

Raman Study of Amorphous Carbon

A Dissertation

Presented to the

Department of Physics and Astronomy

Brigham Young University

In Partial Fulfillment

of the Requirements for the Degree

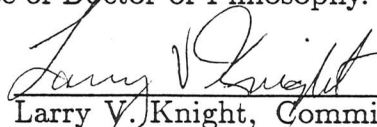
Doctor of Philosophy

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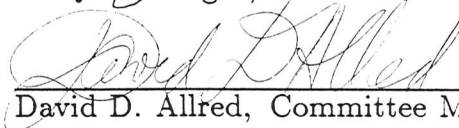
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December 1990

This dissertation, by Qi Wang is accepted in its present form by the Department of Physics and Astronomy of Brigham Young University as satisfying the dissertation requirement for the degree of Doctor of Philosophy.



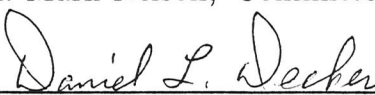
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ABSTRACT

In the Raman spectrum of amorphous carbon (a-C) the low frequency features, in the $200\text{-}900\text{ cm}^{-1}$ region, are an important indication of structural disorder. They may be related to the M-point zone-boundary phonon modes of graphite.

The Raman study of annealed a-C samples reveals that there are dramatic differences in the crystallization process depending upon whether the sample was annealed in air or in an inert gas.

The constrained deconvolution method has been introduced in the analysis of a-C Raman spectrum. The result has been used to verify the assumed relationship between Raman spectrum of a-C and phonon density of states of graphite. This method can also be used in the study of a-C structure and structural changes.

ACKNOWLEDGMENTS

I am greatly indebted to Dr. Larry V. Knight, my academic advisor and the chairman of my dissertation advisory committee for his consistent support and encouragement throughout the completion of my graduate study in Brigham Young University.

I express deep gratitude to Dr. David D. Allred for his insightful guidance in the development of this work and his desire to see his students succeed.

I would like to give my thanks to Dr. J. Gonzalez-Hernandez for his great help in both experimental and theoretical aspects of this work. I extend my thanks to Dr. Brayn G. Peterson, Dr. Robert E. Benner and W. Scott Daniel for their assistance in the experiments.

I appreciate the time and commitment of Dr. Mark W. Lund and Dr. Arturo Reyes-Mena in helping me improve my writing of the dissertation.

Thanks are given also to Dr. H. Mark Nelson of my dissertation advisory committee and Dr. Dorian M. Hatch and Dr. William E. Dibble of my oral examination committee.

I would like to give my special thanks to my family, my wife and daughter for their love, support and patience. I would like also to thank my parents for their love, understanding and encouragement.

This work is dedicated to my fatherland, China.

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I. INTRODUCTION

The purpose of this work is to study amorphous carbon (a-C) using Raman spectroscopy.

Due to the growing interest in amorphous and diamondlike carbon films in industry and interest in multilayers containing carbon for soft x-ray optics, amorphous carbon thin films have been studied intensively during recent years.¹ Raman spectroscopy is one of the techniques used in the area.^{2,3,4} In the study of amorphous materials, especially when the materials are in thin film form, some of the traditional techniques in the characterization of crystal materials, such as x-ray diffraction and neutron scattering, are not efficient or even fail in obtaining useful information. For example, the diffraction of x rays by carbon is so low that a thick film (2 μm) and long time exposures (up to 24 hours) are required to obtain a measurable diffraction pattern.¹ In contrast, Raman spectroscopy can see both crystalline (diamond and graphite) and amorphous carbon and detect structural differences including bonding changes. Because of the high sensitivity of the Raman technique it can be used for ultrathin carbon samples (about 100 $\text{\AA}$). On the other hand, due to the penetration ability of visible light it is possible to use Raman to study not only the surface of the sample but also the material at some depth.⁴ At the same time Raman spectroscopy can work as a non-destructive method. Another advantage of Raman spectroscopy is that the samples do not need special preparation and the measurement can be conducted in air and more quickly. This may make Raman a potential in-situ technique.

One of the contributions made by this work to the Raman study of amorphous materials is to introduce a deconvolution method into the Raman spectrum analysis. For some of the amorphous semiconductors, such as a-Si, a-Ge and a-C, it

is found that the first order Raman spectra are continuous, as opposed to those of corresponding crystals which show only a few sharp lines.⁶ This is due to the disorder in the amorphous materials.⁷ The disorder makes selection rules, which apply to the corresponding crystalline structures, break down and all phonon modes contribute to the first order Raman spectrum. This explanation is supported by a comparison of the reduced Raman spectrum with a broadened phonon density of states (PDOS) of the corresponding crystal.⁸ That means that the comparison is done between two broad continuous curves. Our approach to this problem is from the opposite direction. We deconvolute the Raman spectrum and compare the deconvolution result with the PDOS. Thus the comparison can be done in more detail and more information can be extracted. The deconvolution method is also applied to the Raman study of material structure. Differences in the Raman spectra indicate the diversity of material structures. Due to the same reason discussed above, more structural information can be obtained from the deconvoluted Raman spectrum. The deconvolution result can reveal changes in each phonon mode induced by changes in the structure. Compared with decomposition, the traditional method used in the analysis of a-C Raman spectrum, deconvolution is one step further towards the truth.

Another contribution of this work concerns the a-C Raman spectrum. In the Raman study of a-C materials, most works focus attention on the strongest feature in the 1000-1900 cm^{-1} frequency region.¹ There are also weaker features in the 200-900 cm^{-1} region. The recording of these features can be dated back to the early days of the Raman study of a-C,⁶ but no detailed discussion on these low frequency features is found in the literature. Through our study we found that these features exist in the highly disordered structures and the intensities decrease when the structure becomes more ordered. We point out the clear relationship

between these features and low frequency modes in the PDOS of graphite. These features are used in our discussion of a-C materials having different structures.

In this work we report the observation of the Raman spectrum of W/C multilayers used in soft x-ray optics. It shows that Raman spectroscopy can be used to characterize the physical and geometrical properties of W/C multilayers.

We also studied the annealed a-C materials by using Raman spectroscopy. It is found that for the same annealing temperature different annealing environments may cause great differences in the annealed structure. This finding may have practical applications.

Chapters II and III give some background about Raman spectroscopy and amorphous carbon. Chapters IV and V describe instruments and samples used in the experiments. Chapter VI is about our observed a-C Raman spectra. In chapter VII we make some comments on the decomposition method used in the a-C Raman spectrum analysis. Chapter VIII is to introduce the deconvolution method to the a-C Raman spectrum analysis. In chapter IX we report a new finding on annealed a-C films.

II. BRIEF THEORY OF RAMAN SPECTROSCOPY

Our work has focused mainly on the experimental aspect of Raman spectroscopy. This chapter is intended to give a necessary but brief theoretical background to the subject. In particular, I follow closely the discussion of W. Hayes and R. Loudon.⁹ Some of the equations will be given without derivation. The interested reader is referred to other sources for details.

When an incident beam of monochromatic light passes through a sample, the light will be scattered in all directions from all illuminated parts of the sample. The frequency distribution of the scattered light is shown in Fig. 2.1. The strongest component, which has the same frequency as the incident light, is from elastic scattering, called Rayleigh scattering. The rest of the peaks are from inelastic scattering. According to their frequency shifts from the incident light frequency, the inelastic scattering is divided into two categories. Those with the frequency shift of approximately 1 cm^{-1} or smaller are called Brillouin components which result from scattering by acoustic phonons. The others are Raman components, resulting from scattering by internal vibrations of molecules or optical phonons in solid state materials. According to whether the scattered frequencies are smaller or larger than the incident photon frequency, the inelastic scattering components are further subdivided into the Stokes and anti-Stokes components, respectively.

