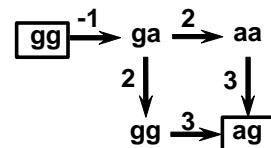
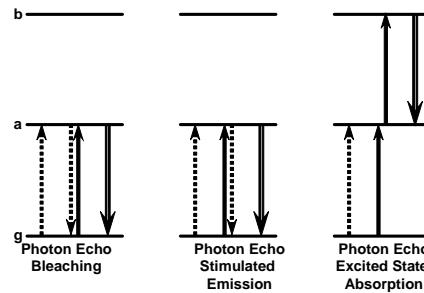
Other effects- phase conjugation (two exactly counter-propagating pump beams interact with a third beam and the third order nonlinearity creates a fourth beam that is the phase conjugate of the third beam so it counter propagates in the exact direction of the third beam), degenerate four wave mixing

- $\vec{k}_1 - \vec{k}_1 + \vec{k}_2$  - Raman, stimulated Raman, fluorescence, stimulated emission, pump-probe, transient grating
- $-\vec{k}_1 + \vec{k}_2 + \vec{k}_2$  - Coherent Stokes Raman spectroscopy (CSRS), photon echo, stimulated photon echo
- $\vec{k}_1 + \vec{k}_1 - \vec{k}_2$  - Coherent Anti-Stokes Raman spectroscopy (CARS)
- $\vec{k}_1 - \vec{k}_2 + \vec{k}_3$  - fully resonant four wave mixing
- $\vec{k}_1 + \vec{k}_2 + \vec{k}_3$  - frequency tripling

**Photon echo-** The figure shows the three photon echo WMEL diagrams. An initial pulse creates a  $ga$  coherence after the first interaction. After a delay time,  $\tau$ , a second pulse induces the second and third interactions (the interactions are drawn close to each other to indicate they come from the same pulse) to create an  $ag$  coherence that reemits. Phase matching is important. For photon echo, the phase matching condition is  $\vec{k}_{PE} = -\vec{k}_1 + 2\vec{k}_2$  where the subscripts indicate the time ordering of the two pulses. The usefulness of photon echo rests on having spectral transitions that are inhomogeneously broadened so molecules that have different environments or conformations have a distribution of different transition frequencies. The temporal dependence of the excited  $ga$  coherences is  $e^{i\omega_{ag}t}$  so after a delay time of  $\tau$ , the phase becomes  $e^{i\omega_{ag}\tau}$ . The temporal dependence of the final  $ag$  coherence is  $e^{-i\omega_{ag}t}$  since an  $ag$  coherence is conjugate to the  $ga$  coherence. After a delay of  $\tau$ , the net phase will be zero, regardless of the  $\omega_{ag}$  frequency. At this point in time, all of the coherences will be again in phase and the re-emission becomes completely coherent. This phased emission scales quadratically with the sample concentration. The large output intensity that results at time  $\tau$  is called the echo. By measuring the echo intensity as a function of delay time between the first two pulses, one can measure the dephasing rate ( $\Gamma_{ag}$ ) of the  $ga$  coherence. The strength of the photon echo experiment is its immunity to inhomogeneous broadening because the echo does not depend on the specific value for the  $ag$  frequency.

**Stimulated photon echo** experiments are three pulse experiments so the three excitation interactions occur at different times and the delay times between pulses are adjustable.<sup>63</sup> The phase matching condition is  $\vec{k}_{SPE} = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$  where the subscripts denote the time ordering. The WMEL diagram shows there are three pathways- a) ground state bleaching, b) stimulated emission, c) excited state absorption. The sign of the polarization is  $(-1)^n$  where  $n$  is the number of bra-side interactions, so excited state absorption has the opposite sign from the other pathways. The negative sign is associated with the intensity decrease caused by excited state absorption.

The Liouville figure shows the coherences and populations for the bleaching and stimulated emission pathways. After the second interaction, one has either a  $gg$  ground state population or an  $aa$  excited



state population. After a delay time  $T$ , the third pulse arrives to create the  $ag$  output coherence (or  $ba$  for the excited state absorption). The decay of the stimulated photon echo intensity during the  $T$  delay time measures the relative population changes of the ground and excited state populations. In the impulsive limit, we can write

$$e^{(-i\omega_{ga}-\Gamma_{ag})(\tau_2-\tau_1)} e^{-\Gamma_{aa}(\tau_3-\tau_2)} e^{(-i\omega_{ag}-\Gamma_{ag})(t-\tau_3)} = e^{(-i\omega_{ga}-\Gamma_{ag})\tau} e^{-\Gamma_{aa}T} e^{(-i\omega_{ag}-\Gamma_{ag})t}$$

where we have redefined the measurement times and delays.

#### Other important pulse propagation effects

- **Ultrafast light pulses-** In order to create ultrafast light pulses, there must be a broad band of frequencies in the pulse and their phases must match at some point in time and space. They constructively interfere at that point in time and space but destructively interfere at every other point. The wider the band of frequencies, the narrower the temporal width of the pulse. The relationship between the band of frequencies and the pulse width is  $\Delta\omega\Delta\tau=2\pi\Delta\nu\Delta\tau=2\pi c_B$  where  $c_B$  depends on the pulse shape

Pulse Shape	$c_B$
Gaussian	0.441
Sech	0.315
Lorentzian	0.142

- **Group velocity dispersion-** The index of refraction changes with frequency. Normal dispersion corresponds to a refractive index that increases as the frequency of light increases. Anomalous dispersion corresponds to a refractive index that decreases as the frequency increases. It is usually observed only in the region above a resonance where the refractive index is changing rapidly.

#### Second Harmonic Generation Phase Matching in Birefringent Crystals

It is very common to create the second harmonic signal from a laser beam by passing the beam through a birefringent crystal. The birefringence is necessary to provide phase matching. Consider light propagating along the optic axis of a uniaxial crystal. Its refractive index is independent of its polarization direction. This refractive index is labeled ordinary,  $n^o$ . Light propagating perpendicular to the optic axis has two refractive indices that depend on the polarization direction. If the light is polarized perpendicular to the optic axis, the refractive index is still  $n^o$ . If it is polarized parallel to the optic axis, the refractive index is labeled extraordinary,  $n^e$ . If the light is propagating at an angle  $\theta$ , the extraordinary refractive index is between  $n^o$  and  $n^e$  and it is labeled  $n(\theta)$  where  $\theta$  is the angle of the light beam relative to the optical axis. If  $\theta = 90^\circ$ ,  $n(\theta = 90^\circ) = n^e$  while if  $\theta = 0^\circ$ ,  $n(0^\circ) = n^o$ . Regardless of the angle, this polarization direction is called the extraordinary ray. It has a value of

$$\frac{1}{n^2(\theta)} = \frac{\cos^2 \theta}{(n^o)^2} + \frac{\sin^2 \theta}{(n^e)^2}.$$

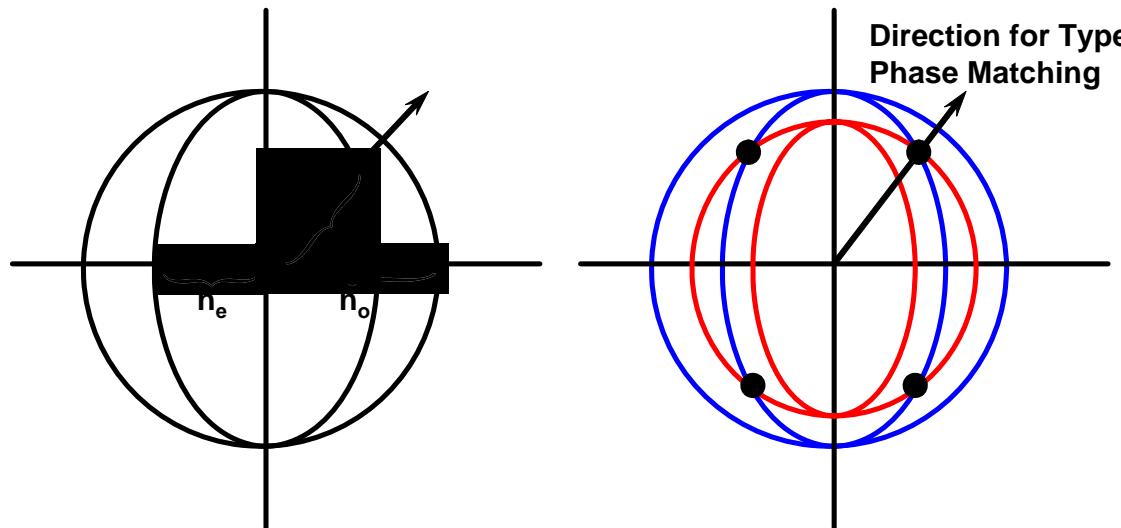
The two refractive indices can be represented graphically by the first graph. The vertical axis is the optical axis. The arrow shows the direction of light propagation. The inner ellipse

shows the extraordinary index of refraction while the outer circle shows the ordinary index of refraction. The intersection of the light ray with the ellipse defines the extraordinary index of refraction while the intersection with the circle defines the ordinary index of refraction.

If there are two frequencies, one needs two sets of circles and ellipses. We show the values for the fundamental frequency,  $\omega$ , in red and the second harmonic frequency,  $2\omega$ , in blue.

The condition for phase matching requires  $\vec{k}_{2\omega} = 2\vec{k}_\omega$  so  $\frac{n_{2\omega}}{c} \frac{2\omega}{c} = \frac{2n_\omega}{c}$ . In order to obtain

phase matching, we require  $n_{2\omega} = n_\omega$ . We can obtain phase matching if the angle of the beam matches that at which the ordinary ray of the fundamental has the same index of refraction as the extraordinary ray of the second harmonic.



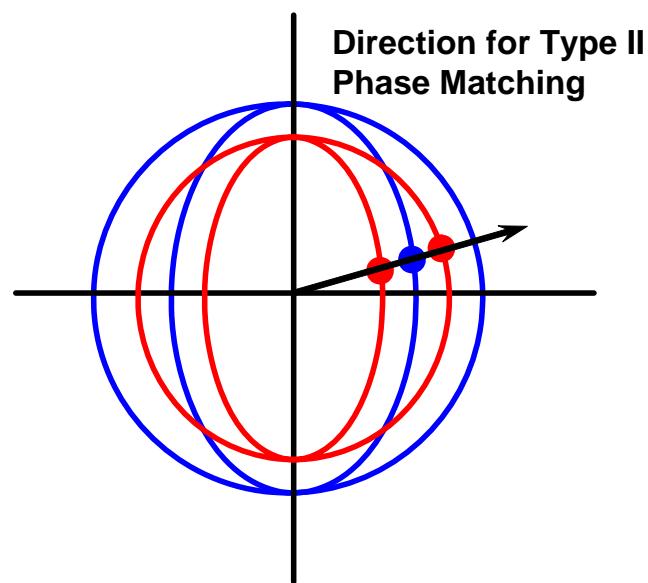
For sum frequency generation, the phase matching condition is  $\vec{k}_{SPE} = \vec{k}_1 + \vec{k}_2$  so

$$\frac{n_{\omega_1+\omega_2}(\omega_1 + \omega_2)}{c} = \frac{n_{\omega_1}\omega_1}{c} + \frac{n_{\omega_2}\omega_2}{c}.$$

Using the same strategy, we can pick a direction such that the two lower frequencies are ordinary rays and the sum frequency is an extraordinary ray. This choice is Type I phase matching and

$$\frac{n_{\omega_1+\omega_2}^e(\theta)(\omega_1 + \omega_2)}{c} = \frac{n_{\omega_1}^o\omega_1}{c} + \frac{n_{\omega_2}^o\omega_2}{c}$$

. We could also pick the extraordinary ray for one of the lower frequencies and the ordinary ray for the other and the extraordinary ray for the sum frequency. That choice corresponds to Type II phase matching and



$$\frac{n_{\omega_1+\omega_2}^e(\theta)(\omega_1 + \omega_2)}{c} = \frac{n_{\omega_1}^o \omega_1}{c} + \frac{n_{\omega_2}^e(\theta) \omega_2}{c}. \text{ In both cases, one solves for the angle that meets}$$

the phase matching criterion. Only some materials are appropriate for phase matching. They must have refractive index dispersions that allow intersections of the ordinary ray of one with the extraordinary ray of the other.

### **Optical Parametric Oscillators and Amplifiers**

Optical Parametric Oscillators (OPO) and Amplifiers (OPA) are based on the same fundamental processes. Here, the sum frequency is designated the pump and the two lower frequencies are designated the signal and idler such that  $\omega_s > \omega_i$  and  $\omega_p = \omega_s + \omega_i$ . The OPO is based on bringing a strong pump beam into a nonlinear birefringent crystal that is mounted within an optical cavity (i.e. two reflective mirrors). The vacuum creates a signal or idler beam and the other beam is created by difference frequency generation. The signal and/or the idler beams are reflected from the cavity end mirrors and remain within the cavity to build up larger fields. Energy essentially flows from the pump beam to the signal and idler beams. The signal and idler frequencies are defined by the phase matching conditions. The signal and idler photons are correlated with each other because they were created by the same photon. They are entangled. That means that if one measures the polarization of one photon at some distant point, the polarization of the other photon will be instantly defined at some other point. Some or all of one or both the signal and idler beams are allowed to leave the cavity for use in an experiment. An OPA is identical except that either a real signal or idler beam is introduced to the nonlinear crystal along with the pump beam. An OPA can be thought of as a difference frequency generation crystal.

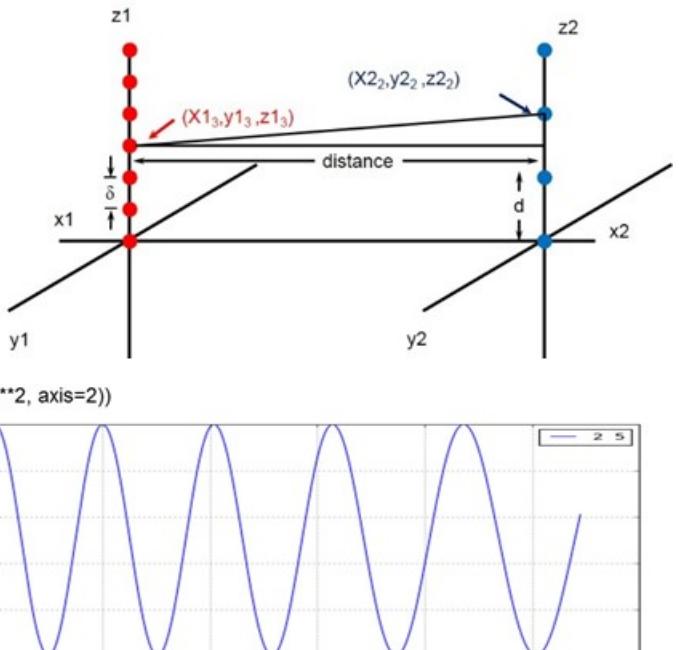
## Physical Optics

### Light, Interference, and Diffraction

- $e^{i(\vec{k} \cdot \vec{z} - \omega t)}$  defines the spatial and temporal dependence of a light wave. For constant  $t$ ,  $\vec{k} \cdot \vec{z}$  defines the spatial variation and  $\vec{k} = \frac{2\pi}{\lambda} \hat{a}$ . For constant  $z$ ,  $\omega t$  defines the temporal variation and  $\omega = 2\pi\nu$ . For constant  $k \cdot z - \omega t$ ,  $k \cdot z = \omega t$  defines how  $z$  changes when  $t$  changes, i.e. the velocity. So,  $\frac{\omega}{k} = \frac{z}{t} = c$  so  $\omega = kc$  or  $c = v\lambda$ .
- Convenient to define  $\bar{v} \equiv \frac{1}{\lambda}$  with units of  $\text{cm}^{-1}$ . **Note, that finding how changes in  $\bar{v}$  are related to changes in wavelength requires differentiation:**  $d\bar{v} = -\frac{d\lambda}{\lambda^2}$
- Huygen's principle- the propagation of a wave front can be defined by an infinite number of light sources along the wave front.
- The intensity is related to the electric field by  $I = \frac{c\varepsilon_0 n_{\text{index}} \xi}{2} |E(z, t)|^2$
- We can use Huygen's principle and MathCAD to describe any interference or diffraction effect. Let's see how. The diagram shows sources (red) and detectors (blue) of light in two separate  $x, y, z$  spaces. We calculate the distances between every source and every detector so we can find the phase of the light at each detector from each source. We then add the phases together to find the net electric field at each detector. The result is a sinusoidally oscillating fringe pattern.

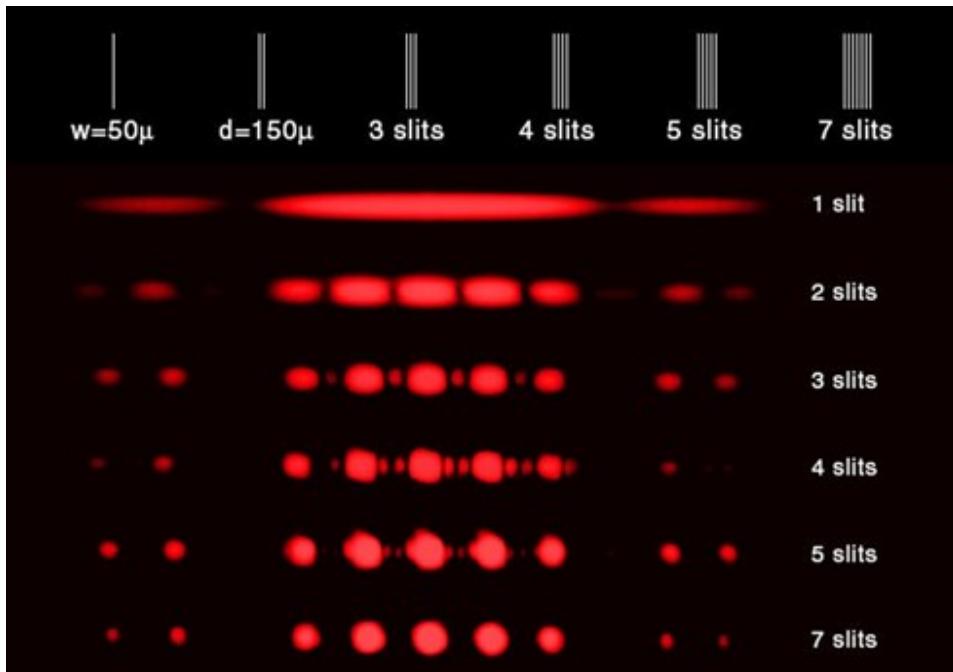
```
wavelength = 0.5 # um
# screen
dist = 1e5 # um
n_screen_points = 500
theta = 0.001
screen_coords = np.zeros((n_screen_points, 3))
screen_coords[:, 0] = dist
screen_coords[:, 2] = dist*np.tan((np.arange(n_screen_points)*theta))
print source_coords
print screen_coords

# 2 slits 5 microns
n_sources = 2
d_sources = 5 # um
source_coords = np.zeros((n_sources, 3))
source_coords[:, 2] = np.arange(n_sources) * d_sources
delta = np.sqrt(np.sum((source_coords[:, None]-screen_coords[:, None])**2, axis=2))
E = np.sum(np.exp(2*np.pi*1j*delta/wavelength), axis=0)
I = E*np.conj(E) / (n_sources)**2
plt.plot(screen_coords[:, 2], I)
```



### Specific Examples- infinite plane wave at normal incidence to slits' plane

- Two thin slits-  $n\lambda = d(\sin \theta)$  where the path difference is  $\Delta = d \sin \theta$
- Multiple slits (a grating)- for N equally spaced slits, the path difference between the first and N<sup>th</sup> slits is  $\Delta = Nd \sin \theta$ 
  - General Principle- condition for constructive interference defined by shortest path length and condition for destructive interference defined by longest path length.
  - Condition for constructive interference:
    - For adjacent slits-  $n\lambda = d \sin \theta$
    - For the N<sup>th</sup> slit-  $nN\lambda = W \sin \theta = nNd \sin \theta$
  - Condition for destructive interference occurs when there is an extra period over the path length difference between the first and last slits, there will be a half wave length of path difference between all pairs of slits- the 1<sup>st</sup> slit and the N/2 slit, the 2<sup>nd</sup> and the N/2+1 slit, etc.
    - For the N<sup>th</sup> slit-  $nN\lambda + \frac{\lambda}{2} = nNd \sin \theta$
    - For adjacent-  $n\lambda + \frac{\lambda}{N} = d \sin \theta$



- Either  $\lambda$  or  $\theta$  can change to go from constructive to destructive interference between the first and middle slits. We will call that change  $d\lambda$  and  $d\theta$ .
  - If  $\lambda$  changes,
  - $nN\lambda_1 = nNd \sin \theta$
  - $nN\lambda_2 + \frac{\lambda}{2} = nNd \sin \theta$
  - so  $nN(\lambda_2 - \lambda_1) = \frac{\lambda}{2}$  or  $\frac{\lambda_2 - \lambda_1}{\Delta\lambda} = nN$

- If  $\theta$  changes,

$$nN\lambda = nNd \sin \theta_1$$

- $nN\lambda + \lambda = nNd \sin \theta_2$
- so  $(\sin \theta_2 - \sin \theta_1) = \frac{\lambda}{nNd}$
- or  $d\theta = \frac{\lambda}{nNd} = \frac{\lambda}{W}$  where  $W$  is the width of the slit array.

- If  $d$  changes,

$$nN\lambda = nNd_1 \sin \theta$$

- $nN\lambda + \lambda = nNd_2 \sin \theta$

$$\Delta d = \frac{\lambda}{N \sin \theta}$$

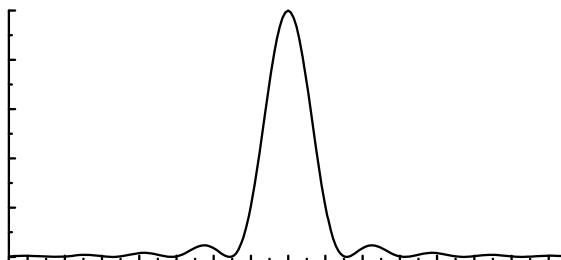
- Finite slit

- The condition for destructive interference at the first minimum is that all the rays coming through the slit must interfere destructively at the minimum. The ray to one extreme must interfere destructively with the ray coming from the center of the slit. If that is the case, there will be a one-to-one pairing of rays that

destructively interfere. The condition for that is  $\frac{\lambda}{2} = \frac{W}{2} \sin \theta$  or

$$\lambda = W \sin \theta \quad \text{where } \theta \text{ is the ray's angle relative to the normal.}$$

- A finite slit creates a sinc function diffraction pattern,  $\frac{\sin^2 x}{x^2}$ . It is graphed below.
- The shape creates a beam that spreads. The divergence is the angular spread of the



beam measured from the center to the first minimum. The divergence is calculated by finding the angle that causes destructive interference between the light coming from the bottom of the slit with the light coming from the middle of the slit, just like the problem with multiple slits. The divergence is then-

$$\sin \theta = \frac{\lambda}{W}$$

- We can reverse the process as well. Huygen's principle says that if we place oscillators on the wavefront of the expanding beam, they will interfere to predict

how the beam will propagate. Thus, if we examine how a beam with a sinc function spatial profile focuses, it becomes the same problem as the diffraction from a single slit except in reverse. The sinc function converges to a width,  $W$

where  $W = \frac{\lambda}{\sin \theta}$  or  $W = \frac{\lambda}{N.A.}$  where  $N.A. \equiv \sin \theta$  is the numerical aperture

(actually,  $N.A. = n \sin \theta$  where  $n$  is the refractive index of the sample medium, either air or oil.)

- A TEM<sub>00</sub> diverging laser beam has a hyperbolic shape that remains Gaussian:

$$w(z)^2 = w_0^2 + \left( \frac{\lambda z}{\pi w_0} \right)^2 \text{ so}$$

$$\begin{aligned} w(z) &= \left[ w_0^2 + \left( \frac{\lambda z}{\pi w_0} \right)^2 \right]^{1/2} \\ &= w_0 \left[ 1 + \left( \frac{\lambda z}{\pi w_0^2} \right)^2 \right]^{1/2} = w_0 \left[ 1 + \left( \frac{z}{z_c} \right)^2 \right]^{1/2} \end{aligned}$$

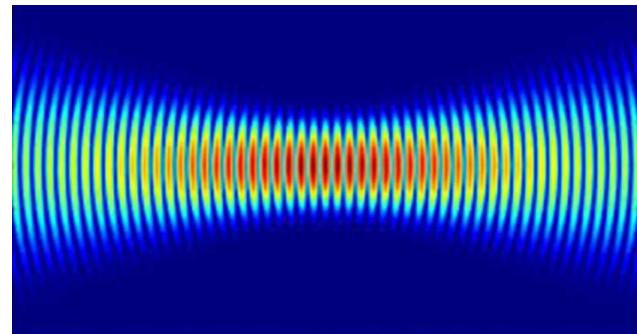
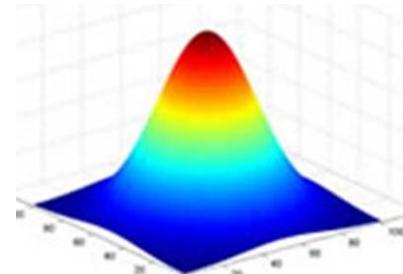
where  $w(z)$  is its beam waist (the radius of the beam from its center to 1/e of its peak intensity,  $w_0$  is its narrowest beam waist at  $z=0$ ,  $z$  is the distance from the narrowest beam waist, and  $z_c$  is the confocal parameter that characterizes how long the beam remains reasonably collimated,

$$z_c = \frac{\pi w_0^2}{\lambda}.$$

- At long distances when  $z/z_c \gg 1$ , the beam waist increases with distance and

$w(z) = \frac{\lambda z}{\pi w_0}$  so the angle of divergence for the beam is given by  $\sin \theta_{div} = \frac{\lambda}{\pi w_0}$ . The

radius of curvature is  $R(z) = z \left( 1 + \left( \frac{z_c}{z} \right)^2 \right)$ . This divergence allows one to define the



spatial and temporal variations of a Gaussian laser beam's intensity distribution:

$$I(r, t) = \frac{E e^{\frac{-r^2}{w_o^2 \left(1 + \left(\frac{z}{z_c}\right)^2\right)}} e^{\frac{-t^2}{\tau^2}}}{\pi^{3/2} w_o^2 \tau \left(1 + \frac{z^2}{z_c^2}\right)}$$

- Focusing laser beams- We treat it as the reverse of a laser beam diverging from its beam waist. Instead it is the convergence of a laser beam with a radius  $w$  that is converging with an angle  $\theta$  to a beam waist of  $w_o$ . We know that  $\sin \theta_{div} = \frac{\lambda}{\pi w_0}$  so rearranging, the diffraction limited beam waist becomes  $w_0 = \frac{\lambda}{\pi \sin \theta_{div}} \approx \frac{\lambda}{\pi \theta_{div}}$  for small angles of divergence.

