Module 4 : Third order nonlinear optical processes

Lecture 23 : Two-photon absorption and Doppler free spectroscopy

Objectives

This lecture deals with

- Two-photon absorption process.
- And its application to Doppler free spectroscopy.

Two Photon absorption and Doppler free spectroscopy

If the photon energies $\hbar\omega_1$ and $\hbar\omega_2$ of light comprising of two monochromatic waves interacting with a quantum system involving two levels having energies E_i and E_f such that

$$E_f - E_i = \hbar(\omega_1 + \omega_2) \tag{23.1}$$

then the transition from E_i to E_f cannot occur by absorption of either the photon of energy $\hbar\omega_1$ or that of $\hbar\omega_2$ alone as both photon energies are nonresonant.

However, the system can be excited from its initial state E_i to higher energy state E_f by *simultaneous* absorption of both frequency photons subject to certain selection rules. In the process energy conservation is obeyed. This is called the two-photon absorption process.

To understand how this process is facilitated, we consider the following facts. A quantum system such as a molecule in a given state $|m\rangle$, even without getting any energy from outside, performs incessant transitions to its other states $|n\rangle$ (*n* represents any other eigen state of the system) with an inevitable return every time to the starting state. Such transitions $|m\rangle \rightarrow |n\rangle \rightarrow |m\rangle$ are called virtual transitions in contrast to the real transitions and are possible due to quantum uncertainty principle when the duration of the journey is such that $\frac{\hbar}{\Delta t} \gg \Delta E$, the energy difference between the states $|m\rangle$ and $|n\rangle$. During the interaction of quantum system undergoing virtual transitions with an electromagnetic field (resonant or nonresonant), the changes in the state of the quantum system and the mode of the electromagnetic field are liable to occur.

such that the initial photon energy is shared between the excitation of quantum system and resulting mode of the electromagnetic field to conserve energy

In two-photon process the initial and final eigen states of the system $|i\rangle$ and $|f\rangle$ are coupled upon excitation with photons of energies $\hbar\omega_1$ and $\hbar\omega_2$ via such virtual transitions to and from an intermediate state, $|j\rangle$ with the excitation of the system to $|f\rangle$ with simultaneous annihilation of both the photons.

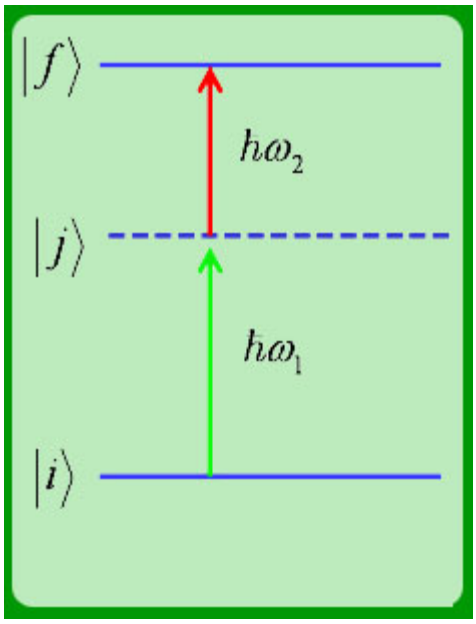

Figure 23.1 Two-photon absorption process

To put it other way, a quantum system in a given eigen state interacting with radiation field ceases to be in this eigen state of the unperturbed system.The new quantum state called a virtual state can be expressed as the superposition of the eigen states of the unperturbed system. The mixed state character to its original state is produced by the virtual transitions. This new state serves as the intermediate state $|j\rangle$.

In the light of the above, Two-photon absorption can be viewed as illustrated in figure 23.1. Quantum system under consideration makes a transition $|i\rangle \rightarrow |j\rangle$ to the virtual state by annihilating a quantum $\hbar\omega_1$ or $\hbar\omega_2$ from the incident field with a simultaneous transition $|j\rangle \rightarrow |f\rangle$ from the intermediate state to the final state exciting the system and annihilating another photon $\hbar\omega_2$ or $\hbar\omega_1$ so as to satisfy the energy conservation.

The transition $|i\rangle \rightarrow |j\rangle \rightarrow |f\rangle$ cannot be factored in time and is to be treated as one single quantum mechanical event.

If $\omega_1 = \omega_2 = \omega$ then both the photons can be absorbed from the same beam. We have already calculated the transition rate for the two-photon process in Lecture 8 on quantum calculations of nonlinear susceptibilities. It is given by

$$W_{if} \propto \frac{\gamma_{if} I_1 I_2}{\left(\left(\omega_{if} - \omega_1 - \omega_2\right)^2 + \gamma_{if}^2\right)} \left| \sum_j \left[\frac{\hat{\mu}_{ij} \cdot \hat{e}_1 \cdot \hat{\mu}_{jf} \cdot \hat{e}_2}{\left(\omega_{ji} - \omega_1\right)} + \frac{\hat{\mu}_{ij} \cdot \hat{e}_2 \cdot \hat{\mu}_{jf} \cdot \hat{e}_1}{\left(\omega_{ji} - \omega_2\right)} \right] \right|^2 \qquad (23.2)$$

where I_1 and I_2 are the intensities of the two light beams of frequency ω_1 and ω_2, respectively $\hat{\mu}_{ij}$ and $\hat{\mu}_{jf}$ are the transition dipole matrix elements from the initial to the intermediate and from the intermediate to the final state ω_{ji} is the frequency separation of the initial and final state and γ_{if} is the corresponding line width for the transition $|i\rangle \rightarrow |f\rangle$.

The first factor gives the line profile of a two-photon transition of a single molecule.