There are basically two approaches to treat inelastic scattering, the microscopic method and the macroscopic method. In the microscopic method atoms are treated quantum mechanically and the interaction of the atoms with light is expressed in terms of matrix elements of the electric-dipole operator. In the macroscopic method, on the other hand, the scattering medium is described as a macroscopic polarization vector formed by combining the individual atomic dipole moments classically and

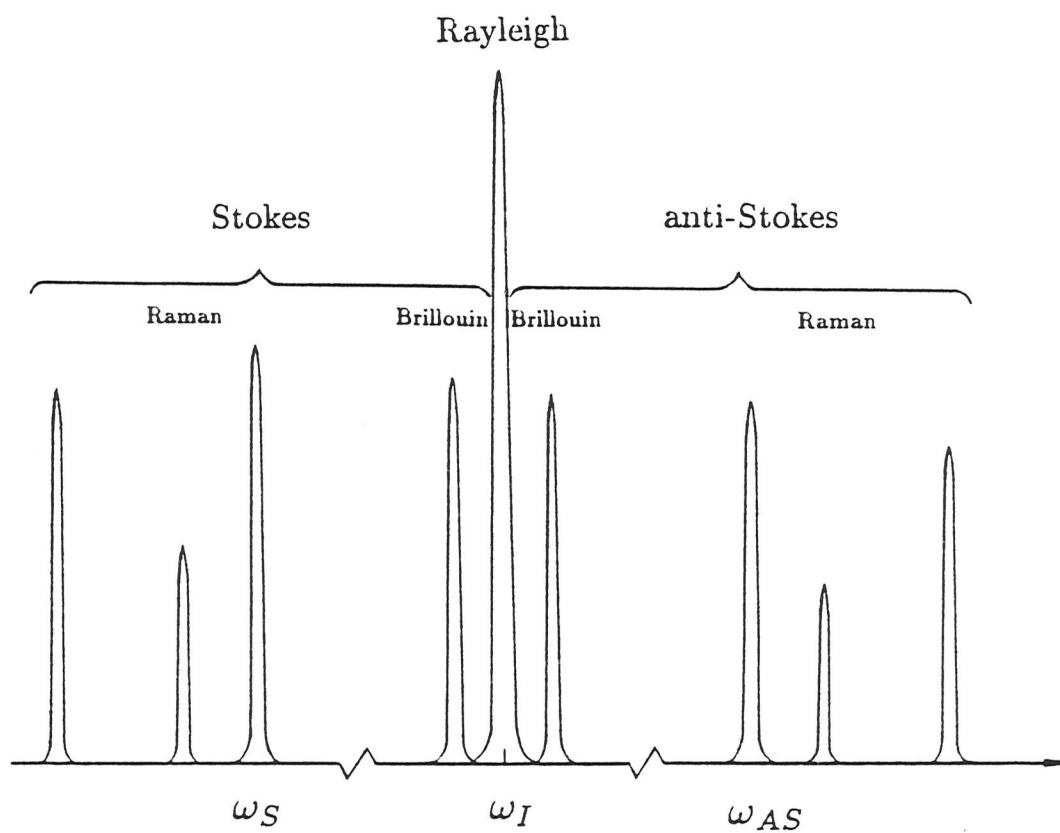


Fig. 2.1 Schematic spectrum of scattered light.

the scattered light is radiated by the oscillatory macroscopic polarization which is subject to classical Maxwell equations. Only the macroscopic method will be discussed here.

Consider an idealized light scattering experiment: the incident light is strictly monochromatic and has a frequency ω_I and a wavevector $\mathbf{k}_I$. The j th Cartesian component of the incident electric field at position $\mathbf{r}$ and time t is written

$$E_I^j(\mathbf{r}, t) = E_I^j \exp(-i\omega_I t + i\mathbf{k}_I \cdot \mathbf{r}) + E_I^{j*} \exp(i\omega_I t - i\mathbf{k}_I \cdot \mathbf{r}). \quad (2.1)$$

In the absence of any excitations of the scattering medium, the polarization induced by the incident field is

$$P^i(\mathbf{r}, t) = \epsilon_0 \chi^{ij}(\omega_I) E_I^j(\mathbf{r}, t), \quad (2.2)$$

where $\chi^{ij}(\omega_I)$ is the first-order or linear susceptibility of the medium at frequency ω_I . The excitation of the medium responsible for the inelastic light scattering is characterized by a space- and time-dependent amplitude

$$X(\mathbf{r}, t) = \sum_{\mathbf{q}} \{X(\mathbf{q}, t) \exp(i\mathbf{q} \cdot \mathbf{r}) + X^*(\mathbf{q}, t) \exp(-i\mathbf{q} \cdot \mathbf{r})\}. \quad (2.3)$$

The effect of the excitations is to modulate the wavefunctions and energy levels of the medium. The changes in these quantities are linear in $X(\mathbf{r}, t)$ to the first order in perturbation theory, and their effect is represented macroscopically by an additional contribution to the susceptibility. Symbolically, (2.2) is replaced by an equation of the form

$$P = \epsilon_0 (\chi E_I + \chi' X E_I), \quad (2.4)$$

where χ' is a second-order susceptibility which describes the modulation.

The linear polarization from (2.2) or the first term of (2.4) oscillates at the same frequency as the incident field and gives the elastic scattering. The second

term of (2.4) is the second-order polarization which oscillates at frequencies different from ω_I because X is itself a time-dependent function. The second-order polarization radiates the inelastically scattered light. Substitute E_I and X from (2.1) and (2.3) into (2.4), the second-order polarization can be separated into a sum of two contributions

$$P_S^i(\mathbf{r}, t) = \sum_{\mathbf{K}_S} \{P_S^i(\mathbf{K}_S, t) \exp(i\mathbf{K}_S \cdot \mathbf{r}) + P_S^{i*}(\mathbf{K}_S, t) \exp(-i\mathbf{K}_S \cdot \mathbf{r})\} \quad (2.5)$$

and

$$P_{AS}^i(\mathbf{r}, t) = \sum_{\mathbf{K}_{AS}} \{P_{AS}^i(\mathbf{K}_{AS}, t) \exp(i\mathbf{K}_{AS} \cdot \mathbf{r}) + P_{AS}^{i*}(\mathbf{K}_{AS}, t) \exp(-i\mathbf{K}_{AS} \cdot \mathbf{r})\}, \quad (2.6)$$

where

$$\mathbf{K}_S = \mathbf{k}_I - \mathbf{q} \quad (2.7)$$

$$\mathbf{K}_{AS} = \mathbf{k}_I + \mathbf{q}. \quad (2.8)$$

To express polarizations in terms of frequency, Fourier transform the polarizations and the excitation with respect to time. Those transformations are defined by

$$P_S^i(\mathbf{K}_S, t) = \int P_S^i(\mathbf{K}_S, \omega_S) \exp(-i\omega_S t) d\omega_S, \quad (2.9)$$

$$P_{AS}^i(\mathbf{K}_{AS}, t) = \int P_{AS}^i(\mathbf{K}_{AS}, \omega_{AS}) \exp(-i\omega_{AS} t) d\omega_{AS} \quad (2.10)$$