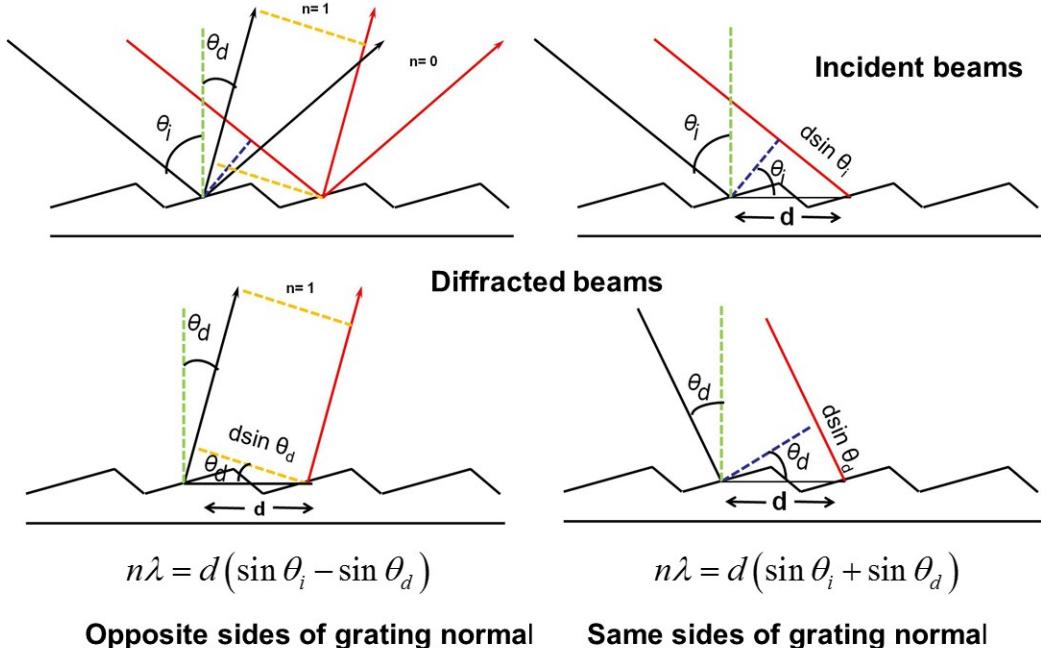
- We can relate the divergence to an f/#. The f/# of the cone of a solid angle is defined as the ratio of the height of the cone to the diameter of its base. Since

$$\frac{w(z)}{z} = \theta = \frac{\lambda}{\pi w_0}, \quad \frac{r}{L} = \theta = \frac{\lambda}{\pi w_0}, \text{ then } f/\# = \frac{L}{2r} \text{ and therefore}$$

$$w_0 = \frac{2\lambda}{\pi} (f/\#) = \frac{2\lambda}{\pi} (f/\#). \text{ This relationship is similar to that seen for a single slit where we saw for small angles, } \theta = \frac{\lambda}{w}.$$

## Gratings

- Condition for **constructive interference**:  $n\lambda = d(\sin \theta_i \pm \sin \theta_d)$ . The positive or negative signs depend on whether the angles of incidence and diffraction lie on the same or opposite sides of the grating normal, respectively.



- Blazing** a grating and blaze angle. The angle of an individual grating groove will reflect light in a preferential direction determined by the angles of incidence and reflection being equal, **as measured by the normal to the groove (not the grating surface)**. Diffraction from the narrow groove will then spread the light around that preferential direction.
- Dispersion-** To see how the direction of different wavelengths changes when the wavelength changes, we just need to differentiate  $n\lambda = d(\sin \theta_i \pm \sin \theta_d)$  with respect to  $\theta$ .

- reciprocal angular dispersion  $\frac{d\lambda}{d\theta_d} = \frac{d \cos \theta_d}{n}$

- angular dispersion-  $\frac{d\theta_d}{d\lambda} = \frac{n}{d \cos \theta_d}$

- reciprocal linear dispersion  $\frac{d\lambda}{dx} = \frac{d \cos \theta_d}{nL}$

- linear dispersion  $\frac{dx}{d\lambda} = \frac{nL}{d \cos \theta_d}$

- Resolution-** Resolution is determined by the interference between the most distant grooves. It is defined by comparing the condition for constructive interference for  $\lambda_1$  and destructive interference for  $\lambda_2$  at the same path length difference,  $Nn\lambda_1 = Nn\lambda_2 + \lambda_2$ . Then,

$$\frac{\lambda}{\Delta\lambda} = nN \quad \text{or} \quad \frac{\lambda}{\Delta\lambda} = N \frac{d}{\lambda} (\sin \theta_i + \sin \theta_d) = \frac{W(\sin \theta_i + \sin \theta_d)}{\lambda}$$

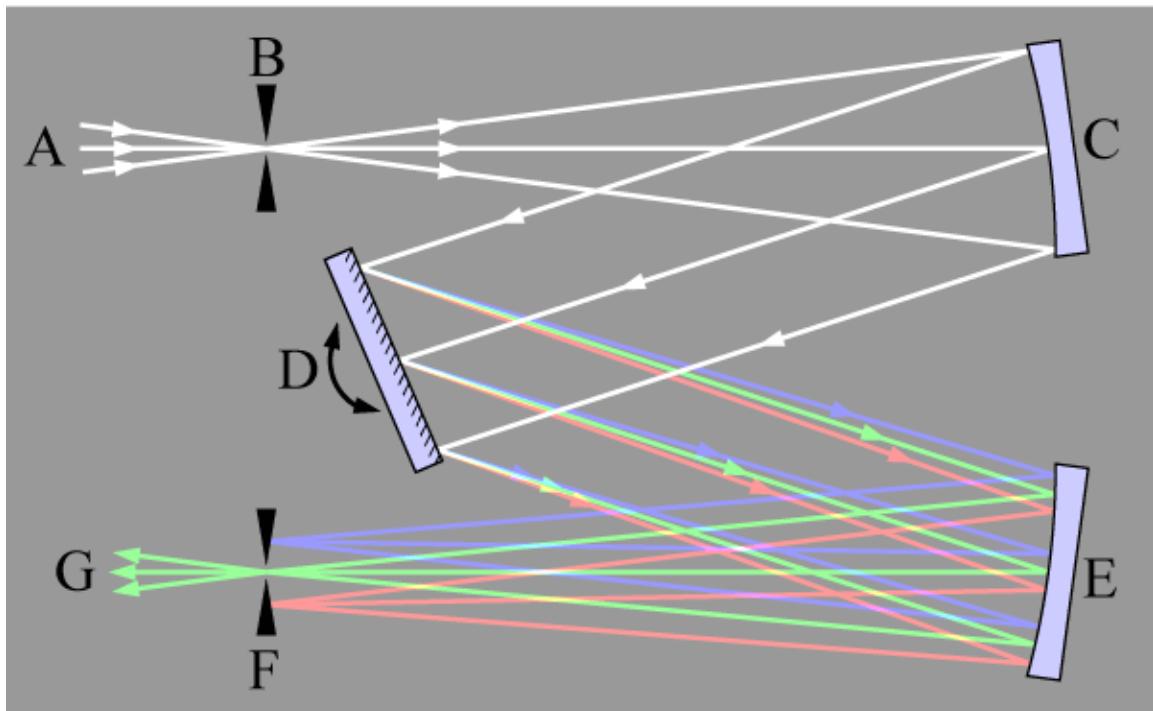
- **Free Spectral Range-** At any given value of  $\theta_i$  or  $\theta_d$ ,  $n\lambda = \text{constant}$  so different wavelengths are present in the different orders and we need filters to isolate the order of interest. Defined by the free spectral range-  $n\lambda = (n+1)(\lambda - \Delta\lambda)$  so

$$\Delta\lambda_{\text{free-spectral-range}} = \frac{\lambda}{n+1}$$

- Polarization dependence
- Ghosts and scattered light
- Holographic gratings
- Concave gratings

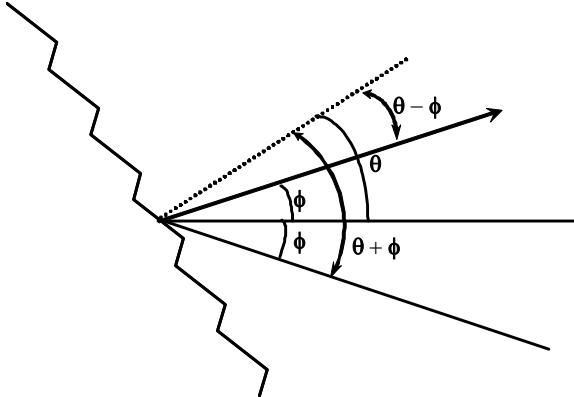
### Monochromators-

- **Physical Construction-** A Czerny-Turner monochromator is the classical design. It has entrance and exit slits, usually taken to be equal. Light is focused on the entrance slit. It enters the monochromator where two concave mirrors collimate light, direct it to the grating, and refocus it on the exit slit. The mirrors form an image of the entrance slit on the exit slit.

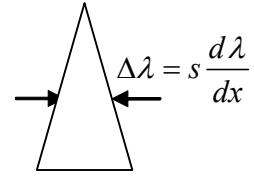


- The relationship of the wavelength to the grating angle,  $\theta$ , is determined by the geometry shown in the following diagram. From the diagram,  $\theta_i = \theta - \phi$  and  $\theta_d = \theta + \phi$  (note that if the monochromator is set up so the grating is tilted in the opposite direction, the incoming and outgoing beams simply interchange).

- $n\lambda = d(\sin(\theta - \phi) + \sin(\theta + \phi))$
- $n\lambda = d(\sin \theta \cos \phi - \sin \phi \cos \theta + \sin \theta \cos \phi + \sin \phi \cos \theta)$
- so  $n\lambda = 2d \sin \theta \cos \phi$



- The dispersion relates the separation in wavelength to a separation in physical space, i.e. the distance between two spectral lines-  $\frac{d\lambda}{dx} = \frac{d \cos(\phi - \theta)}{nf}$  where  $f$  is the focal length of the monochromator.
- Instrumental function- defines the distribution in the measured wavelength spread that an instrument creates for a monochromatic light source.  $\Delta\lambda = \frac{d\lambda}{dx} \Delta x$
- The ultimate resolution of grating is defined by  $\frac{\lambda}{\Delta\lambda} = nN$  or  $\frac{\lambda}{d\lambda} = \frac{d \sin \theta \cos \phi}{\lambda} N = \frac{W \sin \theta \cos \phi}{\lambda}$
- Ultimate resolution of instrument depends on the image size of entrance slit. It is defined by the solid angle focusing it onto the exit slit. That solid angle is the same one defined by the entrance slit's diffraction onto the focusing mirror.
  - $s \sim \lambda f / \# = \frac{f \lambda}{D}$
- The signal,  $s$ , from a monochromator depends on its slit width. The relationship is different depending on whether the light is monochromatic and white light and whether the detector measures the total intensity from the exit slit or an array detector where the array replaces the exit slit.

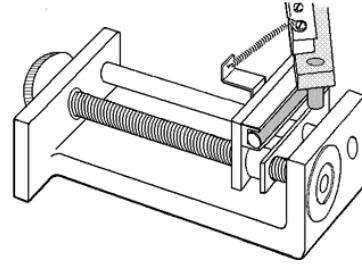


	<b>Array Detector</b>	<b>Photomultiplier</b>
<b>Monochromatic</b>	$s^0$	$s^1$
<b>White Light</b>	$s^1$	$s^2$

- Scattered light rejection is an important variable in monochromators since monochromators role is to pass only the light chosen by the grating angle. The light leaving at other angles must be rejected so the inside of a monochromator is painted a

very deep black. Rejection is typically  $10^4$  or  $10^5$ . Dust inside the monochromator can be a problem.

- Double monochromators can enhance the rejection up to  $10^{10}$ . They become very important for Raman spectroscopy where the Raman scattering is  $10^{-13}$  times weaker than the exciting laser. The dispersion can be subtractive and additive (depends upon whether red goes to the right or left of blue after leaving each grating).
- The wavelength chosen by a monochromator is related to the grating angle by the sine of the angle. One would usually like to have a linear relationship so monochromators use a sine bar drive. The image shows how a screw moves a carriage that pushes an arm that is directly connected to the grating. The angle between the arm and the screw is the angle of the grating. If the screw moves the carriage by  $x$ , the grating changes by  $\sin \theta = \frac{x}{L}$  where  $L$  is the length of the arm.



## Ray Tracing and Gaussian optics

- **Ray Tracing Optics or Geometrical Optics**
  - Geometrical Ray Optics and ABCD matrix- A straight ray leaving some point has the relationship that  $\frac{dr}{r} = \frac{dz}{z}$ , where  $r$  designates the distance of a ray from the optical axis and  $z$  is the distance along the axis so the distance from the optical axis increases linearly with distance along the axis. We define  $r'$  as  $\frac{dr}{dz}$  and we define a vector  $r$  as  $\vec{r} = \begin{pmatrix} r \\ r' \end{pmatrix}$ . An alternative definition is the angle of a ray relative to the optical axis.
  - If we wish to relate two different  $r$  vectors, we use the relationship  $\vec{r}_2 = M\vec{r}_1$  where  $M = \begin{pmatrix} A & B \\ C & D \end{pmatrix}$ . Equivalently, one can expand out the relationship to get  $r_2 = Ar_1 + Br_1'$  and  $r_2' = Cr_1 + Dr_1'$ .
  - $M$  takes on different forms as rays propagate through different optical elements.
    - Propagation a distance  $L$  through free space-  $M = \begin{pmatrix} 1 & L \\ 0 & 1 \end{pmatrix}$
    - Propagation through thin lens, focal length,  $f$ -  $M = \begin{pmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{pmatrix}$

- Refection off a concave mirror, radius of curvature, R-  $M = \begin{pmatrix} 1 & 0 \\ -\frac{2}{R} & 1 \end{pmatrix}$

- Refraction at a planar boundary

$$M = \begin{pmatrix} 1 & 0 \\ 0 & \frac{n_1}{n_2} \end{pmatrix}$$

- Propagation through curved interface with radius of curvature, R, and two different refractive indices

$$M = \begin{pmatrix} 1 & 0 \\ -\frac{n_2 - n_1}{n_2 R} & \frac{n_1}{n_2} \end{pmatrix}$$

- In order to implement the ray tracing strategy, you would start at a point on an object emitting rays in different directions and propagate each ray through free space using the appropriate matrix to find its new r vector. When the new r vector meets an optical interface, you would use the appropriate matrix to propagate it through the optical interface to find the next r vector. You would continue the propagation through free space and additional interfaces until you reached the point of interest. The matrices would multiply together to transform the initial r

vector to the final r vector:  $\begin{pmatrix} r \\ r' \end{pmatrix}_{\text{image}} = \begin{pmatrix} A_1 & B_1 \\ C_1 & D_1 \end{pmatrix} \begin{pmatrix} A_2 & B_2 \\ C_2 & D_2 \end{pmatrix} \begin{pmatrix} A_3 & B_3 \\ C_3 & D_3 \end{pmatrix} \begin{pmatrix} r \\ r' \end{pmatrix}_{\text{object}}$

- One can also describe the propagation of wave fronts instead of rays. Wave fronts are described by their radius of curvature,  $R$ . Remember that a straight ray

is described by  $\frac{dr}{r} = \frac{dz}{z}$ . The radius of curvature of its wave front at any point

is  $z$  so  $R = z = r \frac{dz}{dr} = \frac{r}{r'}$ . So the radius of curvature for wave fronts propagating

through different optical elements transforms according to

$$R_2 = \frac{r_2}{r'_2} = \frac{Ar_1 + Br'_1}{Cr_1 + Dr'_1} = \frac{AR_1 + B}{CR_1 + D} \text{ where } R = \frac{r}{r'}. \text{ Thus, the same ABCD matrix}$$

can transform the wave front curvatures.

- Gaussian beam focusing does not follow the same approach as focusing real objects. The difference arises because imaging of an object depends on the radius of curvature of a wave front increasing linearly with distance. A Gaussian beam profile does not increase linearly with distance until it is outside the confocal region. The A,B,C,D matrices form the best way of describing how a Gaussian beam is imaged. It uses the same ABCD formalism to transform a Gaussian beam as it propagates through different optical elements except a new variable is defined to replace the  $R_1$  and  $R_2$ . The radius of

curvature and the beam waist are combined form the new variables,  $\frac{1}{\tilde{q}} \equiv \frac{1}{R} - \frac{i\lambda}{\pi w_o^2}$ , and

one can now transform this variable using the same ABCD matrix:  $\tilde{q}_2 = \frac{A\tilde{q}_1 + B}{C\tilde{q}_1 + D}$ .

- A more convenient way to relate Gaussian optics to normal imaging is using an approximation developed by Self (Applied Optics-Vol. 22, No. 5 / 1 March 1983).

- Imaging an object obeys the simple equation that relates the object and image

$$\text{distances to the focal length. } \frac{1}{x_o} + \frac{1}{x_i} = \frac{1}{f}. \text{ The magnification is defined by}$$

$$M = \frac{x_i}{x_o}.$$

- Focusing a Gaussian laser beam to a beam waist uses a modified equation to

$$\text{relate the initial and final beam waists. } \frac{1}{x_o + \frac{z_c^2}{x_o - f}} + \frac{1}{x_i} = \frac{1}{f}$$

- The magnification of beam waists (where the original and imaged beam waists are

$$w_o^o \text{ and } w_i^o, \text{ respectively}) \text{ is defined by: } M = \frac{w_i^o}{w_o^o} = \frac{1}{\sqrt{\left(1 - \frac{x_o}{f}\right)^2 + \left(\frac{z_c}{f}\right)^2}}.$$

- The initial and final confocal parameters are also related by the magnification.

$$z_{c,f} = M^2 z_{c,i}$$

## LASERS

### Introduction

- The power in a laser cavity for an arbitrary number of round trips in the cavity is

$$P_{cavity} = \frac{nhvc(1+r^2e^{2\alpha l}+r^4e^{4\alpha l}+\dots)}{2L} \text{ where } \alpha \equiv \sigma(N_2 - N_1), \text{ there}$$

are initially  $n$  photons/cm<sup>2</sup> in cavity,  $L$  is cavity length,  $l$  is length of gain medium, and  $2L/c$  is the round trip time in the cavity.

- Reflection and absorption losses- In order to treat the reflection losses on the same footing as the amplification, we define a new quantity,  $\rho$ , that will appear in the exponential along with the amplification. Here,  $\rho \equiv -\ln(r) + \rho_{cavity\_losses}$  where the last term accounts for other losses in the cavity such as excited state absorption.

- $P_{cavity} = \frac{nhvc}{2L}(1+e^{2(\alpha l-\rho)}+e^{4(\alpha l-\rho)}+\dots) = \frac{nhvc}{2L(1-e^{2(\alpha l-\rho)})}$
- Threshold condition:  $P_{cavity}$  becomes very large (infinite actually) when  $\alpha l = \rho$ . This condition marks threshold. In order to get a more realistic expression, we will have to make our treatment more sophisticated.
- Rate equations and laser performance- The previous approach assumed the gain was independent of the photon flux but in fact the photon flux will deplete the gain until it equals the losses. If it didn't, the photon flux would continue to change in time. Thus, it is important to include the coupling between the photon flux and the gain in our modeling.
  - Let's get a rate equation for the photon intensity first.  $n$  will be photons/sec cm<sup>2</sup>. We will assume there are a finite number of stimulated photons in our cavity and they will be amplified by multiple passes. On a single pass, we can write  

$$n_{out} = n_{in} e^{\sigma_s(N_2 - N_1)l - \rho}$$
. Expanding this expression

$$n_{out} \approx n_{in} \left( 1 + [\sigma_s(N_2 - N_1)l - \rho] + [\sigma_s(N_2 - N_1)l - \rho]^2 + \dots \right) \text{ so}$$

$$\Delta n \equiv n_{out} - n_{in} \approx n_{in} [\sigma_s(N_2 - N_1)l - \rho]. \sigma_s(N_2 - N_1)$$

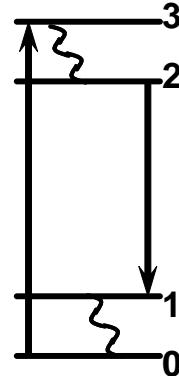
is the gain,  $a$ , on a single pass. The single pass requires an elapsed time of  $\Delta t = \frac{L}{c}$  so the rate of

change in the number of photons  $\text{sec}^{-1}\text{cm}^{-2}$  on a single pass is

$$\frac{\Delta n_s}{\Delta t} = \frac{c(\alpha l - \rho)}{L} n_s \text{ for small } (\alpha l - \rho).$$

- Now we need rate equations for the laser material. We assume a four level system with levels labeled by 0, 1, 2, and 3. We will pump level 3. Level 3 will relax very rapidly to level 2 and we can neglect relaxation to other levels. Level 2 is metastable and relaxes slowly. Level 1 relaxes very rapidly back to level 0. Thus, a population inversion is easily achieved between level 2 and level 1. We will assume rates of  $W_{ij}$  between levels  $i$  and  $j$ .

The lifetime of any level is  $\tau_i^{-1} = \sum_j W_{ij}$ . The stimulated



emission rate constant is  $n_s \sigma_s$  and  $n_p \sigma_p$  is the pump rate constant. The rate equations for the levels and the photon flux (assuming there are stimulated photons in our cavity) are:

- $\dot{n}_s = \frac{cn_s \sigma_s l}{L} (N_2 - N_1) - \frac{\rho cn_s}{L}$  (184)

- $\dot{N}_0 = -P_p (N_0 - N_3) + W_{10} N_1 + W_{20} N_2 + W_{30} N_3$  (185)

- $\dot{N}_1 = n_s \sigma_s (N_2 - N_1) - \tau_1^{-1} N_1 + W_{21} N_2 + W_{31} N_3$  (186)

- $\dot{N}_2 = -n_s \sigma_s (N_2 - N_1) + W_{32} N_3 - \tau_2^{-1} N_2$  (187)

- $\dot{N}_3 = P_p (N_0 - N_3) - \tau_3^{-1} N_3$  (188)

- We assume  $N_1$  and  $N_3$  have negligible populations so  $N = N_0 + N_2$ . (189)
- We also assume the lifetimes of levels 1 and 3 are very much shorter than any other level. Finally, we assume the populations have reached the steady state so the time derivatives are zero. With these approximations, we can solve equations (184) and (188).

- $N_2 = N_1 + \frac{\rho}{\sigma_s l}$  (190)

- $N_3 = \frac{P_p N_0}{\tau_3^{-1}}$  (191)

- If level 1 has zero population, then (190) requires

- $N_2 = \frac{\rho}{\sigma_s l}$ . (192)

This equation means that the population of state 2 is depleted to a value defined by the losses so the gain equals the losses. It also assumes we are above threshold and there is stimulated emission occurring in the cavity.

- Substituting into (189),

$$\blacksquare \quad N_0 = N - \frac{\rho}{\sigma_s l} \quad (193)$$

- Substituting (191), (192), (193) into (187), we find

$$\begin{aligned} \blacksquare \quad & \dot{N}_2 = 0 = -n_s \sigma_s \left( \frac{\rho}{\sigma_s l} \right) + W_{32} \frac{P_p}{\tau_3^{-1}} \left( N - \frac{\rho}{\sigma_s l} \right) - \tau_2^{-1} \frac{\rho}{\sigma_s l} \text{ or} \\ \blacksquare \quad & \frac{n_s \rho}{l} = \frac{W_{32} P_p}{\tau_3^{-1}} \left( N - \frac{\rho}{\sigma_s l} \right) - \tau_2^{-1} \frac{\rho}{\sigma_s l} \approx P_p N - \frac{P_p \rho}{\sigma_s l} - \tau_2^{-1} \frac{\rho}{\sigma_s l} \text{ or} \\ \blacksquare \quad & n_s \approx \frac{P_p N l}{\rho} - \frac{P_p}{\sigma_s} - \frac{\tau_2^{-1}}{\sigma_s} \end{aligned}$$

- Finally, we can write

$$\blacksquare \quad n_s = \frac{P_p (l N \sigma_s - \rho)}{\rho \sigma_s} - \frac{\tau_2^{-1}}{\sigma_s}$$

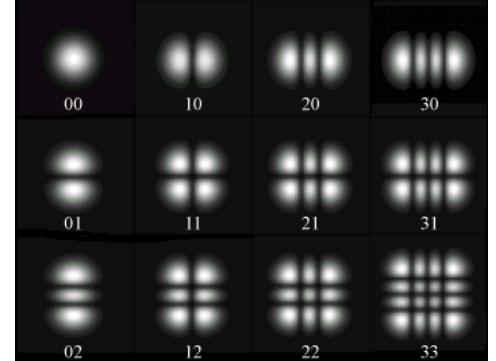
- Threshold occurs when  $\frac{P_p (l N \sigma_s - \rho)}{\rho \sigma_s} = \frac{\tau_2^{-1}}{\sigma_s}$  or  $P_p = \frac{\rho \tau_2^{-1}}{(l N \sigma_s - \rho)}$
- The output results from transmission through an end mirror. The sum of the reflection, transmission, and absorption coefficients has to be one,  $T + R + A = 1$ . The absorption losses can include excited state absorption as well as absorption in the cavity and optics. Thus,

$$n_{out} = T n_s = (1 - R - A) n_s = (1 - R - A) \left( \frac{P_p (l N \sigma_s - \rho)}{\rho \sigma_s} - \frac{\tau_2^{-1}}{\sigma_s} \right)$$

- The **slope efficiency** depends on optimizing  $R$  – decreasing  $R$  increases the light that emerges from the cavity but it also increases the losses,  $\rho$ . The optimum depends on the gain. Large gain lasers are optimized by small  $R$  and low gain

