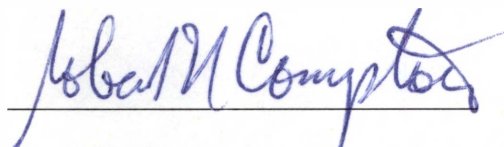


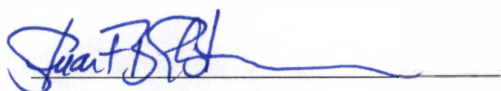
To the Graduate Council:

I am submitting herewith a thesis written by E. Darren Ellis entitled "Raman Under LN₂: A Simple Approach to Low Temperature Raman Spectroscopy." I have examined the final paper copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Physics.



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Raman Under LN₂: A Simple Approach to Low Temperature Raman Spectroscopy

A Thesis

Presented for the

Master of Science Degree

The University of Tennessee, Knoxville

E. Darren Ellis

May 2005

Dedication

To my family, and especially my
wife Kathryn, for their love and
support throughout this endeavor.

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Abstract

Conventional low temperature Raman Spectroscopy techniques utilize expensive equipment to cool a sample to 77° K. In this work, a new technique for performing Raman Spectroscopy at liquid nitrogen temperatures is presented. This technique of taking data with the sample placed under liquid nitrogen provides a low cost alternative to conventional methods, and can be utilized by any lab with a Raman spectrometer without the purchase of additional equipment. Representative spectra for CCl₄, C₆₀, and Single Wall Carbon Nanotubes at room temperature and under liquid nitrogen are shown and compared as validation of the utility of this technique.

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Chapter 1

Introduction

This thesis will attempt to outline the basic tenets of Raman spectroscopy and provide an introduction to a new method for performing Raman spectroscopy: Raman under liquid nitrogen (RUN). We will then qualitatively look at the Raman spectra obtained for Carbon Tetrachloride (CCl_4), C_{60} , and Single Wall Carbon Nanotubes (SWCNTs) both at room temperature and cooled to 77°K (sample under liquid nitrogen) as a verification of the usefulness of this technique. A comparison will be made to literature values and analysis will be presented to explain some of the resolved peaks seen with this technique. In addition, analysis will be presented to show that the isotopically resolved peaks in carbon tetrachloride follow a binomial distribution in peak intensities due to the natural abundances of chlorine isotopes.

1.1 Raman Spectroscopy

Raman spectroscopy has become a standard tool in the study of vibrational and rotational properties of molecules. Theoretically predicted in 1923 by A. Smekal, this inelastic scattering process was experimentally verified by C.V. Raman in 1928 for which he was awarded the Nobel Prize in 1930. In his discovery of the spectroscopy which bears his name, Raman used the Sun as the light source. Early Raman experiments utilized water-cooled low-pressure mercury arc light sources and

photographic plates to record spectra. The advent of high power monochromatic lasers in the 1960s has propelled Raman spectroscopy to a common laboratory technique used today for probing the molecular structure of liquid, solid, and gaseous samples. In addition, the advent of double and triple monochrometers, as well as the use of charge-coupled device arrays (CCDs), has increased the efficiency and resolution of modern experiments in Raman spectroscopy. In fact, prior to the mid-1980s, the application of Raman spectroscopy as a useful analytical tool was impeded by technical issues such as detection efficiency and inefficient light collection techniques.¹ This is certainly a field of science that has benefited greatly by advances in modern technology.

1.2 Raman Versus IR Spectroscopy

Infrared and Raman spectroscopy both provide rotational and vibrational information about molecules, however, the information is often complementary due to the vastly different mechanisms by which each process occurs and the effectiveness by which the photon energy is transferred to the molecule. Additionally, rotations occur at a much lower energy than vibrations and result in a fine structure superimposed on a vibrational band. For the purpose of the work presented in this thesis, rotational effects can be neglected, since for solutions or solids, the energy levels due to rotations are broadened and the fine structure is not observable. In infrared spectroscopy, the intensity of the spectrum obtained depends on how effectively the incident photon energy is transferred to the internal motions of the molecule. This is determined, in large part, by the change in the dipole moment that results from the

molecular vibration. This phenomenon is an absorption process and inherently a single photon event. Infrared spectra are typically collected by measuring the transmittance or reflection of light impinging on a sample. The frequency of the absorption peaks corresponds to the difference between the ground state of the molecule and the excited vibrational state. In contrast, Raman scattering is due to a change in the polarizability of a molecule. Interaction of the incident radiation induces a dipole moment in the molecule. It is the radiation emitted by the induced dipole moment that corresponds to the Raman information that is detected. Thus, the Raman effect is a scattering process and corresponds to a two-photon event. The cross-section for Raman scattering is typically much smaller than that for IR absorption, hence, Raman signals can be difficult to detect from background effects without the use of sensitive detectors. In addition, the scattered light is close in frequency to that of the incident light making it difficult to separate the two signals.

An interesting observation can be made regarding Raman and IR active transitions for molecules with a center of symmetry known as the Rule of Mutual Exclusion. That is, Raman active transitions are disallowed in the Infrared spectrum and likewise, transitions that are allowed in the IR are disallowed in the Raman spectrum. This observation does not, however, mandate that all transitions which are disallowed in the Raman spectrum automatically occur in the IR spectrum; in fact, some transitions may be disallowed in both. These are termed silent modes.

For all molecules without a center of symmetry, with the exception of a few rare point groups (D_{5h} , D_{7h} , O and T_h), there are transitions that are allowed to occur in

both the Raman and IR spectrum.² It is important to note that all molecules will exhibit a Raman spectrum, including homo-nuclear diatomic molecules.

1.3 The Theory of Raman Spectroscopy

In Raman spectroscopy, the intensity of the spectrum depends, among other things, upon the effectiveness by which the incident photon can cause a change in polarizability during the molecular vibration. When a molecule is placed in an external electric field, such as from an incident laser beam, the fundamental charges present will experience forces exerted on them in opposite directions, the positive core of the molecule will experience a force in the direction of the electric field while the negatively charged electron cloud will experience a force anti-parallel to the electric field. If the incident electric field is not strong enough to ionize the molecule, the system will reach a balance where the molecule is left polarized, and will possess an induced dipole moment given by Eq. (1.1),

$$\mathbf{p} = \alpha \mathbf{E} \quad (1.1)$$

where $\mathbf{p}$ is the induced dipole moment, α is the polarizability, and $\mathbf{E}$ is the incident electric field. It is this change in polarizability which determines whether a vibration will be Raman active.

When electromagnetic radiation is incident upon a molecule, the electric field of the radiation varies as,

$$\mathbf{E} = \mathbf{E}_0 \cos(2\pi\nu_0 t) \quad (1.2)$$

where E_0 is the maximum value of the electric field, ν_0 is the frequency of the incident radiation, and t is time. By substituting Eq. (1.2) into Eq. (1.1) we have the following,

$$\mathbf{p} = \alpha \mathbf{E}_0 \cos(2\pi\nu_0 t) \quad (1.3)$$

and hence the incident radiation induces an oscillating dipole moment which has the same frequency as the incident radiation. Since certain vibrations and rotations can cause the polarizability to vary in a molecule, we can approximate α for small vibrations by writing its Taylor series expansionⁱ,

$$\alpha = \alpha_0 + Q \frac{\partial \alpha}{\partial Q} + \frac{Q^2}{2!} \frac{\partial^2 \alpha}{\partial Q^2} + \dots \quad (1.4)$$

where α_0 is the polarizability at equilibrium, Q is the normal coordinate of the system, and the first derivative gives the rate of change of the normal coordinate as measured at the equilibrium position. Second derivative and higher order terms can be neglected in the harmonic approximation. The normal coordinate undergoes oscillation given by,

ⁱ $f(x) = f(0) + x f'(0) + \frac{x^2}{2!} f''(0) + \frac{x^3}{3!} f'''(0) + \dots + \frac{x^n}{n!} f^{(n)}(0) + \dots$

$$Q = Q_0 \cos(2\pi\nu_v t) \quad (1.5)$$

where Q_0 is the maximum value for Q , and ν_v is the frequency of vibration of the normal coordinate due to the incident radiation. Substituting the expression for the normal coordinate, Eq. (1.5), into the expansion for the polarizability, Eq. (1.4), we have the following,

$$\alpha = \alpha_0 + Q_0 \cos(2\pi\nu_v t) \frac{\partial \alpha}{\partial Q} + \dots \quad (1.6)$$

Substitution of this value of the polarizability into the equation for the changing dipole (Eq. (1.3)) yields,

$$p = \alpha_0 E_0 \cos(2\pi\nu_0 t) + E_0 Q_0 \cos(2\pi\nu_0 t) \cos(2\pi\nu_v t) \frac{\partial \alpha}{\partial Q} + \dots \quad (1.7)$$

Neglecting second order and higher terms and invoking the angle-sum and angle-difference relationsⁱⁱ we can write the expression as,

$$p = \alpha_0 E_0 \cos(2\pi\nu_0 t) + \frac{\partial \alpha}{\partial Q} \frac{Q_0 E_0}{2} [\cos(2\pi(\nu_0 - \nu_v)t) + \cos(2\pi(\nu_0 + \nu_v)t)] \quad (1.8)$$

ⁱⁱ Angle-Sum Relation $\cos(\alpha + \beta) = \cos(\alpha)\cos(\beta) - \sin(\alpha)\sin(\beta)$

Angle-Difference Relation $\cos(\alpha - \beta) = \cos(\alpha)\cos(\beta) + \sin(\alpha)\sin(\beta)$

It can be seen from this equation that the induced dipole moment can vary with three distinct frequency components. The first term in Eq. (1.8) gives rise to Rayleigh scattering, the elastic scattering process in which the scattered radiation is the same frequency as that of the incident radiation. The second and third terms correspond to Raman scattering, where the inelastic scattering of the incident radiation is at frequencies above and below that of the incident radiation. Frequencies scattered above the Rayleigh line are known as anti-Stokes lines and frequencies scattered below are known as Stokes lines.³ Fig. (1.1) gives a graphical representation of these processes with a quantum mechanical energy level diagram. Initially, most of the molecules exist in either the ground state ($v=0$, most highly populated) or the lowest excited vibrational state ($v = 1$). The scattering process involves promotion to virtual states and the frequency shifts in the Raman spectrum from the Rayleigh line correspond to vibrational energy levels in the molecule. The classical model predicts equal intensities for the Stokes and anti-Stokes lines. By inspection of the energy level diagram in Fig. (1.1) it can be seen that the intensity of the Stokes lines, in general (i.e. room temperature), will be stronger than the anti-Stokes lines since population of the ground state will be higher than that of the excited vibrational state. Indeed, this is the observed case in Raman Spectra. For a non-degenerate vibration the ratio of the anti-Stokes lines to the Stokes lines is given by,

$$\frac{I_A}{I_S} = \left(\frac{\nu_o + \nu_v}{\nu_o - \nu_v} \right)^4 e^{\left(\frac{-h\nu_v}{kT} \right)} \quad (1.9)$$

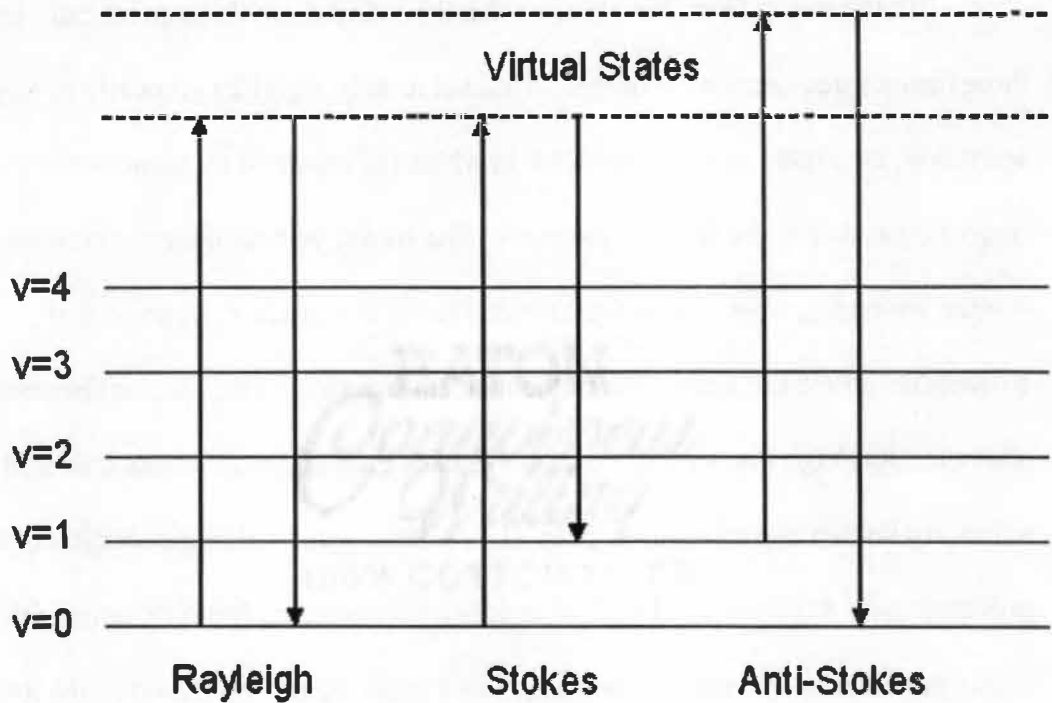


Figure 1.1 Schematic representation of Rayleigh scattering and Raman Stokes/anti-Stokes transitions.

where h is Planck's constant, k the Boltzman constant, and T is the absolute temperature in degrees Kelvin. Thus, measurements of the Stokes and anti-Stokes intensities can be employed to determine the temperature of the sample or access the heating effects of the laser irradiation.

