1991

Raman effect in carbon tetrachloride, silicon and germanium

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DOI: <https://doi.org/10.31979/etd.774c-pud7>
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San Jose State University, 1991

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**RAMAN EFFECT IN CARBON
TETRACHLORIDE, SILICON AND
GERMANIUM.**

A Thesis
Presented to
The Faculty of the Department of Physics
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
Yuqiang Qin

December, 1991

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ABSTRACT

RAMAN SPECTRUM IN CARBON TETRACHLORIDE, SILICON AND GERMANIUM

by Yuqiang Qin

This thesis embodies the experimental study of laser-induced Raman spectra in CCl_4 , Si and Ge. Spectral peaks were found at 460cm^{-1} , 314cm^{-1} , 213cm^{-1} , 760cm^{-1} and 790cm^{-1} for CCl_4 . The line at 460cm^{-1} was found to have fine structure which is due to the isotope effect. Spectral lines were found at 301cm^{-1} for Ge and 511cm^{-1} for Si. All measurements were made at room temperature. All results agree with the reported results. Also, the second order time-dependent Schrodinger equation was solved for the Raman process.

ACKNOWLEDGEMENTS

I am very grateful to several people for their contribution to this thesis. I would like to sincerely thank my thesis advisor, Professor H. Sarma Lakkaraju for the guidance, support and insight he has given me over the past two years. His patient and friendly help made it possible for me to finish this thesis. I would also like to thank Professor Karamjeet Arya for checking the theoretical calculation. He also gave me many constructive criticisms. I would also like to thank Professor Joseph F. Becker for participating as a member of my thesis committee, for the valuable input from the class he taught and his comments and suggestions. I would also like to thank Professor Kiumars Parvin for providing samples and related information. I would like to thank my wife, Z. Zhao, my aunt A. C. Sum and my uncle W. Sum for their love, support and encouragement throughout my graduate career.

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CHAPTER 1. INTRODUCTION

Spectroscopy has been a very important tool in studying material structure for hundred years. Raman spectroscopy has been part of the classical spectroscopy for sixty years. The importance of the Raman spectroscopy is not decreased but increased by the invention of laser and new detection technology. This thesis embodies the experimental study of laser-induced Raman spectra in CCl_4 , Si and Ge. We set up a first complete Raman spectroscopy system in Physics Department of San Jose State University. The spectrum of CCl_4 , Si and Ge were studied and compared with the reported results. Also, the second order time-dependent Schrodinger equation was solved for the Raman process.

1. Raman Effect.

Raman effect was first discovered by Indian physicists C. V. Raman and K. S. Krishnan in 1928. They found that after sunlight was scattered by certain liquids, the incident light suffers a change in frequency.¹ For many years, Raman spectroscopy has been a powerful tool for the investigation of molecular vibrations and rotations. Even when a precise determination of structure is not possible, much can often be said about the arrangement of atoms in a

molecule from empirical information about the characteristic Raman frequencies of groups of atoms. The information from Raman spectra is similar to that provided by infrared spectroscopy. In fact, Raman and infrared spectra often provide complementary information about molecular structure. It can be shown that² for a centrosymmetric molecule no transition appearing in the infrared spectrum can appear in the Raman spectrum and vice versa. But non-centrosymmetric molecules may be both Raman and infra-red active. This is called the mutual exclusion law.

Due to the lack of sufficiently intense radiation sources, Raman spectroscopy was not used much in vibrational spectroscopy until the introduction of lasers which has indeed revolutionized this classical field of spectroscopy.

2. Nature of Raman Scattering

The presence of scattered lines of shifted frequencies can be understood by considering the incident light to consist of photons of energy $\hbar\omega_i$. On collision with a molecule, an incident photon may be elastically or inelastically scattered. For elastic collision, the photon energy remains same, and gives rise to the Rayleigh line in the spectrum. For inelastic collision, the photon will gain

energy from or lose energy to the molecule. In other words, the photon causes the molecule to undergo a transition. If the transition is from higher level to lower level, the anti-Stokes lines are observed. If the transition is from lower level to higher level, the Stokes Raman lines are observed.

The energy level scheme and collision are shown as Fig. 1-1.

The energy levels we are concerned with here include vibrational, rotational and electronic energies of the molecule. The intermediate state $E_k = E_m + \hbar\omega_i$ of the system during the scattering process is a virtual level which is not necessarily a real stationary eigenstate of the molecule. If E_k coincides with one of the molecular eigenstates, the resulting Raman effect is called resonance Raman effect. After collision with an incident photon $\hbar\omega_i$, the molecule will be excited to $E_k = E_m + \hbar\omega_i$, then it will go back to lower level E_n and emit a photon $\hbar\omega_s$, where $E_k = E_n + \hbar\omega_s$. From energy conservation, $E_m + \hbar\omega_i = E_n + \hbar\omega_s$, so $E_n - E_m = \hbar(\omega_i - \omega_s)$.

If initial state E_m is the same as final state E_n , the incident and emitted photon have same frequency, $\omega_i = \omega_s$. This is Rayleigh scattering. If initial state E_m is lower than final state ($E_m < E_n$), the emitted photon will have smaller

frequency ($\omega_i > \omega_s$). In this case Stokes lines are observed. If the initial state is not the ground state and the final state is lower than the initial state ($E_m > E_n$), then $\omega_s > \omega_i$, the emitted photon will have higher energy than the incident photon. Thus it will give anti-Stokes lines. The population distribution at equilibrium is given by Boltzmann distribution. Thus the number of molecules in higher levels is smaller than that in lower levels by a factor $\exp(-\Delta E/kT)$. From Figure 1-1 we can see that population at E_m in case (b) is larger than that in case (a). This is the reason the intensity of anti-Stokes lines are weaker than Stokes lines.

Obviously the shifted frequencies depend on the molecular energy level. The spectral shifts of the modified radiation from the incident line provide a method to measure the rotational or vibrational energy levels of the molecules. Due to the technical difficulties for rotational spectra, which requires higher resolving power of spectrometer, studies on vibrational spectra are more frequent.

In solid state physics, Raman spectrum can be used to measure the energy of phonon. When a photon enters a crystal, it can produce a phonon and a new photon. From an energy point of view, the energy of the phonon is equal to

the energy difference of the two photons. In other words, the frequency change corresponds to the energy of phonon.

3. Classical Treatment of Raman Effect

The Raman scattering can be considered due to the change of electronic polarizability which results from atomic displacements. Consider the incident light having a time dependence $E_i(t) = E_i \cos \omega_i t$. The incident light will interact with the molecules and produce a time varying polarization:

$$P(t) = \alpha E_i(t) \quad (1)$$

In general, P and E are vectors. They usually have different directions. The tensor α is called the polarization tensor. It is also sometimes called the Raman tensor. Thus Equation (1) can be expanded as

$$P_x = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \quad (2)$$

$$P_y = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \quad (3)$$

$$P_z = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z \quad (4)$$

where α_{ij} ($i, j = x, y, z$) is a constant. It can be shown that α is a symmetric tensor.³ Therefore, only six elements of α are independent and they will determine the optical properties of the samples.