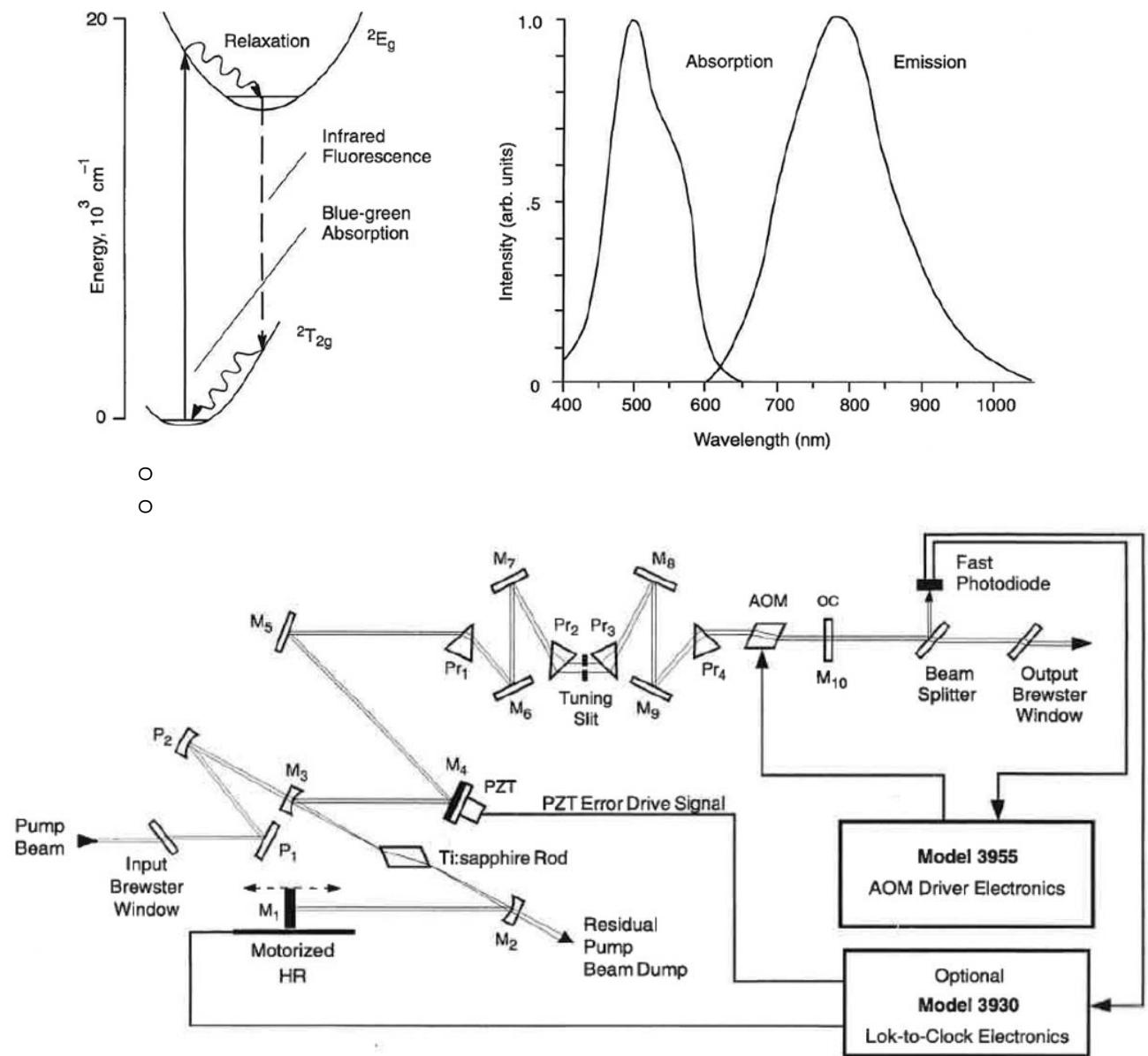
lasers are optimized by  $R$  near 1.  $\frac{dn_{out}}{dn_p} = \frac{(1 - R - A) \sigma_p}{\rho \sigma_s} (\sigma_s N l - \rho)$  where

$$P_p = \sigma_p n_p$$

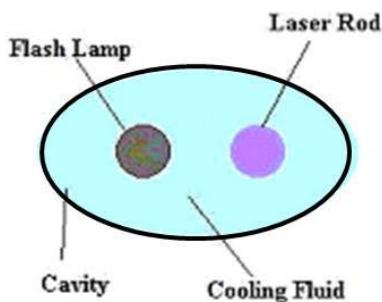
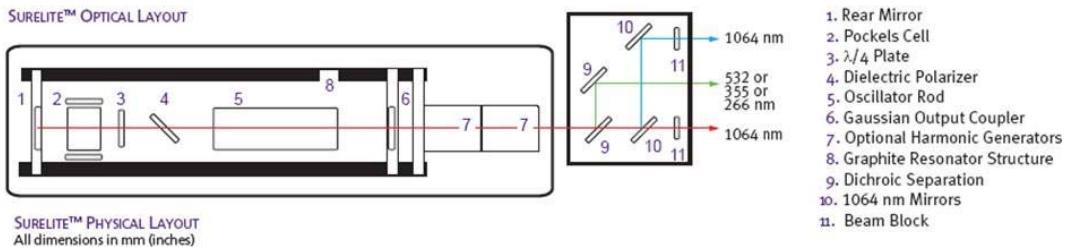


- **Example Lasers**

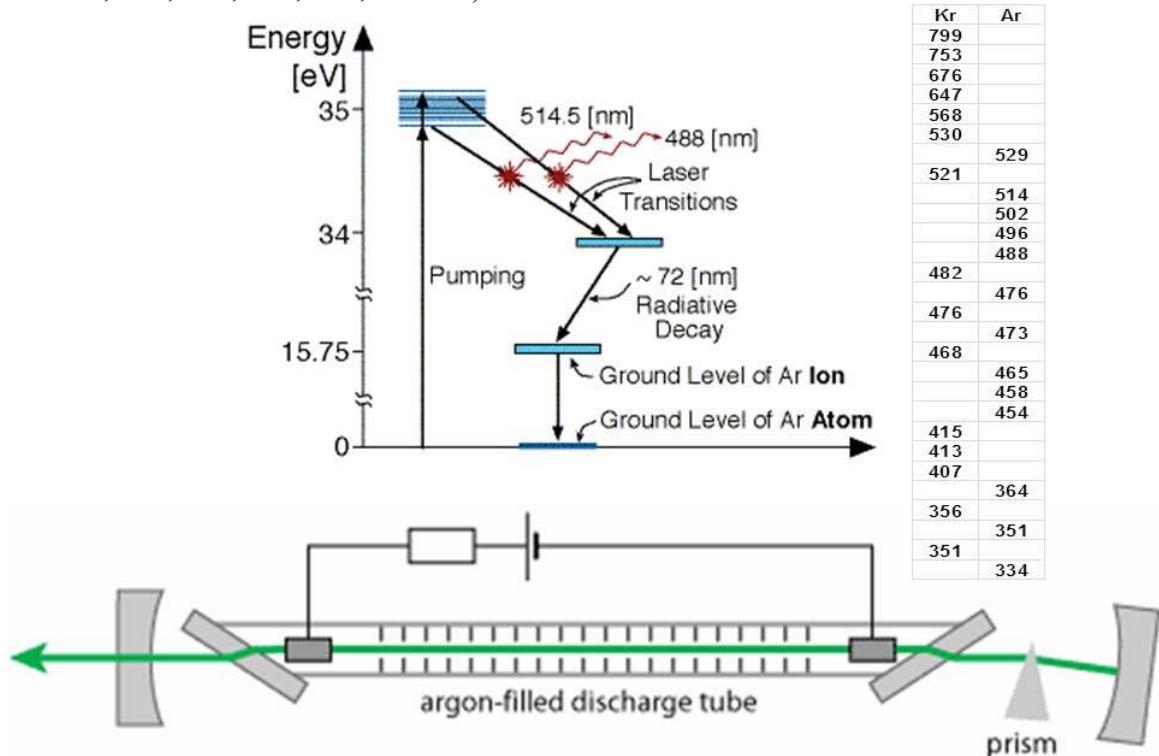
- Ti:Al<sub>2</sub>O<sub>3</sub> Laser (Ti: Sapphire) (800 nm)



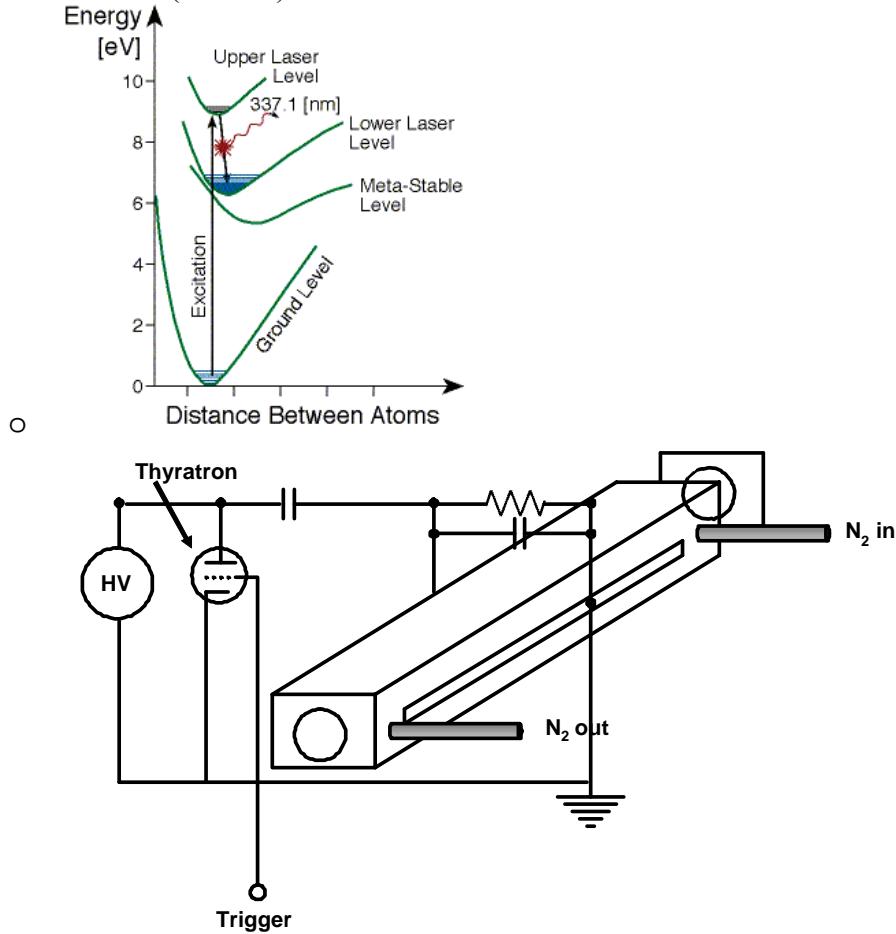
Nd:YAG, Nd:YVO<sub>4</sub>, Nd:LiYF<sub>4</sub>, Nd:Glass, Nd:Fiber Lasers (1.06 microns (2<sup>nd</sup>, 3<sup>rd</sup>, 4<sup>th</sup> harmonics at 532, 355, 266 nm))



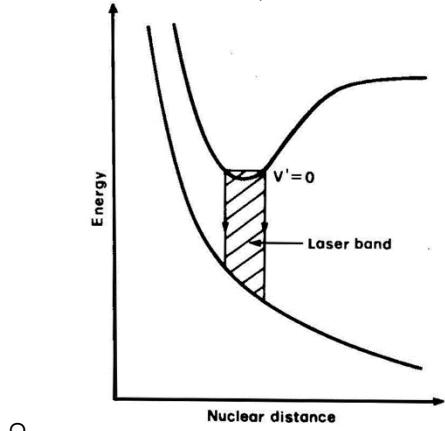
- Ar<sup>+</sup> and Kr<sup>+</sup> Lasers (Ar<sup>+</sup>- 514, 488, 476, 458, 364, 351 nm; Kr<sup>+</sup>- 753, 647, 568, 531, 521, 482, 476, 413, 407 nm)



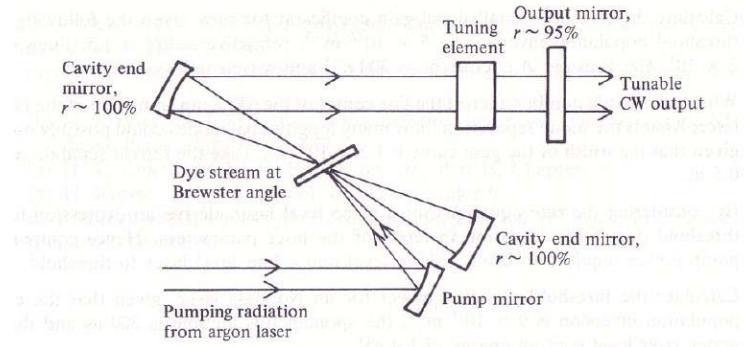
- N<sub>2</sub> Laser(337 nm)



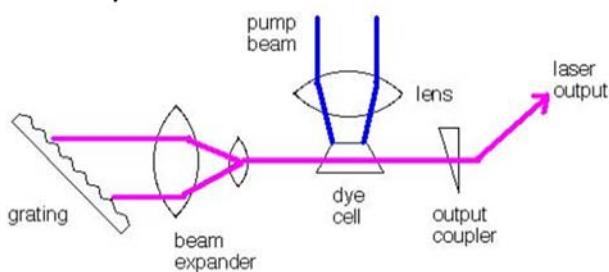
- Excimer Laser (XeCl 308 nm, XeF 351nm, KrF 248 nm, ArF 193 nm)



- CW Dye Laser



- Pulsed Dye Laser



- Ruby laser
- Flashlamp pumped dye

## Cavity design

- Transverse spatial modes- TEM<sub>00</sub>, TEM<sub>10</sub>, TEM<sub>11</sub>,...
- Longitudinal spatial modes- constructive interference occurs when the path length is

$$\Delta = 2L = n\lambda . \text{ Modes are spaced at } \Delta \bar{V} = \frac{1}{2L}.$$

- Mirror Design- For TEM<sub>00</sub>,  $R(z) = z \left( 1 + \left( \frac{z_c}{z} \right)^2 \right)$ ,  $w = w_o \sqrt{1 + \left( \frac{z}{z_c} \right)^2}$ ,  $z_c = \frac{\pi w_o^2}{\lambda}$ .

Select mirrors whose radius of curvature matches that of the diffracted beam's radius of curvature.

- Cavity designs- Plane-parallel ( $\frac{L}{R_1} = \frac{L}{R_2} = 0$ ;  $z_c \gg L$ ),

concentric ( $\frac{L}{R_1} = \frac{L}{R_2} = 2$  and  $R_{1,2} \gg z_c$ ), confocal ( $\frac{L}{R_1} = \frac{L}{R_2} = 1$  and  $R_1 = R_2 = L = 2z_c$ ); hemispherical ( $\frac{L}{R_1} = 0$ ;

$\frac{L}{R_2} = f$  where  $f = 0 \rightarrow 1$ ;  $z_c = \sqrt{L \left( \frac{1-f}{f} \right)}$ );

concave-convex ( $R_1 = aL$ ;  $R_2 = (1-a)L$ ;  $L \gg z_c$ ).

- **Diffractive losses in a plane wave cavity**- If we have a cavity defined by plane mirrors, then diffraction spreading beyond the cavity mirrors causes diffraction losses. Stable cavities are those where a beam does not diverge on successive passes through the cavity. Unstable cavities are those where the beam continuously expands on successive passes through the cavity.

- slit -  $\lambda = 2a \sin \theta \approx 2a\theta_{\text{diffractive}}$  so  $\theta_{\text{diffractive}} = \frac{n\lambda}{2a}$

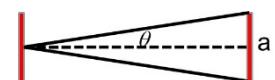
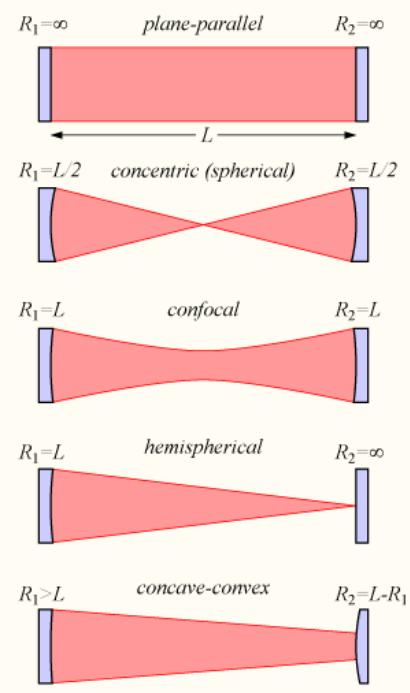
- The cavity acceptance angle is defined as

$$\theta_{\text{cavity}} = \frac{a}{2N_{\text{effective}}L} \text{ where } N_{\text{effective}} \text{ is the number of}$$

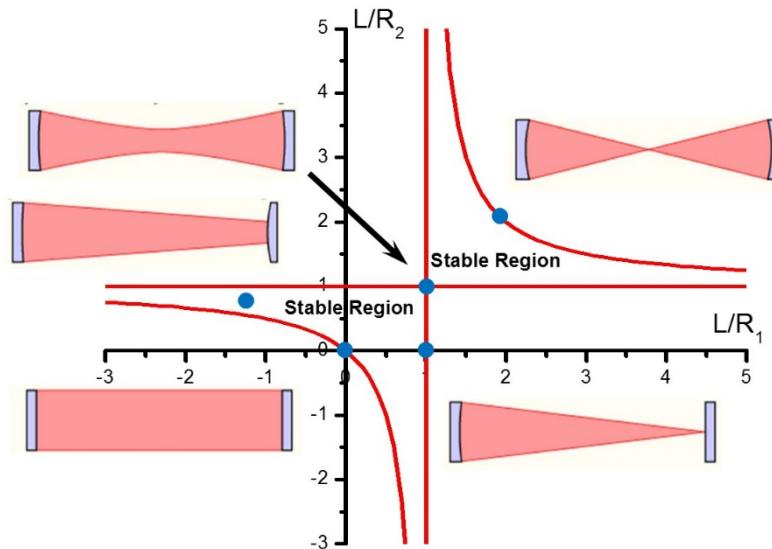
effective passes of light through the cavity.

- One would like the diffractive spreading to be smaller than the cavity acceptance angle.  $\theta_{\text{diff}} < \theta_{\text{cavity}}$  or  $\frac{a^2}{n\lambda L} > N_{\text{effective}}$ .

- Define Fresnel number as  $F \equiv \frac{a^2}{\lambda L}$  and  $F > N_{\text{effective}}$  for minimizing loss



- **Stable and unstable cavities with Gaussian beams-** The stability region is defined by the equation  $0 < \left(1 - \frac{L}{R_1}\right)\left(1 - \frac{L}{R_2}\right) < 1$ . We create a stability graph that defines the regions of stability that obey stability criterion. (You can also define a new variable,  $g \equiv 1 - \frac{L}{R}$ , and plot  $0 < g_1 g_2 < 1$ .)



- **Cavity Design-**
  - Pick the mirrors' radii of curvature and an L that meets the stability criterion.
  - Relate the mirrors' positions relative to the beam waist to the radius of curvature of the wave front. The equations that relate the wave front radius of curvature to the distance from the beam waist are
    - $R_1 = z_1 \left(1 + \left(\frac{z_c}{z_1}\right)^2\right)$  and  $R_2 = (L - z_1) \left(1 + \left(\frac{z_c}{L - z_1}\right)^2\right)$ . Solving for  $z_c$  and substituting in the other equation gives the values for  $z_1$  and  $L - z_1$ . Knowing  $z_1$  allows you to substitute its value into that for  $z_c$ .
    - $z_c = \sqrt{R_1 z_1 - z_1^2}$      $z_1 = \frac{L(R_2 - L)}{R_1 + R_2 - 2L}$     and     $L - z_1 = \frac{L(R_1 - L)}{R_1 + R_2 - 2L}$
  - $z_c$  is now defined and therefore, so also is the beam waist and the size of the beam at the mirrors.
  - Loss mechanisms
    - Diffraction losses
    - Geometrical considerations- spatial modes & apertures
    - Reflection losses
    - Absorption (ground state and excited state)
    - Gain depletion- Gain profile defines frequencies that have gain.
      - Homogeneously broadened gain profiles will lase at the threshold where the maximum in the gain curve matches a minimum loss in

a longitudinal mode and the entire gain curve will contribute to the lasing.

- Frequency domain hole burning- Inhomogeneously broadened gain profiles will lase on the individual longitudinal modes and deplete the gain at those frequencies. Gain at other frequencies will not be depleted.
- Spatial hole burning occurs when there is gain at spatial positions that don't match the particular longitudinal and transverse mode that is lasing. Those areas can support lasing in other less desirable modes.

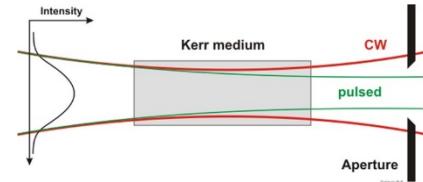
- Ring lasers

- Controlling modes

- Homogeneous & inhomogeneous broadening; transverse & longitudinal spatial hole burning (gain depletion); control of higher order modes; mode noise
- Cavity must be stable; invar or quartz rods define cavity length; very rigid cavity; damp vibrations
- Q-switching – high gain lasers; eliminate lasing on multiple modes as gain builds up
- Cavity dumping – low gain lasers

- Mode locking-

- Passive-
  - Saturable absorber- Relies on positive feedback to create an unstable condition. An intracavity dye solution creates absorption losses but bleaches at high intensities so the losses decrease and the intracavity intensity becomes higher.
  - Kerr lensing or self-focusing causes a narrowing of the beam diameter over that of a c.w. beam. Passive mode locking occurs if the smaller diameter beam experiences either smaller losses or larger gain.
    - An intracavity aperture introduces losses to the c.w. beam since it is larger and can be blocked by the aperture while the pulsed beam is narrower and experiences less loss.
    - Likewise, creating a narrower gain region in the laser will provide a better match to a narrower beam waist of the self-focused pulsed beam than the wider c.w. beam so the laser has larger gains when the pump and laser beam waists match.
    - In a slightly asymmetrical confocal cavity, one can operate in the unstable region for a c.w. beam but in the stable region for a beam that includes self-focusing.
- Active mode locking- gain (synchronous pumping) or loss (acousto-optical) modulation



## Important pulse propagation effects

- Time-Bandwidth Product** - In order to create ultrafast light pulses, there must be a broad band of frequencies in the pulse and their phases must match at some point in time and space. They constructively interfere at that point in time and space but destructively interfere at every other point. The wider the band of frequencies, the narrower the temporal width of the pulse. The relationship between the band of frequencies and the pulse width is

$$\Delta\omega\Delta\tau = 2\pi\Delta\nu\Delta\tau = 2\pi c_B \text{ where } c_B \text{ depends on the pulse shape}$$

3

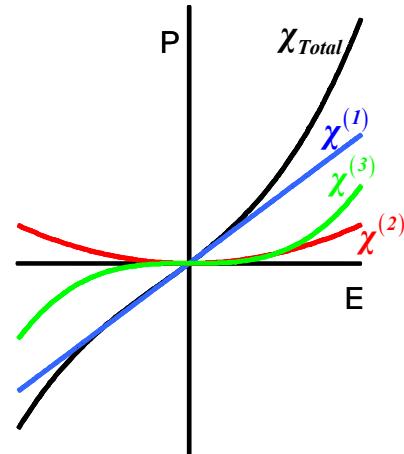
Pulse Shape	$c_B$
Gaussian	0.441
Sech	0.315
Lorentzian	0.142

- Group velocity dispersion**- The index of refraction changes with frequency. Normal dispersion corresponds to a refractive index that increases as the frequency of light increases. Anomalous dispersion corresponds to a refractive index that decreases as the frequency increases. It is usually observed only in the region above a resonance where the refractive index is changing rapidly.

**Nonlinear Methods**- When several light beams are focused into a sample, the electric fields can be comparable to the fields within molecules. The figure shows a schematic relationship between the electric field and the induced polarization. The induced polarization can be distorted because the response to one of the fields can be influenced by another field that changes the sample's polarizability. The result is that new light beams are formed at new frequencies that correspond to all the sums and differences that can be created from the initial excitation frequencies. In addition, the excitation beams leaving the sample at their original frequencies will still have altered intensities and/or phases. We will examine three wave mixing and four wave mixing where two or three excitation waves create a third or fourth output wave. The output beams are coherent because the coherent excitation beams create a phased array of oscillators, i.e. a coherent polarization, which re-emit directional beams. Their directions are defined by momentum conservation. Momentum conservation is defined by the same phase matching relationships between excitation and output  $k$ -vectors. The oscillators have a coherent spatial modulation defined by wave vector addition (i.e. a grating) and a coherent temporal modulation.

Phase matching is a central concept in nonlinear spectroscopy because the directional beams become very intense if the light from all of the molecules in the excitation region constructively interferes to create a much larger electromagnetic wave output. The wave vectors

and frequencies are related to each other by  $\pm(\vec{k} \cdot \vec{z} \pm \omega t)$  where the inner choice of sign



depends on whether the light is traveling to increasing values of  $z$  in which case one chooses the negative sign in decreasing values of  $z$  in which case you chose the positive sign. The choice for the outer sign depends on whether the transition involving  $\omega_{ba}$ , is an absorption or emission. An absorption occurs when state  $b$  is more energetic than state  $a$  so then you chose the sign so

$e^{i(\omega_{ba}-\omega)t}$  the exponent is small. If state  $b$  is less energetic than state  $a$  ( $\omega_{ba} < 0$ ), then you chose the sign that so  $e^{i(\omega_{ba}+\omega)t}$  and again the exponent is small.

### Taylor's Series Expansion of Polarization

It is common to use a Taylor's series expansion of the polarization in order to have a qualitative description of the relationship. The graph shows the individual contributions in the Taylor's series expansion to the total polarization.

$$\vec{P} = \tilde{\chi}_{i,j}^{(1)} \vec{E} + \tilde{\chi}_{i,j,k}^{(2)} \vec{E}^2 + \tilde{\chi}_{i,j,k,l}^{(3)} \vec{E}^3 + \dots \quad (194)$$

$$\text{where } \vec{E} = \sum_i \vec{E}_i. \quad (195)$$

The frequencies will also combine with signs that depend on whether absorption or emission is occurring while the wave-vectors will combine with signs that depend on whether absorption or emission is occurring and whether the waves are traveling forward or reverse.

$$\vec{k}_{out} = \sum_i \pm \vec{k}_i \text{ and } \omega_{out} = \sum_i \pm \omega_i.$$

Note also that the even terms in the polarization are symmetric through reflection through the origin. That means that reversing the electric field does not reverse the polarization. That can't happen in any symmetric material so all even terms in this expansion vanish for symmetric materials. They don't vanish when there is a component of asymmetry such as at surfaces and interfaces.

### Three Wave Mixing

Three wave mixing occurs when two excitation beams create a third beam. This method is based on the  $\chi_{i,j,k}^{(2)}$  term in (181) and therefore all of the effects of three wave mixing are useful for spectroscopy of surfaces and interfaces. Two excitation fields create the output field. It requires an anisotropy in order to obtain a measurable output signal. The importance of anisotropy is most clear when considering that the polarization changes sign if the electric field changes sign in an isotropic material. However, the quadratic term does not change sign if the electric field reverses so it cannot contribute in an isotropic sample. In three wave mixing, we can have two excitation fields whose electric fields add. To find the intensity, we multiply the electric field by its complex conjugate. We then end up with a number of new frequencies.

$$\begin{aligned}
\vec{E} &= \vec{E}_1 + \vec{E}_2 \\
&= \frac{E_1^o}{2} \left( e^{i(\vec{k}_1 \cdot \vec{z} - \omega_1 t)} + e^{-i(\vec{k}_1 \cdot \vec{z} - \omega_1 t)} \right) + \frac{E_2^o}{2} \left( e^{i(\vec{k}_2 \cdot \vec{z} - \omega_2 t)} + e^{-i(\vec{k}_2 \cdot \vec{z} - \omega_2 t)} \right) \\
I &= \frac{cn}{8\pi} \left[ \frac{E_1^o E_2^o}{4} \left( e^{i((\vec{k}_1 - \vec{k}_2) \cdot \vec{z} - (\omega_1 - \omega_2)t)} + e^{-i((\vec{k}_1 - \vec{k}_2) \cdot \vec{z} - (\omega_1 - \omega_2)t)} \right) + \right. \\
&\quad \left. \frac{E_1^o E_2^o}{4} \left( e^{i((\vec{k}_1 + \vec{k}_2) \cdot \vec{z} - (\omega_1 + \omega_2)t)} + e^{-i((\vec{k}_1 + \vec{k}_2) \cdot \vec{z} - (\omega_1 + \omega_2)t)} \right) \right]
\end{aligned}$$

Note the presence of the different k vectors that add and subtract. That means that the output polarization will have a number of different directions given by the vector sums and differences as well as frequencies at all the sums and differences. These new directions and frequencies give rise to four different methodologies.