and

$$X(\mathbf{q}, t) = \int X(\mathbf{q}, \omega) \exp(-i\omega t) d\omega. \quad (2.11)$$

where the frequencies are related by

$$\omega = \omega_I - \omega_S \quad (2.12)$$

for the Stokes component with a gain in energy $\hbar\omega$ by the sample and

$$\omega = \omega_{AS} - \omega_I \quad (2.13)$$

for the anti-Stokes component with a loss in energy $\hbar\omega$ by the sample. Then substitute expressions (2.1) and (2.11) into the second term in equation (2.4) and compare this term with (2.9) and (2.10). Terms with common time dependence can be written

$$P_S^i(\mathbf{K}_S, \omega_S) = \epsilon_0 \chi^{ij}(\omega_I, -\omega) X^*(\mathbf{q}, \omega) E_I^j \quad (2.14)$$

$$P_{AS}^i(\mathbf{K}_{AS}, \omega_{AS}) = \epsilon_0 \chi^{ij}(\omega_I, \omega) X(\mathbf{q}, \omega) E_I^j \quad (2.15)$$

where the second-order susceptibility is here written in an expanded notation to show its dependence on the Cartesian components of the field and polarization and on the frequencies of the incident light and the excitation. Its prime has been dropped. The polarizations (2.14) and (2.15) produce the Stokes and anti-Stokes components of scattered light, respectively.

III. AMORPHOUS CARBON

In this chapter we will discuss the general characteristics of amorphous materials. The materials concerned here are all in solid state and the words amorphous material and amorphous solid will be used to mean the same thing. Since this work focuses on the study of amorphous carbon, particular details relative to it will also be presented.

A. Concept of amorphous solid

The scientific study of amorphous materials, compared with the study of crystalline materials, is relatively new. This is evidenced by the conventional solid-state texts, which deal almost wholly with crystalline materials. What is the amorphous state? An amorphous material is a disordered system. First, in contrast with a perfect crystal, there is no long-range order, i.e., no translational periodicity in an amorphous material. Second, however, there are different degrees of short-range (or local) order. The term here, short-range order, refers to the degree to which factors like coordination number, bond length and bond angle conform to the ideal found in crystals. This short-range order makes amorphous solids different from liquids and gases, and relates the amorphous material to the corresponding crystalline material. The fact that the degree of short-range order can vary continuously gives amorphous solids an important property: the amorphous state is not a single state but a continuum. The distinction between amorphous and polycrystalline materials should also be mentioned. Following the discussion of M. H. Brodsky¹⁰ a polycrystalline solid is composed of crystal grains. Each grain contains a periodic array of atoms surrounded by a layer of boundary atoms. As the grain size is decreased to the microcrystalline range, the surface layer of each grain contains a larger number of atoms relative to the periodically arrayed interior atoms. Eventually for small

enough grains the distinction between the interior and surface is lost, and the concept of microcrystallites with a definable periodic region loses its meaning. While attempts have been made to model amorphous structure by microcrystallites, it is now generally accepted that network models are more applicable.

B. Amorphous carbon

There has been an explosion of interest recently as more materials are produced in an amorphous form, some of which have considerable technological promise. The subject of this study, amorphous carbon, is an example. Hydrogenated amorphous carbon (a-C:H) films are used as hard, transparent coating material.¹ Ultrathin amorphous carbon films are used in the making of soft x-ray mirrors.⁴ In this section we will present some knowledge related to amorphous carbon.

The carbon bonding defines the short-range order in amorphous carbon. J. Robertson² has given a complete review on the bonding structure of carbon. According to his discussion, a carbon atom, in principle, can adopt three different bonding configurations, sp^3 , sp^2 and sp^1 . In the sp^3 configuration, each of the carbon's four valence electrons is assigned to a tetrahedrally directed sp^3 hybrid orbital, which then forms a strong σ bond with an adjacent atom. At a carbon sp^2 site, three of the four electrons are assigned to the trigonally directed sp^2 hybrids which form σ bonds; the fourth electron lies in a p_z orbital lying normal to the σ bonding plane. The p_z orbital forms weaker π bonds with adjacent p_z orbitals. At sp^1 sites, only two of the electrons form σ bonds, along $\pm 0x$, and the two other electrons are left in orthogonal p_y and p_z orbitals to form π bonds. A σ bond between two sites is called a single bond, while a $\sigma - \pi$ bond pair is called a double bond.

There are two commonly seen crystalline forms of carbon: diamond and

graphite. Diamond consists entirely of sp^3 bonded atoms. The saturated bonding produces the wide band gap (5.5 eV) and low conductivity, and the isotropy of the bonding gives it its strength. Graphite consists of hexagonal layers of sp^2 sites, weakly bonded together by van der Waals forces into a ABAB stacking sequence along the c axis. Conductivity and strength are high along the basal plane but are low along the c axis. Amorphous carbon contains largely sp^2 sites and perhaps some sp^3 sites.¹¹ It is a semiconductor and electrical conduction is by variable range hopping in states near E_F .

Carbon is slightly more stable in the graphite lattice, and increasingly unstable in lattices of higher coordination. The fundamental reason for this behavior is that all first row elements are atypical in having no p-like core electrons. This causes their p orbitals to be more compact and more tightly bound, compared to the s states and compared to Si. This effect strengthens carbon's sp^2 σ bonds compared to its sp^3 bonds, and favors the graphite structure. Many disordered forms of carbon have structures based on the lattice of graphite.

There are 4 atoms in the unit cell of graphite and the unit cell has a symmetry consistent with the space group D_{6h}^4 . The point group of D_{6h}^4 is isomorphic with D_{6h} .¹² In crystals, the conservation of wavevector limits only the modes near the Brillouin-zone center to be Raman or IR active. From the properties of the point group and the requirement that all unit cells must vibrate with the same phase ($\mathbf{k}=0$ or corresponding to the totally symmetric mode of the translation lattice), the symmetry properties of the normal modes for $\mathbf{k}=0$ can be calculated. The results are

$$2B_{2g} + 2E_{2g} + A_{2u} + E_{1u}. \quad (3.1)$$

Only the $2E_{2g}$ modes are expected to be Raman active. Raman peaks corresponding to these two modes are at 1581 cm^{-1} and 42 cm^{-1} , respectively.¹³ The main E_{1u}

mode and the out-of-plane A_{2u} mode are infrared active with positions at 1585 cm^{-1} and 868 cm^{-1} , respectively.

In amorphous carbon, due to the loss of long-range order, the k -conservation breaks down and all modes become active. Thus, it is expected that the infrared spectrum should resemble the phonon density of states and that the Raman spectrum resemble the phonon density of states weighted by a matrix element. The infrared and Raman spectra may also reveal disorder-induced changes in the phonon density of states. The main feature in Raman spectrum of amorphous carbon is located at about 1500 cm^{-1} which is a strong evidence in favor of graphite bonding.