In its most general form, the polarizability may be represented by a symmetric tensor,

$$\alpha \rightarrow \alpha_{ij} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{bmatrix} \quad (1.10)$$

This is important for molecules which are anisotropic, where the polarizability may yield different values along orthogonal coordinate directions and hence the induced dipole moment may not be parallel to the incident electric field. Exploiting the polarizability conditions for Raman spectroscopy, depolarization studies can be conducted on isotropic and anisotropic molecules to gain further insight into molecular structure. The depolarization ratio is given as,

$$\rho = \frac{I_{\perp}}{I_{\parallel}} \quad (1.11)$$

where $I_{\perp}$ and $I_{\parallel}$ are defined as the intensities of the scattered radiation perpendicular and parallel to the plane of observation. For symmetric vibrations the depolarization ratio will be approximately zero but can fall within the range $0.75 \geq \rho \geq 0$, however, for totally non-symmetric vibrations the depolarization ratio will be approximately 0.75.⁴ In the experiments to be reported in this thesis, all of the data is collected in back reflection mode and effects of polarization are not studied.

1.4 Selection Rules

The symmetry of a molecule dictates whether a particular vibrational mode will be Raman active or not. In particular, there must be a change in the polarizability during a vibration as shown by the Raman transition moment, R , Eq. (1.12):

$$R = \int \psi_m^* \left[(r - r_e) \left(\frac{\partial \alpha}{\partial r} \right)_e \right] \psi_n d\tau \quad (1.12)$$

where ψ_m and ψ_n are the initial and final states, r and r_e represent the internuclear separation and bond length, and the integration is carried out over all space, $d\tau$. For the transition moment, R , to be non-zero, the product of the initial state, polarizability, and final state must be totally symmetric. Inactive Raman transitions correspond to $R = 0$. Additionally, Raman scattering for the fundamental vibrational modes require that the condition $\Delta v = \pm 1$ be satisfied. Alternatively stated, overtone transitions are not observed in Raman spectra.

Additional methods to determine whether a transition is Raman active or not include the use of group theory while considering the symmetry properties of the polarizability and transition states as well as the visual technique of envisioning a polarizability ellipsoid and its change in shape arising from a vibration. The tensor of Eq. (1.10) can be conceived as a polarizability ellipsoid, as seen in Eq. (1.13):

$$\frac{x^2}{\alpha_{xx}^2} + \frac{y^2}{\alpha_{yy}^2} + \frac{z^2}{\alpha_{zz}^2} + \frac{2xy}{\alpha_{xy}^2} + \frac{2yz}{\alpha_{yz}^2} + \frac{2zx}{\alpha_{zx}^2} = 1 \quad (1.13)$$

Fig. (1.2) illustrates the usefulness of the polarizability ellipsoid in determining whether a vibration is Raman active for the H_2O molecule. In general, the vibration will be Raman active if the size, shape, or orientation of the polarizability ellipsoid changes during a vibration. As seen in Fig. (1.2), all three fundamental vibrations are Raman active. Its ν_1 vibration is Raman active because the size of the polarizability

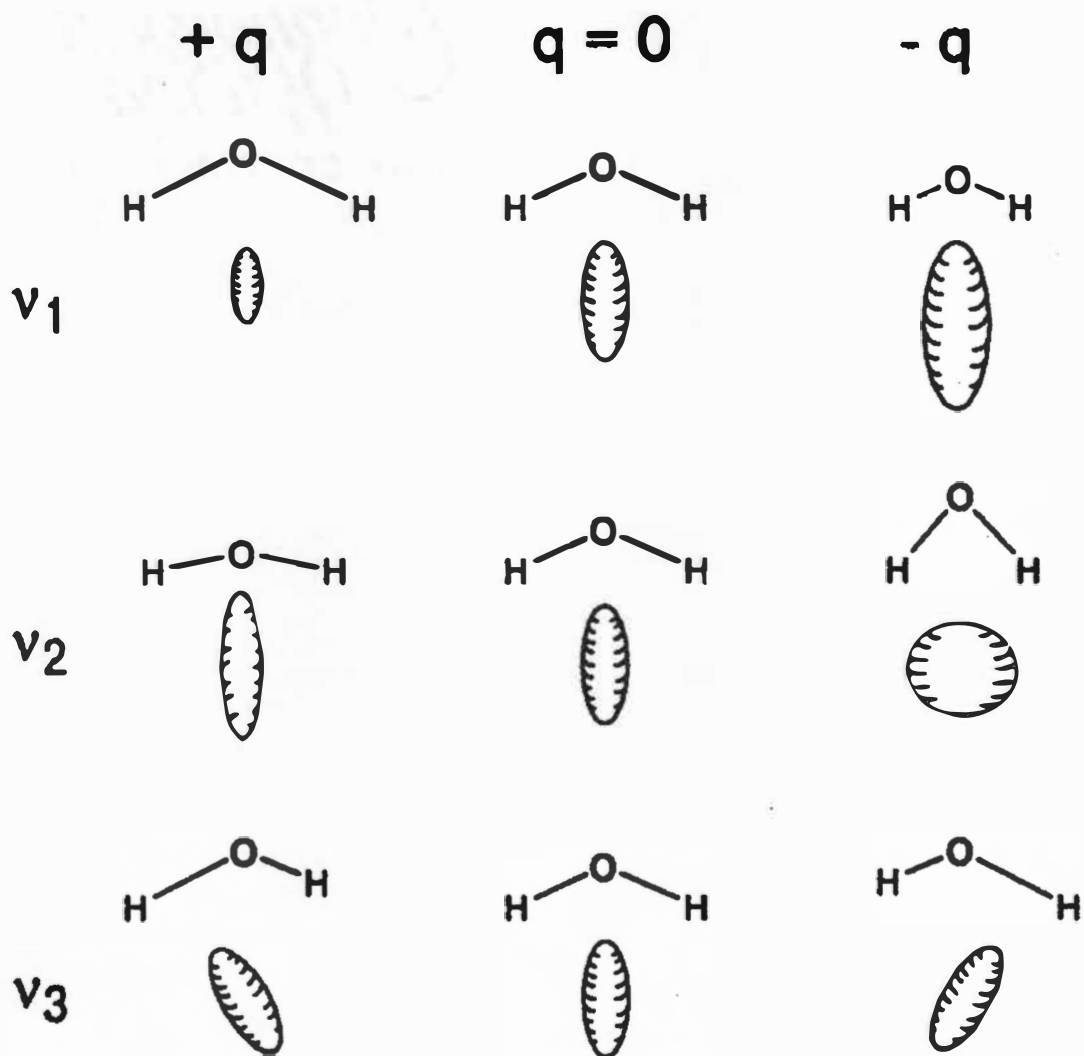


Figure 1.2 Polarizability ellipsoid for the H_2O molecule.²

ellipsoid changes during the vibration. The H_2O molecules' ν_2 vibration is Raman active since the shape of the polarizability ellipsoid changes during the vibration, and finally, the ν_3 vibration is Raman active because the orientation of the polarizability ellipsoid changes during the vibration.

Chapter 2

Raman Under Liquid Nitrogen – (RUN)

2.1 Benefits of RUN

Obtaining Raman spectra under liquid nitrogen has several advantages to the standard practice of employing samples in ambient air at room temperature. Samples are often damaged by overheating and oxidation effects, a problem common with micro-Raman spectroscopy where the excitation laser is focused onto the sample surface at higher laser fluence. Also, line broadening can occur due to ro-vibrational population and concomitant hot band transitions. By having the sample under the inert atmosphere of liquid nitrogen, the oxidation effects are greatly reduced and the sample integrity remains for a much longer time compared to operating at room temperature. Also, by cooling the sample to 77°K, initial ro-vibrational population and hot band transitions are greatly reduced resulting in markedly narrower line peaks and the ability to resolve isotopic effects in some bands.⁵ In some cases a molecule may exist in more than one conformation whose energy difference is small enough that both are populated at room temperatures. Cooling to 77°K can reduce the higher energy conformation to essentially zero.

The RUN technique was performed utilizing both the macro stage as well as the micro-Raman stage of the Dilor Spectrometer. While both techniques yield better results with RUN, the data in this thesis were collected with the micro-Raman stage only. The Dilor XY 800 Spectrometer incorporates a confocal microscope. The

objective lens of the microscope is used to collect the scattered light from the sample under investigation. The confocal optics yield better depth discrimination by allowing the precise collection of scattered light from specific depths within the sample. While the power of this technique is obvious for standard micro-Raman spectroscopy, it does not necessarily pose the most useful conditions for use with RUN. Due to the differing index of refraction ($n=1.207$) and thermal gradients occurring in the liquid nitrogen, the scattered light from the sample under investigation is dispersed at different angles as compared to the sample in air only. This ultimately results in a decrease in the efficiency of the collected Raman scattered light. To counteract this effect, the confocal aperture of the microscope stage is opened as large as possible, thereby increasing the total depth of scattered light collected. While this negates the power of the ability to discriminate between the depth of focus in a sample, in the ensuing chapters, the increase in spectral resolution will become apparent.

Clearly, the power of RUN comes from the use of the liquid nitrogen itself and the protection and benefits it affords to the sample under investigation. The ability to use liquid nitrogen is precipitated by its narrowness and precise location in the Raman spectrum, Fig. (2.1). The peak at 2328.2 cm^{-1} is due to $^{14}\text{N}_2$, while the small peak at 2290.2 cm^{-1} is attributed to isotopic nitrogen, $^{14}\text{N}^{15}\text{N}$. The main liquid nitrogen line itself possesses a very narrow full width at half maximum value of approximately 0.067 cm^{-1} , much smaller than the resolution of high resolution Raman Spectrometers.⁶ The narrowness and precise location of the liquid nitrogen line makes it an excellent calibration source. Data obtained in this thesis were calibrated using a neon lamp source.

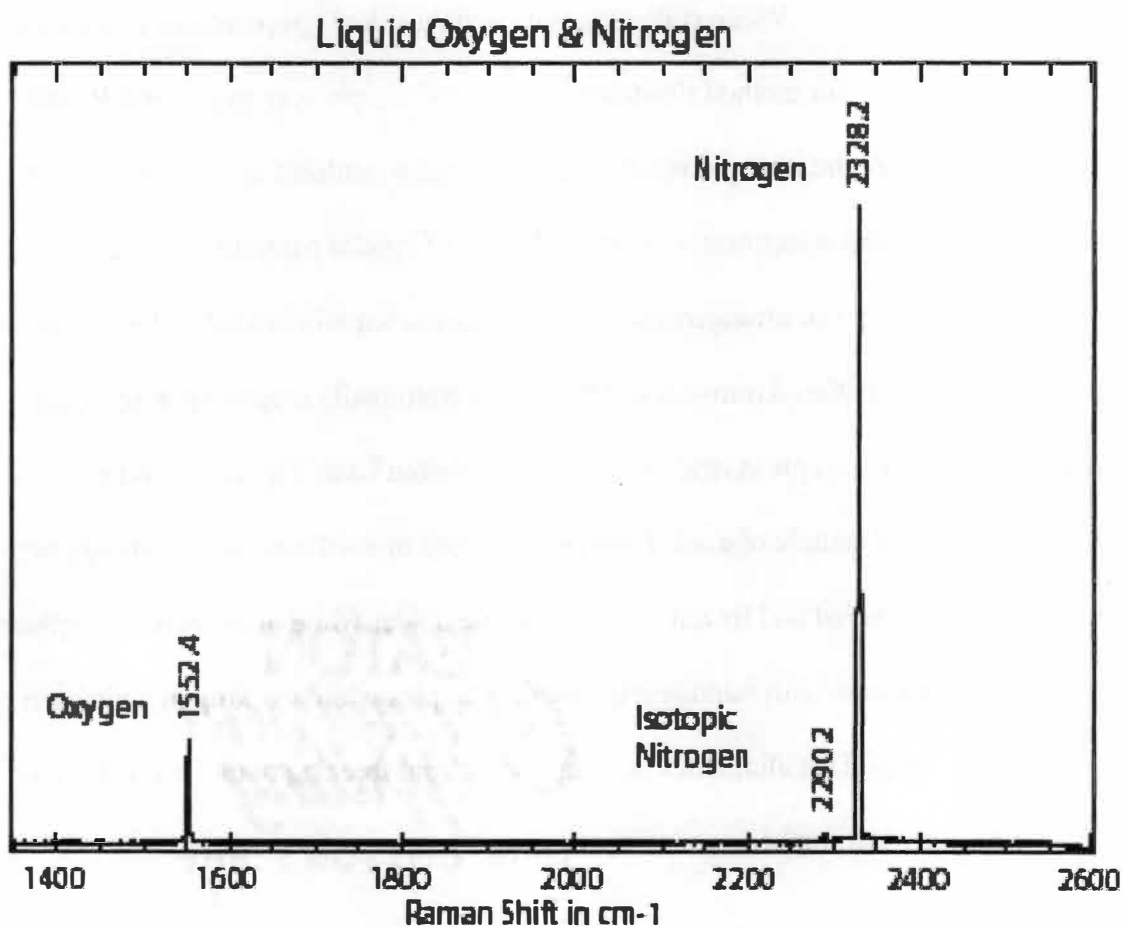


Figure 2.1 Raman spectrum of liquid nitrogen containing a small amount of liquid oxygen.⁷

2.2 RUN Experimental Details

In addition to running spectra at room temperature, we have developed a method of cooling samples by placing them under liquid nitrogen while collecting their Raman spectrum. While collecting Raman data at low temperatures is not a new technique in itself, our method illustrates a novel and simple way to perform Raman Spectroscopy at liquid nitrogen temperatures that can be utilized in any research lab containing a Raman Spectrometer without the use of special equipment and expense. A special double dewar arrangement has been constructed which allows the sample to be immersed under liquid nitrogen and the dewar continually topped up with liquid nitrogen while the sample is irradiated by the excitation laser, Fig. (2.2). When preparing a liquid sample or a solid sample dispersed in a solvent carrier, the samples must be slowly cooled and frozen onto the sample holder while in an inert atmosphere. We have had success with initially freezing the samples while working in a nitrogen purged glove bag. This eliminates any impurities from freezing onto the sample such as O_2 , CO_2 , or water vapor.