- $\vec{k}_1 + \vec{k}_1$ - second harmonic generation (SHG)
- $\vec{k}_1 + \vec{k}_2$ - sum frequency generation (SFG)
- $\vec{k}_1 - \vec{k}_2$ - difference frequency generation (DFG)
- $\vec{k}_1 - \vec{k}_1$ - optical rectification

### Two cases for the relationship between the polarization and the field it creates:

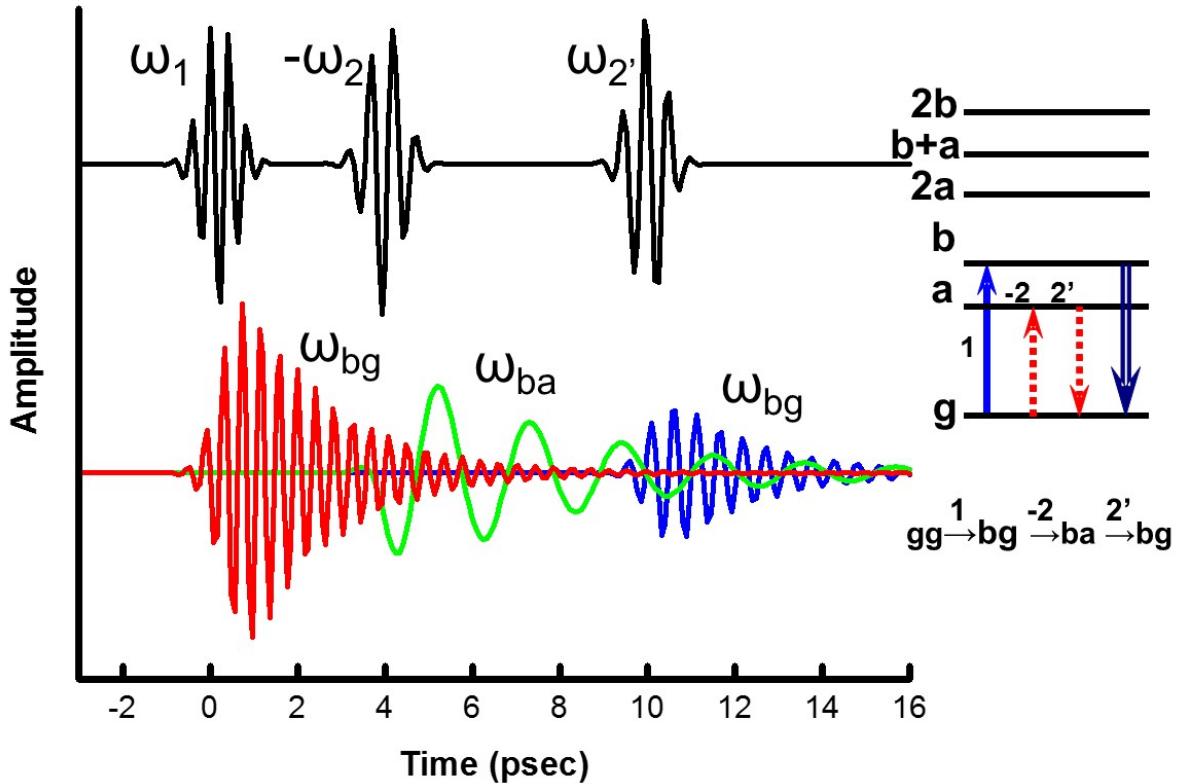
$$\frac{\partial E^o}{\partial z} + \frac{n}{c} \frac{\partial E^o}{\partial t} = \frac{2\pi i F \omega P_{NL}^o}{nc} e^{i\Delta k} \quad (196)$$

- c)  $P_{NL}^o$  depends on  $E^o$  - output frequency is same as an excitation frequency- see earlier discussion on Nonlinear Polarizations, Case 1 (pages 15-19 of notes).
- d)  $P_{NL}^o$  does not depend on  $E^o$  - output frequency is different from any of the excitation frequencies- see earlier discussion on Nonlinear Polarizations, Case 2 (pages 15-19 of notes).

### Four Wave Mixing

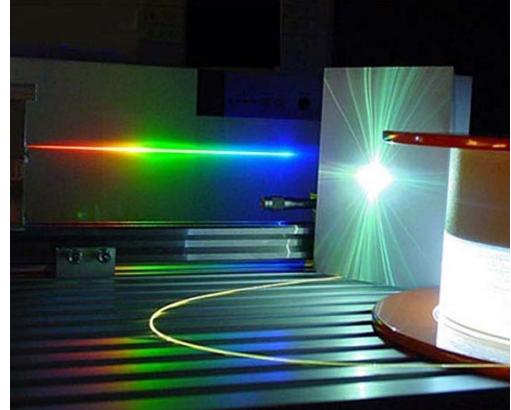
This method is based on the  $\chi_{i,j,k,l}^{(3)}$  term in (181). Three excitation fields create the output fields having all possible sums and differences of the three k vectors and frequencies. In four wave mixing,  $\vec{E} = \vec{E}_1 + \vec{E}_2 + \vec{E}_3$ . The three fields have different frequencies and they create coherences that are oscillating at the frequency differences between the excited quantum states. They also

create populations in quantum states that are stationary. A picture that illustrates these effects appears below.



$\vec{k}_1 - \vec{k}_1 + \vec{k}_1$  - **Pulse propagation effects**- The index of refraction is intensity dependent (optical Kerr effect)-  $n = n_o + n_2 I$ . Typical values of  $n_2$  are  $5-50 \times 10^{-16} \text{ cm}^2/\text{W}$  (CS<sub>2</sub> is  $3.2 \times 10^{-14}$ ) so a  $10^{10} \text{ W/cm}^2$  would change the refractive index by  $10^{-5}$ .

- **Self-phase modulation** occurs because the most intense temporal part of the pulse has a larger refractive index so it slows while the leading and trailing edges travel faster. This effect scrambles the phases in a very complex way and new frequencies are created. The net result is the output appears white. The generation of white light by self-phase modulation has become a very important application because the white light pulse has a very short temporal width and serves as a probe of ultrafast processes.
- **Self focusing** occurs because the most intense spatial part of the pulse has a larger refractive index so a Gaussian pulse shape creates its own lens and the beam

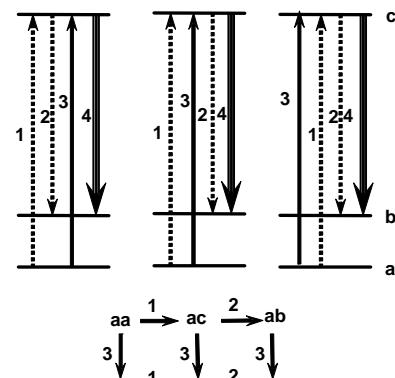
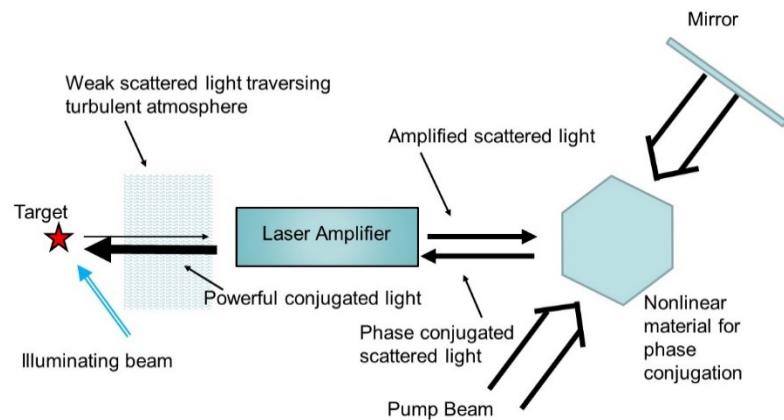


focuses. In the extreme when it is approaching the diffraction limit, the beam will break up into filaments. White light generation usually accompanies self-focusing.

**Phase conjugation-** Phase conjugation occurs when two exactly counter-propagating pump beams interact with a third beam and the third order nonlinearity creates a fourth beam that is the phase conjugate of the third beam so it counter propagates in the exact direction of the third beam. If the third beam has traveled some distance through the atmosphere and has become distorted, the phase conjugation will create an exact replica of the wave front and sent it back in the exact direction that it came from. Phase conjugation can therefore create a different kind of mirror that reflects any incoming light directly back on itself. An example of how a distant target can be illuminated with light and the scattered light travels through the atmosphere until it reaches a laser amplifier where the light is amplified and then directly reflected back on itself by the phase conjugate mirror and amplified by another pass through the laser amplifier. The phase conjugate mirror will reflect a conjugate wave that matches the aberrations of the wave front that were created during the passage through the atmosphere. The result is the beam undoes all the aberrations as it travels back to the target so it can destroy the target.

- $\vec{k}_1 - \vec{k}_1 + \vec{k}_2$  - Raman, stimulated Raman, fluorescence, stimulated emission, pump-probe, transient grating
- $-\vec{k}_1 + \vec{k}_2 + \vec{k}_2$  - Coherent Stokes Raman spectroscopy (CSRS), photon echo, stimulated photon echo
- $\vec{k}_1 + \vec{k}_1 - \vec{k}_2$  - Coherent Anti-Stokes Raman spectroscopy (CARS)
- $\vec{k}_1 - \vec{k}_2 + \vec{k}_3$  - fully resonant four wave mixing
- $\vec{k}_1 + \vec{k}_2 + \vec{k}_3$  - frequency tripling

**Fluorescence and Raman Spectroscopy-** The figure shows the different time ordering of interactions (left to right) with three different electromagnetic fields. These interactions are all occurring at the same time and their effects are additive. The  $\omega_2$  field can be the vacuum fluctuations in which case the methods become spontaneous fluorescence or Raman. If all the fields are real, the methods are stimulated. The major difference between the fluorescence and Raman pathways are whether there is an intermediate population, cc in this case. If there is, the pathway is fluorescence. Fluorescence occurs at the frequency difference between state c and the lower states while Raman occurs at the frequency difference  $\omega - \omega_2$ .



The three pathways in the figure interfere in subtle ways that were discussed earlier in the notes. The net result of the interference is summarized by the equation that was derived earlier:

$$\rho_{cb} \approx \frac{\Omega_{ac}^2 \Omega_{cb} \rho_{aa}}{8|\Delta_{ca}|^2} \left( \frac{1}{\Delta_{ba}^*} + \frac{i\Gamma_{cb}^a}{\Delta_{ba}^* \Delta_{cb}} - \frac{1}{\Delta_{cb}} \frac{(\Gamma_{aa} + 2\Gamma_{ca}^*)}{\Gamma_{cc}} \right). \text{ The first term describes Raman}$$

spectroscopy. The term becomes resonant if  $\omega_1$  and  $\omega_3$  are resonant with the electronic state and  $\omega_1 - \omega_2$  is resonant with a vibrational state. It corresponds to Raman scattering. The last term becomes resonant if  $\omega_1$  and  $\omega_3$  are resonant with the electronic state and  $\omega_2$  is resonant with the transition between the electronic state and the vibrational state. It corresponds to fluorescence. Note that it depends on the dephasing terms. Two of the dephasing terms depend on population relaxation. The third depends on the importance of pure dephasing relative to population relaxation. That means that fluorescence depends on dephasing. If there is no dephasing, there is no fluorescence. Note also that the fluorescence term can be large when the pure dephasing is large compared to the population relaxation. The second term has aspects of both methods and it depends on the presence of pure dephasing. If there is no pure dephasing, only population relaxation, this term will be small.

**Stimulated Raman and stimulated emission** occur when  $\omega_2$  is a real electromagnetic field. **Spontaneous Raman and spontaneous fluorescence** occur when  $\omega_2$  is a vacuum field. Whenever Raman or fluorescence occurs, the intensity of the output field at  $\omega_2$  will increase and the input field at  $\omega_1 = \omega_3$  will decrease. Therefore, you can measure Raman and fluorescence by using two beams at  $\omega_1$  and  $\omega_2$  and measuring the increase in the  $\omega_2$  beam or the decrease in the  $\omega_1$  beam when the frequencies become resonant. The measuring increases or decreases is called Raman gain or Raman loss spectroscopy. In addition, the increase in the  $\omega_2$  beam is related to stimulated Raman spectroscopy and the decrease in the  $\omega_1$  beam is related to inverse Raman spectroscopy.

**Stimulated Raman** can be used to create multiple wavelengths from one excitation laser. For example, focusing an intense pulsed laser into a tube filled with a high pressure of H<sub>2</sub> will create new frequencies whenever  $\omega_1 - \omega_2$  = a vibrational frequency (You can also use other gases including atomic vapors). The amazing thing is that only  $\omega_1$  needs to be present if the intensity is large because the vacuum can supply the  $\omega_2$  frequency. As the beam continues to propagate through the H<sub>2</sub> gas, there will be a real beam at  $\omega_2$  now so the stimulated Raman scattering will become brighter and the conversion can be very efficient. H<sub>2</sub> has the highest vibrational frequency, 4155 cm<sup>-1</sup> so the output beam will be shifted to the red by 4155 cm<sup>-1</sup>. In addition, the H<sub>2</sub> will be vibrationally excited. Now, we can have  $\omega_1$  exciting a Raman transition from the excited vibrational state to the ground state so another frequency will be created such that  $\omega_2 - \omega_1$  matches the H<sub>2</sub> vibrational frequency so a new beam is created at higher energy than  $\omega_1$  by 4155 cm<sup>-1</sup>. In addition, each of the new beams can create new frequencies as well. If a doubled Nd:YAG laser (532 nm) is used, you can create new beams at 1579, 954, 683, 436, 369, 320, 282, 253, 229, 209, and 192 nm.

**Inverse Raman Scattering** is not commonly used. The method uses a strong, narrow band laser ( $\omega_2$ ) and a white light continuum ( $\omega_1$ ). When  $\omega_1 - \omega_2$  matches a vibrational frequency, Raman scattering will cause a decrease at the  $\omega_1$  frequency.

**Photon echo-** The figure shows the three photon echo WMEL diagrams. An initial pulse creates a *ga* coherence after the first interaction. After a delay time,  $\tau$ , a second pulse induces the second and third interactions (the interactions are drawn close to each other to indicate they come from the same pulse) to create an *ag* coherence that re-emits. Phase matching is important. For photon echo, the phase matching condition is  $\vec{k}_{PE} = -\vec{k}_1 + 2\vec{k}_2$  where the subscripts indicate the time ordering of the two pulses. The usefulness of photon echo rests on having spectral transitions that are inhomogeneously broadened so molecules that have different environments or conformations have a distribution of different transition frequencies. The temporal dependence of the excited *ga* coherences is  $e^{i\omega_{ag}t}$  so after a delay time of  $\tau$ , the phase becomes  $e^{i\omega_{ag}\tau}$ . The temporal dependence of the final *ag* coherence is  $e^{-i\omega_{ag}t}$  since an *ag* coherence is conjugate to the *ga* coherence. After a delay of  $\tau$ , the net phase will be zero, regardless of the  $\omega_{ag}$  frequency. At this point in time, all of the coherences will be again in phase and the re-emission becomes completely coherent. This phased emission scales quadratically with the sample concentration. The large output intensity that results at time  $\tau$  is called the echo. By measuring the echo intensity as a function of delay time between the first two pulses, one can measure the dephasing rate ( $\Gamma_{ag}$ ) of the *ga* coherence. The strength of the photon echo experiment is its immunity to inhomogeneous broadening because the echo does not depend on the specific value for the *ag* frequency.

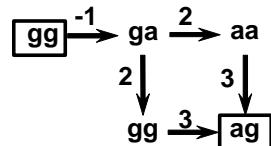
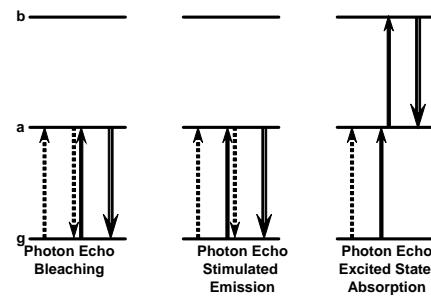
**Stimulated photon echo** experiments are three pulse experiments so the three excitation interactions occur at different times and the delay times between pulses are adjustable.<sup>63</sup> The phase matching condition is  $\vec{k}_{SPE} = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$  where the subscripts denote the time ordering. The WMEL diagram shows there are three pathways- a) ground state bleaching, b) stimulated emission, c) excited state absorption. The sign of the polarization is  $(-1)^n$  where  $n$  is the number of bra-side interactions, so excited state absorption has the opposite sign from the other pathways. The negative sign is associated with the intensity decrease caused by excited state absorption.

The Liouville figure shows the coherences and populations for the bleaching and stimulated emission pathways. After the second interaction, one has either a *gg* ground state population or an *aa* excited state population. After a delay time  $T$ , the third pulse arrives to create the *ag* output coherence (or *ba* for the excited state absorption).

The decay of the stimulated photon echo intensity during the  $T$  delay time measures the relative population changes of the ground and excited state populations. In the impulsive limit, we can write

$$e^{(-i\omega_{ga}-\Gamma_{ag})(\tau_2-\tau_1)} e^{-\Gamma_{aa}(\tau_3-\tau_2)} e^{(-i\omega_{ag}-\Gamma_{ag})(t-\tau_3)} = e^{(-i\omega_{ga}-\Gamma_{ag})\tau} e^{-\Gamma_{aa}T} e^{(-i\omega_{ag}-\Gamma_{ag})t}$$

where we have redefined the measurement times and delays.



**Transient Grating and Pump Probe-** Two interactions with electric fields of the same frequency will create an excited state population and deplete the ground state population. In pump-probe, the two interactions are called the pump and they occur from the same beam. In transient grating, the two interactions occur from two crossed beams so they form a population grating,  $\vec{k}_1 - \vec{k}_2$  where the bright fringes consist of the excited state population and the bleached ground state population and the dark fringes are the equilibrium ground state population. The third interaction then creates the output coherence. In pump-probe, the output electric field created by the third interaction will add to the probe field that created it so the net electric field is the sum of the two. The interference between the two fields can either make the output brighter than the original probe field using the bleaching and stimulated emission pathways or dimmer using the excited state absorption pathway. In transient grating, the output electric field created by the probe field is traveling in a different direction because the probe field essentially reflects off the grating created by the first two fields.

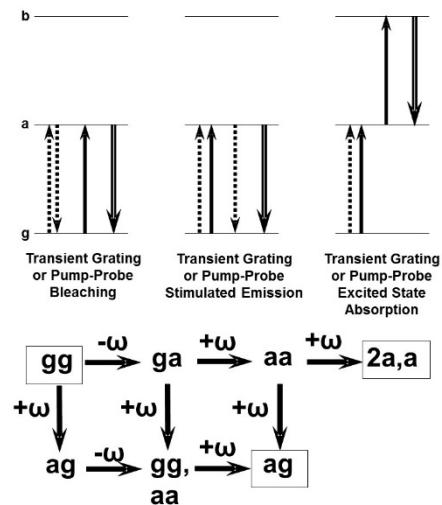
### Second Harmonic Generation Phase Matching in Birefringent Crystals

It is very common to create the second harmonic signal from a laser beam by passing the beam through a birefringent crystal. The birefringence is necessary to provide phase matching. Consider light propagating along the optic axis of a uniaxial crystal. Its refractive index is independent of its polarization direction. This refractive index is labeled ordinary,  $n^o$ . Light propagating perpendicular to the optic axis has two refractive indices that depend on the polarization direction. If the light is polarized perpendicular to the optic axis, the refractive index is still  $n^o$ . If it is polarized parallel to the optic axis, the refractive index is labeled extraordinary,  $n^e$ . If the light is propagating at an angle  $\theta$ , the extraordinary refractive index is between  $n^o$  and  $n^e$  and it is labeled  $n(\theta)$  where  $\theta$  is the angle of the light beam relative to the optical axis. If

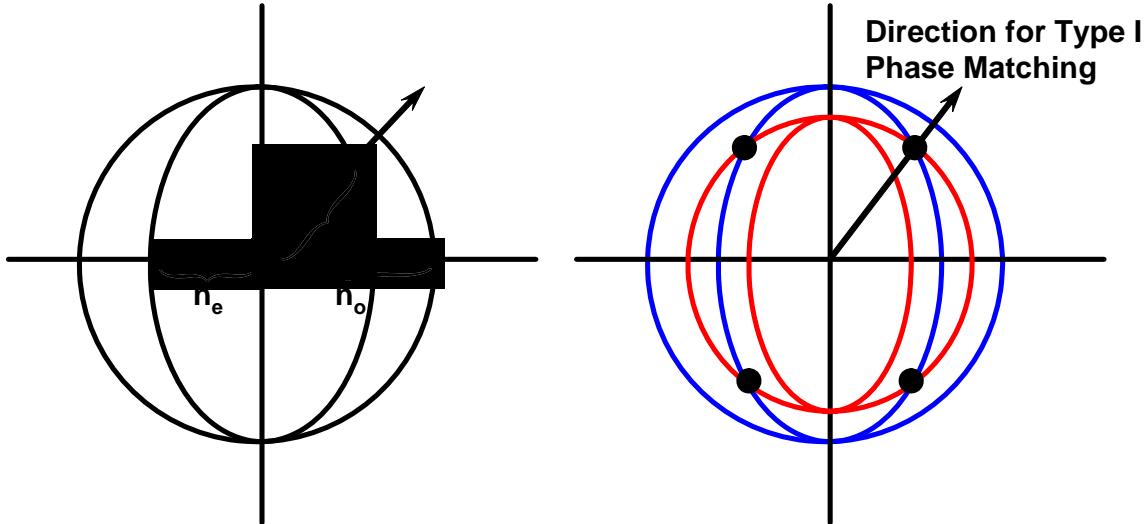
$\theta = 90^\circ$ ,  $n(\theta = 90^\circ) = n^e$  while if  $\theta = 0^\circ$ ,  $n(0^\circ) = n^o$ . Regardless of the angle, this polarization direction is called the extraordinary ray. The wavelength of light traveling in this direction has a different refractive index that lies somewhere between  $n^o$  and  $n^e$ . The real question is: what is the velocity,  $v(\theta)$ , of the wave along its direction? We can break it up into the velocity vector along the optic axis and perpendicular to the axis so

$$v(\theta)^2 = \left( \frac{c}{n(\theta)} \right)^2 = v_o^2 + v_e^2 = \left( \frac{c \cos(\theta)}{n^o} \right)^2 + \left( \frac{c \sin(\theta)}{n^e} \right)^2. \text{ This simplifies to}$$

$$\frac{1}{n^2(\theta)} = \frac{\cos^2 \theta}{(n^o)^2} + \frac{\sin^2 \theta}{(n^e)^2}.$$



The two refractive indices can be represented graphically by the first graph. The vertical axis is the optical axis. The arrow shows the direction of light propagation. The inner ellipse shows the extraordinary index of refraction while the outer circle shows the ordinary index of



refraction. The intersection of the light ray with the ellipse defines the extraordinary index of refraction while the intersection with the circle defines the ordinary index of refraction.

If there are two frequencies, one needs two sets of circles and ellipses. We show the values for the fundamental frequency,  $\omega$ , in red and the second harmonic frequency,  $2\omega$ , in blue.

The condition for phase matching requires  $\vec{k}_{2\omega} = 2\vec{k}_\omega$  so  $\frac{n_{2\omega}}{c} = \frac{2n_\omega}{c}$ . In order to obtain

phase matching, we require  $n_{2\omega} = n_\omega$ . We can obtain phase matching if the angle of the beam matches that at which the ordinary ray of the fundamental has the same index of refraction as the extraordinary ray of the second harmonic.

For sum frequency generation, the phase matching condition is  $\vec{k}_{SPE} = \vec{k}_1 + \vec{k}_2$  so

$\frac{n_{\omega_1+\omega_2}(\omega_1 + \omega_2)}{c} = \frac{n_{\omega_1}\omega_1}{c} + \frac{n_{\omega_2}\omega_2}{c}$ . Using the same strategy, we can pick a direction such that the two lower frequencies are ordinary rays and the sum frequency is an extraordinary ray. This

choice is Type I phase matching and  $\frac{n_{\omega_1+\omega_2}^e(\theta)(\omega_1 + \omega_2)}{c} = \frac{n_{\omega_1}^o\omega_1}{c} + \frac{n_{\omega_2}^o\omega_2}{c}$ . We could also pick the extraordinary ray for one of the lower frequencies and the ordinary ray for the other and the extraordinary ray for the sum frequency. That choice corresponds to Type II phase matching

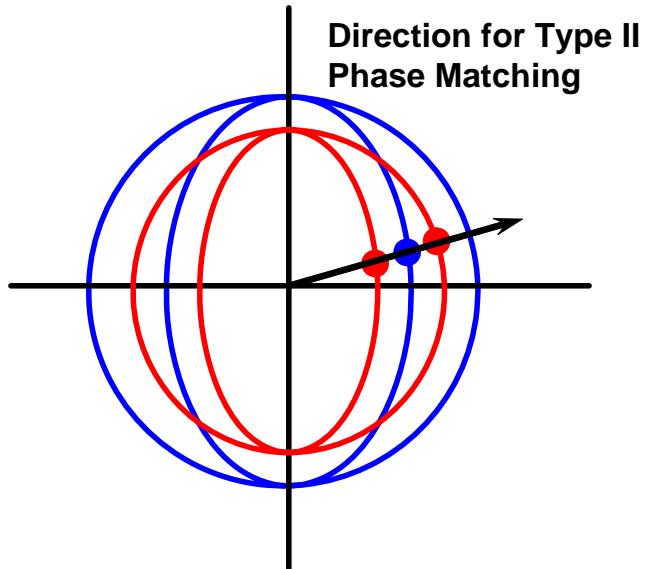
and  $\frac{n_{\omega_1+\omega_2}^e(\theta)(\omega_1 + \omega_2)}{c} = \frac{n_{\omega_1}^o\omega_1}{c} + \frac{n_{\omega_2}^e(\theta)\omega_2}{c}$ . In both cases, one solves for the angle that

meets the phase matching criterion. Only some materials are appropriate for phase matching. They must have refractive index dispersions that allow intersections of the ordinary ray of one with the extraordinary ray of the other.