IV. INSTRUMENTATION

A. Excitation source and fore-optics

The experimental set up is shown in Fig. 4.1. The excitation for the Raman spectrum is from an Ar^+ laser. Six strong laser lines can be used in the experiment. The laser usually operates in the light control mode. In this mode the input electrical power is adjusted by the feedback from the laser light to stabilize laser output power. There is also spontaneous emission light in the laser light beam. Since this spontaneous emission is generated by the gas discharge in the plasma tube of the laser and is in the form of line spectrum it is often called "plasma lines". The intensity of plasma lines is much weaker than laser lines, but is comparable to the intensity of the Raman scattering light. Some plasma lines may fall in the same frequency region as the Raman spectrum. Thus to obtain accurate and unambiguous Raman spectra, a wavelength selector is used in the fore-optics to "clean" the laser light. The key parts of the selector are the grating G1 and slit S1. Fig. 4.2 shows the spectra obtained with and without the selector.

The filtered laser light goes through L1 and is incident on the sample. L1 is a cylindrical lens which focuses the light in one dimension so that the sample is illuminated by a narrow line of light. The purpose for using this lens is to let the image shape of the illuminated sample area formed by lenses L2 and L3 match the shape of the entrance slit of the spectrometer. This makes efficient use of the excitation light. A mirror between L1 and the sample changes the incident angle to the sample to get the best coupling of the excitation light and the sample. The coupling can be monitored by measuring the intensity of the specular reflection from the sample. The weaker the reflected light, the more of the incident light energy is coupled to the sample and more scattered light can be generated. The focal length

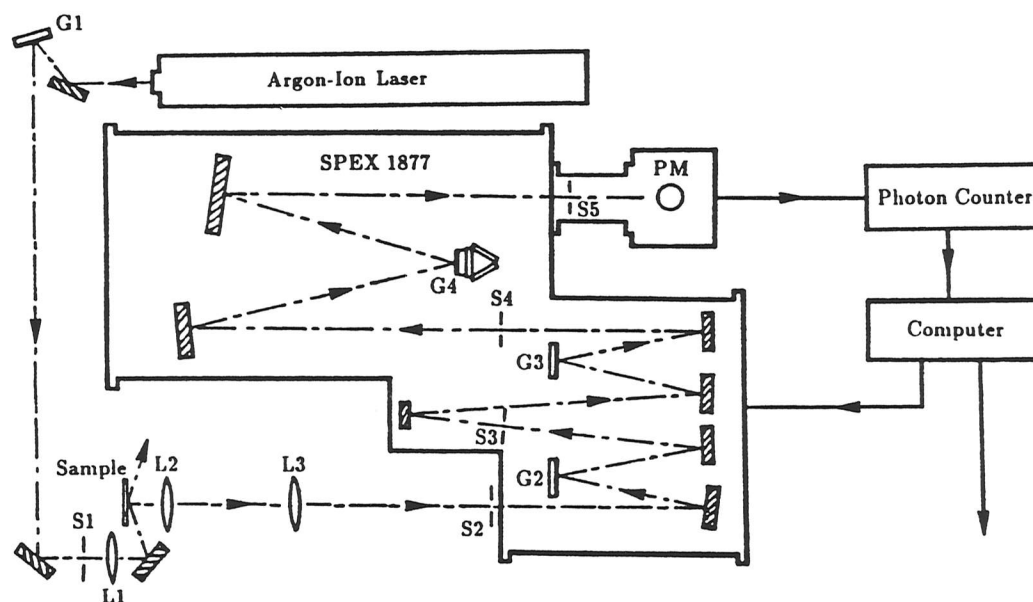


Fig. 4.1 Raman spectroscopy set up. The light from Ar^+ laser is "cleaned" by G1 and S1 and illuminates on the sample. The scattered light from the sample is collected by L2 and L3 and fed to the spectrometer SPEX 1877. The signal from the spectrometer is detected by the photomultiplier PM and the photon counter and stored in the computer. The computer also controls the scan of the spectrometer and sends the measured data to the main computer network.

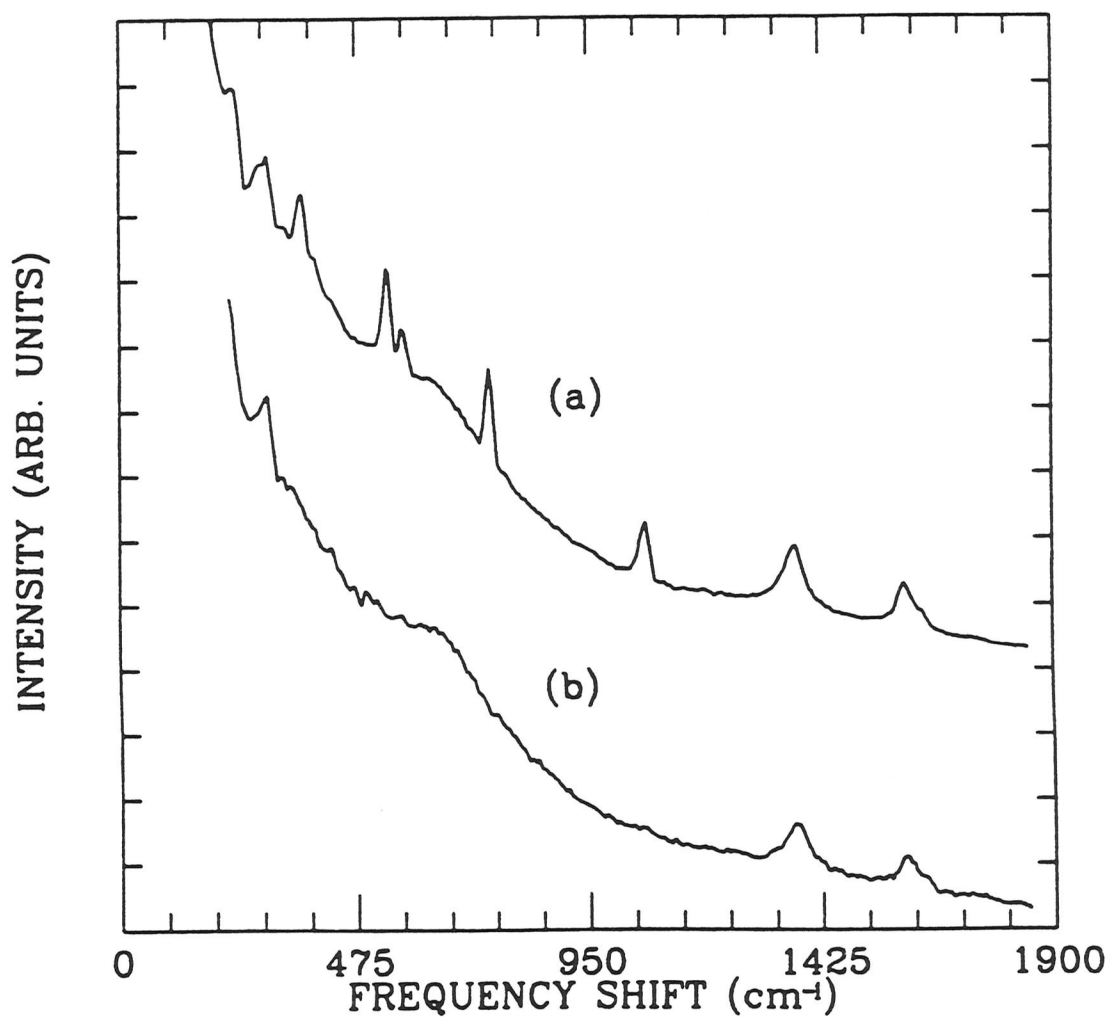


Fig. 4.2. Raman spectrum of polycrystalline graphite. The spectrum (a) was obtained without using the wavelength selector in the fore-optics and (b) with the selector. The peaks at about 1350 and 1580 cm^{-1} are the characteristics of polycrystalline graphite. The source of the feature at about 290 cm^{-1} is unknown.

of L3 determines the spots size on the optical elements inside the spectrometer. Underfilling will reduce the resolving power of the gratings in the spectrometer, overfilling will result in extra stray light.