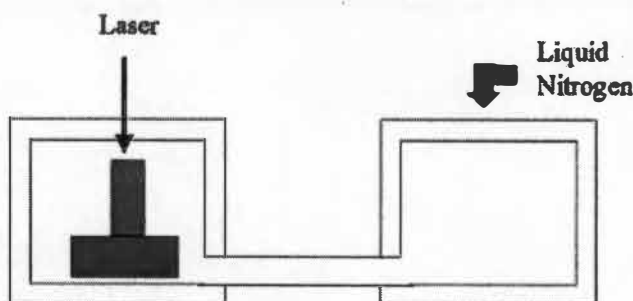


Figure 2.2 Schematic diagram of double liquid nitrogen dewar with connecting tube.

Our Solid C₆₀ samples were vacuum sublimed utilizing a vacuum tube furnace and then immediately transferred to a nitrogen atmosphere for transport to the Raman Spectrometer lab for freezing in the double dewar.

Since my original RUN studies, others⁸ have employed the simple technique of placing one styrofoam cup inside another to facilitate a liquid nitrogen holding cell. This technique has proven to be very effective in recording RUN spectra utilizing the micro-Raman stage.

2.3 Experimental Equipment

Raman Spectra reported in this thesis were recorded with the micro-Raman stage of a Dilor XY 800 Raman Spectrometer located at the University of Tennessee Department of Chemistry, Fig. (2.3) and Fig. (2.4). This spectrometer is equipped with a microscope containing Olympus confocal optics for micro-Raman studies as well as a macro stage. The Dilor Raman Spectrometer utilizes a liquid nitrogen cooled Spectrum One CCD. The Spectrometer is equipped with three 1200 g/mm gratings, two of which are located in the fore-monochromator and one located in the spectrograph. The gratings are of the holographic type and are blazed at 8000 angstroms. The excitation source was the 5145-angstrom line of a Lexel Laser, Inc. 3500 Argon Ion Laser. Liquid samples were pipetted onto a stainless steel time-of-flight mass spectrometer (TOFMS) tip that has been converted to a special holder, while solid samples were either vacuum sublimed onto the tip or dissolved in solvent and deposited on the TOFMS tip.

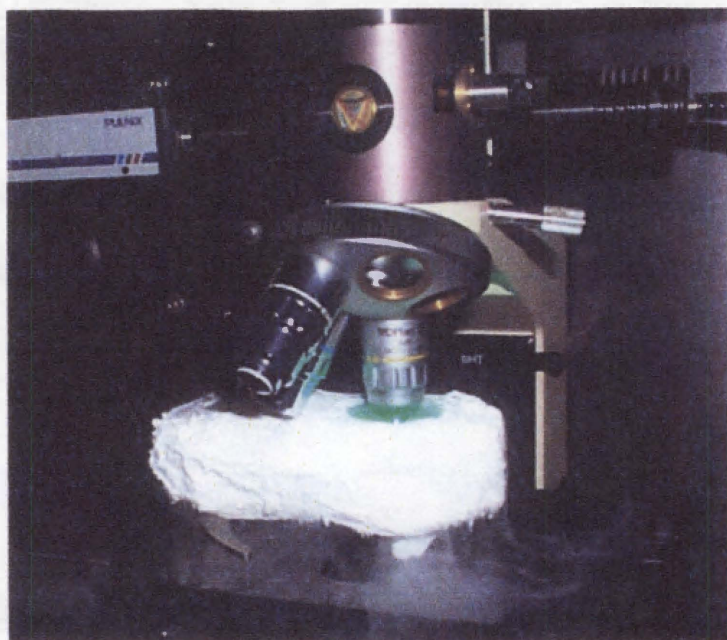


Figure 2.3 Micro-Raman being performed on CCl_4 submerged under liquid nitrogen.

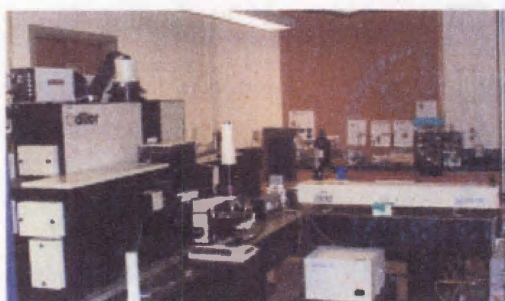


Figure A



Figure B

Figure 2.4 Figure A shows the Dilor XY-Raman spectrometer utilized for these experiments. Figure B shows a close-up of the micro Raman stage with the sample holder in place.

Chapter 3

Raman Spectrum of CCL₄ – Room Temperature and RUN

3.1 Vibrational Modes of CCL₄

Carbon Tetrachloride is a tetrahedral molecule possessing,

$$3N - 6 = 9 \quad (3.1)$$

degrees of freedom, and hence 9 modes of vibration. Fig. (3.1) shows the four observed modes of vibration, where the E mode is doubly degenerate and the T modes are each triply degenerate. The A₁ mode is singly degenerate.

3.2 Experimental Discussion

Liquid carbon tetrachloride was pipetted onto a stainless steel time-of-flight mass spectrometer tip that has been converted to a special holder. When preparing CCL₄ to run a spectrum, the samples must be slowly cooled and frozen onto the sample holder while in an inert atmosphere.

Data was collected with the sample both at room temperature and at 77°K while submerged under liquid nitrogen. The room temperature spectra showing both

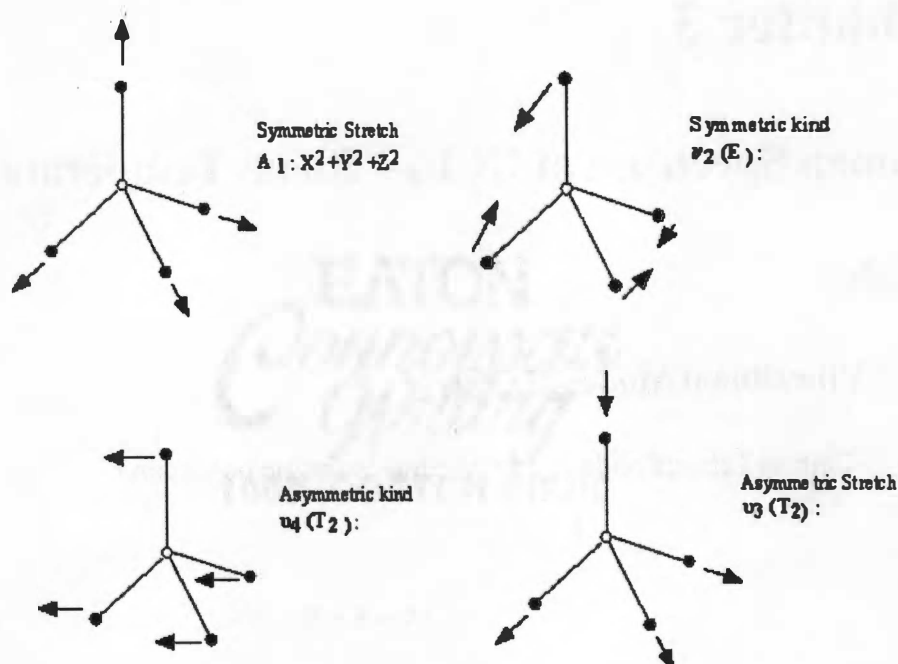


Figure 3.1 Normal modes of vibration for a tetrahedral molecule. Only one of two possible E modes are shown and only one of three possible T modes are shown in the degenerate

the Stokes and anti-Stokes lines can be seen in Fig. (3.2). Due to limitations of the spectrometer, only a maximum window of 1000 cm^{-1} can be scanned at a time, hence the spectrum does not show the doublet peaks at approximately 776 cm^{-1} . An interesting feature to note in Fig. (3.2) are the low frequency peaks superimposed on the Rayleigh line ($<150 \text{ cm}^{-1}$). These peaks are due to inter-molecular vibrations in the CCl_4 solution and involve the motion of two CCl_4 molecules against one another. Additionally, the large peak superimposed on the Rayleigh line is likely due to a laser plasma line. Fig. (3.3) shows the Stokes lines of CCl_4 with all of the fundamental lines present. The observed Raman lines are in good agreement with literature values as summarized in Table (3.1). The conditions under which the spectra were taken are summarized in Table (3.2). In agreement with Eq. (1.9), the Stokes lines are much

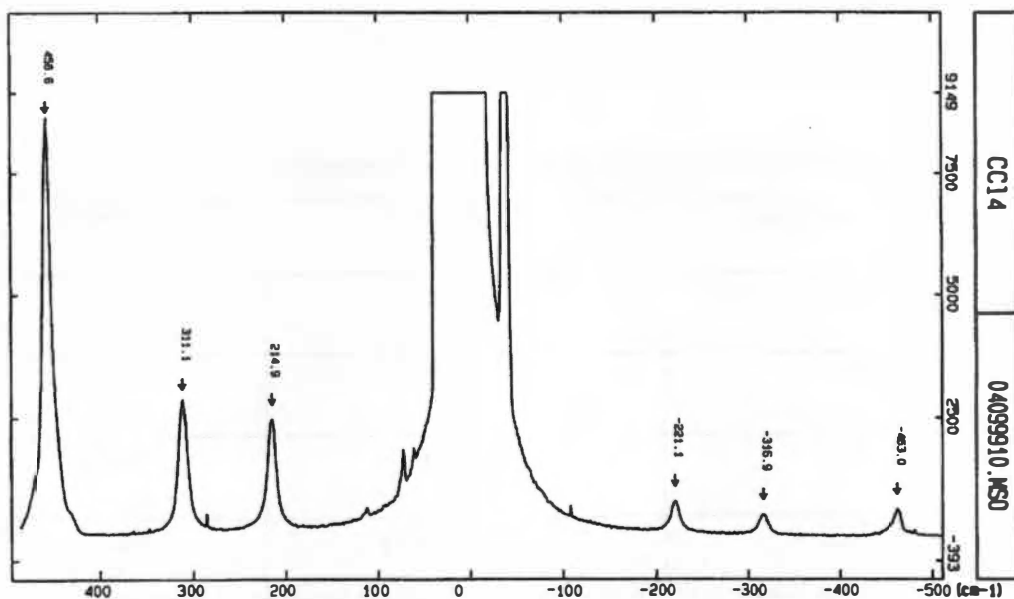


Figure 3.2 Room temperature spectra of CCl_4 showing the Stokes and anti-Stokes lines.

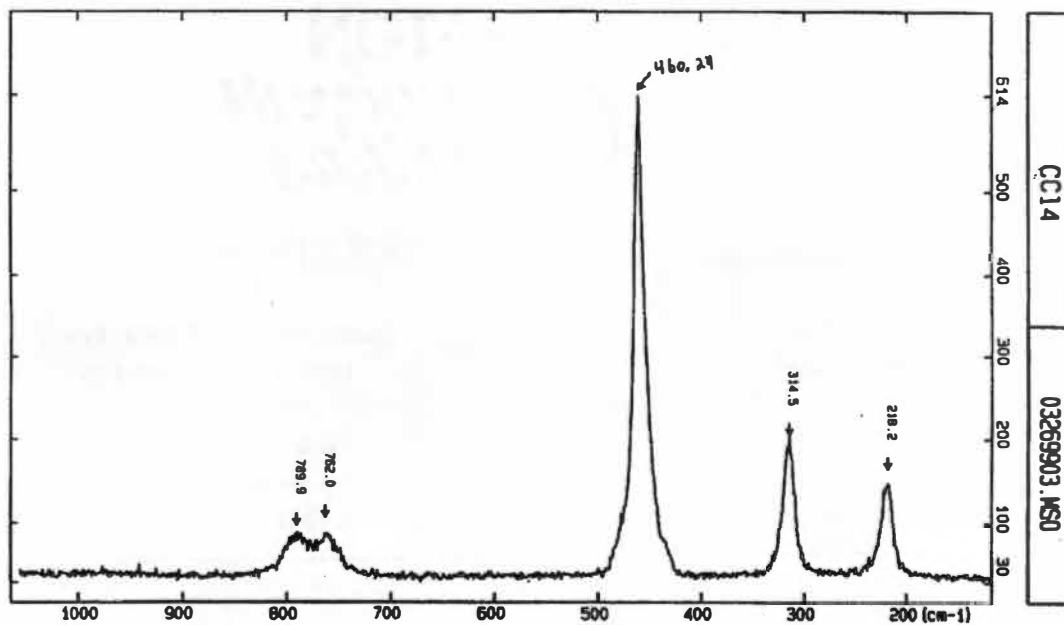


Figure 3.3 Room temperature spectra of CCl_4 showing the Stokes lines.