Under the influence of an electromagnetic wave, the polarizability will vary with the configuration of the molecule, i.e, is a function of the vibrational or rotational coordinates of the nuclei. It can be expanded in powers of the displacements from equilibrium.

$$\alpha(t) = \alpha_0 + \left(\frac{\partial \alpha}{\partial u} \right)_0 u + \left(\frac{\partial^2 \alpha}{\partial u^2} \right)_0 u^2 + \dots \quad (5)$$

where u is the displacement from equilibrium which has a time variation $u = u_0 \cos \omega_0 t$ and ω_0 is the oscillation frequency. For first order approximation, $\alpha(t)$ can be written as

$$\alpha(t) = \alpha_0 + \alpha_1 u_0 \cos \omega_0 t \quad (6)$$

$$\text{where } \alpha_1 = \left(\frac{\partial \alpha}{\partial u} \right)_0$$

substituting Equation (6) and $E = E_i \cos \omega_i t$ into Equation (1)

$$\begin{aligned} P(t) &= (\alpha_0 + \alpha_1 u_0 \cos \omega_0 t) E_i \cos \omega_i t \\ &= \alpha_0 E_i \cos \omega_i t + (1/2) \alpha_1 u_0 E_i (\cos(\omega_0 + \omega_i) + \cos(\omega_0 - \omega_i)) \end{aligned} \quad (7)$$

In classical electromagnetic theory, a time varying polarization, $p(t)$, will yield the radiation.⁴ The scattered light intensity is proportional to $p(t)^2$ and hence to $(E_i)^2$.

$$I = \frac{\omega^4}{3c^3} |p|^2 \quad (8)$$

where p will depend on the angle between source point and field point and the distance from source to field point. The intensity I will have the same spatial distribution as p^2 .

In Equation (7), the first term is the same frequency as the incident light and gives rise to Rayleigh scattering. The second and third terms have the frequencies $\omega_i \pm \omega_0$. The $\omega_0 + \omega_i$ gives anti-Stokes and the $\omega_i - \omega_0$ gives Stokes lines.

The discussion above is for a single molecule. If a single crystal sample is being studied, then rather complex scattering patterns will be observed varying with the direction of polarization, observation and incident angles in the general case.

However, polarization phenomena are observed even when the scatterers are randomly oriented or rotating freely as in a gas or an amorphous crystal. This is because unlike the vector case, the average of the square of polarizability components over all angles is not equal to zero. Equation (1) refers to the laboratory frame of reference. If the

reference frame is changed by altering the angle of observation, then all the quantities have to be transformed to the new frame of reference:

$$\mathbf{P}' = \mathbf{A}\mathbf{P} \quad (9)$$

$$\mathbf{E}' = \mathbf{A}\mathbf{E} \quad (10)$$

where $\mathbf{A}$ is an orthogonal 3×3 matrix and the elements are direction cosines. Substituting Equation (9) and Equation (10) in Equation (1)

$$\mathbf{P}' = \mathbf{A}\alpha\mathbf{A}^{-1}\mathbf{E}' = \alpha'\mathbf{E}' \quad (11)$$

where $\alpha' = \mathbf{A}\alpha\mathbf{A}^{-1}$

In general, a matrix $\mathbf{A}$ always exists to make α' diagonal. That is

$$\mathbf{P}' = \begin{pmatrix} \alpha'_1 & 0 & 0 \\ 0 & \alpha'_2 & 0 \\ 0 & 0 & \alpha'_3 \end{pmatrix} \mathbf{E}' \quad (12)$$

Here α'_1 , α'_2 and α'_3 are called the principal values of the polarizability. For the isotropic case, it is apparent that $\alpha'_1 = \alpha'_2 = \alpha'_3$. The new axes of the coordinate system are called the principle axes of polarizability. We can say that in general, the tensor with six independent elements can be thought of as containing three physical quantities; namely, the half axes of an ellipsoid. The other

three observable quantities give the angles between the laboratory frame of reference and the molecular axes.

If the principal polarizabilities are $\alpha_1, \alpha_2, \alpha_3$, let

$$\bar{\alpha} \equiv \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (13)$$

$$\gamma^2 \equiv \frac{1}{2} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2) \right] \quad (14)$$

It can be shown that⁵:

$$\bar{\alpha}_{xx}^2 = \bar{\alpha}_{yy}^2 = \bar{\alpha}_{zz}^2 = \frac{1}{45}(45\bar{\alpha}^2 + 4\gamma^2) \quad (15)$$

$$\bar{\alpha}_{xy}^2 = \bar{\alpha}_{yz}^2 = \bar{\alpha}_{zx}^2 = \frac{1}{15}\gamma^2 \quad (16)$$

where the average is a spatial average over all randomly oriented molecules. The non zero volume of average polarizability means that we can observe scattered light even in randomly oriented samples.

Two important cases can be distinguished:

1. Unpolarized radiation along Z direction observed along x direction.

In this case, $E_x = E_y$ $E_z = 0$

$$P_y = \alpha_{yx}E_x + \alpha_{yy}E_y$$

$$P_z = \alpha_{zx}E_x + \alpha_{zy}E_y$$

$$\text{so } I_y \approx P_y^2 \approx \bar{\alpha}_{yx}^2 E_x^2 + \bar{\alpha}_{yy}^2 (E_y)^2$$

$$\approx [\bar{\alpha}^2 + (7/45)\gamma^2](E_x)^2 \quad (17)$$

$$I_z \approx P_z^2 \approx \bar{\alpha}_{zx}^2 E_x^2 + \bar{\alpha}_{zy}^2 E_y^2$$

$$\approx (1/15)\gamma^2 (E_x)^2 \quad (18)$$

Thus the ratio of radiation polarized in the y-direction to that polarized in the z-direction is

$$\rho_n = \frac{I_z}{I_y} = \frac{6\gamma^2}{45\bar{\alpha}^2 + 7\gamma^2} \quad (19)$$

2. Irradiation with polarized radiation along z and observation along x.

In this case, $E_x = E_z = 0$

$$I_y \approx P_y^2 \approx \bar{\alpha}_{yy}^2 E_y^2 \approx \bar{\alpha}^2 + (4/45)\gamma^2 (E_y)^2 \quad (20)$$

$$I_y \approx P_z^2 \approx \bar{\alpha}_{zy}^2 E_y^2 \approx (1/15)\gamma^2 (E_y)^2 \quad (21)$$

$$\rho_n = \frac{I_z}{I_y} = \frac{3\gamma^2}{45\bar{\alpha}^2 + 4\gamma^2} \quad (22)$$

ρ_n is an observable physical property called the depolarization ratio. Even if the exact values of α_1 , α_2 and α_3 are difficult to measure, we still can get information about γ and $\bar{\alpha}$ from measurement of ρ_n .

It has been shown that the simple classical treatment of Rayleigh and Raman scattering leads to a fair insight

into the phenomenon, showing how Stokes and anti-Stokes lines arise, how the shifts are related to molecular frequencies, how polarization phenomena arise, and how these are related to the molecular symmetry. However, within classical theory no explanation is given to why anti-Stokes lines are weaker than their Stokes companions, why certain selection rules hold, and what factors govern the intensities of Raman lines.

4. Quantum Theory of The Raman Effect

The rigorous theory describing the Raman effect requires a complete quantum mechanical treatment. Unfortunately, although the general quantum treatment of the Raman effect is completely developed, the calculation for a real system is very difficult. Because some important physical quantities, such as the wave function of the system, are difficult to know either from experiment or from theoretical calculation. In general, the quantum theory of the Raman effect can only give some general information.