B. Raman spectrometer

The Raman spectrometer is a powerful monochromator. This apparatus uses a SPEX 1877 Triplemate. It consists of two main sections. The first is the filter stage which is a 0.22-m double monochromator with gratings G2 and G3 locked in a subtractive-dispersion mode. It acts as a variable-wavelength selectable bandpass filter that feeds a non-dispersed segment of radiation from the spectrometer entrance into the entrance of the second, or spectrograph stage. The second stage is an 0.6-m single-monochromator. It disperses the radiation from the slit S4 over the exit slit S5.

The slit setting determines the resolution and positivity of the spectrometer. The entrance slit S2 lets the scattered light from the sample enter the spectrometer. It should be wide enough to allow the whole sample image to enter the spectrometer. We found that if S2 is too wide more stray light from the outside is admitted. Fig. 4.3 shows the effect of S2. The slit S3 in the filter stage determines the bandpass of the radiation that reaches the spectrograph stage. For the maximum spectral coverage this slit should be wide open, however, for low frequency spectra the slit may be tightened down for additional stray-light rejection or to block the high intensity of laser illumination. Slit S4 controls the resolution of the spectrograph stage. S5 is the exit slit of the spectrometer. When the spectrometer works with the photomultiplier (PM) detector, i.e., in the scanning mode (opposite to the mode with optical multichannel detectors) widths of S4 and S5 decide the slit function of the spectrometer. Let a beam of monochromatic light which can be described as a δ -function in the spectrum strike S4 and fill the whole width of the slit. If

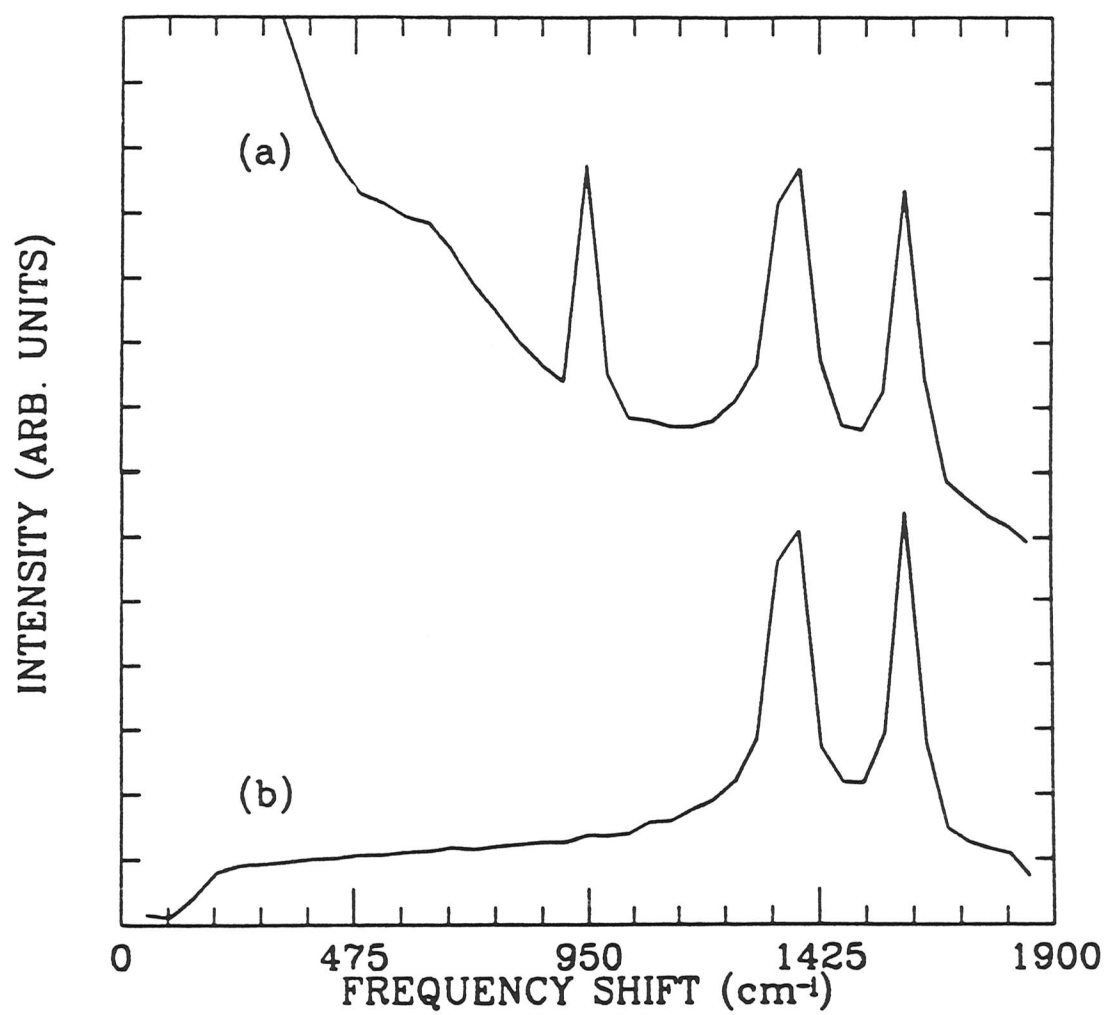


Fig. 4.3. Raman spectrum of polycrystalline graphite with the spectrometer entrance slit (S2) width of (a) 2.5 mm and (b) 1.0 mm.

the magnification of the spectrograph stage is unity, which is the case of SPEX 1877, then the image of S4 on the S5 plane has the same width as S4. In the scanning mode the output from S5 can be calculated by convoluting the function form of S4 with that of S5. The process can be intuitively seen from the cartoon in the upper half of Fig. 4.4. The cartoon shows how the two slits, indicated by two shaded rectangles, slide one relative to the other. The double shaded area represents the proportion of the light that passes through S5. The curve in Fig. 4.4 shows the calculated intensity of the output spectrum in the case where $S_4=0.25$ mm and $S_5=0.50$ mm and the data points are the measured value under the same situation. Now a line spectrum, after going from S4 to S5, is expanded and becomes a triangular or a trapezoidal distribution depending on whether the two widths are equal or not. This process can be expressed as

$$I(\lambda) = \int_0^\infty O(\lambda')S(\lambda' - \lambda)d\lambda' \quad (4.1)$$

where I is the observed spectrum, O is the original or the true spectrum and S is the slit function of the spectrometer. To obtain the slit function S a spectral line from a krypton-86 lamp was used as O . Since the line width is less than 10^{-3} nm, a δ -function can be used to approximate the functional form of O . Substitute this O into Eq. (4.1) and we have I equals S . Therefore the functional form of S is the same as that of measured spectrum. Fig. 4.5 shows the relation between the slit width and the half width of the triangles for measured slit functions. The relation is almost linear and can be expressed as

$$W_T = \alpha W_S \quad (4.2)$$

where W_T is the half width of the triangles, W_S is the slit width for both S4 and S5 and α is the slope which equals 0.92 nm per mm. Recall that the convolution of two identical rectangles gives a triangle with a half width equal to the width of