Table 3.1 Literature values of CCl₄ Raman lines and peak assignments.

Raman Shift (cm ⁻¹)	Assignment	IR Active?
218	$\nu_2(E)$	No
314	$\nu_4(T_2)$	Yes
459	$\nu_1(A_1)$	No
762	$\nu_3(T_2), \nu_1+\nu_4$	Yes
791	$\nu_3(T_2), \nu_1+\nu_4$	Yes

Table 3.2 Dilor XY-Raman spectrometer conditions for the room temperature spectra.

	Excitation (Angstroms)	Laser Power (mW)	Fore Monochromator (cm ⁻¹)	Spectrometer (cm ⁻¹)	Integration Time (sec)
Fig (3.2)	5145	150	0.0	0.0	60
Fig.(3.3)	5145	50	770.0	600.0	10

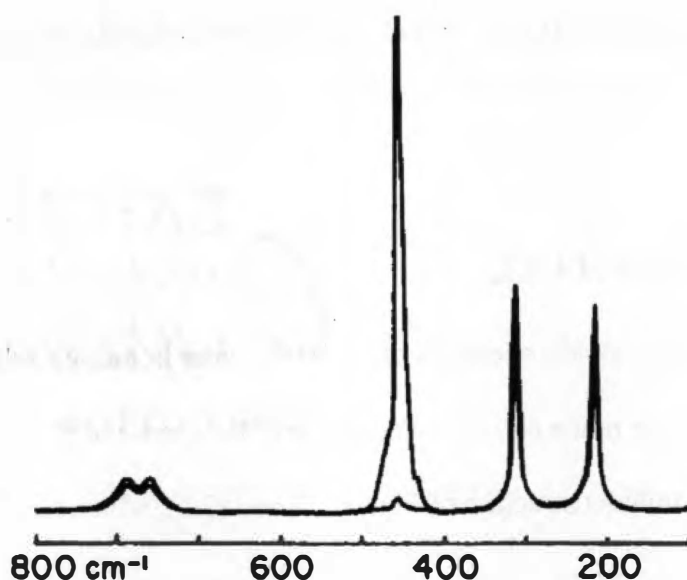


Figure 3.4 The polarized Raman spectrum of CCl_4 . The upper curve corresponds to $I_{//}$ and the lower to $I_{\perp}$.

more intense than the corresponding anti-Stokes lines present as can be clearly see from Fig. (3.2).

While depolarization studies were not conducted during the course of this work, Fig. (3.4) shows a published polarized Raman spectrum of CCl_4 . The upper curve in the spectrum corresponds to $I_{//}$ and the lower curve corresponds to $I_{\perp}$. As expected, the totally symmetric stretch vibration (ν_1 in Fig. (3.1)) has a depolarization value approximately equal to zero. The other vibrations have depolarization values near 0.75 and hence correspond to non-symmetric vibrations. Also, the stretching motions present in the molecule will tend to be a higher frequency vibration hence the 460 cm^{-1} and the doublet at approximately 776 cm^{-1} will correspond to ν_1 and ν_3 respectively. Since the peaks at approximately 776 cm^{-1} and 314 cm^{-1} also possess an IR band, which depends on a change in the dipole moment, we can assign the 314 cm^{-1}

line to ν_4 . The final line at 218 cm^{-1} , which is not active in the IR, can be assigned as the vibration ν_2 .⁹

3.3 RUN Spectrum of CCl_4

Fig. (3.5) shows the Stokes spectrum of CCl_4 run under liquid nitrogen. As can be seen, the line widths are much narrower than those of the room temperature scan of Fig. (3.3). Also, the doublet structure of Figs. (3.3) and (3.5), which has been explained in the literature as a Fermi resonance between ν_3 and $\nu_1 + \nu_4$, appears to have more structure than previously reported.⁹ A Fermi resonance can occur when there is an accidental degeneracy in which two different vibrational states possess the same approximate energy and interact with one another. This effect usually leads to two bands appearing close together where only a single band is expected, lying about either side of the expected peak location. In the case of CCl_4 , the interaction is between the ν_3 vibration and the $\nu_1 + \nu_4$ combination band.

By placing the spectrometer in high dispersion mode, it is possible to zoom in on the various peaks to achieve higher resolution. Fig. (3.6) shows the doublet structure at the location of Fermi resonance both at room temperature and under liquid nitrogen with the same spectrometer settings. As can be seen from Fig. (3.6), the doublet peak is resolved into a complex structure when cooled to liquid nitrogen temperatures. This increase in structure is primarily due to crystal effects as the sample is cooled to liquid nitrogen temperatures.¹⁰ Furthermore, Fig. (3.7) shows structure present in the 460 cm^{-1} and 314 cm^{-1} peaks of Fig. (3.3) when the sample is

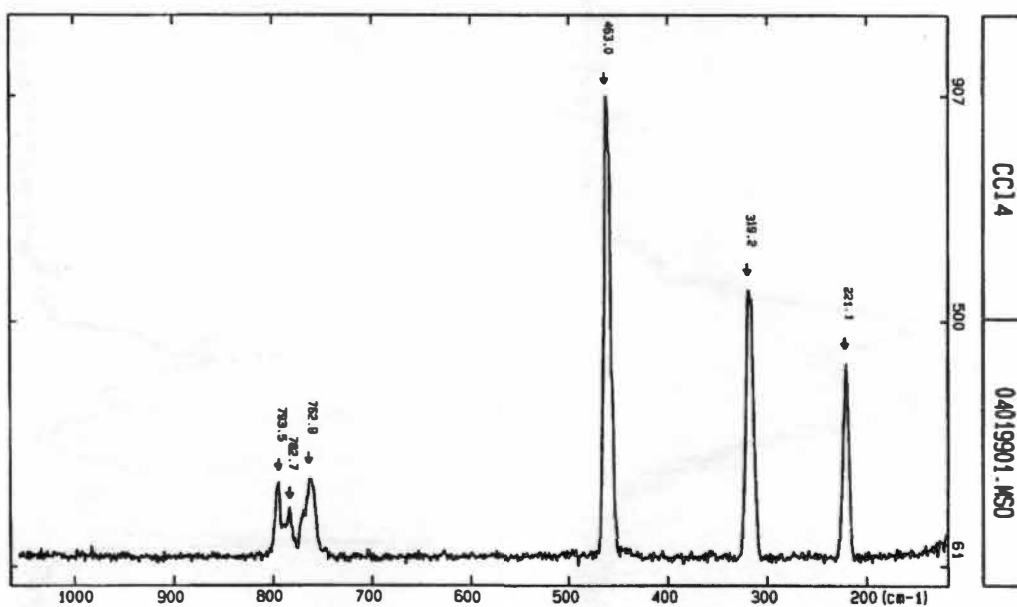


Figure 3.5 Low resolution Raman spectrum of CCl_4 under liquid nitrogen.

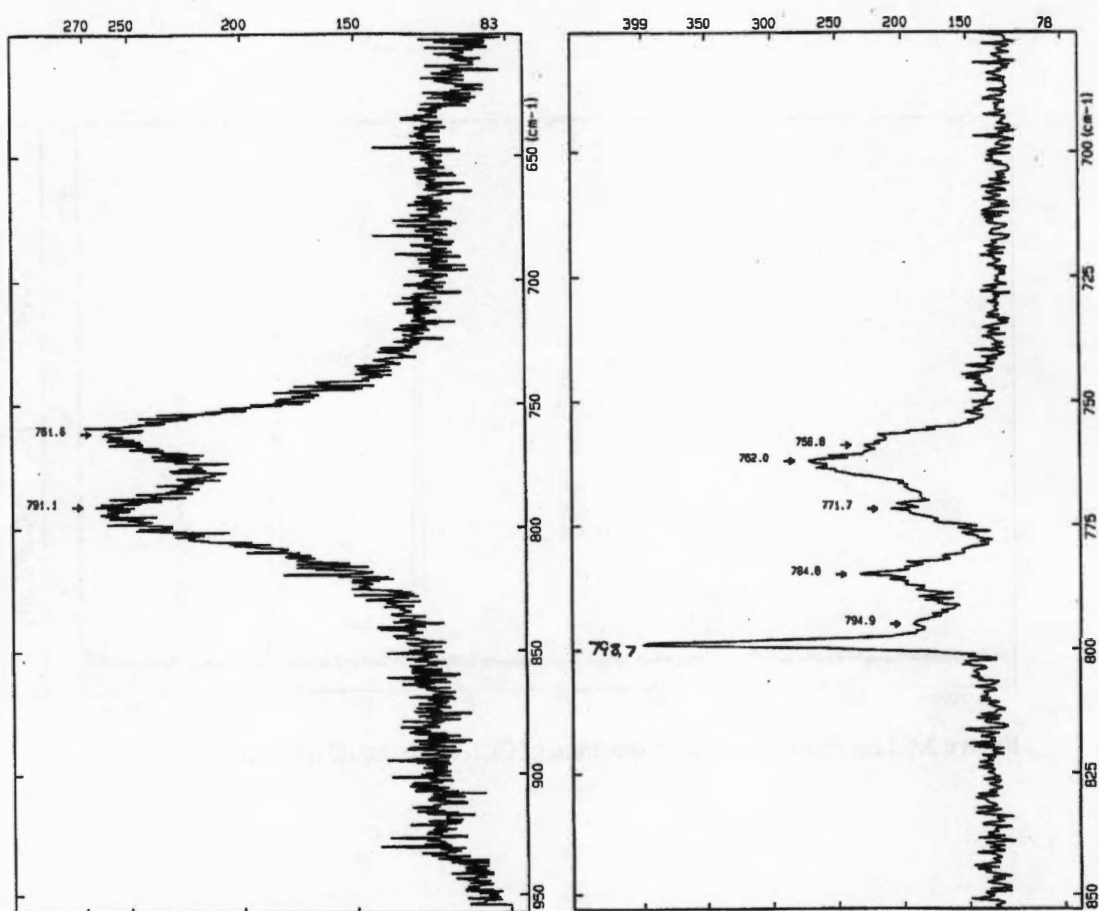


Figure 3.6 High dispersion scan of the doublet peak at ν_3 in CCl_4 . The upper spectrum was taken at room temperature and the lower spectrum was taken with the sample submerged under liquid nitrogen.

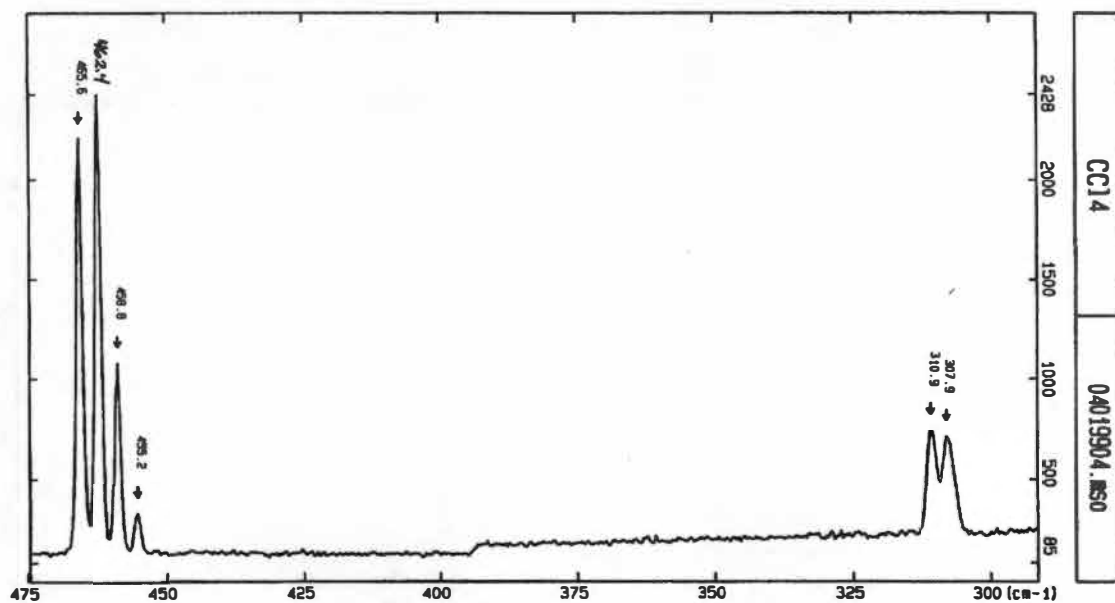


Figure 3.7 High dispersion scan under liquid nitrogen showing structure in the region of the 460 cm^{-1} and the 314 cm^{-1} lines

cooled under liquid nitrogen. The line at 460 cm^{-1} resolves into a structure containing 4 peaks as shown, and the line at 314 cm^{-1} resolves into a doublet. Analysis reported in the literature using isotopically enriched CCl_4 , has shown that the structure which appears in the peaks at 314 cm^{-1} is due to a combination of contributions from isotopic species as well as crystal effects.¹⁰ The peaks at 460 cm^{-1} , shown in Fig. (3.8), are almost completely resolved to the baseline and there may be present a fifth peak. This structure is attributed to the isotopic pattern which follows a binomial distribution as shown in the following section, (3.4).