When the phase matching condition is not met, the fields generated by different sections of the excitation volume will have some destructive interference. The intensity loss is described by a sinc function:

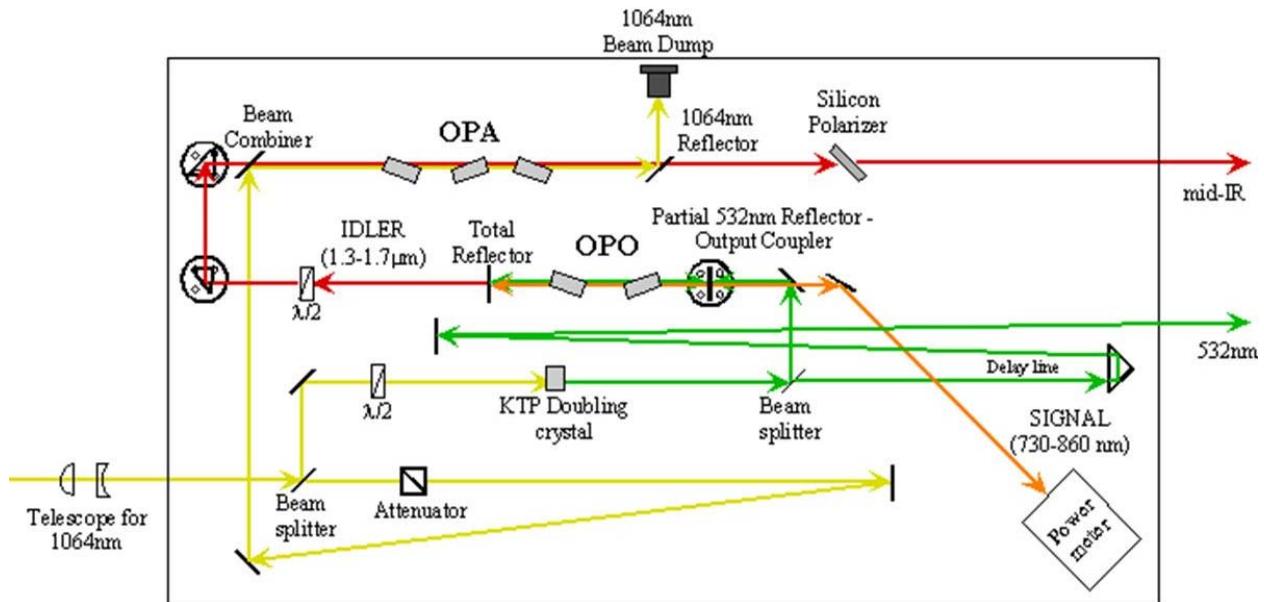
$$\left( \frac{\sin(\Delta kl)}{\Delta kl} \right)^2 \text{ where}$$

$$\Delta \vec{k} = \vec{k}_{\omega_1} + \vec{k}_{\omega_2} - \vec{k}_{\omega_1+\omega_2}.$$



### Optical Parametric Oscillators and Amplifiers

Optical Parametric Oscillators (OPO) and Amplifiers (OPA) are based on the same fundamental processes. Here, the sum frequency is designated the pump and the two lower frequencies are designated the signal and idler such that  $\omega_s > \omega_i$  and  $\omega_p = \omega_s + \omega_i$ . The OPO is based on bringing a strong pump beam into a nonlinear birefringent crystal that is mounted within an optical cavity (i.e. two reflective mirrors). The vacuum creates a signal or idler beam and the other beam is created by difference frequency generation. The signal and/or the idler beams are reflected from the cavity end mirrors and remain within the cavity to build up larger fields. Energy essentially flows from the pump beam to the signal and idler beams. The



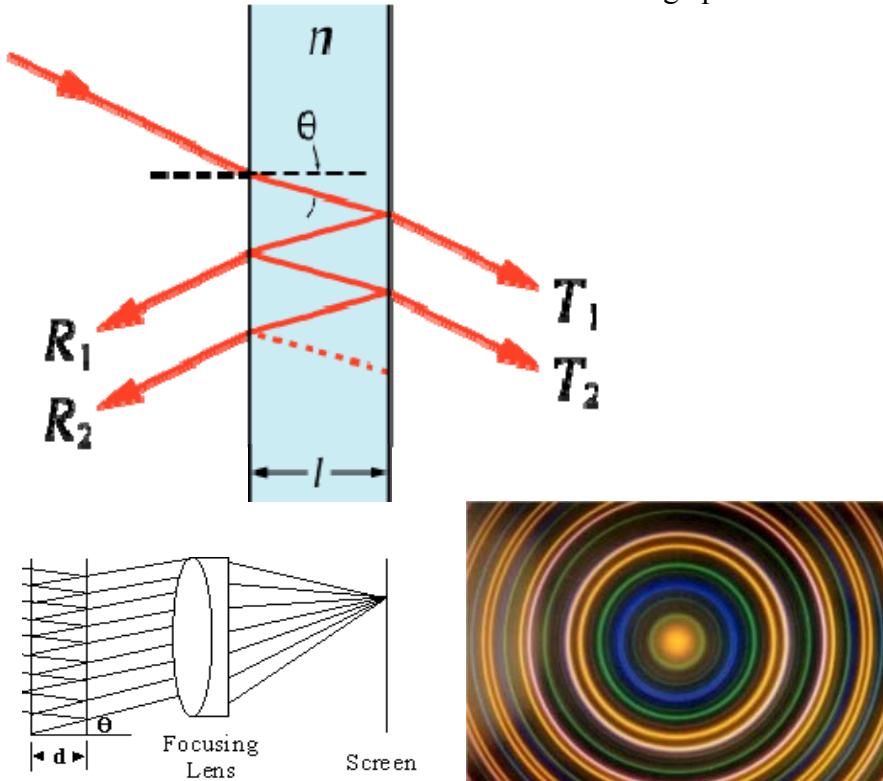
signal and idler frequencies are defined by the phase matching conditions. The signal and idler photons are correlated with each other because they were created by the same photon. They are entangled. That means that if one measures the polarization of one photon at some distant point, the polarization of the other photon will be instantly defined at some other point. Some or all of one or both the signal and idler beams are allowed to leave the cavity for use in an experiment. An OPA is identical except that either a real signal or idler beam is introduced to the nonlinear

crystal along with the pump beam. An OPA can be thought of as a difference frequency generation crystal.

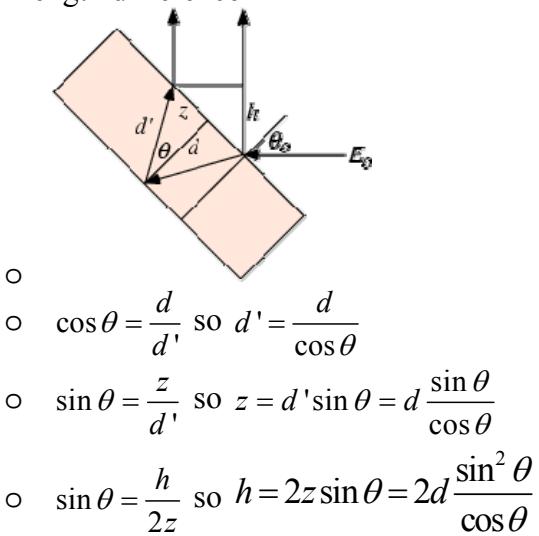
The system shown above is based on excitation by a Nd:YAG laser with 5-10 ns pulses. This laser output occurs at  $1.06\text{ }\mu\text{m}$ . You can see it is frequency doubled in the KTP crystal to 532 nm. The energy of a 532 nm beam is  $18,800\text{ cm}^{-1}$ . The OPO part of the system creates a signal and idler pulse with energies above and below that value such that the sum is  $18,800\text{ cm}^{-1}$ . The idler and signal beams are specified as tunable from  $1.3\text{-}1.7\text{ }\mu\text{m}$  and 860-730 nm, respectively. Thus, an idler beam created at  $1.5\text{ }\mu\text{m}$  ( $6,667\text{ cm}^{-1}$ ) would correspond to a signal beam at 824 nm ( $12130\text{ cm}^{-1}$ ). The frequency range is limited by the phase matching requirements. The OPA part of the design would create mid-IR light at the difference frequency between the  $1.06\text{ }\mu\text{m}$  beam and the idler beam,  $1,700\text{-}3550\text{ cm}^{-1}$  although, in practice, the crystals absorb the light at  $2,000\text{ cm}^{-1}$  and lower.

## Interferometers

- Fabre-Perot interferometer and etalon and their fringe patterns

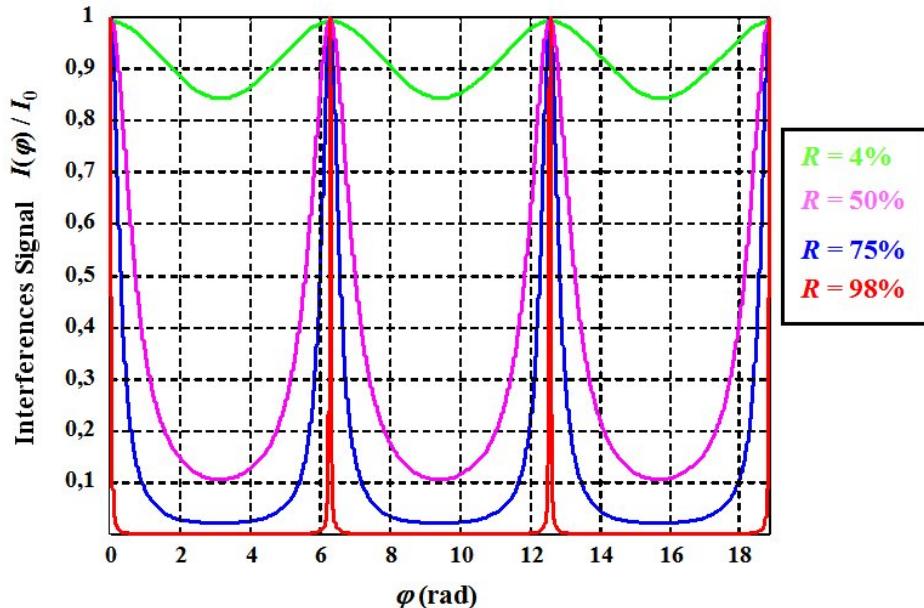


- Path-length difference-



- Constructive interference occurs when  $p\lambda = \Delta = 2nd \cos \theta$  where  $p$  is an integer.
- Let  $a$ ,  $t$  and  $r$  be the absorption, transmission, and reflection coefficients for light's electric field and  $A$ ,  $T$  and  $R$  be the coefficients for light intensity. Fringe patterns result from interference between successive internal reflections

- Note  $|a|^2 + |t|^2 + |r|^2 = A + T + R = 1$  but  $a + r + t \neq 1$
- $t^2 + t^2 r^2 e^{ik\Delta} + t^2 r^4 e^{2ik\Delta} + \dots + t^2 r^{2n} e^{nik\Delta} = \frac{t^2}{1 - r^2 e^{ik\Delta}}$ 
  - The intensity is proportional to
$$I \propto \frac{t^2}{1 - r^2 e^{ik\Delta}} * \frac{t^2}{1 - r^2 e^{-ik\Delta}} = \frac{t^4}{1 + r^4 - r^2(e^{ik\Delta} + e^{-ik\Delta})} = \frac{t^4}{1 + r^4 - 2r^2 \cos k\Delta} = \frac{t^4}{1 + r^4 - 2r^2 \left(1 - 2 \sin^2 \frac{k\Delta}{2}\right)}$$
using  $\sin \frac{x}{2} = \sqrt{\frac{1 - \cos x}{2}}$ . Note  $|a|^2 + |t|^2 + |r|^2 = A + T + R = 1$  but  $a + r + t \neq 1$   
since they are complex
  - $I \propto \frac{t^4}{1 + r^4 - 2r^2 + 4r^2 \sin^2 \frac{k\Delta}{2}} = \frac{t^4}{(1 - r^2)^2 \left(1 + \frac{4r^2}{(1 - r^2)^2} \sin^2 \frac{k\Delta}{2}\right)} = \frac{T^2}{(1 - R)^2 \left(1 + \frac{4R}{(1 - R)^2} \sin^2 \frac{k\Delta}{2}\right)}$
  - $I \propto \frac{1}{\left(1 + \frac{A}{T}\right)^2 \left(1 + \frac{4R}{(1 - R)^2} \sin^2 \frac{k\Delta}{2}\right)} = \frac{1}{\left(1 + \frac{A}{T}\right)^2 \left(1 + \frac{4R}{(1 - R)^2} \sin^2 \pi p\right)}$  where  $p = \frac{\Delta}{\lambda}$
  - Define  $F = \text{the coefficient of finesse} = \frac{4R}{(1 - R)^2}$ . It will be very large if  $R$  is close to 1. The denominator of  $I$  will then be large and  $I$  will be small. It reaches a maximum when  $\sin^2 \pi p$  is zero.
  - The shape of this functionality is



- Resolution defined by the condition when the frequency difference required when the intensity is half the maximum intensity, i.e. the HWHM. The maximum intensity appears when  $\pi p$  is 0,  $\pi$ ,  $2\pi$ ,  $3\pi$ , ....

$$\circ \quad \frac{4R}{(1-R)^2} \sin^2 \pi(p + \delta p) \approx \frac{4R}{(1-R)^2} (\pi \delta p)^2 = 1$$

$$\circ \quad \delta p = \sqrt{\frac{(1-R)^2}{4\pi^2 R}} = \frac{1}{\pi \sqrt{F}} \text{ or } \delta p = \delta \left( \frac{\Delta}{\lambda} \right) = \frac{\delta \lambda \Delta}{\lambda^2} = \frac{p \delta \lambda}{\lambda} = \frac{1}{\pi \sqrt{F}} \text{ or}$$

$$\frac{\delta \lambda}{\lambda} = \frac{1}{\pi p \sqrt{F}}$$

- $\frac{\delta \lambda}{\lambda} = \frac{1}{\pi p \sqrt{F}}$  where  $\delta \lambda$  is the HWHM  $\frac{\lambda}{\delta \lambda_{FWHM}} = \frac{\pi p \sqrt{F}}{2}$
- The shape of a fringe for a Fabre Perot interferometer or etalon is different than those of grating monochromators since the fringe never goes to zero so the effective experimental resolution is more complex to define. If we want the resolution of a Fabre Perot to match that of a monochromator, one can show that the criterion must be changed for a Fabre-Perot.
- $N_{effective}$  can be considered the effective number of reflections that occur within a Fabre-Perot.  $N_{effective}$  is calculated by comparing the resolution of a Fabre-Perot & a grating. The resolution of a Fabre-Perot that is equivalent to a grating can be shown to be

$$\frac{\lambda}{\delta \lambda_{FWHM}} = 1.49 p \sqrt{F} \text{ and for a grating it is } pN. \text{ Comparing the two, we can say}$$

$$N_{effective} = 1.49 \sqrt{F}.$$

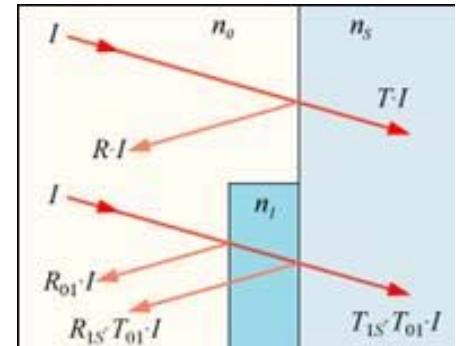
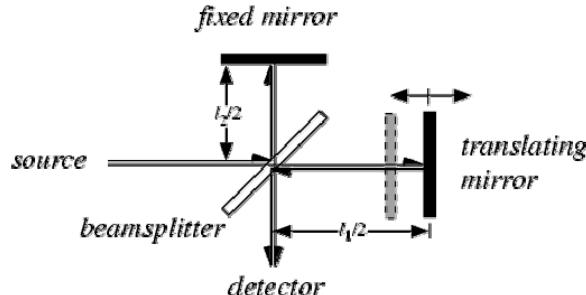
- Free spectral range- If we are scanning the wavelength, we will have constructive interference at two successive wavelengths when  $p\lambda_2 = (p+1)\lambda_1$  (where  $\lambda_2 > \lambda_1$ ) or  $\Delta \lambda_{FSR} = \frac{\lambda_1}{p} = \frac{\lambda_1 \lambda_2}{2nd \cos \theta}$ . Changing to wavenumbers, we find that  $\Delta \bar{v}_{FSR} = \frac{1}{2nd \cos \theta}$
- Finesse =  $\mathfrak{F} = \frac{FSR}{\Delta \lambda_{FWHM}} = \frac{\frac{\lambda}{p}}{\frac{2\lambda}{\pi p \sqrt{F}}} = \frac{\pi \sqrt{F}}{2}$  (large finesse means sharp fringes relative to the FSR)

- The actual resolution depends upon how well you can discern the fringes and that depends upon resolving light traveling along different angles,  $\theta$ .
- Dispersion-  $\frac{d\lambda}{d\theta} = \frac{2nd \sin \theta}{p}$ . Remembering that the order is defined by  $p = \frac{2nd \cos \theta}{\lambda}$ , we can write  $\frac{d\lambda}{d\theta} = \lambda \tan \theta$ . Note that the dispersion is infinite if  $\theta$  is zero.

- For small angles,  $\frac{d\lambda}{d\theta} = \lambda d\theta$  or  $d\lambda = \lambda d\theta^2$ . That means the resolution depends quadratically on the divergence of the light beam.
- Must keep solid angle below  $\Omega_{\max} = \pi(\Delta\theta_{\max})^2 = \pi\left(\frac{\lambda}{\Delta\lambda}\right)$
- Etendue =  $U = A\Omega$  measures light gathering power
- Practical considerations
  - $\frac{1}{\mathfrak{F}_{\text{net}}^2} = \frac{1}{\mathfrak{F}_{\text{reflectivity}}^2} + \frac{1}{\mathfrak{F}_{\text{flatness}}^2}$  where  $\mathfrak{F}_{\text{flatness}} = m/2$  for  $\lambda/m$  flatness
  - also worry about
    - temperature
    - distance
    - alignment
- Solid etalons, air spaced etalons, PZT driven interferometers, pressure tuning
- Interference filters and antireflection coatings- compare the cases when there is no coating (top) and when there is a coating (bottom). If the multiple reflections interfere, there is no net reflection. The condition for destructive interference is dependent on the wavelength.

### Michelson Interferometers and FTIR Instruments

- Michelson interferometer construction:



- An important detail is that reflection from a mirror entails a phase change of the light by 180°. The light heading to the detector has experienced 2 reflections and a transmission so there are no net phase changes from reflections. The light headed back to the source has experienced one reflection and two transmissions so it has had a net 180° phase shift so it is out of phase with the light going to the detector. So when the light headed to the detector is destructively interfering, the light headed to the source is constructively interfering and vice versa. That is an important characteristic because it insures energy conservation, i.e. the light is always headed somewhere.

- $E = E_1 + E_2 = E_1^o e^{\frac{2\pi i \Delta_1}{\lambda}} + E_2^o e^{\frac{2\pi i \Delta_2}{\lambda}}$ 

$$EE^* = |E_1|^2 + |E_2|^2 = |E_1^o|^2 + |E_2^o|^2 + E_1^o E_2^o \left( e^{\frac{2\pi i (\Delta_1 - \Delta_2)}{\lambda}} + e^{-\frac{2\pi i (\Delta_1 - \Delta_2)}{\lambda}} \right)$$

$$= |E_1^o|^2 + |E_2^o|^2 + 2E_1^o E_2^o \cos \frac{2\pi(\Delta_1 - \Delta_2)}{\lambda}$$
- $I = \frac{cn|E|^2}{8\pi}$
- $I = I_1 + I_2 + 2\sqrt{I_1 I_2} \cos \frac{2\pi(\Delta_1 - \Delta_2)}{\lambda}$
- Constructive maxima when  $\frac{2\pi(\Delta_1 - \Delta_2)}{\lambda} = 2\pi n$  or  $\Delta_{\max} = n\lambda$
- Destructive maxima when  $\frac{2\pi(\Delta_1 - \Delta_2)}{\lambda} = 2\pi n + \pi$  or  $\Delta_{\min} = \left(n + \frac{1}{2}\right)\lambda$
- Free spectral range  

$$\Delta = n\lambda_1 = (n+1)\lambda_2 \text{ or } \Delta\lambda_{FSR} = \frac{\lambda}{n} \text{ and since } \Delta\bar{\nu} = \frac{\Delta\lambda}{\lambda^2}, \Delta\bar{\nu}_{FSR} = \frac{1}{\Delta}$$

### Fourier transforms

- Remember,  $\int_0^{2\pi} \sin mx \sin nx dx = \pi\delta(m, n)$  and  $= 0$  if  $m = 0$
- Remember,  $\int_0^{2\pi} \cos mx \cos nx dx = \pi\delta(m, n)$  and  $= 2\pi$  if  $m = 0$
- $\int_0^{2\pi} \sin mx \cos nx dx = 0$
- For  $f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty} a_n \cos nx + b_n \sin nx$  where  $f(x)$  is a periodic function with a period, T.  

$$a_n = \frac{1}{\pi} \int_0^{2\pi} f(x) \cos nx dx \text{ and } b_n = \frac{1}{\pi} \int_0^{2\pi} f(x) \sin nx dx$$

- Egs.  $f(x) = \frac{\pi}{2} + 2 \left( \sin x + \frac{\sin 3x}{3} + \frac{\sin 5x}{5} + \frac{\sin 7x}{7} + \dots \right)$  (square wave)

Resolution (if one  $\lambda$  has  $n+1$  fringes relative to another, Fourier transformation will result in destructive interference between the two)-

$$\Delta_{\max} = n_{\max} \lambda_1 = (n_{\max} + 1) \lambda_2 \quad \text{or} \quad \Delta\lambda = \frac{\lambda}{n_{\max}} \quad \text{which becomes} \quad \Delta\bar{\nu}_{\text{resolution}} = \frac{1}{\Delta_{\max}}$$

### Instrumental details

- Light sources
  - Globar (SiC), Nernst glower ( $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{ThO}_2$ )
- Detectors-
  - $\text{HgCdTe}_2$ ,  $\text{PbS}$ ,  $\text{PbSe}$ ,  $\text{InSb}$ ,  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  ( $8-12\mu$ ),  $\text{Hg}_{0.7}\text{Cd}_{0.3}\text{Te}$  ( $3-5\mu$ ), thermopiles, pyroelectrics, bolometers ( $\text{InSb}$ )
- Fourier transform IR provides Fellgett (measure all  $\omega$ ) and Jaquinot (no slits) advantages that are essential given the disadvantage of weak light sources and inefficient detectors
- Apodization for resolution improvement
- Nyquist criterion

### Important examples of Fourier transforms

Function	Time domain	Frequency domain
Slit	$=1$ for $0 < t < T$ ; $=0$ otherwise	$\sqrt{\frac{2}{\pi}} \frac{\sin \omega T}{\omega}$
Exponential	$e^{-\Gamma t}$	$\sqrt{\frac{2}{\pi}} \left( \frac{\Gamma}{\omega^2 + \Gamma^2} \right)$
Sine wave	$e^{-i\omega_o t}$	$\sqrt{2\pi} \delta(\omega_o - \omega)$
Gaussian	$e^{-t^2/\sigma^2}$	$\frac{\sigma}{\sqrt{2}} e^{-4\sigma^2 \omega^2}$

### Geometric Optics

- Lenses and mirrors- spherical, parabolic, cylindrical, plano convex, biconvex
- Lenses and mirrors will collect the light and deliver it to the monochromator or interferometer that will measure it.
- Lens formula- positions of object and image;  $4f$  is minimum distance; closer to source magnifies and further demagnifies; at the focal position  $f$ , it focuses to infinity. We call that collimation. If the source is at infinity, the image is at the focal distance,  $f$ -

$$\frac{1}{f} = \frac{1}{x_o} + \frac{1}{x_i}$$

- Magnification-  $M = \frac{x_i}{x_o}$

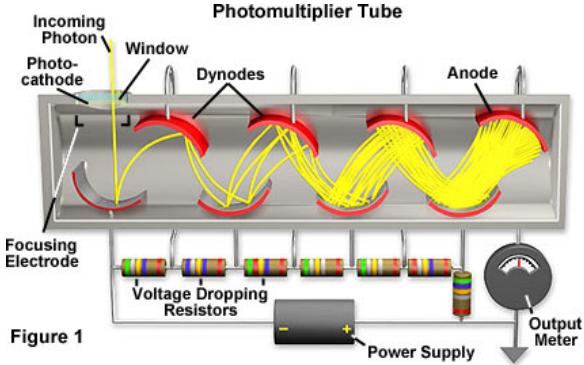
- Solid angle, f/#, numerical aperture, and fraction collected- For a lens,  $f/\# = \frac{x}{D}$ ,  
 $\Omega = \frac{\pi D^2}{4x^2}$ ,  $N.A. = n \sin \theta$  (where  $n$  is the index of refraction and  $\theta$  is the half-angle subtended by the lens), and  $fraction\_collected = \frac{\Omega}{4\pi} = \frac{1}{16(f/\#)^2}$ .
- The area of the image is related to the area of the object by the square of the magnification which is in turn related to the square of the image and object distances. The square image and object distances are also related inversely to the solid angles. Thus,  

$$M^2 = \left( \frac{x_i}{x_o} \right)^2 = \frac{\Omega_o}{\Omega_i}$$
.
- The amount of light entering a monochromator or interferometer is controlled by its solid angle and its slit height and width or its acceptance area, respectively. The product of the area and solid angle is the etendue. If the solid angle feeding the instrument is narrower than the instrument, the feeding solid angle will control the amount of light. If it is wider, the amount of light will be the ratio of the instrument solid angle to the solid angle feeding it. The same is true for the areas. Brightness is the key parameter because it normalizes the amount of light collected to the source's solid angle and area.
- Conservation of brightness
  - Power and intensity are not conserved
  - Brightness is conserved:
    - $P_o, I_o = \frac{P_o}{A_o}, B_o = \frac{P_o}{4\pi A_o}$ ,
    - $P_i = P_o \frac{\Omega_o}{4\pi}, I_i = \frac{P_i}{A_i} = \frac{P_o \Omega_o}{4\pi A_i} = \frac{P_o \Omega_o}{4\pi A_o \frac{\Omega_o}{\Omega_i}} = \frac{P_o \Omega_i}{4\pi A_o}, B_i = \frac{I_i}{\Omega_i} = \frac{P_o}{4\pi A_o}$
    - Note that the brightness of the image is identical to the object but the power and intensity are not the same.
    - To find your signal level, conservation of brightness allows you to avoid the details of the optical system and simply multiply the brightness by the limiting solid angle and aperture dimensions of the optical system.  

$$\text{Signal power} = B A_{\text{limit}} \Omega_{\text{limit}}$$
    - Therefore, for maximum signal, make sure that the detection instrument is the limiting factor, not the optics that you control. ***FILL THE ENTRANCE APERTURE AND THE SOLID ANGLE OF YOUR DETECTION INSTRUMENTATION (MONOCHROMATOR, INTERFEROMETER, ETC.)***
- Aberrations- coma (asymmetrical wave front distortion), astigmatism (symmetrical wave front distortion), spherical aberration (on-axis diameter dependent focal length), chromatic aberration- aspheric lenses, plano-convex with curvature pointed at source, bi-convex for 1:1 imaging

## Photomultipliers

- Physical structure- photocathodes, dynodes, envelopes, pins, voltage divider, gain  $G = \delta^k$
- Quantum efficiency,  $\eta(\lambda)$
- Types of noise- thermionic emission in dynodes and photocathode, shot noise, 1/f noise, Johnson noise  $\sigma_V = \sqrt{4kTR\Delta f}$ , cosmic rays and  $^{40}\text{K}$  in envelope, leakage currents in voltage divider
- Noise at each stage –  $n_p$  and  $n_c$  are the number of counts of photons and dark electrons from photocathode
  - $n_{total} = \eta n_p + n_c$  and  $\sigma_{photocathode} = \sqrt{(\eta n_p + n_c)}$ ,  $\sigma_{1st\_dynode} = \sqrt{\delta(\eta n_p + n_c)}$ ,
  - $\sigma_{2nd\_dynode} = \sqrt{\delta^2(\eta n_p + n_c)}$ , ...