The application of quantum theory can be performed in two stages. Because the Raman effect is due to electromagnetic field interacting with a molecule, we can assume a classical field for the radiation and a fully

quantized molecule. The final stage is considering a quantized field interacting with a quantized molecule. In this work, we follow the former only.

In quantum theory the expectation value of the component α_{ij} of the polarizability tensor is given by

$$\langle \alpha_{ij} \rangle_{mn} = \int \phi_n^*(q) \alpha_{ij} \phi_m(q) dq \quad (23)$$

where the integration extends over all coordinates. The functions $\phi_m(q)$ and $\phi_n(q)$ represent the perturbed time-dependent eigenfunctions of the system in the initial level m and the final level n .

In the Raman effect, the electric field of the incident radiation, acting on the charges of the molecule, perturbs its wave function. The solutions of the time dependent Schrodinger equation are required as the system is subject to a perturbation by an electromagnetic wave. The time dependent Schrodinger equation can be written as

$$\left(H + \frac{\hbar}{i} \frac{\partial}{\partial t} \right) \phi(q, t) = 0 \quad (24)$$

where $H = H_0 + \mathbf{E} \cdot \mathbf{P}$ is the Hamiltonian and H_0 is the unperturbed Hamiltonian. $\mathbf{E} \cdot \mathbf{P}$ is the perturbation terms where $\mathbf{P}$ is the molecular dipole inclusive of the induced moment and $\mathbf{E}$ the electric field arising from the radiation.

$\phi(q,t)$ is the perturbed wave function which can be expressed as an expansion in unperturbed time dependent eigenfunctions $u_n \exp(-iE_n t/\hbar)$:

$$\phi(q,t) = \sum_n a_n(t) u_n e^{-iE_n t/\hbar} \quad (25)$$

Substitution of Equation (25) into Equation (24) gives

$$\begin{aligned} \sum_n (i\hbar \dot{a}_n u_n e^{-iE_n t/\hbar} + a_n E_n u_n e^{-iE_n t/\hbar}) \\ = \sum_n (a_n (H_0 + H') u_n e^{-iE_n t/\hbar}) \end{aligned} \quad (26)$$

where H' is the perturbation operator. Because $u_n e^{-iE_n t/\hbar}$ is the unperturbed wave function.

$$H_0 u_n = E_n u_n \quad (27)$$

We can replace $H_0 u_n$ by $E_n u_n$, multiply both side by u_k and integrate over the whole space to get

$$i\hbar \dot{a}_k e^{-iE_k t/\hbar} = \sum_n a_n(t) e^{-iE_n t/\hbar} \langle k | H' | n \rangle \quad (28)$$

Let $\omega_{kn} = (E_k - E_n)/\hbar$ which is called transition frequency.

$$\dot{a}_k = (i\hbar)^{-1} \sum_n a_n(t) e^{iE_{kn} t/\hbar} \langle k | H' | n \rangle \quad (29)$$

Now, replace H' by $\lambda H'$ and express the a_n 's as power series in λ .

$$a_n = a_n^{(0)} + \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \dots \quad (30)$$

Here λ is a parameter between zero and one and Equation (30) is a continuous analytic function of λ . Substitute Equation (30) into Equation (29) and equate the coefficients of the corresponding powers of λ to get

$$\dot{a}_k^{(0)} = 0 \quad (31)$$

$$\dot{a}_k^{(s+1)} = (i\hbar)^{-1} \sum_n a_n^{(s)} \langle k|H'|n \rangle e^{i\omega_{kn}t} \quad (32)$$

Equation (31) shows that the zero-order coefficients $a_k^{(0)}$ are constant in time. They are determined by the initial conditions of the system before the perturbation is applied.

We assume that:

1. All but one of the a_k are zero, so that the system is initially in a definite unperturbed energy state m .
2. The perturbation is applied at $t=0$, and $H'(t)$ can be written as:

$$H'(t) = 2H' \sin \omega t = \frac{H'}{i} (e^{i\omega t} - e^{-i\omega t}) \quad (33)$$

Substitute Equation (33) into Equation (32) and integrate. The first order probability is

$$a_k^{(1)} = -\frac{\langle k|H'|m \rangle}{i\hbar} \left(\frac{e^{i(\omega_{km} + \omega)t} - 1}{\omega_{km} + \omega} - \frac{e^{-i(\omega_{km} - \omega)t} - 1}{\omega_{km} - \omega} \right) \quad (34)$$

$|a_k^{(1)}|^2$ is the probability that system has made a transition from an initial state m to a virtual state k .

Equation (34) can be interpreted in terms of absorption and emission of quanta of electromagnetic radiation.

From Equation (32)

$$a_n^{(2)} = \frac{1}{i\hbar} \int_0^t \sum_k \langle n | H'(t') | k \rangle a_k^{(1)} e^{i\omega_{nk}t'} dt' \quad (35)$$

We assume that:

1. m is the initial state, k is the intermediate (virtual) state and n is the final state.

2. The perturbation for second order is:

$$H' = 2\sin\omega't = \frac{H'}{i} (e^{i\omega't} - e^{-i\omega't}) \quad (36)$$

Substituting Equation (34) and Equation (36) in Equation (35) and integrating, we get

$$a_n^{(2)} = -\frac{2i}{\hbar^2} \sum_k H'_{nk} H'_{km} \left[\frac{1}{\omega_{km} + \omega} \left(\frac{e^{\frac{1}{2}i(\omega_{nm} + \omega' + \omega)t}}{e^2} \frac{\sin \frac{1}{2}(\omega_{nm} + \omega' + \omega)t}{\omega_{nm} + \omega' + \omega} \right. \right. \\ \left. \left. - \frac{e^{\frac{1}{2}i(\omega_{nm} - \omega' + \omega)t}}{e^2} \frac{\sin \frac{1}{2}(\omega_{nm} - \omega' + \omega)t}{\omega_{nm} - \omega' + \omega} \right) \right]$$

$$\begin{aligned}
& - \frac{e^{\frac{1}{2}i(\omega_{nk} + \omega')t}}{e^2} \frac{\sin \frac{1}{2}(\omega_{nk} + \omega')t}{\omega_{nk} + \omega'} \\
& + \frac{e^{\frac{1}{2}i(\omega_{nk} - \omega')t}}{e^2} \frac{\sin \frac{1}{2}(\omega_{nk} - \omega')t}{\omega_{nk} - \omega'} \Bigg) \\
& + \frac{1}{\omega_{km} - \omega} \left(\frac{e^{\frac{1}{2}i(\omega_{nm} + \omega' - \omega)t}}{e^2} \frac{\sin \frac{1}{2}(\omega_{nm} + \omega' - \omega)t}{\omega_{nm} + \omega' - \omega} \right. \\
& - \frac{e^{\frac{1}{2}i(\omega_{nm} - \omega' - \omega)t}}{e^2} \frac{\sin \frac{1}{2}(\omega_{nm} - \omega' - \omega)t}{\omega_{nm} - \omega' - \omega} \\
& - \frac{e^{\frac{1}{2}i(\omega_{nk} + \omega')t}}{e^2} \frac{\sin \frac{1}{2}(\omega_{nk} + \omega')t}{\omega_{nk} + \omega'} \\
& \left. + \frac{e^{\frac{1}{2}i(\omega_{nk} - \omega')t}}{e^2} \frac{\sin \frac{1}{2}(\omega_{nk} - \omega')t}{\omega_{nk} - \omega'} \right) \Bigg] \quad (37)
\end{aligned}$$

Equation (37) is the complete solution of second order time dependent Schrodinger equation. Among the eight terms, many are so small in general that they are not important in the Raman process. A term is important only when its denominator approaches zero, for example:

1. Since n is the lower state, $\omega_{nk} = (E_n - E_k) / \hbar$ is always negative, ω' is always positive, and therefore $\omega_{nk} - \omega'$ can never be zero.