Table (3.3) summarizes the conditions under which the spectrum from Figs. (3.5), (3.6), (3.7), and (3.8) were taken.

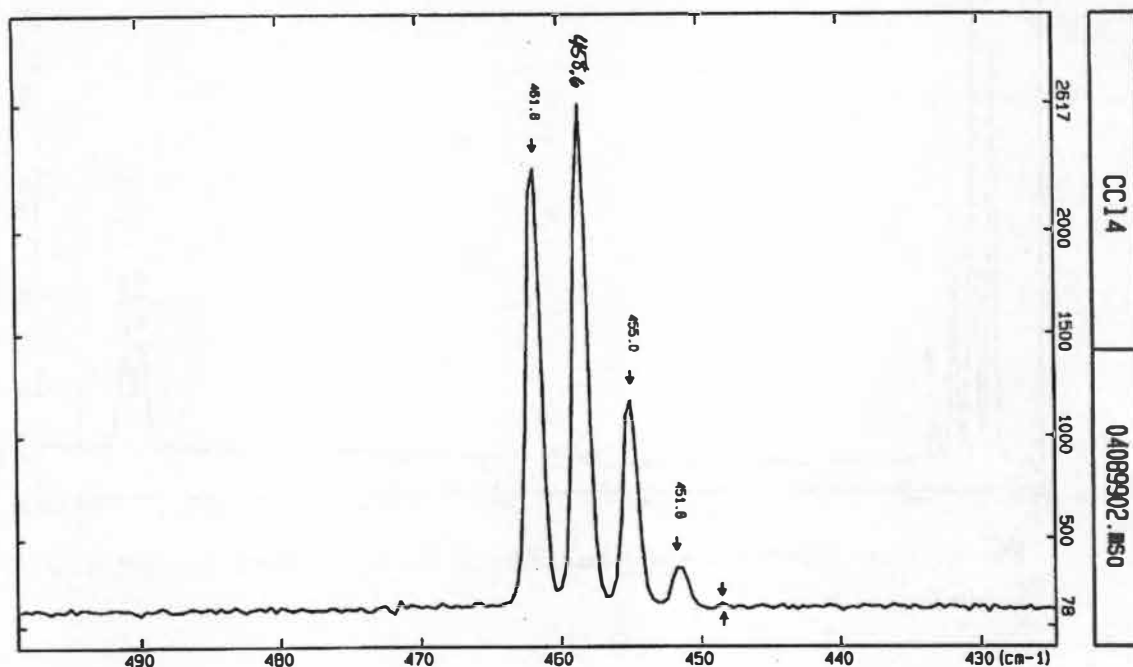


Figure 3.8 High dispersion scan showing the isotopic distribution of the 460 cm^{-1} line. This spectrum was taken with the sample under liquid nitrogen.

Table 3.3 Dilor XY-Raman spectrometer conditions for the RUN spectra.

	Excitation (Angstroms)	Laser Power (mW)	Fore Monochromator (cm^{-1})	Spectrometer (cm^{-1})	Integration Time (Sec)
Fig. (3.5)	5145	50	770.0	600.0	60
Fig. (3.6)	5145	100	780.0	780.0	120
Fig. (3.7)	5145	50	462.0	462.0	120
Fig. (3.8)	5145	50	460.0	460.0	180

3.4 Isotopic Distribution of the 460 cm⁻¹ Peak

Chlorine occurs naturally as two isotopes. The ³⁵Cl and ³⁷Cl isotopes have natural abundances of 75.77% and 24.23% respectively. For a molecule containing one or more isotopic atoms, the expected isotopic abundance for a molecule containing identical atoms can be calculated using the binomial distribution¹¹,

$$\begin{aligned}(A + B)^n = & A^n + nA^{(n-1)}B + n(n-1)A^{(n-2)}\frac{B^2}{2!} + \dots \\ & \dots + n(n-1)(n-2)A^{(n-3)}\frac{B^3}{3!} + n(n-1)(n-2)(n-3)A^{(n-4)}\frac{B^4}{4!} + \dots\end{aligned}\quad (3.2)$$

where A and B represent the naturally occurring abundances of the isotopes and n is the number of isotopic atoms present in a molecule. Setting the integrated intensity of ³⁵Cl to a value of 1.0 and that of ³⁷Cl to be 0.32 relative to ³⁵Cl, we can calculate the expected intensity distribution of a collection of molecules containing 4 Cl atoms. These results are summarized in Table (3.4). Fig. (3.9) shows a plot of these values based on the binomial distribution. As can be seen by comparing the graph in Fig. (3.9) with the actual Raman spectrum in Fig. (3.8), there is good agreement between the observed isotopic distribution and the calculated distribution based on the binomial distribution. The peaks observed in Fig. (3.8) can be assigned as shown in Table (3.5). Additionally, the simulated (m/z) values using the IsoPro software package shown in Fig. (3.10) also show good agreement with the observed and calculated isotopic distribution.

Table 3.4 Results of calculations using the binomial distribution for a molecule containing 4 Cl atoms.

$^{35}\text{Cl}_4$	$^{35}\text{Cl}_3\ ^{37}\text{Cl}$	$^{35}\text{Cl}_2\ ^{37}\text{Cl}_2$	$^{35}\text{Cl}\ ^{37}\text{Cl}_3$	$^{37}\text{Cl}_4$
1.0	$4X$	$6X^2$	$4X^3$	X^4
1.0	1.28	0.614	0.131	0.0105

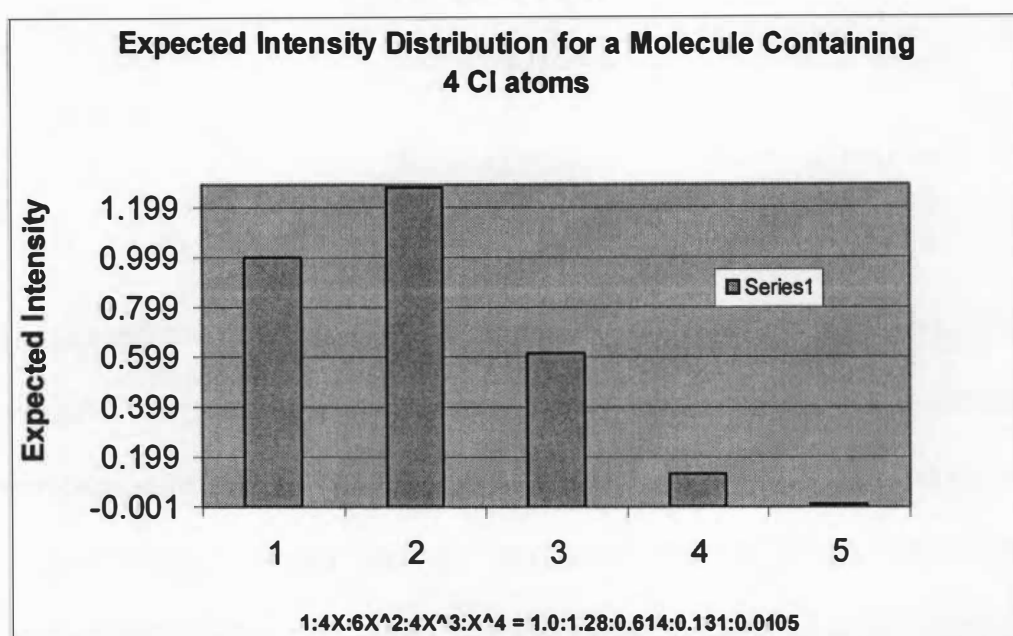


Figure 3.9 Expected intensity distribution for a molecule containing 4 Cl atoms.

Table 3.5 Peak assignments for the resolved 460 cm⁻¹ line.

C $^{35}\text{Cl}_4$	C $^{35}\text{Cl}_3\ ^{37}\text{Cl}$	C $^{35}\text{Cl}_2\ ^{37}\text{Cl}_2$	C $^{35}\text{Cl}\ ^{37}\text{Cl}_3$	C $^{37}\text{Cl}_4$
461.8 cm ⁻¹	458.6 cm ⁻¹	455.0 cm ⁻¹	451.8 cm ⁻¹	Not observed

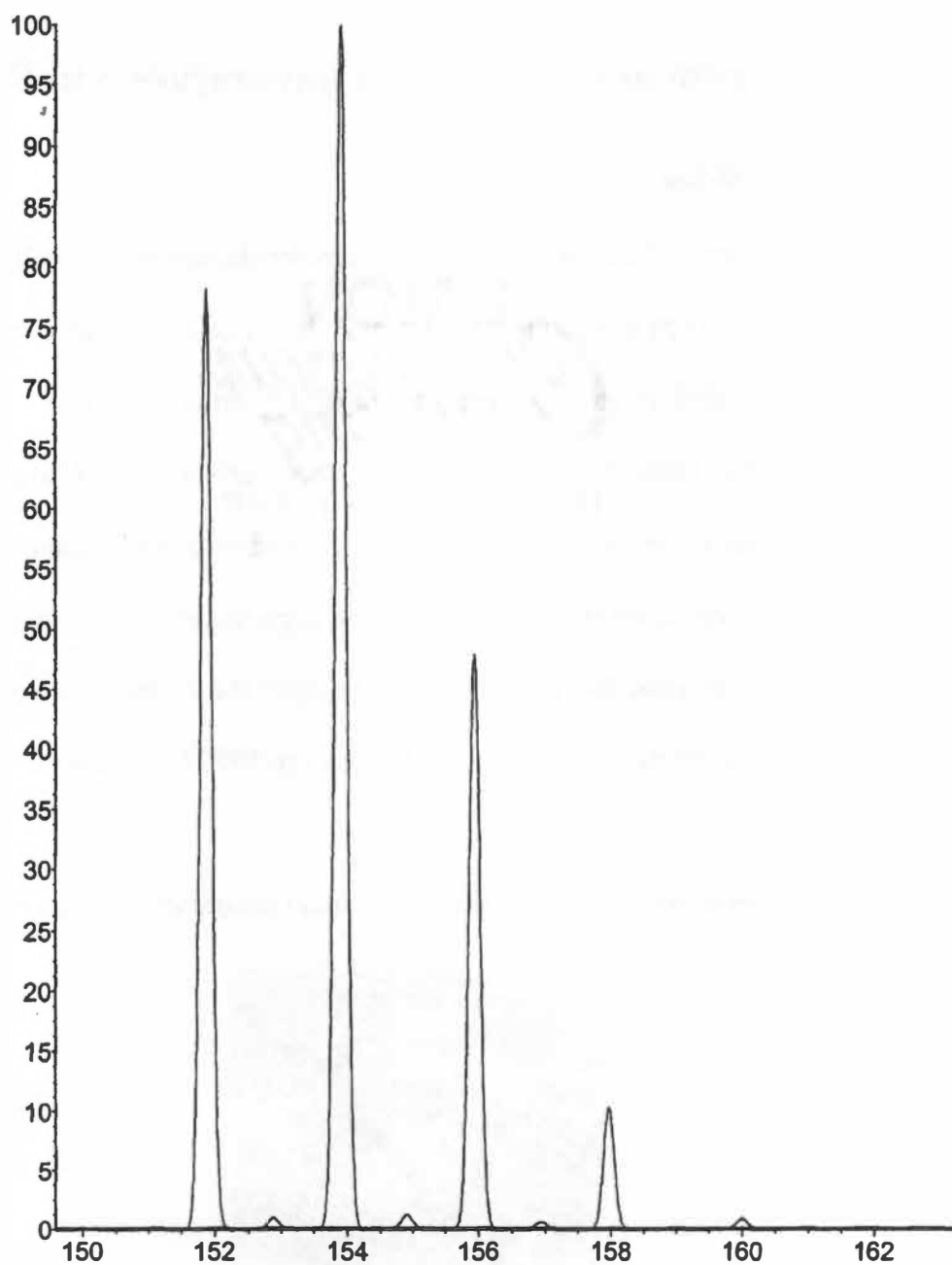


Figure 3.10 IsoPro simulation of the isotopic distribution for a molecule containing 1 C atom and 4 Cl atoms.

Chapter 4

Raman Spectrum of C_{60} – Room Temperature and RUN

4.1 Structure of C_{60}

C_{60} , also known as the Buckminsterfullerene molecule, was theoretically predicted by Ozawa in 1970 as a stable icosahedral molecule containing 60 carbon atoms.¹² This icosahedral structure possesses the highest symmetry possible for a molecule, I_h symmetry, Figure (4.1). It would be another fourteen years before experimental evidence for this molecule emerged from experiments by a group of researchers at the Exxon Research Lab.¹³ A year later, experiments carried out by Smalley, Kroto, et al, verified the existence and structure of the C_{60} and C_{70} molecules. This research earned them the Nobel Prize in Chemistry in 1996 for its discovery and characterization.