- Noise from each stage at the anode – each amplified by effective gain

$$\begin{aligned} & \circ G\sigma_{photocathode} = \sqrt{G^2(\eta n_p + n_c)}, \\ & \circ \frac{G}{\delta}\sigma_{1st\_dynode} = \sqrt{\frac{G^2}{\delta}(\eta n_p + n_c)}, \\ & \circ \frac{G}{\delta^2}\sigma_{2nd\_dynode} = \sqrt{\frac{G^2}{\delta^2}(\eta n_p + n_c)}, \dots \end{aligned}$$

- Total noise at anode- variances add

$$\begin{aligned} & \circ \sigma_T^2 = G^2\sigma_{photocathode}^2 + \frac{G^2}{\delta^2}\sigma_{1st\_dynode}^2 + \frac{G^2}{\delta^4}\sigma_{2nd\_dynode}^2 + \dots \\ & \circ \sigma_T^2 = G^2(\eta n_p + n_c) \left( 1 + \frac{1}{\delta} + \frac{1}{\delta^2} + \dots + \frac{1}{\delta^k} \right) \\ & \circ \sigma_T = G \sqrt{(\eta n_p + n_c) \left( \frac{1 - \frac{1}{\delta^{k+1}}}{1 - \frac{1}{\delta}} \right)} = G \sqrt{(\eta n_p + n_c) \left( \frac{\delta^{k+1} - 1}{\delta^k (\delta - 1)} \right)} \approx G \sqrt{(\eta n_p + n_c) \frac{\delta}{(\delta - 1)}} \end{aligned}$$

- $S/N \approx \frac{\eta n_p G}{G \sqrt{(\eta n_p + n_c) \frac{\delta}{(\delta - 1)}}} = \frac{\eta n_p}{\sqrt{(\eta n_p + n_c) \frac{\delta}{(\delta - 1)}}}$ 
  - For very low light levels (eg. fluorescence and Raman) –
    - $\eta n_p \ll n_c$ ,  $\frac{S}{N_{LowLight}} \approx \frac{\eta n_p}{\sqrt{n_c}} \sqrt{\frac{\delta - 1}{\delta}}$
  - For very high light levels (eg. absorption spectroscopy) –

$$\blacksquare \quad \eta n_p >> n_c, \quad \frac{S}{N_{HighLight}} \approx \sqrt{\eta n_p} \sqrt{\frac{\delta - 1}{\delta}}$$

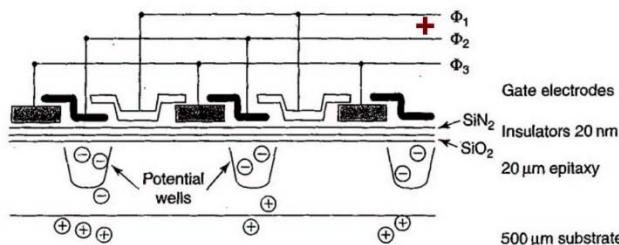
- For multiple sources of noise, variances from each source add.
- Conversion from  $n$  to  $i$  requires measurement time,  $\tau$ .
  - $\tau = 2RC$
  - $\tau = \frac{1}{2B}$
  - $i_{photocathode} = \frac{en}{\tau}$  and  $i_{anode} = \frac{Gen}{\tau}$
- Detection methods
  - dc current
  - photon counting
  - lock-in
- Pulse height distributions
- Temperature dependence of dark current
- Dynode chain construction
- Time response

## Absorption Measurements

- **General Principle-** variances add-  $\sigma_{Total}^2 = \sum_i \sigma_i^2$
- $A = \log\left(\frac{I_o}{I}\right)$
- $dA^2 = \left(\frac{\partial A}{\partial I_o}\right)^2 \Delta I_o^2 + \left(\frac{\partial A}{\partial I}\right)^2 \Delta I^2$
- $\frac{\partial A}{\partial I_o} = \frac{\log e}{I_o}$  and  $\frac{\partial A}{\partial I} = \frac{\log e}{I}$  and  $dA = \sqrt{\left(\frac{0.434 \Delta I_o}{I_o}\right)^2 + \left(\frac{0.434 \Delta I}{I}\right)^2}$

## Charge Transfer Devices (CTD)- Charge Coupled Detector Arrays (CCD arrays) and Charge Injection Detector Arrays (CID arrays)

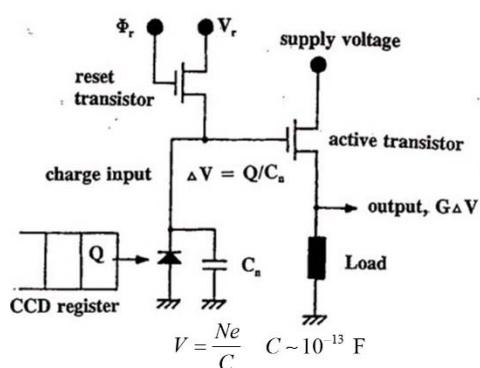
- CCD detector arrays are based on metal oxide semiconductor (MOS) capacitors. CMOS detector arrays are based on photodiode arrays that are individually read out.
- n-type Si use negative bias to collect photogenerated holes in depletion region and detect charge nondestructively by the voltage change induced by moving charge from a collection electrode to the sensing electrode within a single detector element (CID).
- p-type Si use positive bias to collect photogenerated electrons in depletion region and move the charge to a charge-sensing amplifier (CCD). We'll concentrate on CCD arrays
- Array size- linear, rectangular, square; number of pixels



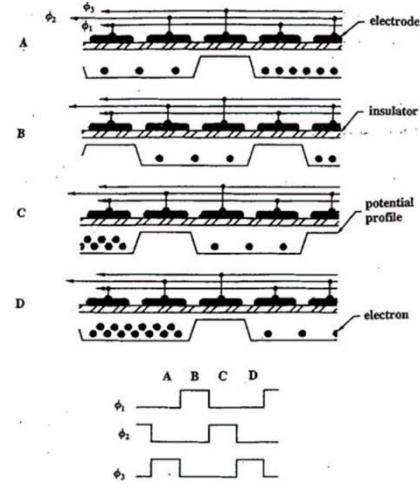
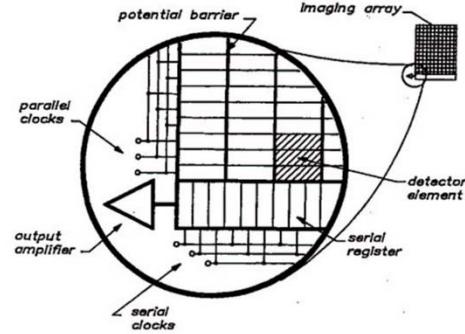
CCD arrays use p-type Si with positive bias to collect electrons

absorption (100's of microns at 1,000 nm). Limited by strong reflection from silicon surface (30-50% from 1090 to <400 nm). QE can be near 100%.

- Increase QE by back-thinning and antireflection coating the back side (front has the SiO and SiN electrodes which have different indices of refraction)
- Down conversion is used for UV sensitivity
- Pixel size defines resolution
- Full-well capacity (10K-500K electrons, depending upon pixel size)
- ADC limits dynamic range-ADU defines smallest signal (perhaps 4 e<sup>-</sup>'s if that is the noise level) and then # of bits defines the upper limit. May not be the full-well capacity of a pixel.

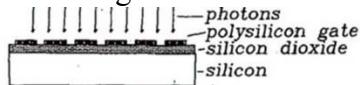


- 10 bits- 1,024; 16- 65,535
- can change gain or get higher number of bits
- Dark current depends strongly on temperature (50% decrease/6 C temp. change). Thermoelectric coolers are part of chip. Cooling too much prevents ability to move



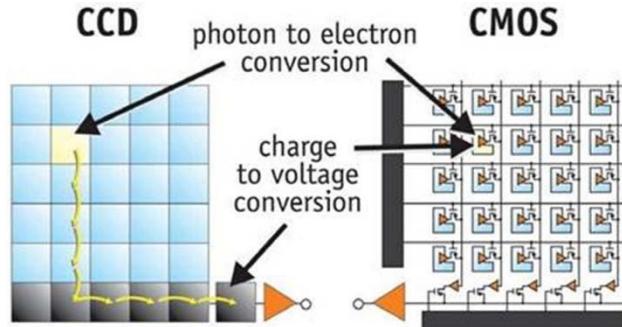
the electrons (not as much of a problem in CID's). Can be 0.03-  
 $<0.001 \text{ e}^-/\text{sec}$ . for properly cooled  
 CCD's and  $<0.008 \text{ e}^-/\text{sec}$  for CID's.

- Noise sources- dark current; read noise (2-20 e-'s /pixel depending on readout rate)
- cosmic rays create strong features
- Blooming occurs at high intensities to signal overflows to other pixels

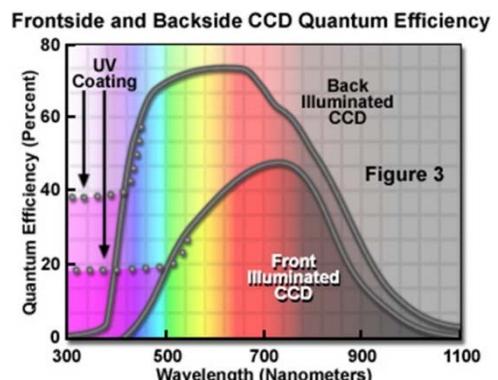


pixels and using software to add together.

- Time-delayed integration (TDI)- use CCD parallel shifts to synchronize the pixel movement with an image
- frame transfer CCD's use 1/2 pixels to record (unmasked) and 1/2 to read-out so after acquiring data, transfer it to the masked area for reading
- Defects in pixels- high dark current, unresponsive, charge traps, differences in quantum efficiency
- Etaloning from epitaxial layer
- Must use shutter to prevent exposure during readout



- read-out speed is 50-200kHz for best noise and >5MHz for best speed. Choose depending upon noise and speed. Read-out noise is typically 2->20 electrons.
- sub-array readout, charge binning. Binning theoretically reduces read noise (binning vs reading all



iXon Ultra 897

Neo sCMOS

	iXon Ultra 897	Neo sCMOS
Active pixels (H x V)	512 x 512	2560 x 2160
Pixel size (W x H; $\mu\text{m}$ )	16 x 16	6.5 x 6.5
Sensor area (mm)	8.2 x 8.2	16.6 x 14.0
Pixel well depth ( $\text{e}^-$ , typical)	160,000	30,000
Maximum full frame rate (fps)	56	100
Read noise ( $\text{e}^-$ , typical)	< 1 to 98 @ 17 MHz	1 @ 200 MHz
Dark current ( $\text{e}^-$ / pix / sec)	0.001	0.03
Vertical clock speeds ( $\mu\text{s}$ )	0.3 to 3.3	N/A
Minimum sensor temperature ( $^{\circ}\text{C}$ )	-100	-40
Digitization	16-bit	16-bit (Data Range)
Pixel readout rates (MHz)	17, 10, 5, 1	560, 200
PC interface	USB 2.0	Camera Link
Sensor QE options	EX2, BV, UVB	sCMOS

## Light Sources

- Black body radiation
- Spectral brightness  $B = \frac{2hc^2}{\lambda^5 \left( e^{\frac{hc}{\lambda kT}} - 1 \right)}$  watts/cm<sup>2</sup>steradian nm

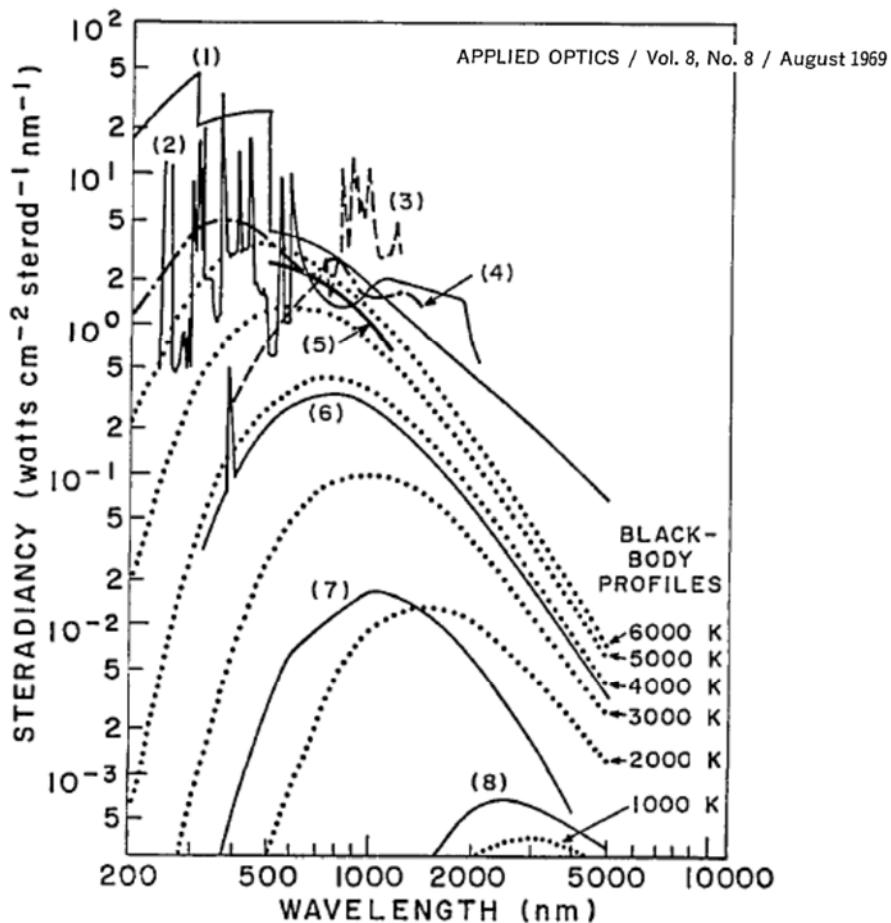


Fig. 10. Intensities of light sources for the visible and near visible: (1)—argon arc continuum (approximate calculation neglecting selfabsorption); (2)—mercury compact arc (PEK 110); (3)—xenon compact arc (PEK X75); (4)—Giannini vortex stabilized radiation source; (5)—high current carbon arc (brightness temperature 5800 K);<sup>31</sup> (6)—low current-carbon arc (brightness temperature 3900 K);<sup>36</sup> (7)—tungsten ribbon lamp (true temperature 2600 K, emissivities from De Vos<sup>153</sup> and Larabee<sup>154</sup>); (8)—globar (color temperature 1175 K, emissivities from Silverman<sup>169</sup>).

## APPENDIX A- SELECTED LAPLACE TRANSFORMS

### LAPLACE OPERATIONS

$F(t)$	$\int_0^\infty dt e^{-st} F(t)$
$AF(t) + BG(t)$	$Af(s) + Bf(s)$
$\frac{dF(t)}{dt}$ (or $\dot{f}(t)$ )	$sf(s) - F(0)$
$\frac{d^n F(t)}{dt^n}$	$s^n f(s) - s^{n-1} F(0) - s^{n-2} \frac{dF(0)}{dt} - \dots - \frac{d^{n-1} F(0)}{dt^{n-1}}$
$\int_0^t d\tau F(\tau)$	$\frac{1}{s} f(s)$
$\int_0^t \int_0^\tau d\tau d\lambda F(\lambda)$	$\frac{1}{s^2} f(s)$
$\int_0^t d\tau F_1(t-\tau) F_2(\tau)$ (or $F_1 * F_2$ )	$f_1(s) f_2(s)$

### LAPLACE TRANSFORMS

$\frac{1}{s}$	1
$\frac{1}{s^2}$	$t$
$\frac{1}{(s-a)}$	$e^a t$
$\frac{1}{(s-a)^2}$	$t e^{at}$
$\frac{1}{(s-a)(s-b)}$	$\frac{1}{(a-b)} (e^{at} - e^{bt})$
$\frac{s}{(s-a)(s-b)}$	$\frac{(ae^{at} - be^{bt})}{(a-b)}$
$\frac{1}{(s^2 + a^2)}$	$\frac{1}{a} \sin at$

$$\begin{aligned}
& \frac{s}{(s^2 + a^2)} \cos at \\
& \frac{1}{(s-a)(s-b)(s-c)} - \frac{(b-c)e^{at} + (c-a)e^{bt} + (a-b)e^{ct}}{(a-b)(b-c)(c-a)} \\
& \frac{s}{(s-a)(s-b)(s-c)} \\
& - \frac{ae^{at}}{(a-b)(c-a)} - \frac{be^{bt}}{(a-b)(b-c)} - \frac{ce^{ct}}{(b-c)(c-a)} \\
& \frac{(s-d)}{(s-a)(s-b)(s-c)} \frac{(a-d)(b-c)e^{at} + (b-d)(c-a)e^{bt} + (c-d)(a-b)e^{ct}}{(a-b)(b-c)(a-c)} \\
& \frac{s}{(s^2 + a^2)(s^2 + b^2)} \quad (a^2 \neq b^2) \quad \frac{\cos at - \cos bt}{b^2 - a^2} \\
& \frac{1}{(s-a)(s^2 + b^2)} \quad \frac{be^{at} - b \cos bt - a \sin bt}{b(a^2 + b^2)}
\end{aligned}$$

## APPENDIX B- GENERALIZED LIOUVILLE EQUATION

### Generalized Derivation of Liouville Equation

In order to write the Liouville equation to describe the temporal evolution of our density matrix elements, we examine how an electromagnetic field can induce transitions involving either  $\psi_i$  or  $\psi_j$  states in the  $\Psi = c_i\psi_i + c_j\psi_j$  wave function. We will assume that an electromagnetic field can induce a transition where either  $\psi_k \rightarrow \psi_i$  or  $\psi_l \rightarrow \psi_j$ . We first rewrite our equations relating the amplitudes for being in a particular state:

$$\dot{c}_i = -i\omega_i c_i - \frac{i}{\hbar} V_{ik} c_k - \Gamma_i c_i \quad (1)$$

$$\dot{c}_j = -i\omega_j c_j - \frac{i}{\hbar} V_{jl} c_l - \Gamma_j c_j \text{ or its complex conjugate} \quad (2)$$

$$\dot{c}_j^* = i\omega_j c_j^* + \frac{i}{\hbar} V_{jl} c_l^* - \Gamma_j c_j^* \quad (3)$$

We also rewrite the temporal evolution of the density matrix, equation:

$$\dot{\rho}_{ij} = \dot{c}_i c_j^* + c_i \dot{c}_j^* \quad (4)$$

and we substitute

$$\dot{\rho}_{ij} = \left( -i\omega_i c_i - \frac{i}{\hbar} V_{ik} c_k - \Gamma_i c_i \right) c_j^* + c_i \left( i\omega_j c_j^* + \frac{i}{\hbar} V_{jl} c_l^* - \Gamma_j c_j^* \right) \quad (5)$$

and simplify,

$$\dot{\rho}_{ij} = -i\omega_i \rho_{ij} - \frac{i}{\hbar} V_{ik} \rho_{kj} + i\omega_j \rho_{ij} + \frac{i}{\hbar} V_{jl} \rho_{il} - \Gamma_{ij} \rho_{ij} \quad (6)$$

Defining  $\omega_{ij} \equiv \omega_i - \omega_j$  and  $\Gamma_{ij} \equiv \Gamma_i + \Gamma_j$ , this becomes:

$$\dot{\rho}_{ij} = -i\omega_{ij} \rho_{ij} - \frac{i}{\hbar} (V_{ik} \rho_{kj} - V_{jl} \rho_{il}) - \Gamma_{ij} \rho_{ij} \quad (7)$$

### Differential Form of Time Evolution

The general equation defining the time evolution of coherences and populations is

$$\dot{\rho}_{ij} = -i\delta_{ij} \rho_{ij} + \frac{i}{2} (e^{-i\omega t} + e^{i\omega t}) (\Omega_{ik} \rho_{kj} - \Omega_{jk} \rho_{ik}) \quad (8)$$

where  $\delta_{ij} = \omega_{ij} - i\Gamma_{ij}$ . If  $\omega_{ij}$  is a high frequency, it is useful to make the rotating wave approximation. If it is not, one simply uses the equation given above. Let  $\rho_{ij} = \tilde{\rho}_{ij} e^{-i\omega_{RW} t}$  (Choices might be  $\omega_{RW} \sim \omega_{ij}$  or  $\omega$  or the center of an inhomogeneous distribution,  $\omega_0^2$ ). This

transformation into the rotating frame makes integrals easier since there are no rapidly oscillating terms. Then,

$$\dot{\tilde{\rho}}_{ij} e^{-i\omega_{RW}t} - i\omega_{RW} \tilde{\rho}_{ij} e^{-i\omega_{RW}t} = -i\delta_{ij} \tilde{\rho}_{ij} e^{-i\omega_{RW}t} + \frac{i}{2} (e^{-i\omega t} + e^{i\omega t}) (\Omega_{ik} \rho_{kj} - \Omega_{jk} \rho_{ik}) \quad (9)$$

**Note that the frequencies for the  $kj$  and  $ik$  coherences can be either the free induction decay frequency and/or the driven frequency.** We are going to assume the initial coherences are oscillating at their free induction decay frequencies and that they are not themselves being driven by laser fields. If they are being driven, then the  $\omega_{kj}$  and  $\omega_{ik}$  frequencies should be chosen to be the laser excitation frequencies.

$$\dot{\tilde{\rho}}_{ij} = i\omega_{RW} \tilde{\rho}_{ij} - i\delta_{ij} \tilde{\rho}_{ij} + \frac{i}{2} (e^{-i(\omega-\omega_{RW})t} + e^{i(\omega+\omega_{RW})t}) (\Omega_{ik} \tilde{\rho}_{kj} e^{-i\omega_{kj}t} - \Omega_{jk} \tilde{\rho}_{ik} e^{-i\omega_{ik}t}) \quad (10)$$

The rotating wave approximation neglects one of the two terms oscillating at  $(\omega - \omega_{RW})$  or  $(\omega + \omega_{RW})$  because it will average to zero in comparison with the term that has a similar

frequency to either  $\rho_{kj}$  or  $\rho_{ik}$ . Then, the net phase associated with the exponentials will be

$$e^{-i(\pm\omega-\omega_{ij})t-i\omega_{kj}t} = e^{-i(\pm\omega-\omega_{ik})t} \text{ or } e^{-i(\pm\omega-\omega_{ij})t-i\omega_{ik}t} = e^{-i(\pm\omega-\omega_{kj})t} \text{ where } \omega_{ik} \text{ or}$$

$\omega_{kj}$  is the frequency of the transition initiated by  $\omega$ . One chooses the sign on  $\omega$  according to which makes the smallest exponent, ideally zero. Equation (10) can then be written:

$$\dot{\tilde{\rho}}_{ij} = i(\omega_{RW} - \delta_{ij}) \tilde{\rho}_{ij} + \frac{i}{2} (\Omega_{ik} \tilde{\rho}_{kj} e^{-i(\pm\omega-\omega_{RW}+\omega_{kj})t} - \Omega_{jk} \tilde{\rho}_{ik} e^{-i(\pm\omega-\omega_{RW}+\omega_{ik})t}) \quad (11)$$

In order to have the slowest rate of change for  $\tilde{\rho}_{ij}$ , we want  $\omega_{RW} = \pm\omega + \omega_{kj}$  for the ket side transition or  $\omega_{RW} = \pm\omega + \omega_{ik}$  for the bra side transition. (As an example, a common choice for  $\omega_{RW}$  is to have the excitation frequency,  $\omega$ , resonant with the  $k \rightarrow i$  or  $k \rightarrow j$  transitions. Then,  $\omega_{RW} = \omega_{ij}$ .)

There are two cases to consider for evaluating the equation:

$$\text{Ket side transition- } \dot{\tilde{\rho}}_{ij} = i(\pm\omega + \omega_{kj} - \delta_{ij}) \tilde{\rho}_{ij} + \frac{i\Omega_{ik}}{2} \tilde{\rho}_{kj} \text{ and } \rho_{ij} = \tilde{\rho}_{ij} e^{-i(\pm\omega+\omega_{kj})t} \quad (12)$$

$$\text{Bra side transition- } \dot{\tilde{\rho}}_{ij} = i(\pm\omega + \omega_{ik} - \delta_{ij}) \tilde{\rho}_{ij} - \frac{i\Omega_{jk}}{2} \tilde{\rho}_{ik} \text{ and } \rho_{ij} = \tilde{\rho}_{ij} e^{-i(\pm\omega+\omega_{ik})t}$$

These equations form the basis for a numerical integration to find the temporal dependence of the density matrix. The time dependence of the amplitude is typically defined by the time dependence of the electric field amplitude contained within the Rabi frequency,  $\Omega = \frac{\mu E^o(t)}{\hbar}$ .

It is also interesting to note that the equation for the bra side transition could be obtained by simply taking the complex conjugate of the ket side transition.

### Steady State Expressions

In the steady state, equations (12) become:

$$\tilde{\rho}_{ij} = -\frac{i\Omega_{ik}}{2i(\pm\omega + \omega_{kj} - \delta_{ij})} \tilde{\rho}_{kj} \quad \text{and} \quad \tilde{\rho}_{ij} = \frac{i\Omega_{jk}}{2i(\pm\omega + \omega_{ik} - \delta_{ij})} \tilde{\rho}_{ik}$$

which in turn become:

$$\text{Ket side- } \tilde{\rho}_{ij} = -\frac{i\Omega_{ik}}{2i(\pm\omega + \omega_{kj} - (\omega_{ij} - i\Gamma_{ij}))} \tilde{\rho}_{kj} = \frac{\Omega_{ik}}{2(\omega_{ik} \mp \omega - i\Gamma_{ij})} \tilde{\rho}_{kj}$$

$$\text{Bra side- } \tilde{\rho}_{ij} = \frac{i\Omega_{jk}}{2i(\pm\omega + \omega_{ik} - (\omega_{ij} - i\Gamma_{ij}))} \tilde{\rho}_{ik} = -\frac{\Omega_{jk}}{2(\omega_{kj} \mp \omega - i\Gamma_{ij})} \tilde{\rho}_{ik}$$

We have assumed that the initial coherence was not being driven but was undergoing free induction decay. If it was driven at some  $\omega_1$  frequency and now it is being driven at  $\omega_2$ , these equations become:

$$\text{Ket side- } \tilde{\rho}_{ij} = -\frac{i\Omega_{ik}}{2i(\pm\omega_2 \pm \omega_1 - (\omega_{ij} - i\Gamma_{ij}))} \tilde{\rho}_{kj} = \frac{\Omega_{ik}}{2(\omega_{ij} \mp \omega_1 \mp \omega_2 - i\Gamma_{ij})} \tilde{\rho}_{kj}$$

$$\text{Bra side- } \tilde{\rho}_{ij} = \frac{i\Omega_{jk}}{2i(\pm\omega_2 \pm \omega_1 - (\omega_{ij} - i\Gamma_{ij}))} \tilde{\rho}_{ik} = -\frac{\Omega_{jk}}{2(\omega_{ij} \mp \omega_1 \mp \omega_2 - i\Gamma_{ij})} \tilde{\rho}_{ik}$$

where the signs are defined by the resonance conditions for the initial and final coherences.

