

Explanation of Raman Scattering Spectrum on the Basis of Semi Classical Model and Klein Gordon Equation 2

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Abstract: Raman scattering process and its correspondings spectrum is widely used in science and industry. This process was explained by using classical physics and quantum harmonic model. Recently Schrödinger equation was used to explain this phenomenon. In this work semi classical model is used to provide mathematical equation framework of this phenomenon. A quantum model based on Klein-Gordon equation is also established to explain Raman scattering process. The advantage of this model is that it can explain and solve some problems in this process like Stokes and anti Stokes asymmetry.

Keywords: Raman Scattering, Klein Gordon, photons, electrons.

I. Introduction

The spectra of atoms and molecules play an important role in civilization. They are widely used in mineral exploration and remote sensing^(1,2). They are utilized in soil tests^(3,4) and analysis for building constructions⁽⁵⁾ and for agriculture. Atoms and molecules display different spectral types and patterns. Among these Raman spectroscopy plays a central role.

Raman spectroscopy is one of the most popular phenomena used to find the concentration of trace elements⁽⁶⁾. In this phenomenon a photon interacts with atoms to produce spectrum of three peaks. One is related to the original photon frequency, while the two others are related to the interaction of photons with atoms or molecules. The frequency shifts are related to rotational and vibration energies of molecules.

Simple electromagnetic and quantum interpretations are made to describe Raman spectra⁽⁷⁾. Attempts are also made to describe this phenomenon by using Schrödinger equation⁽⁸⁾. As far as special relativity (SR) can describe atomic world more accurately⁽⁹⁾, thus one needs a theoretical (SR) framework that can describe Raman spectra. This is done in sections 3 and 4 by using time independent and time dependent Klein –Gordon equations. However section 2 is devoted to describe photons molecules interactions by using the classical second Newton law for a circular motion⁽¹⁰⁾ by treating the photon as a particle and by using (SR) and plank expressions for energy.

II. The Interaction of the Photons with the Electrons

One can study the interaction of the electrons with the external force with the aid of the centrifugal force and the nucleus attraction. When the force field on the electrons is only the attraction force of the nucleus (F_e), then the centrifugal force of the oscillating electrons with the angular frequency of ω_0 will be equal to the attraction force of the nucleus. This means that

$$\frac{m_0 v_0^2}{r} - \frac{m_0 \omega_0^2 r^2}{r} = m_0 \omega_0^2 r = F_e \dots \dots \dots (1)$$

But when the outer electrons interact with external force of the photons (F_p), then the centrifugal force of the electrons will be equal to F_e plus F_p or

$$m_0 \omega^2 r = m_0 \omega_0^2 r + F_p \dots \dots \dots (2)$$

One can express the force by means of the energy in the form

$$F = - \frac{\partial E}{\partial r} \dots \dots \dots (3)$$

This is in conformity with the ordinary relation

$$F = - \frac{\partial V}{\partial x}$$

One can utilize equations (2) and (3) to show that the photon can change the electron frequency from ω_0 to ω if it is in resonance with the electron original frequency ω_0 . Using the relation of Bohr radius (r) with the wavelength λ , one gets

$$\lambda = 2\pi r C = \lambda f = 2\pi f \left(\frac{\lambda}{2\pi}\right) = \omega_0 r \dots\dots\dots(4)$$

Thus the photon energy is given by

$$E_p = m_p C^2 = m_p \omega_0^2 r^2 \dots\dots\dots(5)$$

And from (3)

$$F_p = -\frac{\partial E_p}{\partial r} = -\frac{\partial m_p \omega_0^2 r^2}{\partial r} = -2m_p \omega_0^2 r \dots\dots\dots(6)$$

Inserting (6) in (2) by assuming the photon force to oppose the electron motion

$$m_0 \omega^2 r = m_0 \omega_0^2 r + 2m_p \omega_0^2 r$$

$$m_0 (\omega^2 - \omega_0^2) r = 2m_p \omega_0^2 r$$

$$m_0 (\omega + \omega_0)(\omega - \omega_0) = 2m_p \omega_0^2 \dots\dots\dots(7)$$

Assuming ω to be very near to ω_0 as in Lang vein model:

$$\omega \approx \omega_0 \omega + \omega_0 \approx 2\omega_0 \omega - \omega_0 \approx \Delta\omega \dots\dots\dots(8)$$