C_{60} belongs to a class of carbon caged molecules containing an even number of

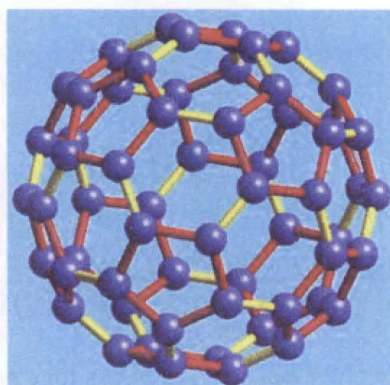


Figure 4.1 Structure of the C_{60} molecule. Red indicates single bonds and yellow indicates double bonds.¹⁴

carbon atoms, beginning at C_{20} , known as Fullerenes. The carbon atoms are arranged in 5 (hexagonal) and 6 (pentagonal) -membered rings and using Euler's Theorem it can be shown that C_{60} possesses twelve 5-membered rings and twenty 6-membered rings. The structure is that of a truncated icosahedron and resembles the shape of a soccer ball. As seen in Figure (4.1), each carbon atom is equivalent to all others in the molecule, each sharing two single bonds and a double bond with its nearest neighbors. Given its high chemical and structural stability, C_{60} has been referred to as the third major allotrope of pure carbon following graphite and diamond.

4.2 Vibrational Modes of C_{60}

A group theoretical treatment for a C_{60} molecule, which possesses I_h symmetry, predicts a total of fourteen first order vibrational modes as indicated in Table (4.1). Columns two and six represent experimental values of the allowed vibrational modes and columns three and seven represent theoretical values from the literature.^{15, 16} Of the fourteen allowed vibrational modes for C_{60} , there are four distinct IR-active modes ($4F_{1u}$). The remaining ten allowed vibrational modes shown in Table (4.1) are Raman active vibrations ($8H_g + 2A_g$).

The most intense peak in the Raman spectrum for C_{60} is attributed to the $A_g(2)$ mode, which is known as the pentagonal pinch mode of vibration. This contribution to the Raman spectrum is a result of the tangential breathing mode of the five carbon atoms making up the twelve 5-membered rings. Due to the intensity of this peak the $A_g(2)$ mode of vibration is the focus of our study of the RUN technique as applied to C_{60} .

Table 4.1 Experimental and theoretical values of vibrational frequencies for C₆₀.

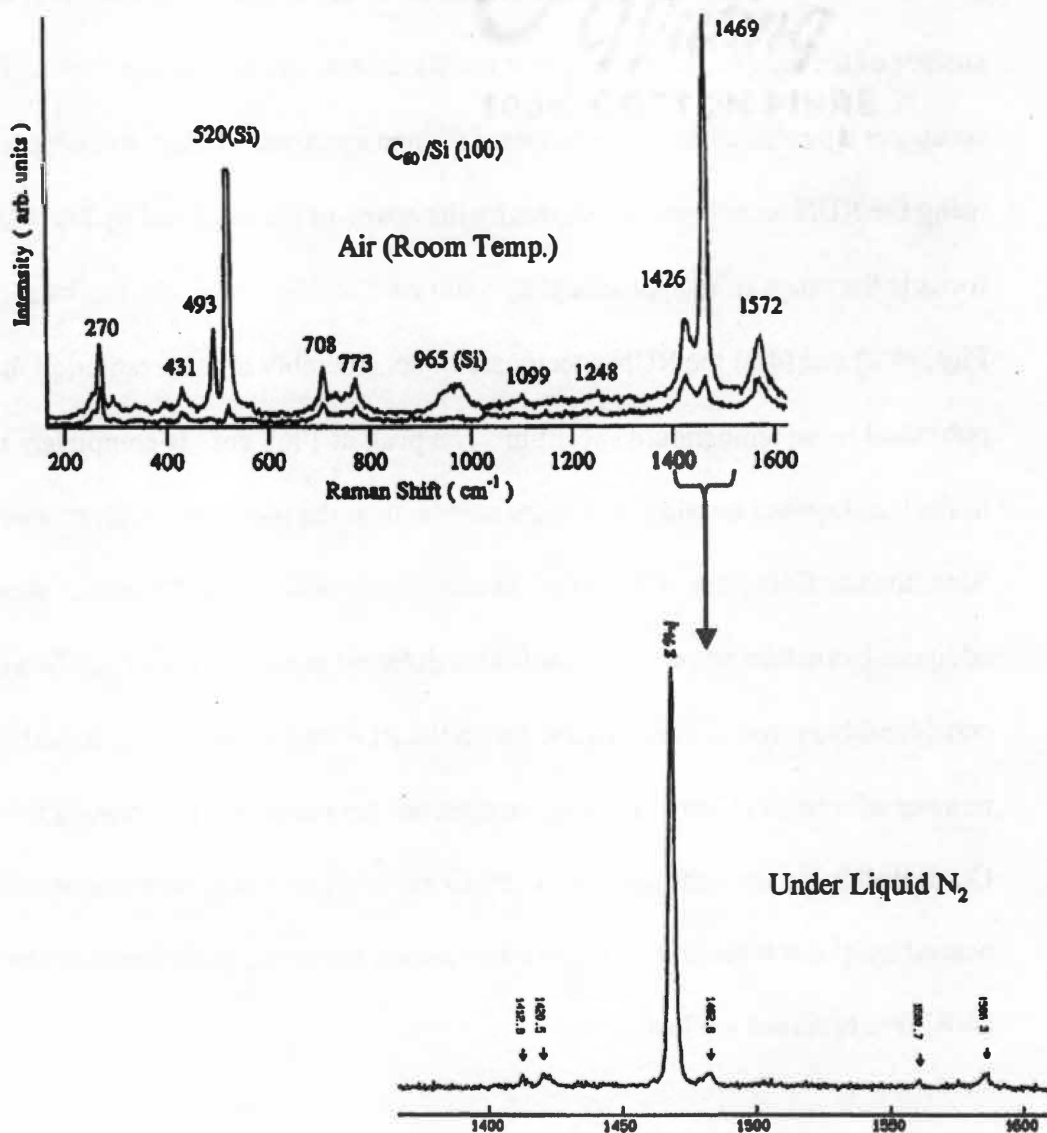
Mode	Exp. (cm ⁻¹)	Theory (cm ⁻¹)		Mode	Exp (cm ⁻¹)	Theory (cm ⁻¹)
A _g (1)	497.5	492		H _g (2)	432.5	439
A _g (2)	1470	1468		H _g (3)	711	708
F _{1u} (1)	526.5	505		H _g (4)	775	788
F _{1u} (2)	575.8	589		H _g (5)	1010	1102
F _{1u} (3)	1182.9	1208		H _g (6)	1251	1217
F _{1u} (4)	1429.2	1450		H _g (7)	1426.5	1401
H _g (1)	273	269		H _g (8)	1577.5	1575

4.3 Raman Spectrum of C₆₀

A sample of C₆₀ was vacuum sublimed onto a modified time-of-flight mass spectrometer tip in a vacuum tube furnace for our RUN experiment. After the sample was removed from the vacuum chamber, it was immediately immersed in liquid nitrogen for transport to the Raman Spectroscopy lab for investigation in order to minimize the exposure to oxygen. As previously mentioned, due to the intensity of the A_g(2) mode of vibration, this is the vibrational peak we chose to compare to literature values in the RUN spectra. Due to sample burning effects, we were unable to obtain a satisfactory room temperature spectrum of C₆₀ using our Raman spectrometer. It has been reported in the literature that obtaining Raman spectra of

fullerenes is often difficult due to sample burning and oxidation effects as well as peak shifting effects due to oxygen adsorbed into the fullerene lattice. Subsequent studies of the Raman spectra of C_{60} obtained with the Dilor XY 800 Raman Spectrometer have been successful with the implementation of dry nitrogen blowing over the surface of the sample; however, these results are not reported in this thesis. Fig. (4.2) compares a published room temperature Raman spectrum of C_{60} ¹⁵ to our spectrum using the RUN technique. As shown by the arrow in the inset and by Fig. (4.3), our focus is the range from approximately 1400 cm^{-1} to 1600 cm^{-1} . As can be seen from Figs. (4.2) and (4.3) the RUN spectra are of considerably higher resolution than the published room temperature spectrum. The peak at 1468 cm^{-1} is completely resolved to the baseline and considerably more narrow than the room temperature spectrum. Also, the shoulder peak at 1426 cm^{-1} is completely resolved and possibly shows some additional structure and a new peak is also detected at approximately 1482 cm^{-1} . The considerably narrower lines obtained with the RUN technique are attributed to smaller number of rotational lines at liquid nitrogen temperatures and the absence of oxygen. C_{60} molecules in the solid state form are found to rotate freely with respect to their nearest neighbor molecules at room temperature, however, at temperatures below 260K free rotations are lost.

Raman Spectrum of C₆₀



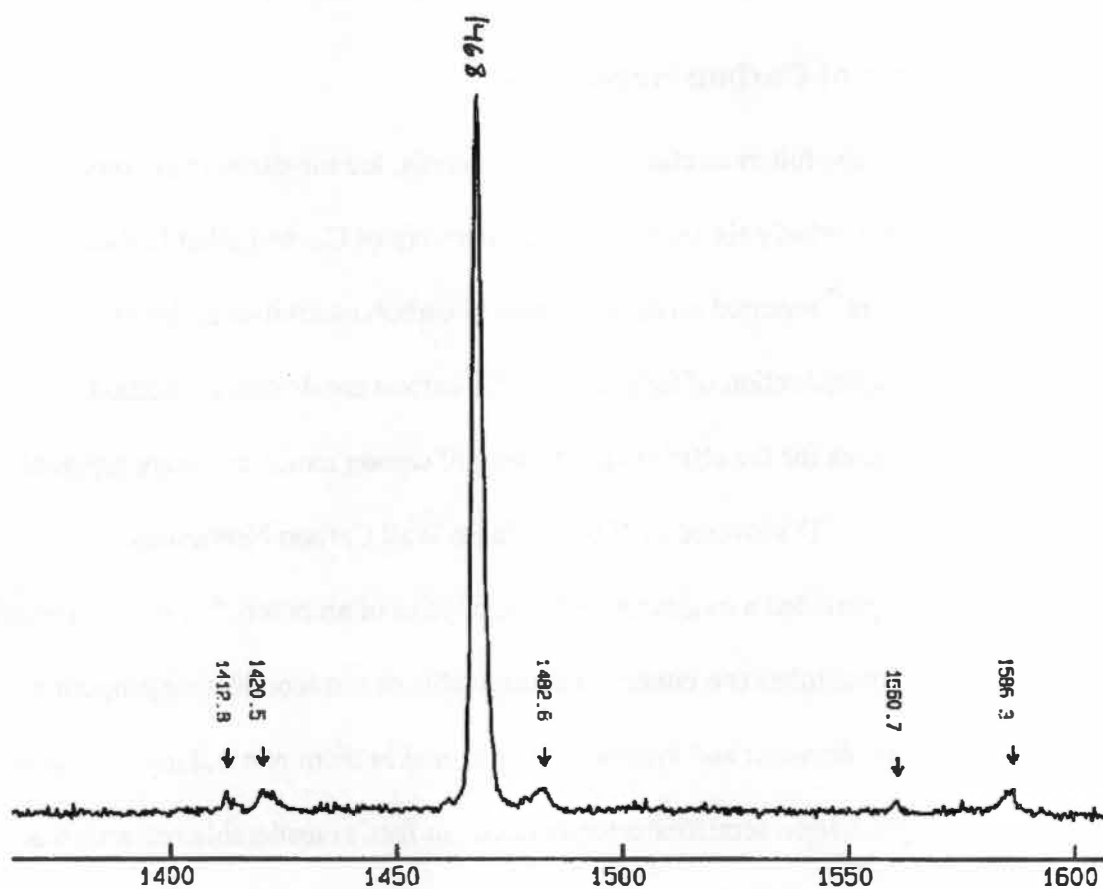


Figure 4.3 Raman Spectrum of C₆₀ under liquid nitrogen.

Chapter 5

Raman Spectrum of Single Wall Carbon Nanotubes (SWCNT) – Room Temperature and RUN

5.1 Structure of Carbon Nanotubes

A close kin to the fullerene class of nano-materials, are the carbon nanotube structures. Approximately six years after the discovery of C_{60} and other higher fullerenes, S. Iijima¹⁷ reported on the existence of carbon nanotubes in the soot resulting from the production of fullerenes by the carbon arc discharge method. A year later, techniques for the efficient production of carbon nanotubes were reported by Ebbensen et al.¹⁸. Discovered in 1993¹⁹, Single Wall Carbon Nanotubes (SWCNTs) have provided a means to study the physics of an ordered one-dimensional system. Carbon nanotubes can either possess metallic or semiconducting properties depending on their diameter and symmetry, which makes them particularly attractive for use in next generation semiconductor devices. In fact, considerable research has already shown their promise for use in nano-transistors and nano-vacuum tube devices.^{20, 21, 22} In addition, owing to their large aspect ratio, carbon nanotubes show considerable promise for use as field emission devices.²³ The ability to fabricate fullerenes and carbon nanotubes in bulk quantities has spawned an entirely new interdisciplinary area of research, popularly known as nanotechnology.