2. $\omega_{nk} + \omega'$ can be zero only in the case of resonant Raman scattering where $\omega_{nk} = -\omega'$.

3. In Raman scattering, the energy difference between the final and initial state is very small compared to the incident and emitted photon energy, $\omega_{nm} \pm (\omega' + \omega)$ can not be satisfied. Actually those two terms that include the denominator of $\omega_{nm} \pm (\omega' + \omega)$ give rise to two-photon absorption and two-photon emission which is not covered in this thesis.

After neglecting terms whose denominators are not zero, $a_n^{(2)}$ can be written as

$$\begin{aligned}
 a_n^{(2)} &= -\frac{2i}{\hbar^2} \sum_k H'_{nk} H'_{km} \left[\frac{1}{\omega_{km} + \omega} \cdot \frac{e^{\frac{1}{2}i(\omega_{nm} - \omega' + \omega)t} \sin \frac{1}{2}(\omega_{nm} - \omega' + \omega)t}{\omega_{nm} - \omega' + \omega} \right. \\
 &\quad \left. + \frac{1}{\omega_{km} - \omega} \cdot \frac{e^{\frac{1}{2}i(\omega_{nm} + \omega' - \omega)t} \sin \frac{1}{2}(\omega_{nm} + \omega' - \omega)t}{\omega_{nm} + \omega' - \omega} \right] \\
 &= \frac{2\pi^2 i}{\hbar^2} \sum_k H'_{nk} H'_{km} \left(\frac{\delta(\omega_{nm} - \omega' + \omega)}{\omega_{km} + \omega} e^{\frac{1}{2}i(\omega_{nm} - \omega' + \omega)t} \right.
 \end{aligned}$$

$$\left. + \frac{\delta(\omega_{nm} + \omega' - \omega)}{\omega_{km} - \omega} e^{\frac{1}{2}i(\omega_{nm} + \omega' - \omega)t} \right) \quad (38)$$

where use has been made of the result⁶:

$$\lim_{a \rightarrow \infty} \frac{2\sin(a-b)}{a-b} = 2\pi\delta(a-b) \quad (39)$$

In Equation (38), ω_{km} and ω are always positive, the first term is always much smaller than the second term. If we assume that incident photon energy is close to one of the molecular state k , we can neglect the first and keep only second term:

$$a_n^{(2)} = \frac{2i\pi^2}{\hbar^2} H'_{nk} H'_{km} \frac{\delta(\omega_{nm} + \omega' - \omega)}{\omega_{km} - \omega} e^{\frac{1}{2}i(\omega_{nm} + \omega' - \omega)t} \quad (40)$$

Assuming ω is the frequency of incident photon and ω' is scattered photon frequency, from Equation (40) we get following results:

1. When $\omega_{nm} = \omega - \omega'$, if $E_n > E_m$, $\omega > \omega'$, Stokes lines are observed; if $E_n < E_m$, $\omega < \omega'$, anti-Stokes lines are observed; if $E_n = E_m$, $\omega_{nm} = 0$, $\omega = \omega'$, Rayleigh lines are observed.

2. The intensity of the scattered light is proportional to $|a_n^{(2)}|^2$, therefore:

$$I_{\text{scattered}} \sim |H'_{nk} H'_{km}|^2 \sim E^4 |\langle n | \alpha | k \rangle \langle k | \alpha | m \rangle|^2 \sim I_{\text{incident}}^2$$

3. The intensity of scattered light proportion to $1/(\omega_{kn}-\omega)^2$.

5. Selection Rules for Raman Scattering

The expression for the transition moment may be written in the form:

$$\int \phi_n^* \hat{P} \phi_m d\tau = E \int \phi_n^* \alpha \phi_m d\tau \quad (41)$$

where E is incident field and α is the molecular polarizability tensor with six distinct components, α_{ij} .

The general selection rule is as follows: A transition between states characterized by the wave functions ϕ_n and ϕ_m is forbidden in Raman scattering unless for at least one of the components α_{ij} of the molecular polarizability tensor the product $\phi_n \alpha_{ij} \phi_m$ belongs to a representation whose structure contains the totally symmetric species.

The application of above selection rule is simple in the case of fundamental transitions. The wave function of ground state is always totally symmetric. Then the necessary condition for Raman activity is that the product of the wave function of upper level and the polarizability component α_{ij} shall be totally symmetric. It can be proved that this can

only be so provided that the two factors belong to the same species.⁷ Thus a fundamental mode is Raman inactive unless its species is the same as that of at least one of the components of the polarizability tensor or one combination of these components.

The description of symmetry of polarizability and wave function requires the knowledge of group theory. A detail discussion for CCl_4 , S_6 , and G_e is given in Chapter 3 and Chapter 4.

CHAPTER 2 EXPERIMENTAL METHODS

1. Introduction

One of the purposes of this experimental thesis was to set up a Raman spectrometer and characterize laser-induced Raman scattering in CCl_4 , Si, and Ge. The spectrum was characterized by intensity and corresponding wavelength at room temperature. To accomplish this, the experiment was designed and constructed to:

- Produce a laser-induced Raman spectrum in several samples at room temperature,
- Resolve the spectra as a function of wavelength and
- Collect, average and store this data for later analysis.

Figure 2-1 shows a schematic diagram of the experimental set-up used in this experiment. The basic components of the set-up consist of:

- The source and illumination system.
- Monochromator.
- The radiation detection system.

A detailed explanation of the apparatus and methods used in this experiment follows.

2. Argon Ion Laser

Among the light sources used in Raman spectroscopy the lasers are the most widely used sources today. Lasers as pumping sources have the following advantages compared to other sources:

1. There are a variety of excitation lines available with a clear spectral region on each side of the excitation line.
2. The band width of the laser line is usually much smaller than a vapor-arc lamp line.
3. The polarization of the laser beam is well defined and could be controlled to within 0.1%.
4. The large amount of energy available can be concentrated in a narrow beam .
5. The intensity can be easily controlled.

An argon ion laser is one of the most often used pumping sources in Raman spectroscopy. It can produce

reliable high power in cw operation on several lines across the visible and near ultraviolet region. Hence we can choose a suitable line to excite the sample to be studied.

The principal excitation mechanism of argon ion laser is electron impact in high current DC discharges. Atoms are ionized on collision with electrons. The ions then relax, cascading to lower excited states with many possible relaxation routes.

By considering the equilibrium populations of excited atoms in a gas discharge, Basov and Krokhin (1962) have derived expressions defining the conditions under which gain will exist.⁸ However, the real collision processes occurring in a gas discharge are very complex. Often the important information, such as cross-sections, is unknown with sufficient accuracy making it impossible to predict theoretically which atomic and molecular species will be useful, and in which pathways inversion will be obtained.

