

Interpretation of Raman Effect on the Basis of Quantum Theory

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ABSTRACT

Raman spectrum is explained on the basis of classical electromagnetic theory. There is a need for quantum treatment. In this work semi classical and quantum treatments based on Schrödinger equation are utilized to describe photon molecular interaction. The semi classical treatment gives results consistent with the quantum one. The Schrödinger treatment explains theoretically Raman spectrum.

Keywords: Raman effect, quantum theory, photons, electrons

INTRODUCTION

Raman spectroscopy is one of the important techniques used in material science for knowing the degree of purity of elements or compounds⁽¹⁾. It can detect sensitively the impurities existing in chemical compounds or foods. This technique is based on Raman Effect in which atoms or molecules absorb a photon of certain frequency, to emit three photons. One has frequency higher than the original one, the second has lower frequency, and the third has the same frequency as the original one⁽²⁾.

This effect can easily be explained by using electromagnetic Maxwell's theory⁽³⁾. The techniques of Raman spectroscopy which is based on this classical theory are used in a wide variety of applications^(4, 5, 6).

Despite the successes of this technique, there is a need to promote its application on the micro scale, like nano particles and nano materials^(7, 8). This means a need for a quantum mechanical treatment.

THE THEORY OF THE CLASSICAL RAMAN SPECTROSCOPY

When electromagnetic waves are incident on atoms they cause them to form oscillating dipoles. These oscillating dipoles themselves, also emit electromagnetic waves with characteristic radiation. To know the characteristic of this emitted radiation, one can use the relation between the incident electromagnetic field (E_0) and polarization (P) were written as;

$$E = E_0 \cos \omega_0 t \dots \dots \dots (1)$$

Where E , ω_0 , t are electromagnetic field, angular frequency and time.

$$P = \chi E \dots \dots \dots (2)$$

Where χ is the susceptibility, which written in real (χ_0) and imaginary (χ_1) parts as;

$$\chi = \chi_0 + \chi_1 \cos \omega_1 t \dots \dots (3)$$

Then the polarization will be;

$$P = (\chi_0 + \chi_1 \cos \omega_1 t) E_0 \cos \omega_0 t \Rightarrow$$

$$P = E_o \chi_o \cos \omega_o t + \frac{1}{2} E_o \chi_1 [\cos(\omega_o + \omega_1) t + \cos(\omega_o - \omega_1) t] \dots (4)$$

Thus this interaction lead to the splitting of the original line ω_o to three distinct lines $\omega_o + \omega_1, \omega_o$, and $\omega_o - \omega_1$.

The problem with this model is related to the fact that it is based on classical electromagnetic theory. Thus there is a need for a quantum version.

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_o will be equal to the attraction force of the nucleus. This means that ⁽⁹⁾

$$\frac{mv_o^2}{r} = \frac{m\omega_o^2 r^2}{r} = m\omega_o^2 r = F_e \dots (5)$$

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 the total of F_e and F_p as;

$$m\omega^2 r = F_e - F_p \dots (6),$$

where the photon force opposes the nuclear attractive force which causes the electron to move away from the nucleus.

Substitute (5) in (6) it yields

$$m\omega^2 r = m\omega_o^2 r - F_p \dots (7)$$

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

$$F = - \frac{\partial E}{\partial r} \dots (8)$$

This is inconformity with the ordinary relation

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

If one integrates equation (7) with respect to r, the resulting equation takes the form

$$\frac{m\omega^2 r^2}{2} = \frac{m\omega_o^2 r^2}{2} + E_p$$

and so

$$\frac{m\omega^2 r^2}{2} - \frac{m\omega_o^2 r^2}{2} = E_p \dots (9)$$

One can write equation (9) in terms of electron kinetic energy in the form

$$\frac{mv^2}{2} - \frac{mv_o^2}{2} = E_p \dots (10)$$

And Equation (10) will be

$$E - E_o = E_p \dots (11)$$

which is equal to

$$\Delta E = E_p \dots (12)$$

So the change of the energy of the electrons is due to the interaction with the photons.

The Interaction of The Photons with the Molecule according to Time Independent Schrödinger Equation

For free particles time independent Schrödinger equation for particles with energy E_o , is given by⁽¹⁰⁾

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi_o}{\partial x^2} = E_o \Psi_o \dots\dots\dots (13)$$

In equation (13) the potential vanishes since the particles are free, that is means $V = 0$

The solution of this equation is

$$\Psi_o = e^{iax} \text{ or } \Psi_o = A_o \cos ax \dots\dots\dots (14)$$

Substitute (14) in (13) yields

$$\frac{\partial \Psi_o}{\partial x} = -a A_o \sin ax, \text{ and}$$

$$\frac{\partial^2 \Psi_o}{\partial x^2} = -a^2 A_o \cos ax = -a^2 \Psi_o$$

Then equation (14) becomes

$$\frac{\hbar^2 a^2}{2m} \Psi_o = E_o \Psi_o$$

And because $E_o = \frac{\hbar^2 k^2}{2m}$

So

$$\frac{\hbar^2 a^2}{2m} \Psi_o = \frac{\hbar^2 k^2}{2m} \Psi_o$$

And the value of a is equal to k

$a = k$

Then the wave equation of the molecule is

$$\Psi_o = A_o \cos k_o x \dots\dots\dots (15)$$

If one substitutes the Eigen function Ψ_p of the photon in Schrödinger equation (14) the equation will be

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi_p}{\partial x^2} = E_p \Psi_p \dots\dots\dots (16)$$