Single wall carbon nanotubes can be envisioned as a graphene sheet (hexagonal array of carbon atoms), which has been seamlessly rolled into a cylindrical geometry. A nanotube can be uniquely defined by its chiral vector, Eq. (5.1);

$$\mathbf{c} = n\mathbf{a}_1 + m\mathbf{a}_2 \quad (5.1)$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ represent unit vectors which form the elementary cell of the graphene sheet and n and m are integer values. Figure 5.1 illustrates this configuration for the case $(n,m) = (4,2)$. The chiral angle, θ , is measured relative to the direction defined by the unit vector $\mathbf{a}_1$. The cylindrical nanotube contains end caps on each end consisting of “hemispheres” of a fullerene molecule.

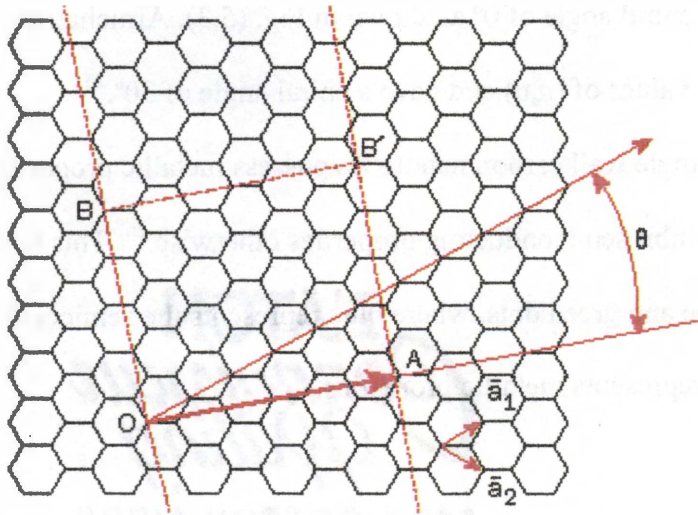


Figure 5.1 Graphene sheet which serves as the basis for carbon nanotubes.²⁴

A wide variety of nanotube structures can be formed due to differences in tube diameters, end cap structure, as well as the chirality of the particular nanotube. There are two primary symmetry classifications for carbon nanotubes; chiral and achiral. A chiral nanotube is one in which its mirror image cannot be superimposed on the original image. Chiral nanotubes exhibit spiral symmetry, as can be seen in part (c) of Fig. (5.2). They have general values for (n,m) and a chiral angle that can vary between 0° and 30° . The second classification of carbon nanotubes are the achiral type. An achiral nanotube is one in which the mirror image is identical to the original. These can be broken down into two distinct configurations; armchair and zigzag nanotubes as shown in part (a) and (b) of Fig. (5.2).

The terms armchair and zigzag originate from the shape of the cross sectional ring of the nanotube. The zigzag nanotubes correspond to (n,m) values of either $(n,0)$ or $(m,0)$ and have a chiral angle of 0° as shown in Fig. (5.3). Armchair nanotubes correspond to (n,m) values of (n,n) and have a chiral angle of 30° .²⁵

In general, single wall carbon nanotubes possess metallic properties if $(n-m)/3$ is an integer, and exhibit semiconducting properties otherwise.²⁶ This is illustrated in Fig. (5.3) by the blue and green dots, where blue represents the semiconducting property and green represents metallic properties.

5.2 Vibrational Modes of Carbon Nanotubes

Single wall carbon nanotubes exhibit two main first order vibrational modes. These vibrational modes fall into the low energy and high energy regions. The low

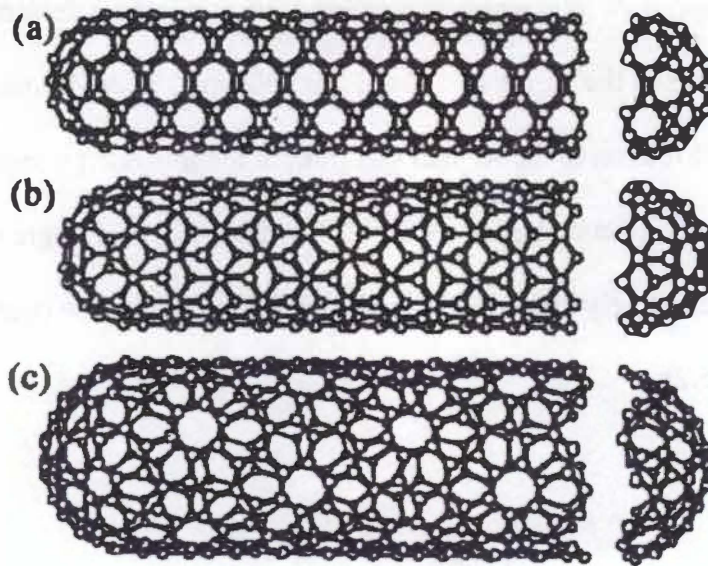


Figure 5.2 Classification of carbon nanotubes: (a) armchair, (b) zigzag, and (c) chiral.²⁵

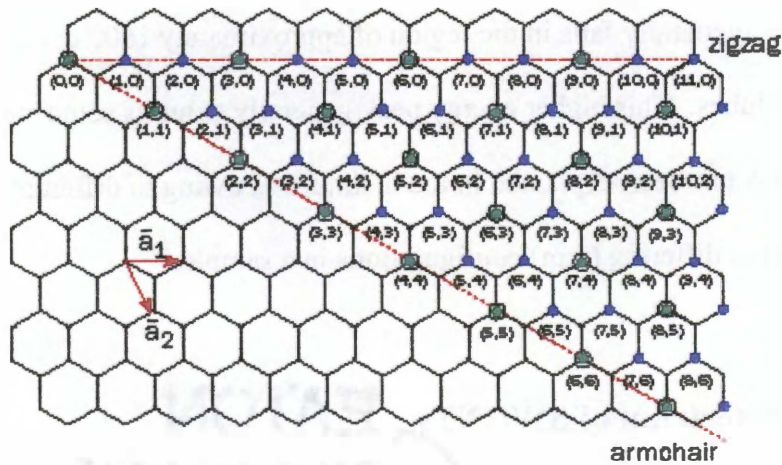


Figure 5.3 Armchair and zigzag configurations for carbon nanotubes.²⁴

energy mode of vibration (A_{1g}), corresponds to a totally symmetric radial breathing vibration of the carbon nanotube where the carbon atoms undergo a uniform radial displacement, and falls in the region of 150 cm^{-1} to 200 cm^{-1} . There is also often a Van-Der-Waals contribution to the Raman spectrum in the low energy region arising from neighboring carbon nanotubes as well.^{27,28} The diameter of a single wall carbon nanotube can be qualitatively estimated from the frequency of the low energy vibration²⁹ by Eq. (5.2);

$$d \approx \frac{223.75}{\omega} \quad (5.2)$$

The high energy modes of vibration (E_{1g} , E_{2g} , and A_{1g}) corresponds to a longitudinal mode of vibration due to the bond stretching motion of neighboring carbon atoms, and generally falls in the region of approximately 1600 cm^{-1} for single wall carbon nanotubes. This higher energy peak generally exhibits some structure in its intensity, which has been explained in the literature as owing to different nanotube diameters as well as differing (n,m) configurations in a sample.³⁰

5.3 Raman Spectrum of SWCNTs

The single wall carbon nanotubes used in our Raman experiments were obtained from Rao, Eklund, et al. These nanotubes were fabricated via a pulsed laser vaporization process in which a carbon target containing 1%-2% concentration of a

nickel/cobalt catalyst were vaporized in a vacuum tube furnace at 1200°C by a pulsed sequence of two lasers (532-nm concentric with a 1064-nm laser). The debris from the plasma formed in the process is collected by an argon gas flow downstream onto a cold finger used for collection. The collected soot is soaked in CS₂ to dissolve fullerenes from the mix. The remaining insoluble material was then dispersed into distilled H₂O with 0.1% (by weight) Benzalkonium Chloride and subjected to an ultrasonic bath to separate carbon and catalyst particles. The SWCNTs were then separated from the remaining material using microfiltration techniques.(insert reference). The result is a bundle of SWCNTs ranging from 10 nm to 20 nm in diameter and having lengths ranging from approximately 10 μm to 100 μm in length.³¹

Transmission Electron Micrograph (TEM) images for our SWCNT sample were obtained using the Hitachi HF-2000 high resolution transmission electron microscope located at the High Temperature Materials Lab of Oak Ridge National Laboratory (ORNL). Images were obtained to verify the diameter as well as to qualitatively determine the amount of impurities contained in the sample. As can be seen from Fig. (5.4), our sample does contain some carbonaceous material (dark matter) in addition to nickel/cobalt catalyst particles which are represented by the bright dots in the image. Fig. (5.5) represents a close-up image of a single SWCNT from our sample. Investigation of our sample has shown that the diameter distribution was in the 10μm – 20μm range while the lengths of the nanotubes varied considerably from tens of microns to several hundred microns in length.

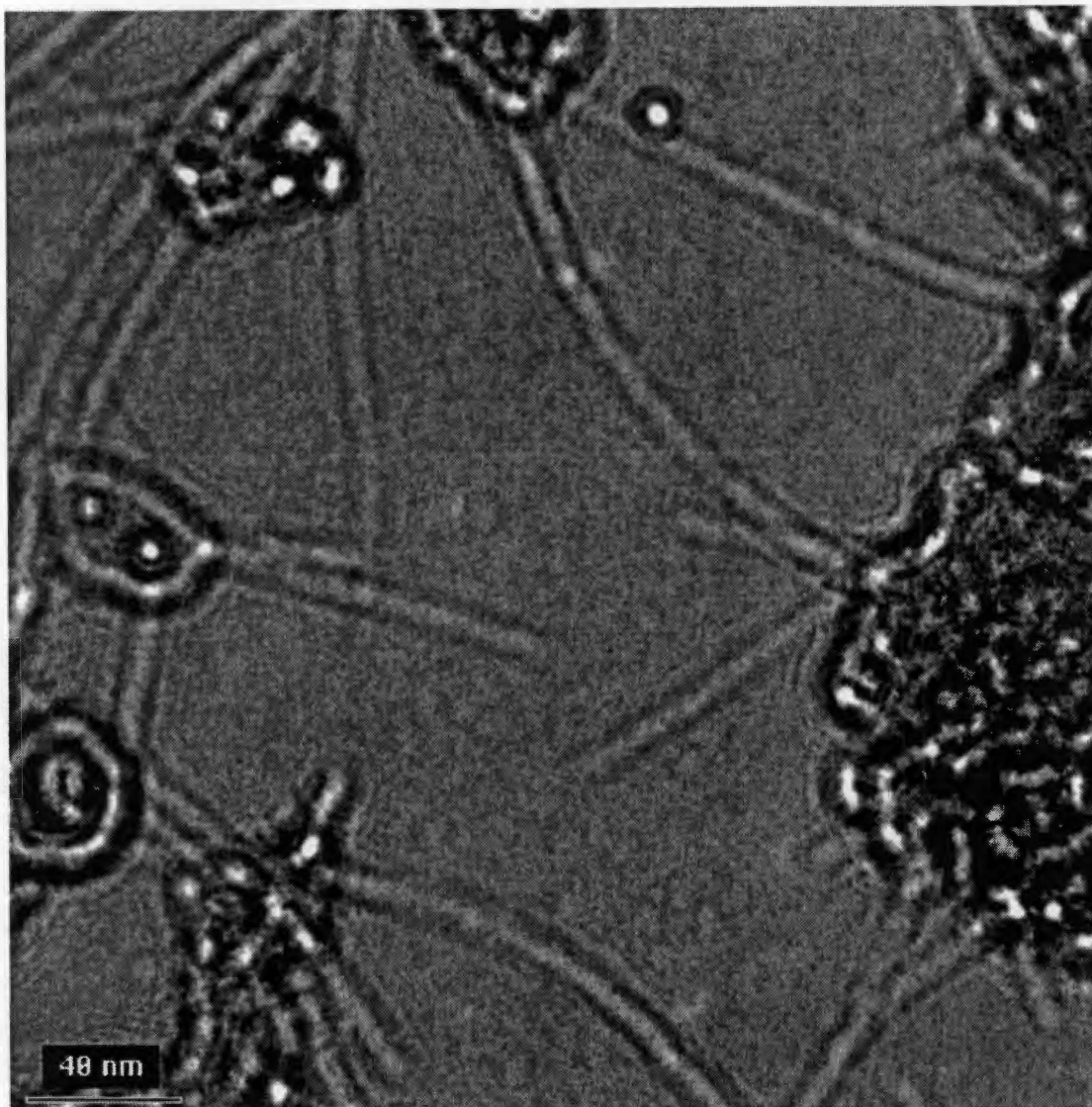


Figure 5.4 TEM image of single wall carbon nanotubes utilized for RUN experiments.