### Integral Form of Time Evolution

Let's get an integral form for this equation. Multiply both sides by  $e^{i(\delta_{ij} - \omega_{RW})t}$ .

$$\dot{\tilde{\rho}}_{ij} e^{i(\delta_{ij} - \omega_{RW})t} - i(\omega_{RW} - \delta_{ij}) \tilde{\rho}_{ij} e^{i(\delta_{ij} - \omega_{RW})t} = \frac{i}{2} (\Omega_{ik} \rho_{kj} - \Omega_{jk} \rho_{ik}) e^{-i\omega t} e^{i\delta_{ij}t}. \quad (13)$$

Notice that the left side can be written as an exact differential,

$$\frac{d}{dt} \left( \tilde{\rho}_{ij} e^{i(\delta_{ij} - \omega_{RW})t} \right) = \frac{i}{2} (\Omega_{ik} \rho_{kj} - \Omega_{jk} \rho_{ik}) e^{i(\delta_{ij} - \omega)t} \quad (12)$$

so we can now integrate from  $t = -\infty$  to  $t$  remembering that  $\rho_{ij}(t = -\infty) = 0$ .

$$\tilde{\rho}_{ij} = \frac{i}{2} e^{-i(\delta_{ij} - \omega_{RW})t} \int_{-\infty}^t (\Omega_{ik}(t') \rho_{kj}(t') - \Omega_{jk}(t') \rho_{ik}(t')) e^{i(\delta_{ij} - \omega)t'} dt' \quad \text{or} \quad (13)$$

$$\tilde{\rho}_{ij} = \frac{i}{2} \int_{-\infty}^t (\Omega_{ik}(t') \rho_{kj}(t') - \Omega_{jk}(t') \rho_{ik}(t')) e^{-i(\omega - \omega_{RW})t'} e^{-i(\delta_{ij} - \omega_{RW})(t-t')} dt' \quad (14)$$

If we make the assignment that  $\omega_{RW} = \omega_{ij}$ , then (14) becomes

$$\tilde{\rho}_{ij} = \frac{i}{2} \int_{-\infty}^t (\Omega_{ik}(t')\rho_{kj}(t') - \Omega_{jk}(t')\rho_{ik}(t')) e^{i(\delta_{ij}-\omega)t'} e^{-\Gamma_{ij}t'} dt' \quad (15)$$

This equation forms the basis for many treatments when a specific excitation pulse is applied to the system. The excitation pulse can be described by the temporal dependence of the Rabi frequency since the Rabi frequency depends on  $\Omega = \frac{\mu E^o(t)}{\hbar}$ . One simply substitutes the temporal dependence on  $E^o(t)$  and integrates.

The easiest and therefore most common assumption is to work in the impulsive limit where the excitation pulse is essentially instantaneous and can be described by a delta function,  $\delta(t' - \tau)$ . This function is infinite when the argument is zero and it is zero at all other times. By

definition, it is normalized so its integral is one. Under this assumption,  $\Omega = \frac{\mu E^o}{\hbar} \delta(t' - \tau)$

, and the integral in eqn. (15) is easy to evaluate. It is simply the value of each function when the argument is zero so we replace  $t'$  by  $\tau$ . Then, (15) becomes

$$\tilde{\rho}_{ij} = \frac{i}{2} (\Omega_{ik}(\tau)\rho_{kj}(\tau) - \Omega_{jk}(\tau)\rho_{ik}(\tau)) e^{i(\delta_{ij}-\omega)\tau} e^{-\Gamma_{ij}\tau} \quad (16)$$

and therefore

$$\rho_{ij} = \frac{i}{2} (\Omega_{ik}(\tau)\rho_{kj}(\tau) - \Omega_{jk}(\tau)\rho_{ik}(\tau)) e^{i(\delta_{ij}-\omega)\tau} e^{-(i\omega_{ij} + \Gamma_{ij})\tau} \quad (17)$$

The first part of this function simply defines the amplitude. It depends upon the size of the coherence and the electromagnetic field that drives the transition at the time of the excitation pulse, a phase factor at the time of the excitation, and an exponentially decaying oscillation at the free induction decay frequency of the  $ij$  coherence. This function can be used as the Green's function for describing any other shaped excitation pulse and forms another equivalent way of deriving the effects of a specific temporal shape of an excitation pulse.

## APPENDIX C TEMPORAL COHERENCE EVOLUTION AFTER STEP FUNCTION EXCITATION

It is informative to solve the Liouville equation using Laplace transforms. We will assume the excitation field turns on at time=0 and remains on. That assumption will create a transient term that will die out and a steady state term that will persist at long times. We will also assume there is an initial coherence present at time=0 and that it is feed by other coherences or populations that have reached a steady state value. The Liouville equation states:

$$\dot{\rho}_{ij} = -i\delta_{ij}\rho_{ij} + \frac{i}{2}(e^{-i\omega t} + e^{i\omega t})(\Omega_{ik}\rho_{kj} - \Omega_{jk}\rho_{ik}). \quad (1)$$

We will write the oscillations of the feeding coherences,  $\rho_{kj}$  and  $\rho_{ik}$ , in the form

$$\rho_{kj} = \tilde{\rho}_{kj}e^{-i\omega_{kj}t} \text{ and } \rho_{ik} = \tilde{\rho}_{ik}e^{-i\omega_{ik}t}. \quad (2)$$

**Note that these frequencies can be either the free induction decay frequency and/or the driven frequency.** Substituting into (1), we obtain

$$\dot{\rho}_{ij} = -i\delta_{ij}\rho_{ij} + \frac{i}{2}(e^{-i\omega t} + e^{i\omega t})(\Omega_{ik}\tilde{\rho}_{kj}e^{-i\omega_{kj}t} - \Omega_{jk}\tilde{\rho}_{ik}e^{-i\omega_{ik}t}) \quad (3)$$

Expanding this expression and combining the exponents,

$$\dot{\rho}_{ij} = -i\delta_{ij}\rho_{ij} + \frac{i}{2}\left(\Omega_{ik}\tilde{\rho}_{kj}\left(e^{-i(\omega_{kj}+\omega)t} + e^{-i(\omega_{kj}-\omega)t}\right) - \Omega_{jk}\tilde{\rho}_{ik}\left(e^{-i(\omega_{ik}+\omega)t} + e^{-i(\omega_{ik}-\omega)t}\right)\right) \quad (4)$$

Now we take the Laplace transform,

$$(s + i\delta_{ij})\rho_{ij} - \rho_{ij}^o = \frac{i}{2}\begin{cases} \Omega_{ik}\tilde{\rho}_{kj}\left(\frac{1}{s + i(\omega_{kj} + \omega)} + \frac{1}{s + i(\omega_{kj} - \omega)}\right) \\ -\Omega_{jk}\tilde{\rho}_{ik}\left(\frac{1}{s + i(\omega_{ik} + \omega)} + \frac{1}{s + i(\omega_{ik} - \omega)}\right) \end{cases} \quad (5)$$

Solving for the coherence,

$$\rho_{ij} = \frac{\rho_{ij}^o}{(s + i\delta_{ij})} + \frac{i}{2}\begin{cases} \Omega_{ik}\tilde{\rho}_{kj}\left(\frac{1}{[s + i(\omega_{kj} + \omega)][s + i\delta_{ij}]} + \frac{1}{[s + i(\omega_{kj} - \omega)][s + i\delta_{ij}]}\right) \\ -\Omega_{jk}\tilde{\rho}_{ik}\left(\frac{1}{[s + i(\omega_{ik} + \omega)][s + i\delta_{ij}]} + \frac{1}{[s + i(\omega_{ik} - \omega)][s + i\delta_{ij}]}\right) \end{cases} \quad (6)$$

Taking the inverse Laplace transform,

$$\rho_{ij} = \rho_{ij}^o e^{-i\delta_{ij}t} + \frac{i}{2}\begin{cases} \Omega_{ik}\tilde{\rho}_{kj}\left(\frac{e^{-i(\omega_{kj}+\omega)t} - e^{-i\delta_{ij}t}}{(-i(\omega_{kj} + \omega) + i\delta_{ij})} + \frac{e^{-i(\omega_{kj}-\omega)t} - e^{-i\delta_{ij}t}}{(-i(\omega_{kj} - \omega) + i\delta_{ij})}\right) \\ -\Omega_{jk}\tilde{\rho}_{ik}\left(\frac{e^{-i(\omega_{ik}+\omega)t} - e^{-i\delta_{ij}t}}{(-i(\omega_{ik} + \omega) + i\delta_{ij})} + \frac{e^{-i(\omega_{ik}-\omega)t} - e^{-i\delta_{ij}t}}{(-i(\omega_{ik} - \omega) + i\delta_{ij})}\right) \end{cases} \quad (7)$$

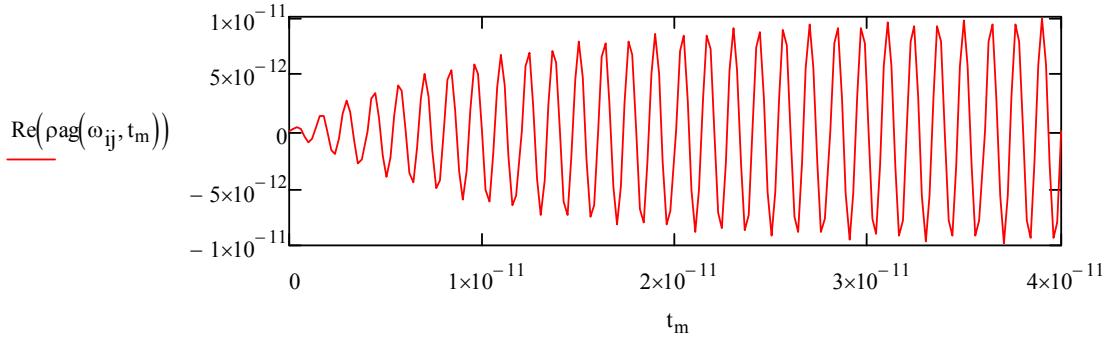
Simplifying,

$$\rho_{ij} = \rho_{ij}^o e^{-i\delta_{ij}t} + \frac{1}{2} \left( \Omega_{ik} \tilde{\rho}_{kj} \left( \frac{e^{-i(\omega_k+\omega)t} - e^{-i\delta_{ij}t}}{(\delta_{ij} - \omega - \omega_{kj})} + \frac{e^{-i(\omega_k-\omega)t} - e^{-i\delta_{ij}t}}{(\delta_{ij} + \omega - \omega_{kj})} \right) \right. \\ \left. - \Omega_{jk} \tilde{\rho}_{ik} \left( \frac{e^{-i(\omega_k+\omega)t} - e^{-i\delta_{ij}t}}{(\delta_{ij} - \omega - \omega_{ik})} + \frac{e^{-i(\omega_k-\omega)t} - e^{-i\delta_{ij}t}}{(\delta_{ij} + \omega - \omega_{ik})} \right) \right) \quad (8)$$

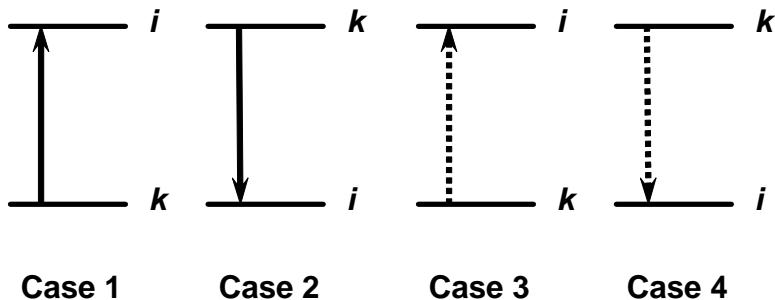
Let's now understand this expression. The first term is the exponential decay of the initial coherence  $\rho_{ij}^o$  in the absence of any driving field. It has an oscillatory component and a decay component:

$$\rho_{ij} = \rho_{ij}^o e^{-i\omega_{ij}t} e^{-\Gamma_{ij}t}. \quad (9)$$

The next four terms correspond to the 4 different cases that are possible when either the ket- or bra-side state undergoes either an absorption or emission. Each case has two terms. The first term corresponds to the steady state response and the second corresponds to the transient response that dies away exponentially because it has the same form as equation (9). An example of the temporal response for the real part of the coherence is shown below. The imaginary part is identical except for a 90° phase shift.



The interpretation of the 4 cases depends on the resonance condition defined by the excitation frequency required to minimize the denominators. At resonance, the coherence reaches its maximum. The first two cases correspond to ket-side transitions and the last two cases correspond to bra-side transitions. They have opposite signs. In our diagrams that show the transitions between states, we will use solid arrows for ket-side transitions and dotted arrows for bra-side transitions. The diagrams for each case are



**It is important to remember that for each case, the frequencies of the initial coherence ( $\rho_{kj}$  or  $\rho_{ik}$ ) can be either the free induction decay frequency and/or the driven frequency.**

**Case 1- ket-side absorption transition from state  $k$  to state  $i$ .**

This case corresponds to the term

$$\rho_{ij} = \frac{\Omega_{ik} \tilde{\rho}_{kj} \left( e^{-i(\omega_{kj} + \omega)t} - e^{-i\delta_{ij}t} \right)}{2(\delta_{ij} - \omega - \omega_{kj})} \quad (10)$$

It reaches its minimum value of  $-i\Gamma_{ij}$  when  $\omega = \omega_{ij} - \omega_{kj} = \omega_{ik}$ . For this condition to be met, state  $i$  must have a higher energy than state  $k$  so the  $k \rightarrow i$  transition must be an absorption. That also means that the second term in equation (8) cannot reach resonance because  $\omega$  has the opposite sign. The term is antiresonant and corresponds to the term that is ignored in the rotating wave approximation.

**Case 2- ket-side emissive transition from state  $k$  to state  $i$ .**

This case corresponds to the term

$$\rho_{ij} = \frac{\Omega_{ik} \tilde{\rho}_{kj} \left( e^{-i(\omega_{kj} - \omega)t} - e^{-i\delta_{ij}t} \right)}{2(\delta_{ij} + \omega - \omega_{kj})} \quad (11)$$

It reaches its minimum value of  $-i\Gamma_{ij}$  when  $\omega = \omega_{kj} - \omega_{ij} = \omega_{ki}$ . For this condition to be met, state  $i$  must have a lower energy than state  $k$  so the  $k \rightarrow i$  transition must be an emission. That also means that the first term in equation (8) cannot reach resonance because has the opposite sign. The term is antiresonant and corresponds to the term that is ignored in the rotating wave approximation.

**Case 3- bra-side emission transition from state  $k$  to state  $j$ .**

This case corresponds to the term

$$\rho_{ij} = -\frac{\Omega_{jk} \tilde{\rho}_{ik} \left( e^{-i(\omega_{ik} + \omega)t} - e^{-i\delta_{ij}t} \right)}{2(\delta_{ij} - \omega - \omega_{ik})} \quad (12)$$

It reaches its minimum value of  $-i\Gamma_{ij}$  when  $\omega = \omega_{ij} - \omega_{ik} = \omega_{kj}$ . For this condition to be met, state  $j$  must have a lower energy than state  $k$  so the transition must be an emission. That also means that the fourth term in equation (8) cannot reach resonance because  $\omega$  has the opposite sign. The term is antiresonant and corresponds to the term that is ignored in the rotating wave approximation.

**Case 4- bra-side absorption transition from state  $k$  to state  $j$ .**

This case corresponds to the term

$$\rho_{ij} = -\frac{\Omega_{jk}\tilde{\rho}_{ik}\left(e^{-i(\omega_{ik}-\omega)t} - e^{-i\delta_{ij}t}\right)}{2(\delta_{ij} + \omega - \omega_{ik})} \quad (13)$$

It reaches its minimum value of  $-i\Gamma_{ij}$  when  $\omega = \omega_{ik} - \omega_{ij} = \omega_{jk}$ . For this condition to be met, state  $j$  must have a higher energy than state  $k$  so the transition must be an absorption. That also means that the third term in equation (8) cannot reach resonance because  $\omega$  has the opposite sign. The term is antiresonant and corresponds to the term that is ignored in the rotating wave approximation.

### TEMPORAL COHERENCE EVOLUTION AFTER SQUARE EXCITATION PULSE

A square excitation pulse with a width of  $\tau$  can be represented by the equation (8) when  $t = \tau$  and the response given by (9) where

$$\rho_{ij} = \rho_{ij}(t = \tau)e^{-i\omega_{ij}(t-\tau)}e^{-\Gamma_{ij}(t-\tau)} \quad (14)$$

## APPENDIX D- MATRIX FORM OF LIOUVILLE EQUATION AND ROTATING WAVE APPROXIMATION

The Liouville equation in matrix form is

$$\dot{\rho} = -\frac{i}{\hbar} [H, \rho] - \rho^R \quad (15)$$

or equivalently,

$$\dot{\rho}_{ij} = -\frac{i}{\hbar} [H_{ik} \rho_{kj} - \rho_{ik} H_{kj}] - \Gamma_{ij} \rho_{ij} \quad (16)$$

**where repeated subscripts imply a summation over the subscripts.** If we now state that

$$\rho_{ij} = \tilde{\rho}_{ij} e^{-i\omega_{ij}^{RW} t} \quad (17)$$

where  $\omega_{ij}^{RW}$  can be chosen as  $\omega_j$  but it can also be chosen differently, depending on the circumstances of the particular problem. Substituting into (16),

$$\dot{\tilde{\rho}}_{ij} e^{-i\omega_{ij}^{RW} t} - i\omega_{ij}^{RW} \tilde{\rho}_{ij} e^{-i\omega_{ij}^{RW} t} = -\frac{i}{\hbar} [H_{ik} \tilde{\rho}_{kj} e^{-i\omega_{kj}^{RW} t} - \tilde{\rho}_{ik} e^{-i\omega_{ik}^{RW} t} H_{kj}] - \Gamma_{ij} \tilde{\rho}_{ij} e^{-i\omega_{ij}^{RW} t} \quad (18)$$

which becomes

$$\dot{\tilde{\rho}}_{ij} = i\omega_{ij}^{RW} \tilde{\rho}_{ij} - \frac{i}{\hbar} [H_{ik} \tilde{\rho}_{kj} e^{-i\omega_{kj}^{RW} t} - \tilde{\rho}_{ik} e^{-i\omega_{ik}^{RW} t} H_{kj}] e^{i\omega_{ij}^{RW} t} - \Gamma_{ij} \tilde{\rho}_{ij} e^{-i\omega_{ij}^{RW} t} e^{i\omega_{ij}^{RW} t} \quad (19)$$

or

$$\dot{\tilde{\rho}}_{ij} = i\omega_{ij}^{RW} \tilde{\rho}_{ij} - \frac{i}{\hbar} [H_{ik} \tilde{\rho}_{kj} e^{i\omega_{kj}^{RW} t} - \tilde{\rho}_{ik} e^{i\omega_{ik}^{RW} t} H_{kj}] - \Gamma_{ij} \tilde{\rho}_{ij} \quad (20)$$

where  $\omega_{ik}^{RW} \equiv \omega_{ij}^{RW} - \omega_{kj}^{RW}$  and  $\omega_{kj}^{RW} \equiv \omega_{ij}^{RW} - \omega_{ik}^{RW}$

The Hamiltonian matrix elements will have the form

$$H_{ii} = \hbar \omega_i \text{ and } H_{ij} = -\frac{\mu_{ij} E^o}{2\hbar} (e^{i\omega t} + e^{-i\omega t}) \quad (21)$$

so substituting into equation (20), we have

$$\dot{\tilde{\rho}}_{ij} = i\omega_{ij}^{RW} \tilde{\rho}_{ij} - \frac{i}{\hbar} \hbar \omega_{ij} \tilde{\rho}_{ij} + \frac{i}{\hbar} \left[ \frac{\mu_{ik} E^o}{2\hbar} (e^{i\omega t} + e^{-i\omega t}) \tilde{\rho}_{kj} e^{i\omega_{kj}^{RW} t} - \tilde{\rho}_{ik} e^{i\omega_{ik}^{RW} t} \frac{\mu_{kj} E^o}{2\hbar} (e^{i\omega t} + e^{-i\omega t}) \right] - \Gamma_{ij} \tilde{\rho}_{ij} \quad (22)$$

Multiplying the exponentials together will give terms that oscillate slowly and terms that oscillate quickly.

If we throw away the latter in the rotating wave approximation and if we take  $\omega_{ij}^{RW} = \omega_{ij}$ , then

$$\dot{\tilde{\rho}}_{ij} = \frac{i}{\hbar} \left[ \frac{\mu_{ik} E^o}{2} \tilde{\rho}_{kj} e^{i(\pm\omega + \omega_{ik})t} - \frac{\mu_{kj} E^o}{2} \tilde{\rho}_{ik} e^{i(\pm\omega + \omega_{kj})t} \right] - \tilde{\rho}_{ij}^R \quad (23)$$

We can write this equation in matrix form as

$$\dot{\tilde{\rho}} = \frac{iE^o}{2\hbar} [\tilde{\mu}, \tilde{\rho}] - \tilde{\rho}^R \quad (24)$$

where  $\mu$  is an off-diagonal matrix with elements  $\mu_{ba} e^{i(\pm\omega+\omega_{ba})t}$ . For a two state system,

$$\mu = \begin{pmatrix} 0 & \mu_{ab} e^{i(\pm\omega+\omega_{ab})t} \\ \mu_{ba} e^{i(\pm\omega+\omega_{ba})t} & 0 \end{pmatrix} \text{ and } \tilde{\rho}^R = \begin{pmatrix} \Gamma_{aa}\rho_{aa} & \Gamma_{ab}\rho_{ab} \\ \Gamma_{ba}\rho_{ba} & \Gamma_{bb}\rho_{bb} \end{pmatrix}. \quad (25)$$

If we still employ the rotating wave approximation but instead assume that  $\omega_{ij}^{RW} \neq \omega_{ij}$ , then (22) becomes

$$\dot{\tilde{\rho}}_{ij} = i(\omega_{ij}^{RW} - \omega_{ij} + i\Gamma_{ij})\tilde{\rho}_{ij} + \frac{i}{\hbar} \left[ \frac{\mu_{ik}E^o}{2} \tilde{\rho}_{kj} e^{i(\pm\omega+\omega_{ik})t} - \frac{\mu_{kj}E^o}{2} \tilde{\rho}_{ik} e^{i(\pm\omega+\omega_{kj})t} \right]. \quad (26)$$

We can write this equation in matrix form as

$$\dot{\tilde{\rho}} = \frac{iE^o}{2\hbar} [\tilde{\mu}, \tilde{\rho}] - \tilde{\rho}^T \quad (27)$$

where for a two state system,

$$\tilde{\rho}^T = \begin{pmatrix} (i(\omega_{aa}^{RW} - \omega_{aa}) + \Gamma_{aa})\rho_{aa} & (i(\omega_{ab}^{RW} - \omega_{ab}) + \Gamma_{ab})\rho_{ab} \\ (i(\omega_{ba}^{RW} - \omega_{ba}) + \Gamma_{ba})\rho_{ba} & (i(\omega_{bb}^{RW} - \omega_{bb}) + \Gamma_{bb})\rho_{bb} \end{pmatrix}. \quad (28)$$

## APPENDIX E- ELECTROMAGNETIC FIELDS OF THE VACUUM

In addition to real electromagnetic fields, we must also consider the zero-point fluctuations of the vacuum. These fluctuations are predicted by the quantum mechanical quantization of light. They arise from the uncertainty principle which states that you can't know exactly the energy of a state, even if the state contains no photons. Zero point fluctuations define the limit on an excited state lifetime. The vacuum fluctuations have an intensity (photons/sec. cm<sup>2</sup>) that results in a radiative relaxation rate that is  $I\sigma_{SE}$  where  $\sigma_{SE}$  is the stimulated emission cross-section. If there are  $m$  photons in a mode, the energy is  $\hbar\omega\left(m + \frac{1}{2}\right)$  for the mode where

the  $\frac{1}{2}$  comes from the contribution of the vacuum fluctuations. To define the vacuum fluctuations and the quantum mechanical representation of the electromagnetic field, one defines a cavity, in our case a rectangular box. The modes are the standing waves that can be created in the box. The intensity of a light beam corresponding to single mode will be

$$I = \frac{\hbar\omega\left(m + \frac{1}{2}\right)}{A\Delta t} \quad (\text{watts/cm}^2) \quad (29)$$

If we release  $m$  photons traveling in the  $z$  direction over an area,  $A$ , of our cavity, then after  $\Delta t$  seconds the photons will occupy a volume of  $V = A\frac{c}{n}\Delta t$  in volume where  $n$  is the index of

refraction. So,  $A\Delta t = \frac{nV}{c}$ . We can now write (5) as

$$I = \frac{\hbar\omega\left(m + \frac{1}{2}\right)}{V\frac{n}{c}} = \frac{\hbar c\omega\left(m + \frac{1}{2}\right)}{nV}. \quad (30)$$

We will use this relationship between intensity and photons.

If there are  $\frac{n^3\omega^2d\omega}{2\pi^2c^3}$  modes per unit volume (see Appendix for derivation), the number of modes,  $dM$ , within the volume with two polarizations will be:

$$dM = \frac{n^3\omega^2Vd\omega}{\pi^2c^3}. \quad (31)$$

Here, we are assuming a single oriented molecule where the transition moment and the driving electric field are aligned so  $\vec{\mu} \cdot \vec{E}$  is a maximum. To get a better expression, one should perform an ensemble average over all the orientations in the sample so one gets both the isotropic and anisotropic response.

If  $m$  (the number of photons in mode) = 0, the intensity associated with all modes and polarizations, ( $dI_{zero\ pt}^o$ ), in the volume that can interact with a molecule over the frequency range,  $d\omega$ , will be

$$dI_{zero\ pt}^o = \frac{\hbar c\omega}{2Vn} \frac{n^3\omega^2Vd\omega}{\pi^2c^3} = \frac{n^2\hbar\omega^3d\omega}{2\pi^2c^2}.$$

## APPENDIX F- OPTICAL NUTATION, DYNAMIC STARK EFFECTS, and RABI CYCLES

The equations we derived earlier to the amplitudes and a wave function (e.g.  $c_a \psi_a + c_b \psi_b$ ) contain the key information that describes some of the most fundamental insights to spectroscopy so it is important to fully understand them. The amplitudes have real and imaginary components in quantum mechanics and the rate of change of the amplitudes depends on the amplitudes. For example, equation 15 states that the rate of change of the real part of state b is proportional to the imaginary part of its amplitude with its frequency as the proportionality constant and it also depends on the imaginary part of state a with a frequency as the proportionality constants that depend on the electric field of the light. The former is the Bohr frequency and it is very fast. The latter is the Rabi frequency and it is quite slow and dependent on the light intensity.

At this point, one can define two paths for spectroscopy- coherent spectroscopy that depends on having lasers and incoherent spectroscopy which is by far the most common. Let's first look at coherent spectroscopy. The key to understanding coherent spectroscopy is understanding optical nutation. Equations (13) and (14) (or (15) and (16)) are coupled. We will solve them for the case where a resonant electromagnetic field causes transitions between states  $a$  and  $b$ . Let's assume first we can separate time scales into fast and slow. The slow time scale corresponds to the time dependence of the excitation pulse amplitude and the second time scale corresponds to the frequency of the amplitude. The amplitude can be oscillating either at the frequency of the state or the frequency of the excitation pulse, depending on whether the superposition state is oscillating after the excitation pulse or whether the excitation pulse itself is driving the transition during the time that the excitation pulse is on. We will assume the former. Then,

$$c_a = \tilde{c}_a(t) e^{-i\omega_{ag}t} \quad (32)$$

where  $\omega_{ag}$  is the **Bohr** frequency.  $\tilde{c}_a(t)$  is the amplitude for state  $a$  that can still vary slowly in time in comparison with the Bohr frequency, perhaps as the state's population changes from the laser excitation or as the population decays after it is excited. We can now substitute (32) into equations (13) and (14) (we must remember to use the chain rule to differentiate (32)).

$$-i\omega_{ag} \tilde{c}_a(t) e^{-i\omega_{ag}t} + \dot{\tilde{c}}_a(t) e^{-i\omega_{ag}t} = -i\omega_{ag} \tilde{c}_a(t) e^{-i\omega_{ag}t} + i\bar{\mu}_{ab} \cdot \vec{\sigma} \frac{E^o}{2\hbar} (e^{i\omega t} + e^{-i\omega t}) \tilde{c}_b(t) e^{-i\omega_{bg}t} \quad (33)$$

$$-i\omega_{bg} \tilde{c}_b(t) e^{-i\omega_{bg}t} + \dot{\tilde{c}}_b(t) e^{-i\omega_{bg}t} = -i\omega_{bg} \tilde{c}_b(t) e^{-i\omega_{bg}t} + i\bar{\mu}_{ab} \cdot \vec{\sigma} \frac{E^o}{2\hbar} (e^{i\omega t} + e^{-i\omega t}) \tilde{c}_a(t) e^{-i\omega_{ag}t} \quad (34)$$

We will now use the **rotating wave approximation (RWA)** which states that terms that oscillate quickly in time will average to zero over times that are long compared to the oscillation period.<sup>†</sup> We must be careful in picking the neglected term since some of the frequencies may be negative ( $\omega_{ba} \equiv \omega_{bg} - \omega_{ag} = -\omega_{ab}$ ). For example, gathering all the exponentials in eqn. (34) gives  $(e^{i\omega t} + e^{-i\omega t}) e^{-i\omega_{ab}t}$  where  $\omega_{ab} = \omega_{ag} - \omega_{bg}$  so if  $\omega_{ab} < 0$ , we will keep the

---

<sup>†</sup> The RWA is appropriate for almost all cases except when the excitation pulse widths are short compared to the period. The equations should then be solved numerically.