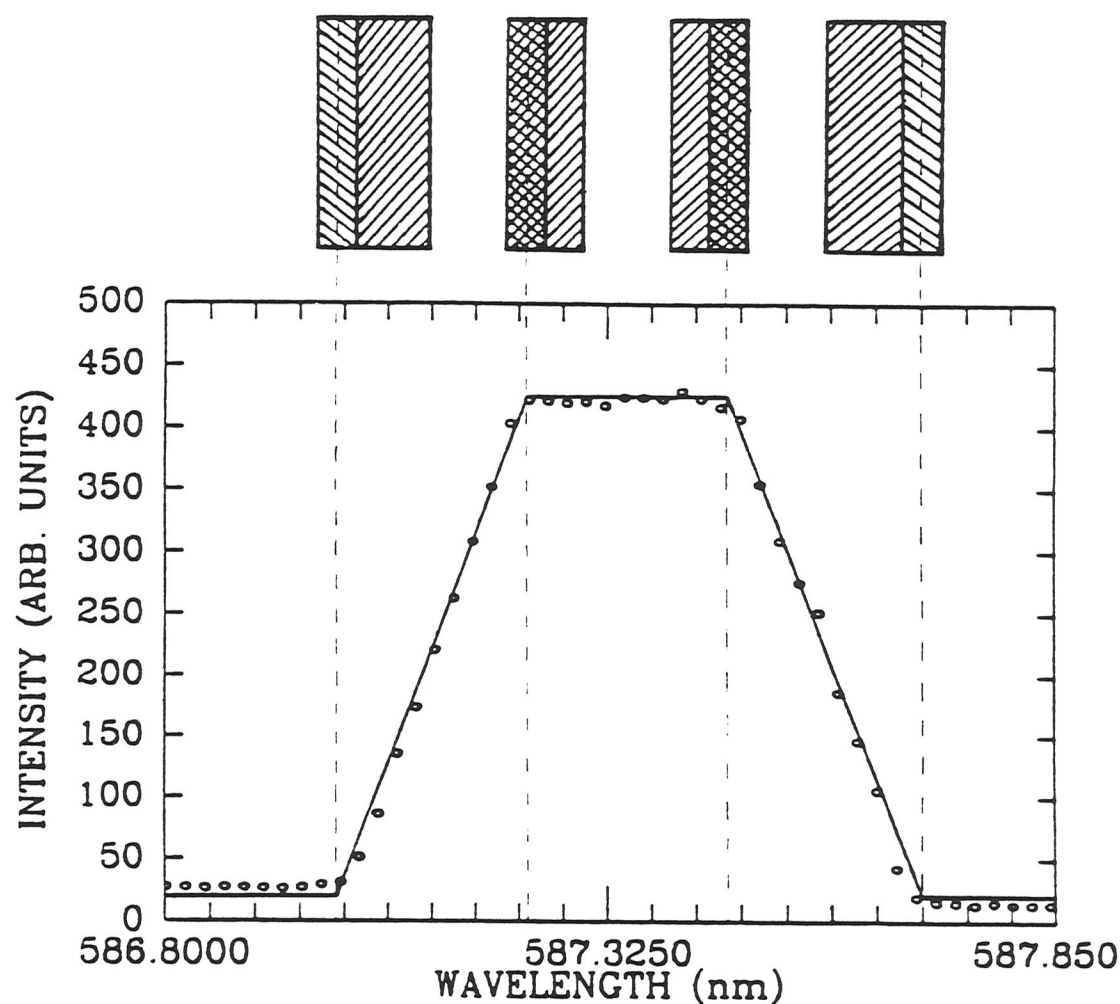


Fig. 4.4. The spectrometer output of a line spectrum with $S_4=0.25$ mm and $S_5=0.50$ mm. The solid line curve is the calculation result of Eq. (4.1) and the circles are the measurement of a Kr-86 spectral line which has line width less than 10^{-3} nm. The shaded rectangles above indicate the corresponding positions of the image of S_4 relative to S_5 . The double shaded area is where the input light can pass through S_5 .

the rectangles. Thus, if the model used for S is correct, α should have the same value as the dispersion of G4 at the exit slit S5. From the SPEX 1877 Triplemate instrument manual this value is 0.92 nm/mm for the 1800 gr/mm grating that we used. Checking with the data in Fig. 4.5 the agreement is very good. The deviation from the fitted line at narrow slit widths is due to the fact that the assumption about O is only correct when the value of slit width is much greater than the width of krypton-86 spectral line which is in the order of 10^{-3} nm. The above discussion about the slit function also suggests that while working on spectra involving narrow peaks, it is necessary to deconvolute the observed data using the slit function to recover the true spectrum.

Generally, the finer the grating the higher the resolution. In the filter stage the higher the resolving power the greater the rejection of stray light. This is important for Raman spectroscopy because of strong Rayleigh scattering. In the spectrograph stage the higher resolving power enables you to see more details of the spectrum. But the finer the gratings the narrower the total spectral coverage for both stages.

C. Scanning control and data acquisition

The spectral scan of the spectrometer and data acquisition is done by a 7000-MDAS Modular Data Acquisition System (MDAS). An HP computer is connected to MDAS to input instructions and store the data. The photo-electrons from the photomultiplier are counted by an SSR Model 1110 Photon Counter (PC). The photon counter works in the chopper mode and the output of the photon counter is the number of photo-electrons in each chopper cycle which is 1 second in our case. The whole data taking process can be divided into five steps as follows:

1. Input the scanning start position, scan length, number of data points and the data taking time at each point to MDAS through the computer key board.
2. MDAS drives the spectrometer to the start position. The measurement begins.