The majority of transitions have very small gains and most of the lines can not be observed and are, in general, not important. But in Raman spectroscopy these lines become important. The good thing about these plasma lines is that we can use them to calibrate the spectrometer. These lines can be obtained by detuning the laser and collecting the scattered radiation from a Kimaz melting point tube as

suggested by Craig and Levin.⁹ This method gives a calibration better than 1cm^{-1} accuracy. The disadvantage associated with the plasma lines is that they will appear along with the Raman lines in the spectrum. When using some particular configuration to obtain Raman spectra from solid samples, this problem can be serious. One method to solve this problem is by using an interference filter (band pass filter) which will allow one frequency to pass through without significant attenuation of intensity and block other frequencies. They are somewhat troublesome in that filters are needed for each laser line and they may allow plasma lines to leak through. For those plasma lines very close to the laser line, the filter does not work effectively. For those plasma lines which can not be suppressed, we can distinguish them by comparing to the known spectrum of the plasma lines. We also can change the laser line. The Raman line will not change with the laser line, but the plasma lines will disappear or shift. In general, a plasma line is sharper and stronger than a Raman line. A list of discharge lines that may interfere with Raman lines is given by Strommen and Loader.^{10,11}

The discharge lines we got from Argon Ion laser are shown in Figure 2-2. The measurement was made using the 488nm laser line.

3. Monochromator

The monochromator used in this project was a Raman spectrometer (Model 1401, Spex Industries, Inc., Metuchen, NJ). Its schematic is shown in Figure 2-3. The monochromator has three slits s1, s2 and s3. The slit widths are set manually and are therefore constant throughout the scan. The resolution of the instrument will vary almost continuously with wavelength. Two spectral lines are resolved if the slit images of the two wavelengths are sufficiently separated as distinguished by Rayleigh criterion. The geometrical separation of the slit images depends on the angular dispersion of the monochromator, the focal length of the focusing lens, and the width of the entrance slit. The actual image depends also on diffraction effects, whose dimensions depend on the numerical aperture of the image-forming cones. The maximum theoretical resolution (band pass, BP) may be calculated as¹²

$$BP = D_L^{-1} * SW$$

where D_L^{-1} is the inverse linear dispersion characteristic of the spectrometer and SW is the mechanical slit width. Linear dispersion is determined by the gratings used in the spectrometer and the geometry of the optical system. Table

2-1 shows the resolution and the slit setting suggested by Stromment¹³ for two main frequencies of the argon ion laser. Both of them are for Spex Model 1401 monochromator only.

Table 2-1. Suggested Slit Settings for Spex Model 1401 Monochromator.

Resolution, cm ⁻¹	Spectral Slit Width in μm for Laser Frequency	
	514.5 nm	488.0 nm
0.5	25-100-25	22-100-22
1.0	50-100-50	45-100-45
2.0	100-100-100	90-100-90
5.0	250-250-250	225-225-225
10.0	500-500-500	450-450-450
20.0	1000-1000-1000	900-900-900

Another factor affecting resolution is scanning speed. For the photon counting(PC) detection mode.¹⁴

$$\text{BP}(\text{cm}^{-1}) > \{\text{scan speed}(\text{cm}^{-1})/\text{min}\} * 4(\text{time constant}) / 60$$

The suggested maxium scan speed for the Spex Model 1401 Monochromator is given by Strommen.¹⁵

The operation of the spectrometer is controlled by Spex CompuDrive (CD2A) via an IBM compatible computer/data acquisition system. It interfaces with the computer

accepting commands from the keyboard to control the scan mode, speed, step, spectral region, etc. It also outputs the spectrometer position and scan status, and accepts trigger inputs. The BASIC program used to control the CD2A is listed in the appendix.

4. Detector

A photomultiplier is one of the most commonly used optical detectors. The detector located at the monochromator exit slit is a RCA 14018 photomultiplier (PM). It can be used to measure radiation in the near ultraviolet, visible, and near infrared regions of the spectrum. With proper techniques which include long integration time, cooling of the photocathode using proper coolant and pulse-height discrimination, the PM tube can be used to detect power levels as low as about 10^{-19} Watts.¹⁶

A PM tube consists of a photocathode, which emits electrons when photons strike it, and a series of dynodes. Each dynode emits a number of secondary electrons when struck by an electron. The potential distribution at dynodes/cathode, which is always biased negatively with respect to ground for photon counting(PC) experiments, will determine how many electrons are given off per photon

striking the cathode, and thus, the total gain or multiplication factor of the tube. The typical voltage difference from dynode to dynode is about 100 Volts. Adding more dynodes and applying higher voltage can increase the number of secondary electrons for each incident photon and reduce the response time of photomultiplier. If the average secondary emission multiplication at each dynode is δ and the number of dynodes is N , the total current multiplication between the cathode and anode is $G=\delta^N$. For typical values of $\delta=5$ and $N=9$, $G\approx 2\times 10^6$.

In practice a high gain PM does not mean it can be used to measure weak signal. The primary limiting factor in PM tube performance is the noise due to background electron perturbation called dark current. This dark current is due to

1. Cathode shot noise. This is due to random thermal excitation of electrons from the surface of cathode as well as excitation by cosmic rays and radioactive bombardment.

2. Dynode shot noise. This is due to the random secondary emission process at the dynodes. The contribution of all the dynodes to the total shot noise output is smaller by a factor of δ^{-1} than that of the cathode.

3. Johnson noise. It due to the thermal noise associated with the output resistance connected across the anode.

One of the effective methods used to reduce the dark current is to thermoelectrically cool the PM tubes. Cooling will reduce the thermal emission from the cathode and the thermal noise from the resistance. The coolant we used in this project is water at room temperature. After cooling the noise was considerably reduced and the sensitivity was increased by about 10^2 .

5. Data Collection And Analysis System

In this experiment we used a data acquisition system to acquire and transfer data into a computer system. The signal produced by the PM tube was very small. We used a Digital Photometer(DPC-2, Spex Industries, Inc., Metuchen, NJ) as a pre-amplifier. It can operate in either DC or photon counting (PC) mode. For the photon counting mode, the average signal is of the order of 10^{-5} V. After being amplified by DPC-2, the signal is of the order of 100 mV. We built an amplifier which amplified the signal from 100 mV to 1V. This analog signal was digitized using an A/D board (model DASH-16F manufactured by Metra byte Corporation,

Stoughton, MA) installed in an AT&T model 6300 PC (an IBM XT clone) with an Intel 8087 math coprocessor. The software packages used in this project are Labtech Notebook (Laboratory Technologies Corporation, Wilmington, MA) and Lotus 1-2-3 (Lotus Development Corporation, Cambridge, MA).

The data flow chart is as Figure 2-4. The computer sends scan parameters such as scan mode, step, start and stop position, etc. After receiving a scan command, the CD2A will start the scan. The scan speed depends on the scan step and the frequency of the trigger signal produced by the computer to control both the scan frequency and the rate of receiving intensity data as well. Thus computer can record the intensity and corresponding position correctly. Using Labtech Notebook, the data is written directly to the computer hard disk. This method is good for a large volume of data but the rate of receiving data can not be higher than 20Hz. Fortunately, low light intensities due to band pass limitation eliminate the need for high data rate. Recorded data are stored as data files using Lotus 1-2-3, and analyzed subsequently.