And after the solution of this equation the wave equation of the photon will be

$$\Psi_p = A_p \cos k_p x \dots\dots\dots (17)$$

And when the photons interact with the electrons of the molecule the wave equation of the composite system will become Ψ_T , where

$$\Psi_T = \Psi_o \Psi_p$$

Therefore

$$\Psi_T = A_o A_p \cos k_o x \cos k_p x \dots\dots\dots (18)$$

Substituting $A_o A_p$ by A_T and using trigonometric relations, one can rewrite (18) in the form

$$\Psi_T = \frac{A_T}{2} [\cos(k_o + k_p)x + \cos(k_o - k_p)x] \dots\dots\dots (19)$$

Equation (19) contains two parts:

The first part $(k_o + k_p)$ represents the absorption of the photons by the electron

The second part $(k_o - k_p)$ represents the emission of the photons by the electron

If some of the photons passes without interaction with the molecules, it will be represented by Ψ_p . Then the wave function of all the photons Ψ is equal to the algebraic sum of the function of the interacting photons Ψ_T plus the function of the noninteracting photons Ψ_p , that is

$$\Psi = \Psi_T + \Psi_p$$

Thus

$$\Psi = \frac{A_T}{2} [\cos(k_o + k_p)x + \cos(k_o - k_p)x] + A_p \cos k_p x \dots\dots\dots (20)$$

From this equation it is clear that the spectrum of the atoms contains three wavelengths

$\lambda_o + \lambda_p$, $\lambda_o - \lambda_p$ and λ_p .

The Interaction of the Photon with the Molecule according to Time Dependent Schrödinger Equation

Time dependent Schrödinger equation for time independent potential is given by⁽¹¹⁾

$$i\hbar \frac{\partial \Psi_o}{\partial t} = E_o \Psi_o \dots\dots\dots (21)$$

The solution of this equation is

$$\Psi_o = A_o e^{bt} \dots\dots\dots (22)$$

Substituting (22) in (21) and then differentiate yields

$$i\hbar b = E_o \rightarrow b = -\frac{iE_o}{\hbar} \dots\dots\dots (23)$$

Substituting (23) in (22) the function will be

$$\Psi_o = A_o e^{-\frac{iE_o}{\hbar}t} \dots\dots\dots (24)$$

Because the molecule energies may assumed negative or positive values, that is $\pm E_o$ then the wave function of the molecule is

$$\Psi_o = A_1 e^{-\frac{iE_o}{\hbar}t} + A_2 e^{+\frac{iE_o}{\hbar}t} \dots\dots\dots (25)$$

But the wave function of the photon will be

$$\Psi_p = A_p e^{-\frac{iE_p}{\hbar}t} \dots\dots\dots (26)$$

And when the photons interact with the electrons of the molecule the wave equation of the composite system will become Ψ_T , where

$$\Psi_T = \Psi_o \Psi_p$$

Then

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

$$= B_1 e^{\frac{-i(E_o+E_p)t}{\hbar}} + B_2 e^{\frac{i(E_o-E_p)t}{\hbar}} \dots\dots\dots (27)$$

If one represents the part of the photons that interacts with the molecules by Ψ_T and the other parts that penetrate without interaction by Ψ_p then the total wave function of the photon will be

$$\Psi = \Psi_T + \Psi_p = B_1 e^{\frac{-i(E_o+E_p)t}{\hbar}} + B_2 e^{\frac{i(E_o-E_p)t}{\hbar}} + A_p e^{\frac{iE_p t}{\hbar}} \dots\dots\dots (28)$$

Substituting

$$E_o by \hbar\omega_o \text{ and } E_p by \hbar\omega_p,$$

and then take only the real part of equation (28) the wave function will be

$$\Psi = B_1 \cos(\omega_o + \omega_p)t + B_2 \cos(\omega_o - \omega_p)t + A_p \cos \omega_p t \dots\dots\dots (29)$$

This equation represents a photon with a spectrum of $\omega_o + \omega_p$, $\omega_o - \omega_p$ and ω_p .

The first frequency represents the case of the absorption of the photon by the molecule, the second frequency represents the case of the emission of the photon by the molecule and the third one represents the case when the photon penetrates without interaction.

DISCUSSION

Considering the electron moving in a circular orbit with frequency ω_o , the centrifugal force counter balance the electric nuclear force as shown by equation (5). When a photon incident on it, a force F_p produced by the photon changes the electron frequency to ω , as shown by equation (6). It is very striking to note that these relations show that the new electron energy E is equal to the old one E_o , beside photon energy E_p as shown by equations (11) and (12). This happens when the photon force F_p opposes the nuclear force F_e . See equation (6), which is quite reasonable as far as F_p pulls the electron far from the nucleus, thus move it from the ground state E_o to the excited state E .

Raman spectrum is explained by using time independent Schrödinger equation for free particles. Treating molecules and photons as free particles their wave functions are obtained in equations (15) and (17). The composite wave for molecules interacting with photons is found in (19). The total wave function for interacting and non interacting photons is given by (20). Equation (20) shows existence of three wavelengths $\lambda_o + \lambda_p$, $\lambda_o - \lambda_p$ and λ_p corresponding to Raman spectrum.

Using the same arguments for time dependent Schrödinger equation for any molecules or photons, even those which are affected by radial or any time independent potential, the total wave functions is also found in (29). It again gives a theoretical umbrella for Raman spectrum.

CONCLUSION

The interaction of photons with molecules can be described by semi classical treatment or by using time dependent and independent Schrödinger equation. The quantum Schrödinger treatment of this interaction describes a suitable theoretical frame work for Raman spectroscopy.

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