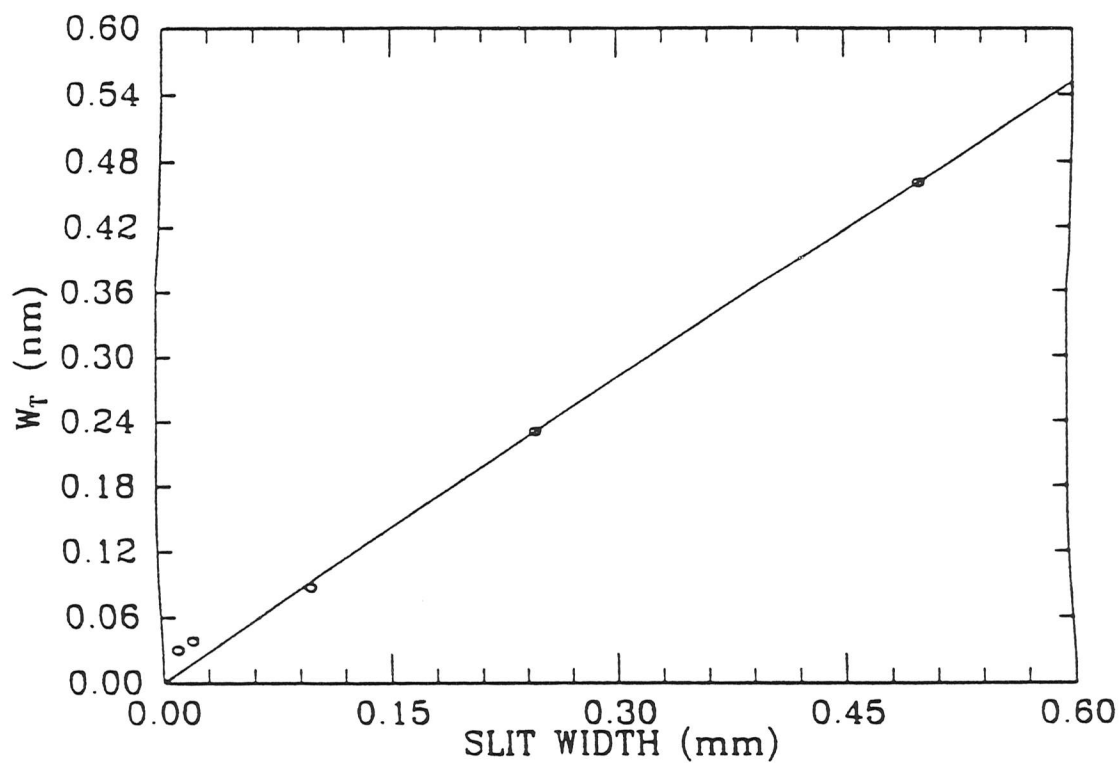


Fig. 4.5. The half width of the slit function vs. the slit width. Slits S4 and S5 have the same widths. Circles are the measured data of a Kr-S6 spectral line. The straight line is from the calculation of Eq. (4.2) with $\alpha=0.92$ nm/mm.

3. MDAS collects the output from PC and sends it to the computer where the total number of photo-electrons for a time specified in step 1 is summed and stored in memory.

4. MDAS drives the spectrometer to the next data taking position.

Step 3 and 4 are repeated until the scanning is done. The process may be real-time monitored through the computer.

5. Transfer the data from the memory to a floppy disc. The data can also be transferred to the main computer network for further processing.

Because of the statistical nature of the data, the longer the data acquisition time at each data point, the better the signal to noise ratio. This is a time averaging effect which is effective but is not efficient for the scanning mode in which the data are taken serially. For some samples with weak Raman signal the data taking time at each point can be as long as 60 seconds for an acceptable signal to noise ratio.

D. System calibration

In Fig. 4.1 the scattered photons from the sample go through collecting lenses L2 and L3 and the spectrometer. Then they are detected by a photomultiplier tube which generates a measurable electrical signal. The efficiency of the conversion from photons into an electrical signal varies with the energy or the wavelength of the photons. The cause for this variation is that the absorption of the lenses, the reflection of the mirrors, the diffraction efficiency of the gratings and the sensitivity of the photomultiplier tube are all functions of the photon energy. Let us call the relationship between the conversion efficiency and the wavelength the Raman system spectral response characteristic, or system response for short. It is clear that before conducting the actual spectral measurement the system response has to be found, i.e., the system has to be calibrated.

Different methods can be used in the calibration. The method we used utilizes

a continuous spectrum from a standard lamp. The lamp used was an Optronic Laboratories 45-watt Tungsten-Halogen Lamp. The total irradiance of the lamp is based on the radiance of a blackbody as defined by the Stefan-Boltzman radiation law. The spectral irradiance from the lamp over the wavelength range of 250 nm to 1600 nm is based on the National Bureau of Standards 1973 scale of spectral irradiance. The lamp was placed in the position of the sample and the irradiance from the lamp was taken as the input to the system. The conversion process can be expressed as

$$I_o(\lambda) = T(\lambda)I_i(\lambda) \quad (4.3)$$

where $I_o(\lambda)$ is the measured output irradiance, $T(\lambda)$ is the conversion factor and $I_i(\lambda)$ is the input irradiance. The functional form of $I_i(\lambda)$ can be found by fitting the spectral irradiance data given in the manufacturer's instructions to Planck's equation

$$I_i(\lambda) = \varepsilon(\lambda) \frac{C_1}{\lambda^5} \left[\frac{1}{e^{\frac{C_2}{\lambda T}} - 1} \right] \quad (4.4)$$

where $\varepsilon(\lambda)$ is the emissivity of tungsten whose value is near unity, T is the temperature of the lamp filament which will be found in the fitting and the two constants, C_1 and C_2 have values

$$C_1 = 2\pi hc^2 = 3.7415 \times 10^{-16} (Wm^2)$$

$$C_2 = \frac{hc}{k} = 1.43879 \times 10^{-2} (mK)$$

where h is Planck's constant, c is the velocity of light in vacuum and k is Boltzmann's constant. Fig. 4.6 shows the given spectral irradiance data and the fitting curve with the temperature $T=2800.114K$. The data points in Fig. 4.7 are measured irradiance values. The whole spectrum is divided into five segments and the data in each segment are fitted to a Gaussian function to find the functional form of I_o . The solid line in Fig. 4.7 is the fitting curve. $T(\lambda)$ can be calculated by substituting

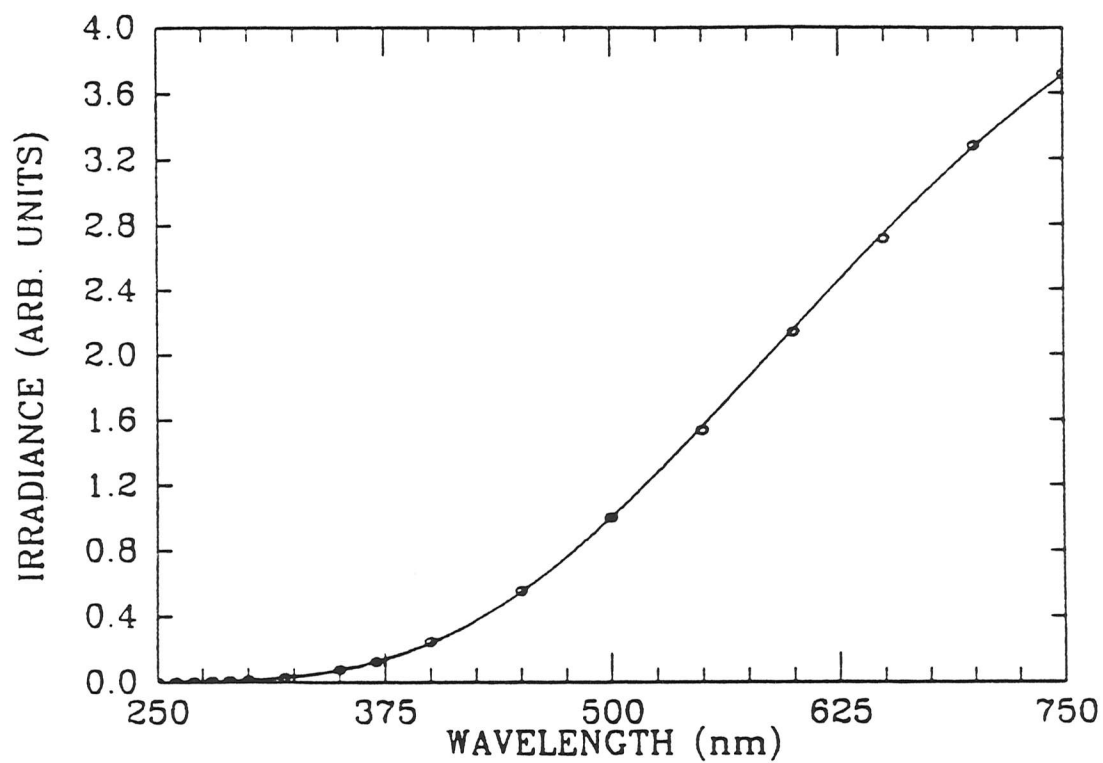


Fig. 4.6. The tungsten-halogen lamp radiation curve. Circles are the data provided by the Optronic Laboratories, Inc. and the solid line curve is from Planck's equation with $T=2800.114\text{K}$.