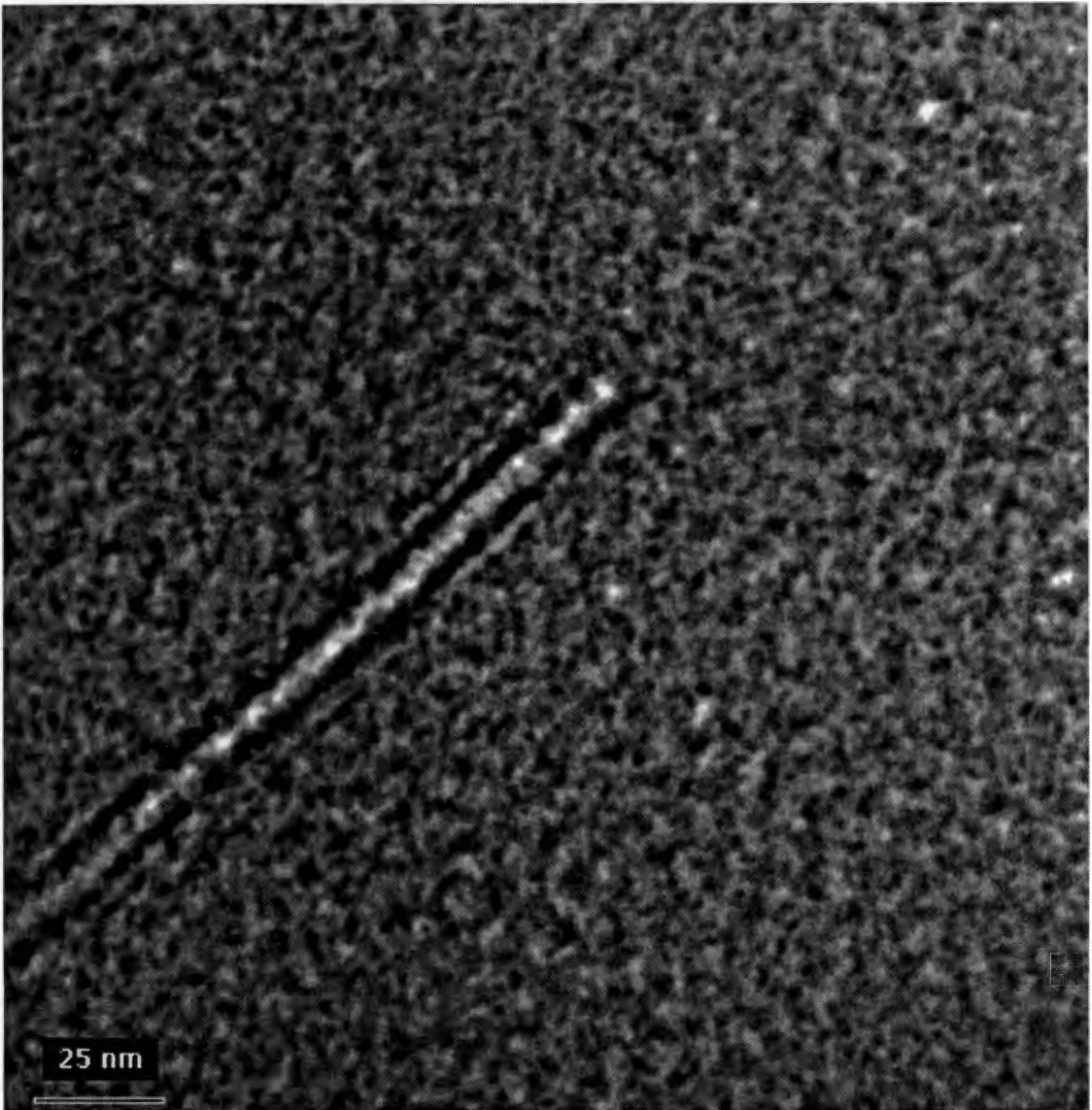


Figure 5.5 Close-up image of a single carbon nanotube utilized for the RUN experiments.

Due to limitations with the operation of our Raman spectrometer, the low frequency region (radial breathing mode of vibration) centered on approximately 200 cm^{-1} was not studied in these experiments. Due to this, we present a comparison between the room temperature spectrum and the RUN spectrum for our SWCNT sample in the high energy region. This region represents the longitudinal mode of vibration of the SWCNT. Fig. (5.6) illustrates a comparison between the room temperature spectrum and the RUN spectrum for a SWCNT. As can be seen from the Figs. (5.6) and (5.7), the peak at approximately 1590 cm^{-1} is considerably more resolved in the RUN spectrum. In fact, the low frequency shoulder in the room temperature spectrum is resolved into a doublet structure. A high dispersion scan of the 1600 cm^{-1} region is shown in Fig. (5.7). The peak in the vicinity of 1340 cm^{-1} is likely due to carbon impurities present in the bulk sample.³² These images show considerably more structure in the vibrational peaks of the sample under liquid nitrogen as compared to the room temperature spectra and illustrate the usefulness of this technique.

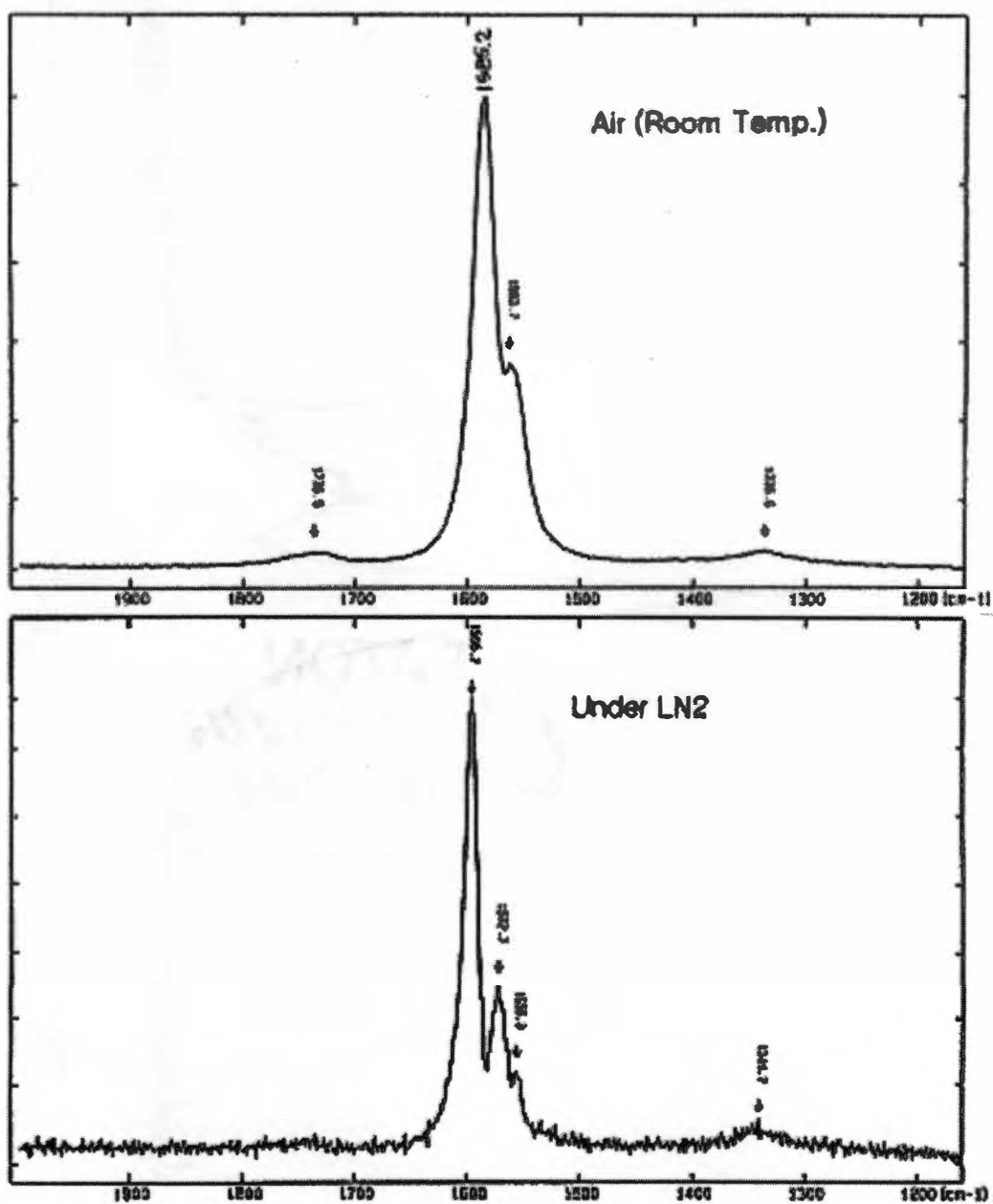


Figure 5.6 Room temperature and RUN spectrum of carbon nanotubes.

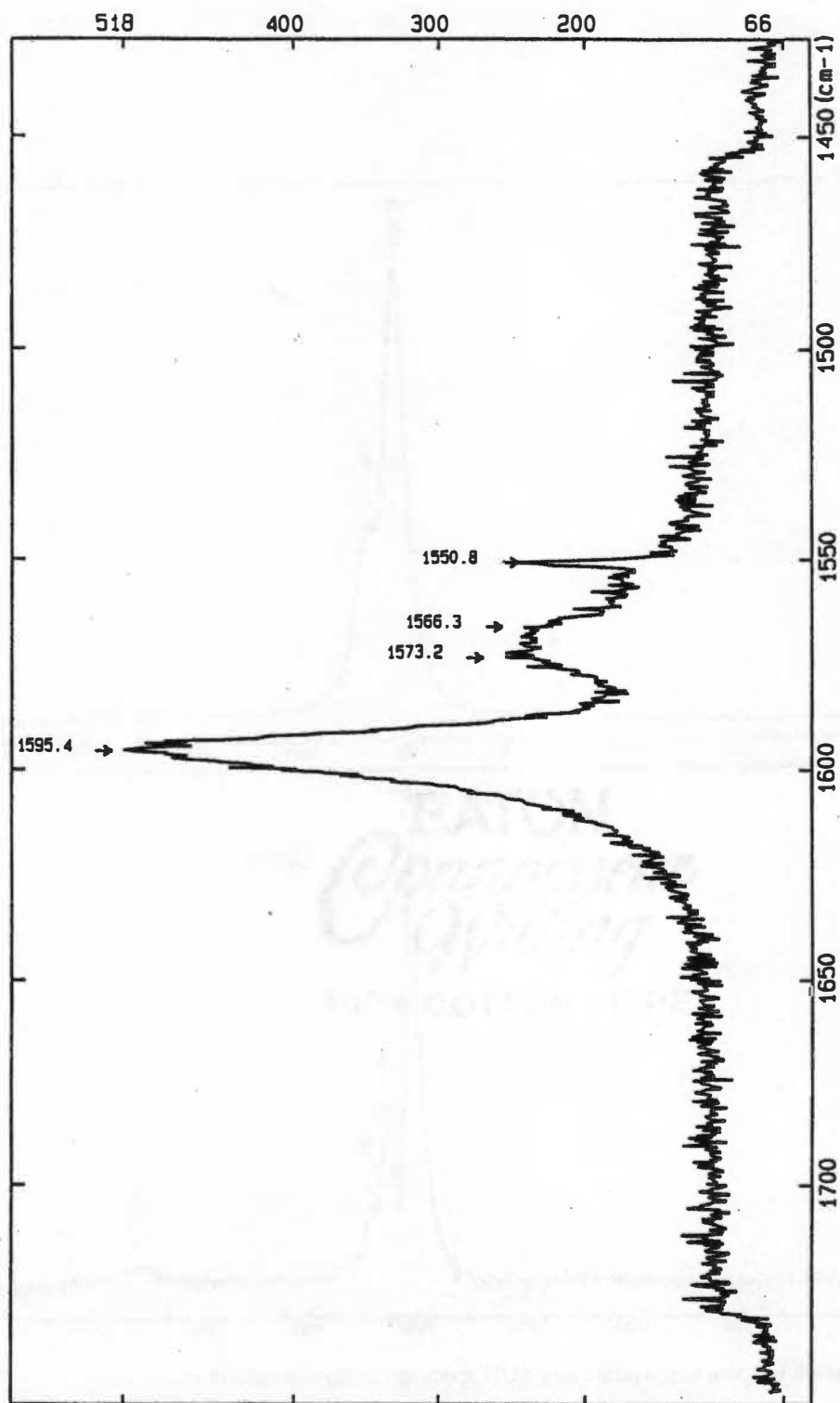


Figure 5.7 High dispersion RUN scan of the 1600 cm^{-1} region of a SWCNT sample.

Chapter 6

Summary

This thesis presents a new technique for performing Raman Spectroscopy at liquid nitrogen temperatures. Conventional low temperature Raman techniques utilize expensive equipment to cool the sample to 77° K. Our technique of taking data with the sample placed under liquid nitrogen provides a low cost alternative to conventional methods, and can be utilized by any lab with a Raman spectrometer without the purchase of additional equipment.

It has also been shown that obtaining Raman spectra under liquid nitrogen has several advantages to the standard practice of employing samples in ambient air at room temperature. Samples are often damaged by overheating and oxidation effects, a problem which is compounded by micro-Raman spectroscopy due to the higher laser fluence experienced by the sample under investigation. Additionally, line broadening due to ro-vibrational population and hot band transitions is greatly reduced with the RUN technique.

Several molecules have been investigated to test the RUN technique including CCl₄, C₆₀, and single wall carbon nanotubes. In each case, considerably enhanced spectra have been obtained, to include narrower vibrational peaks, increased structure as compared to room temperature spectra, and the ability to resolve isotopic patterns in the case of CCl₄. In addition, since the initial investigation of the RUN technique reported in this thesis, Dr Robert N. Compton and Dr. J. Stewart Hager have extended

this technique to include a wide array of molecular systems and have found it to be universally applicable.

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VITA

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