Substituting (8) in (7) yields

$$2m_0 \omega_0 \Delta\omega = 2m_p \omega_0^2 \text{ and so } \Delta\omega = \frac{m_p \omega_0}{m_0}$$

Thus

$$\hbar \Delta\omega = \frac{\hbar c^2 m_p \omega_0}{m_0 c^2} \dots\dots\dots(9)$$

Following De Broglie hypothesis by assuming the electron to behave as a harmonic oscillator

$$E_0 = \hbar \omega_0 = m_0 c^2 \text{ is the initial electron energy}$$

$$E = \hbar \omega = mc^2 \dots\dots\dots(10) \text{ is the final electron energy.}$$

Substituting (10) in (9) yields

$$\hbar \Delta\omega = m_p c^2 \text{ and so}$$

$$\Delta E = E - E_0 = \hbar(\omega - \omega_0) = \hbar \Delta\omega = m_p c^2 \dots\dots\dots(11)$$

Similarly equation (7) for the photon force in the direction of electron motion is given by $m_0 (\omega^2 - \omega_0^2) r = -2m_p \omega_0^2 r$. to get $\omega_0 - \omega \approx \Delta\omega$ in (8) and (9) to get finally $\Delta E = E_0 - E = \hbar(\omega_0 - \omega) = \hbar \Delta\omega = m_p c^2 \dots\dots\dots(12)$

This equation explains the change in the electron energy which appears from the influence of the photon, which gives its energy to the electron to change it from E_0 to E and to change its frequency from ω_0 to ω . The electron or the molecule frequency may increase or decrease as shown by equations (11) and (12). This result is inconformity with Raman scattering phenomenon.

III. The Interaction of the Photon with the Molecule According to Klein- Gordon Time Independent Equation

Time Independent Klein- Gordon Equation⁽¹¹⁾:

$$\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} = P^2 \Psi \dots\dots\dots(13)$$

The solution of this equation for the molecule is

$$\Psi_0 = A_1 e^{\frac{P_0 x}{\hbar}} + A_2 e^{-\frac{P_0 x}{\hbar}} \dots\dots\dots(14)$$

Because the molecule momentums may assume negative or positive values, that is $\pm P_0$ so the wave function of the molecule in equation (14) has two parts. And if one write equation (14) in the trigonometric form it yields

$$\Psi_0 = A_1 \cos\left(\frac{iP_0}{\hbar}x\right) + A_2 \cos\left(\frac{-iP_0}{\hbar}x\right)$$

but the solution for the photon is

$$\Psi_p = A_p e^{\frac{P_p x}{\hbar}} \dots\dots\dots(15)$$

To find the composite system Ψ_T multiply the wave function of the interacting molecules Ψ_0 with the Eigen function of the interacting photons Ψ_p

$$\Psi_T = \Psi_0 \Psi_p$$

It will be

$$\Psi_T = A_1 A_p e^{\frac{(P_0 + P_p)x}{\hbar}} + A_2 A_p e^{-\frac{(P_0 - P_p)x}{\hbar}} \dots\dots\dots(16)$$

And if some of the photons wave Ψ_p passes without interacting with the molecules, the function of all the photons Ψ will be

$$\Psi = \Psi_T + \Psi_p, \text{ which is equal to}$$

$$\Psi = A_1 A_p e^{\frac{(P_0+P_p)x}{\hbar}} + A_2 A_p e^{-\frac{(P_0-P_p)x}{\hbar}} + A_p e^{\frac{P_p}{\hbar}x} \dots\dots\dots(17)$$

If one write

$$A_1 A_p = A_{T1} \text{ and } A_2 A_p = A_{T2}$$

$$\alpha_0 = \frac{iP_0}{\hbar} \text{ and } \alpha_p = \frac{iP_p}{\hbar}$$

Equation (17) in the trigonometric form will be like this

$$\Psi = A_{T1} \cos(\alpha_0 + \alpha_p)x + A_{T2} \cos(\alpha_0 - \alpha_p)x + A_p \cos(\alpha_p)x \dots\dots\dots(18)$$

The first part of equation (18) represents the absorption of the photon by the molecule and the increase of the momentum the second part represents the emission of the photon by the molecule and the decrease of the momentum but the third part represents the noninteracting photons.