CHAPTER 3. RAMAN SPECTRUM OF CCl_4

1. Sample and Configuration

The sample of CCl_4 we used was Baker Analyzed Reagent made by J. T. Baker Chemical Co., Phillipsburg, NJ. The sample was held in a glass tube ($\phi=4\text{mm}$) which was cleaned with detergent followed by ethanol rinse to avoid scattering by dust and to reduce the loss of light energy. Figure 3-1 shows the geometry configuration of sample, incident beam, and scattered beam. Selection of the collecting lens should satisfy two conditions:

- It should be as large as possible to collect the most scattered light possible.
- The numerical aperture of the image-forming cone meets the requirement for monochromator getting maximum resolving power.

The incident beam is taken as propagating along z axis. There is an analyzer between the collecting lens and the spectrometer for measuring the depolarization ratio ρ_n .

2. Selection Rules for CCl_4

CCl_4 has a tetrahedral structure with one carbon atom at the center. This structure belongs to point group T_d , i.e., it has three mutually perpendicular two-fold axes and four three-fold axes (point group T). Besides, it has a plane of symmetry σ_d through each pair of three-fold axes, in all, six planes of symmetry. The molecule structure of CCl_4 is shown in Figure 3-2.

The detailed description of the symmetry properties of CCl_4 requires the knowledge of group theory. The character table of T_d is given in Table 3-1.

Table 3-1.Character Table of Point Group T_d

T_d	I	$8C_3$	$6\sigma_d$	$6S_4$	$3C_2$
A_1	1	1	1	1	1
A_2	1	1	-1	-1	1
E	2	-1	0	0	2
F_1	3	0	-1	1	-1
F_2	3	0	1	-1	-1

Along the top are the symmetry elements with the numbers before the symmetry elements giving the number of

the symmetry elements N_e . Along the left are the vibration types or species that correspond to the irreducible representations. The vibration types or species represented are given, according to the symmetry operation.

- A: symmetric with respect to the principal axis of symmetry.
- B: antisymmetric with respect to the principal axis of symmetry
- E: doubly degenerate vibrations.
- F: triply degenerate vibrations.
- g and u (subscripts): symmetric or antisymmetric with respect to a center of symmetry.
- 1 and 2 (subscripts): symmetric or antisymmetric with respect to a rotation axis (cp) or rotation-reflection axis (sp) other than the principal axis or, in those point groups with only one symmetry axis with respect to a plane of symmetry.

The characters in the character table are symbolized by $\chi_i(R)$ and are equal to the trace of transformation matrices of the symmetric operations. $\chi_i(R)$ can be calculated from the molecular structure and the symmetry operation. For the 32

point groups, the character tables have been calculated and can be found in many reference books.¹⁷

As mentioned in Chapter 1, the polarizability tensor is another factor to determine the selection rules. The polarizability is a tensor that has certain transformation properties under symmetry operations. The character $\chi_{\alpha}(R)$ for the transformation of the polarizability tensor for the symmetry operation R is given by Wilson¹⁸, et al., and Bauman¹⁹

$$\chi_{\alpha}(R) = 2 \pm 2 \cos \phi + 2 \cos 2\phi$$

Where ϕ is the rotated angle during symmetry operation. The plus sign is for proper rotations and the minus sign for improper rotations. An improper rotation is a rotation followed by a reflection in a plane which is perpendicular to the axis of rotation. In the case of CCl_4 , only σ_d and S_4 are improper rotations.

It can be proved that a fundamental is Raman active only when the quantity N_i defined is not zero.²⁰

$$N_i = \sum N_e \chi_{\alpha}(R) \chi_i(R)$$

Here N_e is the number of elements in each class and the summation is over all classes. For CCl_4 , N_i can be calculated as follows:

Table 3-2. Calculation of N_i

	I	$8C_3$	$6\sigma_d$	$6S_4$	$3C_2$
N_e	1	8	6	6	3
ϕ	0°	120°	0°	90°	180°
$\pm 2\cos\phi$	2	-1	-2	0	-2
$2\cos 2\phi$	2	-1	2	-2	2
$\chi_{\alpha(R)} = 2\pm 2\cos\phi + \cos\phi$	6	0	2	0	2
$\chi_{A_1(R)}$	1	1	1	1	1
$\chi_{A_2(R)}$	1	1	-1	-1	1
$\chi_E(R)$	2	-1	0	0	2
$\chi_{F_1(R)}$	3	0	-1	1	-1
$\chi_{F_2(R)}$	3	0	1	-1	-1
N_{A_1}	$1*6*1+8*0*1+6*2*1+6*0*1+3*2*1=24$				
N_{A_2}	$1*6*1+8*0*1+6*2*(-1)+6*0*(-1)+3*2*1=0$				
N_E	$1*6*2+8*0*(-1)+6*2*0+6*0*0+3*2*2=24$				
N_{F_1}	$1*6*3+8*0*0+6*2*(-1)+6*0*1+3*2*(-1)=0$				
N_{F_2}	$1*6*3+8*0*0+6*2*1+6*0*(-1)+3*2*(-1)=24$				

From the above calculation, A_2 and F_1 are not allowed in a Raman spectrum and therefore Raman inactive, whereas A_1 , E and F_2 are Raman active. Therefore, three fundamentals should appear in the Raman spectrum of CCl_4 . Our experiments

are in excellent agreement with this result. We have observed three lines at 459cm^{-1} , 315cm^{-1} and 213cm^{-1} shown in Figures 3-3 through 3-8. The lines at 760cm^{-1} and 790cm^{-1} shown in Figure 3-8 are overtones.

3. Isotope Effect

The high resolution spectrum of the line at 459cm^{-1} shown in Figure 3-4, indicates the presence of a fine structure, with three separate lines readily visible. The isotope effect can explain the existence of this fine structure. There are two types of chlorine atoms in bound nature, Cl^{35} and Cl^{37} . The abundance and atomic masses of these two isotopes are²¹:

	<u>% Natural abundance</u>	<u>Atomic mass (u)</u>
Cl^{35}	75.77	34.968852
Cl^{37}	24.33	36.965903

Combinations of Cl^{35} and Cl^{37} give five isotopically different CCl_4 molecules. The relative abundance of every kind of CCl_4 can be calculated as follows:

$$\begin{aligned}
\text{CCl}_4^{35}: (75.77\%)^4 * C_4^4 &= 0.3296 \\
\text{CCl}_3^{35}\text{Cl}^{37}: (75.77\%)^3 * (24.23\%) * C_4^3 &= 0.4216 \\
\text{CCl}_2^{35}\text{Cl}_2^{37}: (75.77\%)^2 * (24.23\%)^2 * C_4^2 &= 0.2022 \\
\text{CCl}^{35}\text{Cl}_3^{37}: (75.77\%) * (24.23\%)^3 * C_4^1 &= 0.0431 \\
\text{CCl}_4^{37}: (24.23\%)^4 * C_4^0 &= 0.0034
\end{aligned}$$

Here $C_m^n = \frac{m!}{(m-n)!n!}$ is the combination. Since the intensity of scattered light is proportional to the number of molecules, the molecules $\text{CCl}^{35}\text{Cl}_3^{37}$ and CCl_4^{37} are not abundant enough to be observed. So only three lines appear in the Raman spectrum. In our intensity measurements we observed the intensity ratios of the three lines as 3:4:2, in excellent agreement with the calculation.