$e^{-i\omega_a t} e^{-i\omega_{ab} t} = e^{i(\omega_{ba}-\omega)t}$  term. We can therefore eliminate one of the electromagnetic field terms in each equation as well as the two identical terms. We can also combine the exponential factors.

$$\dot{\tilde{c}}_a(t) = \frac{i\mu_{ab}E^o}{2\hbar}\tilde{c}_b(t)e^{-i(\omega_{ba}-\omega)t} \quad (35)$$

$$\dot{\tilde{c}}_b(t) = \frac{i\mu_{ba}E^o}{2\hbar}\tilde{c}_a(t)e^{i(\omega_{ba}-\omega)t} \quad (36)$$

These two equations are coupled. We will solve them on resonance when  $\omega = \omega_{ba}$ . The easiest way to solve them is to differentiate one and substitute it into the other.

$$\ddot{\tilde{c}}_a(t) = i\vec{\mu}_{ab} \cdot \vec{\sigma} \frac{E^o}{2\hbar} \dot{\tilde{c}}_b(t) = \left( i\vec{\mu}_{ab} \cdot \vec{\sigma} \frac{E^o}{2\hbar} \right)^2 \tilde{c}_a(t) e^{i(\omega_{ba}-\omega)t} = -\frac{\Omega_{ba}^2}{4} \tilde{c}_a(t) \quad (37)$$

where we have defined the **Rabi frequency** as  $\Omega \equiv \frac{\vec{\mu} \cdot \vec{\sigma} E^o}{\hbar}$ . We can solve (37) assuming we start in state  $a$  at  $t=0$ .

$$\tilde{c}_a(t) = \cos \frac{\Omega t}{2} \text{ and then } \tilde{c}_b(t) = \sin \frac{\Omega t}{2}. \quad (38)$$

We can now define the temporal evolution of our final wave function.

$$\psi = \left[ \cos \left( \frac{\Omega t}{2} \right) \right] \psi_a(x) e^{i\omega_{ag}t} + \left[ \sin \left( \frac{\Omega t}{2} \right) \right] \psi_b(x) e^{i\omega_{bg}t} \quad (39)$$

Equation (39) has two time scales: a slow time scale where the amplitude is changing at the Rabi frequency and a rapid time scale where the phase is changing at the Bohr frequency. Equation (39) is fundamental because it defines how an electromagnetic field causes the wave

function to evolve in time from state  $a$  to a higher state  $b$ . After a time of  $\frac{\pi}{\Omega}$ , half the Rabi period, the system has evolved to state  $b$ . During this time, energy has been extracted from the electromagnetic field and placed in the quantum system. Absorption is therefore occurring. During the next half of the Rabi period, the system has returned to state  $a$ . Emission is occurring during this time as the quantum system transfers its energy back to the field. No net change has occurred. Absorption and emission are equal. This Rabi cycling occurs forever, as long as the quantum system is not disturbed in its interaction with the light field.

Experimentally, coherent light passing through a sample would progressively weaken because of absorption and then brighten because of stimulated emission. The cycle would continue forever at the Rabi frequency. Making the light brighter would increase the frequency. This intensity modulation is **optical nutation**. Very strong lasers cause fast optical nutation and very weak lasers cause very slow optical nutation.

An animation of the optical nutation of a H atom undergoing a transition from its 2p state to its 1s state appears in the class website. Note the two time scales- the fast oscillations that occur at the Bohr frequency in synchronization with the light and the slow change in the relative

amounts of 1s and 2p character as the system undergoes a transition from the initial 2p state to the 1s state at the Rabi frequency. Note also the strong oscillations of the charge density. It is this oscillation that creates light. Any time that a charge distribution oscillates, light is generated because a distant charge will experience the changing Coulombic force as it interacts with the changing charge distribution. Note also that the light emission is strongest at the mid-point of the oscillation where there is an equal admixture of 1s and 2p character.

When the Rabi frequency exceeds the normal relaxation rate of the coupled states, the state perturbation becomes strong and the light field and quantum system become tightly coupled. The transition line-width broadens in this limit because the lifetime of the states is shortened by the rapid transitions. In addition, the transition will split. This effect is called the **dynamic Stark effect**.

## APPENDIX G- DERIVATION OF INTENSITY-PHOTON RELATIONSHIP

Consider a rectangular volume and we release m photons traveling in the z direction over an area, A. After  $\Delta t$  seconds, the volume will be  $V = A \frac{c}{n} \Delta t$  in volume. The intensity will be

$$I = \frac{\hbar\omega(m + \frac{1}{2})}{A\Delta t} = \frac{\hbar\omega(m + \frac{1}{2})}{V \frac{n}{c}} = \frac{\hbar c \omega(m + \frac{1}{2})}{n V}.$$

## APPENDIX H- DERIVATION OF MODES/VOLUME

In a cubic volume with sides, L, the modes are characterized by the requirement that  $\frac{2L}{\lambda} = n$

where  $n$  is an integer for each side of the box. Since there are three dimensions, we can define three integers to characterize a mode. We will only need the magnitude that results from having all three integers so we will define an effective  $n$  as  $n = \sqrt{n_x^2 + n_y^2 + n_z^2}$ . The total number of modes having effective values of  $n$  less than  $n$  is the volume of a sphere in a space defined by the

three integers-  $\frac{4\pi n^3}{3}$ . We are only concerned about the volume contained in the first quadrant of

this sphere since we require the  $n_x$ ,  $n_y$ , and  $n_z$  values to be positive so  $N = \frac{4\pi n^3}{3} \frac{1}{8} = \frac{\pi n^3}{6}$ . The

number of modes in a thin shell between  $n$  and  $n + \Delta n$  is the derivative-  $\frac{dN}{dn} = \frac{\pi n^2}{2}$  so

$dN = \frac{\pi n^2}{2} dn$ . We can relate  $n$  to the wavelength so  $dN = \frac{\pi}{2} \frac{4L^2}{\lambda^2} \frac{2L}{\lambda^2} d\lambda = \frac{4\pi L^3}{\lambda^4} d\lambda$ . Since

$\frac{c}{n} = v\lambda = \frac{\omega\lambda}{2\pi}$  or  $\lambda = \frac{2\pi c}{n\omega}$ , we can rewriting this expression in terms of angular frequency,

$$dN = \frac{4\pi L^3}{16\pi^4 c^4} \frac{2\pi c d\omega}{n\omega} = \frac{n^3 \omega^2 V d\omega}{2\pi^2 c^3 n^4 \omega^4}$$

We have assumed there is only one mode for each set of  $n$  values but in fact there are two polarizations so we need to multiply our expression by 2.

$$dN = \frac{n^3 \omega^2 V d\omega}{\pi^2 c^3}$$

## APPENDIX I- DERIVATION OF RADIATIVE TRANSITION RATE

We saw before that  $c_b = \frac{\mu E^o c_g}{2\hbar} \frac{e^{ikz} (e^{-(i\omega_b + \Gamma_b)t} - e^{(-i\omega)t})}{(-(i\omega_b + \Gamma_b) + i\omega)}$  (here we kept the term that was resonant and ignored the nonresonant term). The first term describes the oscillation of the excited state and the second term describes the oscillation created by the excitation field. If we turn off the excitation field after the state is excited, we can keep just the first term. We can now find the decay of the b state population.

$$c_b c_b^* = \frac{\mu^2 E^{o2} c_g c_g^*}{4\hbar^2} \frac{e^{ikz} e^{-ikz} (e^{-(i\omega_b + \Gamma_b)t} - e^{(-i\omega)t})(e^{(i\omega_b + \Gamma_b)t} - e^{i\omega t})}{(-(i\omega_b - i\omega) + \Gamma_b)((i\omega_b - i\omega) + \Gamma_b)}$$

This becomes

$$= \frac{\mu^2 E^{o2} c_g c_g^* (2 - 2e^{-\Gamma_b t} \cos(\omega_b - \omega)t)}{4\hbar^2 ((\omega_b - \omega)^2 + \Gamma_b^2)} \approx \frac{\mu^2 E^{o2} c_g c_g^* (2 - 2(1 - \Gamma_b t))}{4\hbar^2 ((\omega_b - \omega)^2 + \Gamma_b^2)} \approx \frac{\mu^2 E^{o2} c_g c_g^* (\Gamma_b t)}{2\hbar^2 ((\omega_b - \omega)^2 + \Gamma_b^2)} \text{ for}$$

small values of  $t$ . The time derivative of the population is therefore

$$\frac{dc_b c_b^*}{dt} \approx \frac{\mu^2 E^{o2} c_g c_g^* \Gamma_b}{2\hbar^2 ((\omega_b - \omega)^2 + \Gamma_b^2)}$$

We now need to change  $E^{o2}$  to an intensity.

$$I = \frac{c}{8\pi} E^{o2} \quad \text{so} \quad E^{o2} = \frac{8\pi}{cn_{index}} I \quad (\text{or } E^{o2} = \frac{2}{cn_{index} \epsilon_0} I \text{ in mks units})$$

Substituting,

$$\frac{dc_b c_b^*}{dt} \approx \frac{\mu^2 c_g c_g^* \Gamma_b}{2\hbar^2 ((\omega_b - \omega)^2 + \Gamma_b^2)} \frac{8\pi}{c} I \approx \frac{4\pi \mu^2 c_g c_g^* \Gamma_b}{\hbar^2 c ((\omega_b - \omega)^2 + \Gamma_b^2)} I$$

If there are  $m$  photons in a mode, the energy is  $\hbar\omega(m + 1/2)$  for the mode. If the photons are all contained within a volume,  $V$ , the intensity will be (see notes for derivation):

$$I = \frac{\hbar c \omega (m + 1/2)}{n V} \quad (\text{watts/cm}^2)$$

where  $n$  is the index of refraction.

If there are  $\frac{n^3 \omega^2 d\omega}{2\pi^2 c^3}$  modes per unit volume (see notes for derivation), the number of modes

within the volume with two polarizations will be:

$$\frac{n^3 \omega^2 V d\omega}{\pi^2 c^3}.$$

Here, we are assuming a single oriented molecule where the transition moment and the driving electric field are aligned so  $\vec{\mu} \cdot \vec{E}$  is a maximum. To get a better expression, one should perform an ensemble average over all the orientations in the sample so one gets both the isotropic and anisotropic response.

If  $m$  (the number of photons in mode) = 0, the intensity associated with all modes and polarizations in the volume will be

$$I = \frac{\hbar c \omega n_{cb}^3 \omega^2 V d\omega}{2Vn \pi^2 c^3} = \frac{n_{cb}^2 \hbar \omega^3 d\omega}{2\pi^2 c^2}.$$

So,

$$\frac{dc_b c_b^*}{dt} \approx \frac{4\pi\mu^2 c_g c_g^* \Gamma_b}{\hbar^2 c \left( (\omega_b - \omega)^2 + \Gamma_b^2 \right)} \frac{n_{cb}^2 \hbar \omega^3 d\omega}{2\pi^2 c^2} \approx \frac{2\mu^2 n_{cb}^2 c_g c_g^* \Gamma_b \omega^3 d\omega}{\pi c^3 \hbar \left( (\omega_b - \omega)^2 + \Gamma_b^2 \right)} \approx \frac{4\mu^2 n_{cb}^2 c_g c_g^* \Gamma_b \omega^3 d\omega}{c^3 h \left( (\omega_b - \omega)^2 + \Gamma_b^2 \right)}$$

We now need to integrate over all frequencies where we assume that  $\omega$  does not change appreciably over the line profile,

$$= \int_0^\infty \frac{4\mu^2 \Gamma_b n_{cb}^2 \omega^3 d\omega}{c^3 h \left( (\omega_b - \omega)^2 + \Gamma_b^2 \right)} = \frac{4\pi\mu^2 \Gamma_b n_{cb}^2 \omega^3}{2c^3 h \Gamma_b} = \frac{2\pi\mu^2 n_{cb}^2 \omega^3}{c^3 h} \quad (\text{or } \frac{8\pi^2 \mu^2 n_{cb}^2 \omega^3}{c^3 h \epsilon_o} \text{ in mks units})$$

## APPENDIX J- INTENSITY DEPENDENT REFRACTIVE INDEX

The index of refraction becomes intensity dependent at high intensities because of processes like  $gg \rightarrow ag \rightarrow gg \rightarrow ag$ . The first  $ag$  coherence is responsible for the normal index of refraction,  $n_o$  while the second  $ag$  is intensity dependent but also contributes to the total polarization. In steady state, the two  $ag$  coherences are

$$\rho_{ag} = \frac{\mu_{ag} E^o}{2\hbar\Delta_{ag}} \text{ and } \rho_{ag} = \frac{(\mu_{ag} E^o)^3}{8\hbar^3 \Delta_{ag} \Delta_{gg} \Delta_{ag}}.$$

The total polarization will therefore be

$$P = \frac{NF \mu_{ag}^2 E^o \rho_{gg} e^{i(kz-\omega t)}}{2\hbar\Delta_{ag}} \left( 1 + \frac{(\mu_{ag} E^o)^2}{4\hbar^2 \Delta_{gg} \Delta_{ag}} \right) + c.c.$$

The correct approach would be to find the electric field resulting from this polarization but that strategy leads to a nonlinear differential equation that cannot be solved in closed form. So instead, we neglect the higher order dependence on the electric field and treat it as an intensity dependent correction to the first order susceptibility. With this approach,

$$P = \frac{NF \mu_{ag}^2 E^o \rho_{gg} e^{i(kz-\omega t)}}{2\hbar\Delta_{ag}} \left( 1 + \frac{8\pi\mu_{ag}^2 I}{4\hbar^2 c n_o \Delta_{gg} \Delta_{ag}} \right) + c.c.$$

and

$$\chi^{(1)} = \left( \frac{NF \mu_{ag}^2 \rho_{gg}}{\hbar\Delta_{ag}} + \frac{2\pi NF \mu_{ag}^4 \rho_{gg}}{cn_o \hbar^3 \Delta_{ag} \Delta_{gg} \Delta_{ag}} I \right)$$

The index of refraction is then

$$n = \text{Re} \left( \sqrt{1 + 4\pi\chi^{(1)}} \right) = \text{Re} \left( \sqrt{1 + 4\pi \left( \frac{NF \mu_{ag}^2 \rho_{gg}}{\hbar\Delta_{ag}} + \frac{2\pi NF \mu_{ag}^4 \rho_{gg}}{cn_o \hbar^3 \Delta_{ag} \Delta_{gg} \Delta_{ag}} I \right)} \right)$$

Let  $n_o^2 = 1 + \frac{4\pi NF \mu_{ag}^2 \rho_{gg}}{\hbar\Delta_{ag}}$ . Then,

$$\begin{aligned} n &= \text{Re} \left( \sqrt{n_o^2 + \frac{2\pi F_2 \mu_{ag}^2 \rho_{gg}}{cn_o \hbar^2 \Delta_{gg} \Delta_{ag}} I} \right) = \text{Re} \left( n_o \sqrt{1 + \frac{8\pi^2 NF \mu_{ag}^4 \rho_{gg}}{cn_o^3 \hbar^3 \Delta_{ag} \Delta_{gg} \Delta_{ag}} I} \right) \\ &\approx \text{Re} \left( n_o + \frac{4\pi^2 NF \mu_{ag}^4 \rho_{gg}}{cn_o^2 \hbar^3 \Delta_{ag} \Delta_{gg} \Delta_{ag}} I \right). \end{aligned}$$

Finally,  $n = n_o + n_2 I$  where

$$n_2 = \text{Re} \left( \frac{4\pi^2 NF \mu_{ag}^4 \rho_{gg}}{cn_o^2 \hbar^3 \Delta_{ag} \Delta_{gg} \Delta_{ag}} I \right)$$

## APPENDIX K- FORCED SIMPLE HARMONIC OSCILLATOR

The simple harmonic oscillator problem is central to much of physics. It starts with:

$$m\ddot{x} + b\dot{x} + kx = Fe^{-i\omega t+i\theta}$$

$$\ddot{x} + \Gamma\dot{x} + \omega_o^2 x = \frac{F}{m} e^{-i\omega t+i\theta} \quad \text{where } \Gamma = \frac{b}{m} \text{ and } \omega_o^2 = \frac{k}{m}$$

Taking the Laplace Transforms

$$s^2 x - sx_o - \dot{x}_o + s\Gamma x - x_o + \omega_o^2 x = \frac{F}{m} e^{i\theta} \frac{1}{s + i\omega}$$

where the subscript o designates initial conditions for position and velocity. Solving for x,

$$x = \frac{F}{m} e^{i\theta} \frac{1}{(s + i\omega)(s - a)(s - b)} + \frac{sx_o + \dot{x}_o + x_o}{(s - a)(s - b)}$$

where

$$(s - a)(s - b) = s^2 x + s\Gamma x + \omega_o^2 x \text{ and}$$

$$a = \frac{-\Gamma + \sqrt{\Gamma^2 - 4\omega_o^2}}{2} \approx \frac{-\Gamma + 2\omega_o \sqrt{\frac{\Gamma^2}{4\omega_o^2} - 1}}{2} \approx \frac{-\Gamma + 2i\omega_o}{2}$$

$$b = \frac{-\Gamma - \sqrt{\Gamma^2 - 4\omega_o^2}}{2} \approx \frac{-\Gamma - 2\omega_o \sqrt{\frac{\Gamma^2}{4\omega_o^2} - 1}}{2} \approx \frac{-\Gamma - 2i\omega_o}{2}.$$

Taking the inverse Laplace Transforms,

$$x = \frac{F}{m} e^{i\theta} \frac{(a - b)e^{-i\omega t} + (b + i\omega)e^{at} + (-i\omega - a)e^{bt}}{(a - b)(b + i\omega)(-i\omega - b)} + \frac{ae^{at} - be^{bt}}{a - b} x_o + \frac{e^{at} - e^{bt}}{(a - b)} (\dot{x}_o + x_o)$$

Simplifying this expression:

$$x \approx \frac{F}{m} e^{i\theta} \frac{2i\omega_o e^{-i\omega t} + \left(-\frac{\Gamma}{2} - i\omega_o + i\omega\right) e^{-\frac{\Gamma}{2}t} e^{i\omega_o t} + \left(-i\omega + \frac{\Gamma}{2} - i\omega_o\right) e^{-\frac{\Gamma}{2}t} e^{-i\omega_o t}}{(2i\omega_o) \left(-\frac{\Gamma}{2} - i\omega_o + i\omega\right) \left(-i\omega + \frac{\Gamma}{2} + i\omega_o\right)}$$

$$+ \frac{i\omega_o e^{i\omega_o t} + i\omega_o e^{-i\omega_o t}}{2i\omega_o} e^{-\frac{\Gamma}{2}t} x_o + \frac{e^{i\omega_o t} - e^{-i\omega_o t}}{2i\omega_o} e^{-\frac{\Gamma}{2}t} (\dot{x}_o + x_o)$$

and further

$$x \approx -\frac{F}{m} e^{i\theta} \frac{2i\omega_o e^{-i\omega t} - \left(\frac{\Gamma}{2} + i(\omega_o - \omega)\right) e^{-\frac{\Gamma}{2}t} e^{i\omega_o t} + \left(\frac{\Gamma}{2} + i(\omega_o - \omega)\right) e^{-\frac{\Gamma}{2}t} e^{-i\omega_o t}}{(2i\omega_o) \left(\frac{\Gamma}{2} + i(\omega_o - \omega)\right)^2}$$

$$+ \frac{i\omega_o e^{i\omega_o t} + i\omega_o e^{-i\omega_o t}}{2i\omega_o} e^{-\frac{\Gamma}{2}t} x_o + \frac{e^{i\omega_o t} - e^{-i\omega_o t}}{2i\omega_o} e^{-\frac{\Gamma}{2}t} (\dot{x}_o + x_o)$$

Or finally,

$$x \approx -\frac{F}{m} e^{i\theta} \frac{e^{-i\omega t}}{\left(\frac{\Gamma}{2} + i(\omega_o - \omega)\right)^2} - e^{-\frac{\Gamma}{2}t} \left( \frac{(e^{i\omega_o t} - e^{-i\omega_o t})}{(2i\omega_o) \left(\frac{\Gamma}{2} + i(\omega_o - \omega)\right)} - \frac{(e^{i\omega_o t} + e^{-i\omega_o t})}{2} x_o - \frac{e^{i\omega_o t} - e^{-i\omega_o t}}{2i\omega_o} (\dot{x}_o + x_o) \right)$$

## APPENDIX L- SOME USEFUL CONVERSIONS AND UNITS:

- The Electrostatic System of units (esu) chooses Coulomb's Law as its fundamental relationship so
$$F = \frac{Q^2}{r^2} \text{ and } E \equiv \frac{F}{Q} = \frac{Q}{r^2}. \text{ Then } \vec{F} = \frac{1}{c} Q \vec{v} \times \vec{B}. \text{ A statcoulomb of charge then has units}$$
of  $\text{dyne}^{1/2} \text{cm}$ . The electric field is statvolts/cm.
- The MKS system chooses the Lorentz force as its fundamental relationship so
$$\vec{F} = Q \vec{v} \times \vec{B}. \text{ Then, } F = \frac{Q^2}{4\pi\epsilon_0 r^2} \text{ and } E \equiv \frac{F}{Q} = \frac{Q}{4\pi\epsilon_0 r^2}. \text{ A Coulomb of charge then has}$$
units of  $\text{newton}^{1/2} \text{meters}$ . The electric field is volts/m.
- The permittivity of free space is  $\epsilon_0 = 8.85 \times 10^{-12}$  Farad/meter.
- $e = 1.602 \times 10^{-19}$  coulombs in mks units or  $4.803 \times 10^{-10}$  statcoulombs in esu units
- The conversion factor between statcoulombs and coulombs is therefore,
- $$\frac{Q_{\text{esu}}^2}{Q_{\text{mks}}^2} = \frac{1}{4\pi\epsilon_0} \frac{F_{\text{dynes}} r_{\text{cm}}^2}{F_{\text{newtons}} r_{\text{meter}}^2} = 9 \times 10^{18}.$$
- In general,  $\chi_{\text{MKS}}^{(n)} = \frac{4\pi}{(10^{-4} c)^{n-1}} \chi_{\text{Gaussian}}^{(n)}$  where  $c = 3 \times 10^8$  m/s.
- The conversion factor between electric field in esu and mks units is therefore,
$$\frac{E_{\text{mks}}}{E_{\text{esu}}} = \frac{\frac{1}{4\pi\epsilon_0} Q_{\text{mks}} r_{\text{esu}}^2}{Q_{\text{esu}} r_{\text{mks}}^2} = 3 \times 10^4.$$
- The intensity is related to the electric field.
$$I_{\text{esu}} = \frac{C_{\text{esu}}}{4\pi} E_{\text{esu}}^2 = 2.390 \times 10^9 E_{\text{esu}}^2 \text{ and } I_{\text{mks}} = \epsilon_0 C_{\text{mks}} E_{\text{mks}}^2 = \frac{1}{\mu_0 C_{\text{mks}}} E_{\text{mks}}^2 = 2.655 \times 10^{-3} E_{\text{mks}}^2$$

$$E_{\text{esu}} = \sqrt{4.189 \times 10^{-10} I_{\text{esu}}} \text{ and } E_{\text{mks}} = \sqrt{377 I_{\text{mks}}}$$
- A dipole moment is defined as the product of the difference in charges, q, and the separation between the two charges.  
 $\vec{\mu} \equiv q\vec{r}$   
The units are coulomb-meter for mks units and statcoulomb-cm for esu units so the conversion factor between them is  $\frac{\mu_{\text{esu}}}{\mu_{\text{mks}}} = \frac{Q_{\text{esu}} r_{\text{esu}}}{Q_{\text{mks}} r_{\text{mks}}} = 3 \times 10^9 \times 10^2 = 3 \times 10^{11}.$
- 1 Debye =  $10^{-18}$  esu or  $3.336 \times 10^{-30}$  C m =  $0.0208 e \text{ A}^\circ$
- 1 amu = 2.541 Debye (J. Chem. Educ. **65**, 1981 (1988))
- In Gaussian units, E and P have the same units, statvolt/cm or statcoulomb/cm<sup>2</sup> or  $\sqrt{\frac{\text{erg}}{\text{cm}^3}}$  or dyne/statcoulomb. In  $P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3$ ,  $\chi^{(1)}$  is dimensionless,  $\chi^{(2)}$  is

measured in cm/statvolt or  $\sqrt{\frac{cm^3}{erg}}$ , and  $\chi^{(3)}$  is measured in  $cm^2/statvolt^2$  or  $\frac{cm^3}{erg}$ . It is common in the literature to use only the designation *esu* to indicate the units without explicitly stating the true units. It is unfortunately left to the reader to figure out the units for themselves.

- In MKS units, E has units of volts/meter or newtons/coulomb and P has units of coulombs/meter<sup>2</sup>. If the convention is to define  $P \equiv \epsilon_0 (\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3)$ ,  $\chi^{(1)}$  is again dimensionless,  $\epsilon_0\chi^{(2)}$  is measured in coulombs/volt<sup>2</sup> (or  $\chi^{(2)}$  is measured in meter/volt) and  $\epsilon_0\chi^{(3)}$  is measured in  $\frac{coulomb * m}{volt^3}$  (or  $\chi^{(3)}$  is measured in meter<sup>2</sup>/volt<sup>2</sup>). If the convention is to define  $P \equiv \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3$ , then the units for  $\chi$  are those in parentheses.
- linear Rabi frequency in  $cm^{-1} = 4.62 \times 10^{-4} \mu \sqrt{\frac{I}{n}}$  where  $\mu$  is measured in Debye and I is measured in watts/cm<sup>2</sup>. Here,  $\frac{10^{-18}}{2\pi\hbar c} \sqrt{\frac{8\pi 10^7}{c}} = 4.62 \times 10^{-4}$ .
- 1 a.u. (atomic units) =  $8.641 \times 10^{-33} \text{ cm}^5/\text{esu}$  in esu units and  $3.206 \times 10^{-53} \text{ coulomb}^3 \text{ m}^3/\text{J}^2$  in SI units (see Chem. Rev. **94**, p. 239, footnote 49)