IV. The Interaction of the Photon with the Molecule According to Klein- Gordon Time Dependent Equation

Time Dependent Klein- Gordon Equation⁽¹²⁾:

$$\hbar^2 \frac{\partial^2 \Psi}{\partial t^2} = E^2 \Psi \dots\dots\dots(19)$$

The solution of this equation for the molecules is

$$\Psi_0 = A_1 e^{\frac{iE_0 t}{\hbar}} + A_2 e^{-\frac{iE_0 t}{\hbar}} \dots\dots\dots(20),$$

or

$$\Psi_0 = A_1 \cos\left(\frac{E_0}{\hbar}\right)t + A_2 \cos\left(-\frac{E_0}{\hbar}\right)t, \text{ because the molecules energies may take positive or negative values}$$

But the solution for the photon is

$$\Psi_p = A_p e^{\frac{iE_p t}{\hbar}} \dots\dots\dots(21),$$

or

$$\Psi_p = A_p \cos\left(\frac{E_p}{\hbar}\right)t$$

After the interaction of the electrons of the molecules having wavefunction Ψ_0 with the photons of wave function Ψ_p the composite system Ψ_T will become

$$\Psi_T = \Psi_0 \Psi_p,$$

it yields

$$\Psi_T = A_1 A_p e^{\frac{i(E_0+E_p)t}{\hbar}} + A_2 A_p e^{-\frac{i(E_0-E_p)t}{\hbar}} \dots\dots\dots(22)$$

If one suppose

$$A_1 A_p = A_{T1} \text{ and } A_2 A_p = A_{T2}$$

$$\alpha_0 = \frac{E_0}{\hbar} \text{ and } \alpha_p = \frac{E_p}{\hbar}$$

And if only the real part of equation (22) is written it will yields

$$\Psi_T = A_{T1} \cos(\alpha_p + \alpha_0)t + A_{T2} \cos(\alpha_p - \alpha_0)t$$

Which is equal to

$$\Psi_T = A_{T1} \cos(\alpha_0 + \alpha_p)t + A_{T2} \cos(\alpha_0 - \alpha_p)t \dots\dots\dots(23)$$

If some of the photons penetrates without interaction with the molecules then the whole wave function Ψ becomes

$$\Psi = \Psi_T + \Psi_p, \text{ or}$$

$$\Psi = A_{T1} \cos(\alpha_0 + \alpha_p)t + A_{T2} \cos(\alpha_0 - \alpha_p)t + A_p \cos\left(\frac{E_p}{\hbar}\right)t \dots\dots\dots(24)$$

$$= A_{T1} \cos(\omega_0 + \omega_p)t + A_{T2} \cos(\omega_0 - \omega_p)t + A_p \cos \omega_p t$$

This equation consists of three parts the first part represents the absorption of the photon by the molecule, the second part represents the emission of the photon by the molecule and the third part represents the case when the photons penetrate without interaction.

V. Discussion

According to equation (2) the photon force exerted on the molecule can change its frequency from ω_0 to ω . By using (SR) expression for energy, utilizing plank theory, and treating the electron as a harmonic oscillator, a useful expression relating change of electron energy and photon energy is obtained in equation (12). This expression indicates that photons energy change the electrons energy and frequency. This expression agrees with what is observed in Raman spectrum.

Section (3) utilizes time independent Klein-Gordon equation to find the wave function of molecules and photons for free particles systems. The wave function of the photons and the molecules which are

considered as a composite system, describing excited molecules is shown by the wave function (16). Since there are photons which do not interact with molecules, the total wave function of the whole system is described by equation (17). This equation shows existence of three different wavelengths, which are stocks, anti stocks and original photon frequency. This agrees with experimentally observed Raman spectrum.

The time dependent Klein-Gordon equation treatment is shown in section (4). Again the total wave function is that of excited molecules and free photon. This wave function shows that the spectrum should display three frequencies stokes, anti stokes and original photon frequency. This result is in conformity with classical Raman theory.

VI. Conclusion

This model shows that Raman spectrum can be described semi classically by treating the molecule as a harmonic oscillator and a photon as a particle exerting force on the molecule according to (SR) and plank hypothesis. It shows also the possibility of describing Raman scattering with the frame work of Klein-Gordon.

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