The mass difference between two isotopes is so small that we can think of it as a perturbation. The vibrational frequency can be calculated classically as

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

so
$$df = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \left(-\frac{dm}{2m} \right) = -f_0 \frac{dm}{2m}$$

Minus sign means the frequency will decrease when mass increases. The frequency shift between CCl_4^{35} and CCl_4^{37} is

$$df = -459 * \frac{2}{2 * 35} = 13.1 \text{cm}^{-1}$$

The spacing for the five possible lines is about $13.1/5=2.6 \text{cm}^{-1}$. This also agrees with our experimental result (Figure 3-4).

4. Intensities and Polarization Properties

From quantum theory, we know that for any molecule there is a large number of possible energy states. In thermal equilibrium the molecules will distribute among these possible levels according to Boltzmann distribution:

$$N_e = N_0 e^{-E/kT}$$

where N_e is the number of molecules in the state with energy E . Under the influence of the electromagnetic field, the number of molecules available for Stokes scattering will be larger than that for anti-Stokes scattering. Thus the intensities of Stokes and anti-Stokes lines are also given according to the Boltzmann distribution.

$$\frac{I_{\text{Stokes}}}{I_{\text{anti-Stokes}}} = \frac{N_m}{N_n} = \frac{g_m e^{-E_m/kT}}{g_n e^{-E_n/kT}} = \frac{g_m}{g_n} e^{-(E_m - E_n)/kT}$$

Here the subscript m and n are for ground and upper level states, respectively. g_m and g_n are the degeneracies

of the ground and upper level states. For line at 459cm^{-1} , both ground and upper levels are nondegenerate and $g_m=g_n=1$.

Since $E_n - E_m = \hbar\omega_s = hc/\lambda$ we have $\frac{I_{\text{Stokes}}}{I_{\text{anti-Stokes}}} = e^{\left(\frac{hc}{\lambda}\right)/kT}$.

For $1/\lambda = 459\text{cm}^{-1}$, $T = 300\text{K}$, $I_{\text{Stokes}}:I_{\text{anti-Stokes}} = 9.1$. From Figure 3-3, it can be seen that our experimental result agrees well with this calculation.

There are many factors which influence the observed Raman intensities. Most of the factors depend upon the characteristics of the particular spectrometer system used.

1. The absorbance of the sample.
2. The variation in sensitivity of the photomultiplier detector as a function of frequency.
3. The variation of the monochromator transmission as a function of frequency.
4. The effect of recorder response and scan rate.

Due to the above reasons the determination of the absolute intensities of Raman lines is difficult. In our experiments, measurements of relative intensities instead of absolute intensities were made, as is often found in the literature. Figure 3-3 through Figure 3-8 show the

experimental results we obtained. Some figures consist of two lines corresponding to I_x and I_z . The figures show that the line at 459cm^{-1} is totally polarized. Thus it must belong to symmetric species A_1 .

CHAPTER 4. RAMAN SPECTRUM OF SILICON AND GERMANIUM

1. Sample and Configuration

The sample of Ge we used was from Crystal Specialties, Intl.. The dopant was Antimony. The carrier concentration was not available. The sample of Si was p-type. The dopant and carrier concentration were not available. Both Ge and Si are single crystal. The orientations are $\langle 100 \rangle$ off $6\langle 111 \rangle \pm 0.5^\circ$.

Si and Ge are opaque for argon laser lines at $\lambda=488\text{nm}$ and 514.5nm . Consider a photon incident on a semiconductor. If the energy of photon is smaller than the band gap, there is no absorption in the material and the light will pass through the solid except for reflection. If the energy of the photon is larger than the band gap of the semiconductor, the light can excite electron from the valence band to the conduction band. Therefore, some of the incident light will be absorbed. For Si and Ge, their band gaps are 1.12eV and 0.66eV . If we use laser line 488nm or 514.5nm , the photon energies are 2.54eV or 2.41eV , which are larger than the

band gaps of Si and Ge, thus the laser lines will be absorbed.

Since this absorption makes it difficult to obtain Raman spectra of Si and Ge using transmission geometry, we used reflection geometry in this experiment. The different geometries used in this experiment are shown in Figure 4-1 (a) and (b). We select a coordinate system such that the z-axis is always vertical and the y-axis is along the observation direction. The sample was set at origin in x-z plane. Figure 4-1 (a) shows the backscattering geometry. The incident beam propagates along -y direction. There is a small mirror in front of the sample. The incident laser beam is reflected back along the same path it incidents. The scattered light is collected by a lens. The observation direction is along y-direction. Figure 4-1(b) shows right angle scattering geometry. The angle between incident and reflected beams is 90° , and observation is along the +y-direction.

2. Raman Effect in a Solid

Raman measurements, like infrared measurements, can be used to determine the frequencies of the $k=0$ phonons. When an incident photon interacts with the crystal lattice, it

will change to a new photon and create or annihilate a phonon. Let the incident light have energy and momentum $\hbar\omega_i$ and k_i , the scattered light have energy and momentum $\hbar\omega_s$ and k_s , and a phonon has energy $\hbar\omega$ and momentum k . Conservation of energy and crystal momentum require that

$$\omega_i = \omega_s \pm \omega \quad \text{and} \quad k_i = k_s \pm k$$

where the plus sign refers to the annihilation of a phonon which gives anti-Stokes lines, the minus sign refers to the creation of a phonon which gives Stokes lines. From energy conservation, we can see that the frequency shift between incident and scattered photons gives the frequency of the phonon.

There are two types of phonons in solids: optical phonons and acoustic phonons. For the acoustic phonon, the atoms in each unit cell are moving in phase as in a sound wave. Its dipole moment does not change with time; therefore, the acoustic phonon does not interact with a photon. For the optic phonon, the atoms in each unit cell are moving in opposite directions simultaneously, and if the atoms have opposite charges, this motion will create a changing dipole moment. Therefore, the optical phonon can interact strongly with a photon.

The k-vector of light is very much smaller than the dimension of the Brillouin zone. For the argon ion laser ($\lambda=488\text{nm}$) the wave vector is $k=2\pi/\lambda\approx 2\pi/488\text{nm}\approx 1.3\times 10^5\text{cm}^{-1}$. The dimension of the Brillouin zone is $k_{\text{max}}=2\pi/a\approx 2\pi/0.5\text{nm}=1.3\times 10^8\text{cm}^{-1}$. The k-vector is a factor 10^3 larger than the dimension of the Brillouin zone. From the phonon dispersion curve, the plot of ω vs. k for light is essentially a vertical line starting at the origin (Figure 4-2). Thus from the conservation of crystal momentum, light interacts only with optic phonons that have $k\approx 0$.

In most cases, Raman scattering in solids is a one-phonon process, that is, during the scattering only one phonon is emitted or absorbed. However, it is possible to have a two-phonon process. From quantum theory calculations, a two-phonon Raman process is a higher order process. Its matrix elements are much smaller than that of the one-phonon process in most cases.

From Raman scattering, we also can measure the lifetime of the phonon. The profile of every spectral line has a finite width and characteristic shape. The width of the spectral line is determined by following factors.

1. Instrument broadening due to the width of the entrance slit of spectrometer.

2. Natural width due to the uncertainty principle. This line shape has a Lorentzian distribution, and

$$\Delta E \cdot \Delta t = \hbar \Delta \omega \cdot \tau = \hbar$$

$$\Delta \omega = 1/\tau$$

where τ is the lifetime of phonon.