The second factor gives the transition probability for the two photon transition. This involves the product of the transition dipole moment matrix elements $\hat{\mu}_{ij}$ between initial state $|i\rangle$ and the

intermediate state $|j\rangle$ and the transition matrix element $\hat{\mu}_{jf}$ between intermediate state $|j\rangle$ and final state $|f\rangle$. It is obvious that for nonzero two-photon transition probability, the transitions involving the intermediate state be one-photon allowed. Selection rules require that states $|i\rangle$ and $|j\rangle$ as well as $|j\rangle$ and $|f\rangle$ have opposite parity.

It thus transpires that the two-photon transition will be allowed if the states $|i\rangle$ and $|f\rangle$ have same parity. Thus the two-photon absorption spectroscopy allows us to probe states which are not accessible by one-photon transition from the ground state. It thus complements the one-photon absorption spectroscopy to unravel more complete information on the electronic structure.

The summation over *j* includes all one-photon allowed states. The denominator implies that only nearly resonant states have dominant contributions. Thus to enhance the two-photon absorption probability, we must choose ω_1 and ω_2 such that the virtual state $|j\rangle$ is close to a real state.

Matrix cements $\hat{\mu}_{ij}\cdot\hat{e}_1$ and $\hat{\mu}_{jf}\cdot\hat{e}_2$ etc. depend on the polarization of the incident radiation. This enables the selection of the upper state by choosing the incident beams polarization states of the two beams appropriately.

If the molecule moves with velocity $\vec{v}$, the transition probability can be written as

$$W_{if} \propto \frac{\gamma_{if} I_1 I_2}{\left(\left(\omega_{if}-\omega_1-\omega_2-\vec{v}.(\vec{k}_1+\vec{k}_2)\right)^2+\gamma_{if}^2\right)}\left|\sum_j\left[\frac{\hat{\mu}_{ij}\cdot\hat{e}_1\cdot\hat{\mu}_{jf}\cdot\hat{e}_2}{\left(\omega_{ji}-\omega_1-\vec{v}.\vec{k}_1\right)}+\frac{\hat{\mu}_{ij}\cdot\hat{e}_2\cdot\hat{\mu}_{jf}\cdot\hat{e}_1}{\left(\omega_{ji}-\omega_2-\vec{v}.\vec{k}_2\right)}\right]\right|^2\sqrt{b^2-4ac} \quad (23.3)$$

(see lecture #23)

We can see that when $\vec{k}_1=-\vec{k}_2$, the Doppler broadening in two-photon line profile completely vanishes and pure homogeneously broadened Lorenzian line shape is obtained provided the laser line width is $<\gamma_{if}$.

Two-photon absorption process thus opens the gateway for performing high resolution Doppler free spectroscopy. Note that unlike Doppler free saturation spectroscopy all molecules contribute to the signal. Because of this, despite smaller two-photon absorption cross sections, the signals can be quite large. An experimental setup for two-photon spectroscopy with counter propagating beams is shown in figure 23.2 using one single tunable laser.

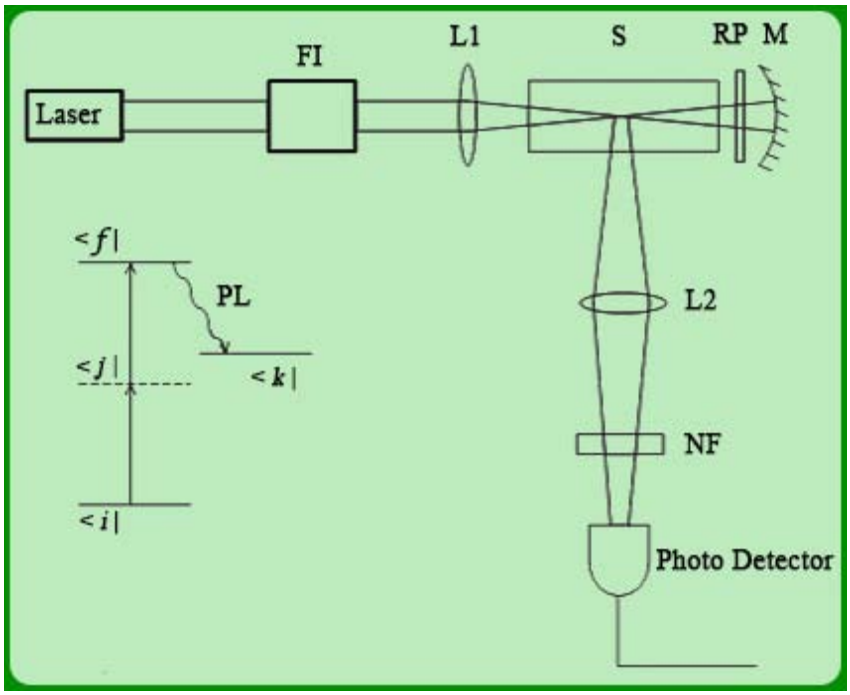

Figure 23.2 Two-photon Doppler free spectroscopy setup, FI-Faraday isolator, $L_{1,2}$ lenses, NF-notch filter

Here, Doppler free signal will be riding on the homogeneously broadened line profile. Because the two-photon absorption from each beam is also present there. Often the background can be completely removed by polarizing the two counter propagating beams appropriately so that one photon from each beam is annihilated to enable background free two-photon absorption. Alternatively, two counter propagating beams of different wavelengths can be employed.

Recap

In this lecture we have looked at the

- Two-photon absorption process – a qualitative picture.
- Two-photon transition rate.
- And its application to Doppler free spectroscopy.