3. Collision broadening due to the interaction of neighboring molecules. This line shape also has a Lorentzian distribution. Its half width has a small temperature dependence²²:

$$\Delta \omega_{1/2}(\text{collision}) \propto T^{3/10}$$

Among those factors, instrument broadening can be reduced by reducing the width of the entrance slit. The collision broadening can be reduced by lowering the temperature (300K in our experiment). We reduced the width of entrance slit to minimum without losing the signal. Thus we consider the real line shape includes two parts: natural and collision widths.

Klemens²³ and Cowley²⁴ calculated the phonon lifetime using the same physical idea but different mathematical methods. They considered one optical phonon to decay into two acoustical phonons. At $T=0$ K, Klemens gives

$$1/\tau = 0.007\omega_0$$

From $\Delta\omega = 1/\tau$ and $\omega = 2\pi c/\lambda$ we get

$$\Delta(1/\lambda) = 0.007 (1/\lambda)$$

The temperature factor given by Klemens is $1 + 2/(e^x - 1)$, where $x = \hbar\omega_0/2kT$ and ω_0 is the frequency of phonons.

Our measured results for Si and Ge are shown in Figures 4-4 through 4-6. The results given by Klemens' calculation at 300K and the results reported by Parker²⁵ are shown in Table 4-1 and compared with our experimental results.

Table 4-1. Experimental Results

	$(1/\lambda)_{\text{Si}}$	$(1/\lambda)_{\text{Ge}}$	$\Delta(1/\lambda)_{\text{Si}}$	$\Delta(1/\lambda)_{\text{Ge}}$
our results (cm^{-1})	521.0 ± 0.5	300.0 ± 0.5	7.1 ± 0.3	5.0 ± 0.3
Klemens' calculation (cm^{-1})			6.6	4.0
Parker's results (cm^{-1})	520.2 ± 0.5	300.7 ± 0.5	4.6	5.3

Our experimental results are in good agreement with the reported results and the theoretic calculation.

CHAPTER 5. CONCLUSION

This Thesis work developed an experimental system, the first of its kind in Physics Department of San Jose State University, to measure the Raman spectrum from liquid and solid samples. It is ready to measure other liquid and solid samples. The only change needed is the sample handling part. The data obtained from this experiment can be used as a basis to perform further research work.

There are some improvements of this system that can be made for better performance. The Raman lines are sensitive to temperature. A temperature control system for controlling the temperature of sample is recommended. Since the width of the Raman lines decrease when temperature decreases, the low temperature experimental set up (i.e., cryostat) is recommended. Another difficulty in this experiment is the low intensity. There are two possible ways to improve the sensitivity of the system. One way is to change the coolant of the photo multiplier, such as liquid nitrogen, instead of tap water. The another way is to change the amplifier after the photomultiplier. A high gain and low noise amplifier will increase the signal-noise ratio. With these

improvements, this system can be used to study a variety of specimens including solids and liquids.

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APPENDIX: Program for control CD2A. This program
provide the input information and scan command.

```
10 OPEN "com1:1200"AS#1
20 STX$=CHR$(2):ETX$=CHR$(3):CAN$=CHR$(24):ACK$=CHR$(6)
30 EOT$=CHR$(4):NAK$=CHR$(21):NUL$=""
40 PRINT"ENTER YOUR CHOICE:"
50 PRINT"1. START POSITION."
60 PRINT"2. END POSITION."
70 PRINT"3. BURST INCREMENT."
80 PRINT"4. CONTINUOUS SCAN RATE."
90 PRINT"5. DWELL TIME."
100 PRINT"6. REP SCAN."
110 PRINT"7. SCAN DELAY."
120 PRINT"8. LASER LINE."
130 PRINT"9. SCAN TYPE."
140 PRINT"10. SCAN."
150 INPUT CHOICE
160 ON CHOICE GOSUB 170, 180, 190, 200, 210, 220, 230,
    240, 250, 290
170 PRINT"START POSITION=?":
    INPUT VALUE$:A$=STX$+"ST"+VALUE$+ETX$:GOTO 270
180 PRINT"END POSITION=?":
    INPUT VALUE$:A$=STX$+"EN"+VALUE$+ETX$:GOTO 270
```

```

190 PRINT"INC/RATE=?":
      INPUT VALUE$:A$=STX$+"BI"+VALUE$+ETX$:GOTO 270
200 PRINT"CONTINUOUS SCAN RATE=?":
      INPUT VALUE$:A$=STX$+"SR"+VALUE$+ETX$:GOTO 270
210 PRINT"DWELL TIME=?":
      INPUT VALUE$:A$=STX$+"DT"+VALUE$+ETX$:GOTO 270
220 PRINT"REP SCAN=?":
      INPUT VALUE$:A$=STX$+"NS"+VALUE$+ETX$:GOTO 270
230 PRINT"SCAN DELAY=?":
      INPUT VALUE$:A$=STX$+"SD"+VALUE$+ETX$:GOTO 270
240 PRINT"LASER LINE=?":
      INPUT VALUE$:A$=STX$+"LL"+VALUE$+ETX$:GOTO 270
250 PRINT"SCAN TYPE=? C FOR CONTIUE AND B FOR BURST
      MODE.":
      INPUT VALUE$:A$=STX$+"TY"+VALUE$+ETX$:GOTO 270
260 A$=CAN$+"S"+ETX$
270 PRINT #1, A$
280 GOTO 40
290 A$=CAN$+"S"+ETX$
300 PRINT #1, A$
310 END

```


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Figure 2-1. Basic arrangement of experimental set up.

Figure 2-2. Discharge lines from argon ion laser.

Laser line is at 488nm.

Slits setting: 20 μ m/40 μ m/20 μ m.

Scan speed: 50cm⁻¹/min.

Figure 2-3. Monochromator layout.

Figure 2-4. Data flow chart.

Figure 3-1. Optical geometry for CCl₄ Raman measurements.

Figure 3-2. Molecular structure of CCl₄.

Figure 3-3. Spectrum of CCl₄.

Laser line: 488nm, which is not shown in this Figure.

Slits setting: 50 μ m/100 μ m/50 μ m.

Scan speed: 100cm⁻¹/min.

Figure 3-4. Spectrum of CCl₄.

Laser line: 488nm.

Slits setting: 20 μ m/40 μ m/20 μ m.

Scan speed: 2cm⁻¹/min.

Figure 3-5. Spectrum of CCl₄.

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Scan speed: 10cm⁻¹/min.

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Scan speed: $5\text{cm}^{-1}/\text{min}$.

(a)

(b) Stokes case

(c) anti-Stokes case.

Figure 1-1. Vibrational states involved in Raman scattering.

Figure 2-1

Figure 2-2.

Figure 2-3. Monochromator.

Fig. 2-4. Data Flow Chart.

Figure 3-1. Optical geometry for CCl_4 .

Figure 3-2. Molecule structure of CCl_4

Figure 3-3

Figure 3-4

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Figure 3-8

(a) Backscattering geometry.

(b) Right angle geometry.

Figure 4-1.

Figure 4-2. Phonon dispersion curve.

Figure 4-3. Crystal structure of Si, Ge.

Figure 4-4

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Figure 4-6