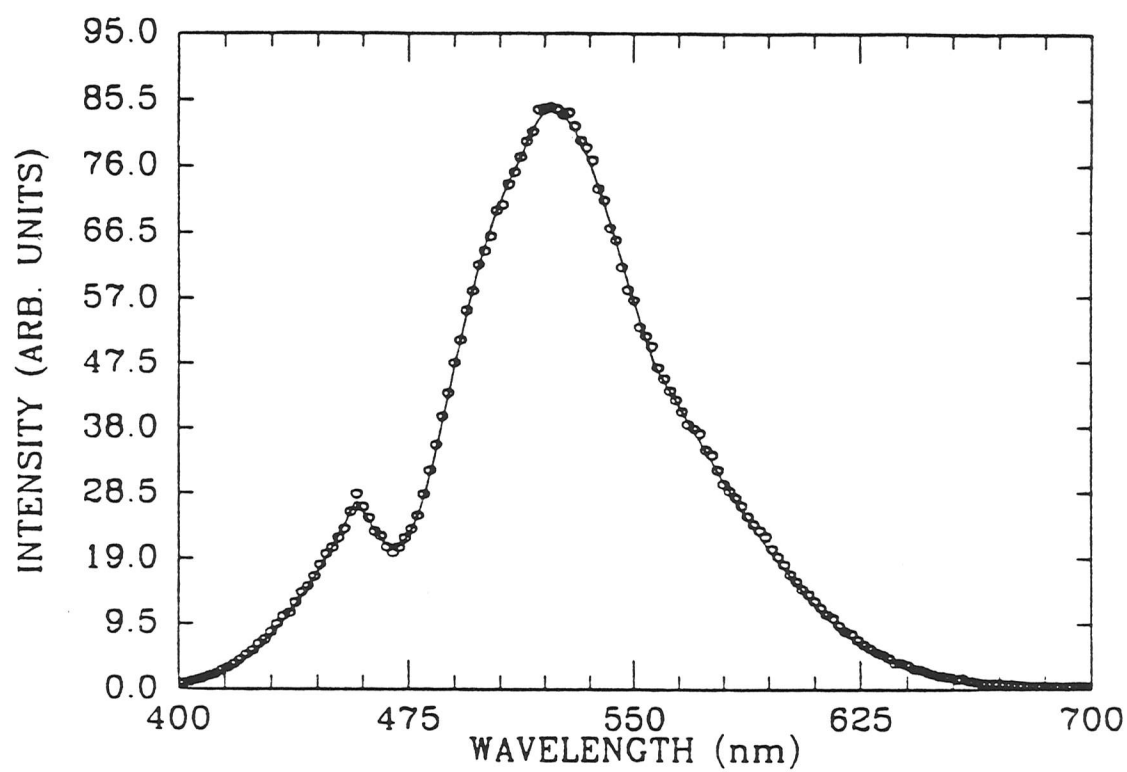


Fig. 4.7. The measured spectrum of the tungsten-halogen lamp. The solid line is the fitting curve to the measured data.

the function form of $I_i(\lambda)$ and $I_o(\lambda)$ obtained above into Eq. (4.4). $T(\lambda)$ will be used in the experiments to correct measured spectra.

In the above discussion we have neglected the effect of the slit function. The spectrum discussed here is slowly varying in a range of several hundreds nm. On the other hand, in section B we found that the half width of the slit function is only about 0.5 nm wide. So the convolution in Eq. (4.1) would not give much difference between the observed spectrum and the slit effect free spectrum.

V. SAMPLE PREPARATION

All the samples were made by DC-magnetron sputtering. The sputtering method consists of the bombardment of a target by energetic ions from a low-pressure plasma, causing erosion of the target material, either atom by atom or as clusters of atoms. The sputtered material is subsequently deposited as film on a substrate. The plasma is generated by the discharge in argon gas. Before introducing Ar, the vacuum chamber was pumped down to about 2×10^{-6} Torr. The supporting substrates were crystal Si wafers. During the deposition the substrate temperature was estimated at about 60°C. The control of the thickness of the deposited film was achieved by controlling the deposition time. Because of the relatively low temperature of the substrate the adatom mobility is sufficiently low that the material deposited on the substrate usually forms an amorphous film.

Two kinds of samples were used in this work: single layered carbon films and W/C multilayers. For the single layered carbon samples, the thickness of the film is about 4000 Å. Both as-deposited and annealed carbon film samples were studied. The annealed samples were made from as-deposited samples by two different ways. One annealing procedure was to put the sample in a vacuum chamber, pump the chamber down to 10^{-2} Torr and then introduce Ar into the chamber. With the Ar gas flowing the sample was heated to the desired temperature, kept at that temperature for certain time and then cooled down naturally to near room-temperature. The annealing temperature range for this method was from 400 to 1000 °C, determined by the capability of the vacuum chamber. The other way of annealing was simply to heat the sample in a furnace in the atmosphere. To avoid burning the carbon film in the air, the highest annealing temperature used in this method was below 500°C. The W/C multilayer samples are similar to those used as mirrors in

soft x-ray optics. They consist of two sputtered materials: carbon and tungsten, arranged alternately in layers of thickness d_C and d_W , respectively, so that the periodicity of the structure is $d=d_C + d_W$. For all multilayer samples the number of periods is 30 and the nominal thickness of each tungsten layer, d_W , is 20 Å. The nominal thickness of each carbon layer, d_C , is 20, 40 and 80 Å, respectively, for the three multilayer samples used in this work.

VI. RAMAN SPECTRUM OF a-C

Raman spectra reveal the structure and structural changes in a-C materials. The a-C Raman spectrum can be related to the phonon density of states (PDOS) of crystalline graphite.⁸ One evidence that this is a worthwhile approach is the similarity between the first order Raman spectrum of a-C and that of polycrystalline graphite in the 1000-1900 cm^{-1} region (Fig. 6.1). On the other hand, the structural differences between a-C and polycrystalline graphite materials suggest that in addition to the broadening of the graphitic features there should be some new features appear in the a-C Raman spectrum due to the further breakdown of selection rules in the highly disordered a-C material. P. Lespade and R. Al-Jishi¹⁴ calculated the Raman intensity of disordered carbon materials based on the phonon density of states of graphite. Their calculation predicts a weak feature at about 800 cm^{-1} but they failed to observe it experimentally.

In Fig. 6.2 we display the Raman spectrum obtained from an as-deposited carbon film sample. It is a typical Raman spectrum of a-C material. Fig. 6.3 shows the Raman spectra of W/C multilayer samples. Compared with Fig. 6.2, the Raman spectrum of W/C multilayer is almost identical to that of a-C. The reason is that metal, such as tungsten, usually has very weak Raman signal. Thus in the W/C multilayer case only carbon layers give significant Raman scattering and the tungsten layers act primarily as attenuator to the incident and scattered light.

The distinct characteristic of the first order a-C Raman spectrum is the asymmetric feature in the 1000-1900 cm^{-1} region with the summit at about 1550 cm^{-1} . A lot of research has been done on this feature to obtain information about material structure.^{3,15,16,17} There are also features in the 200-900 cm^{-1} region with two maxima at about 400 cm^{-1} and 750 cm^{-1} . The intensity of maxima is about

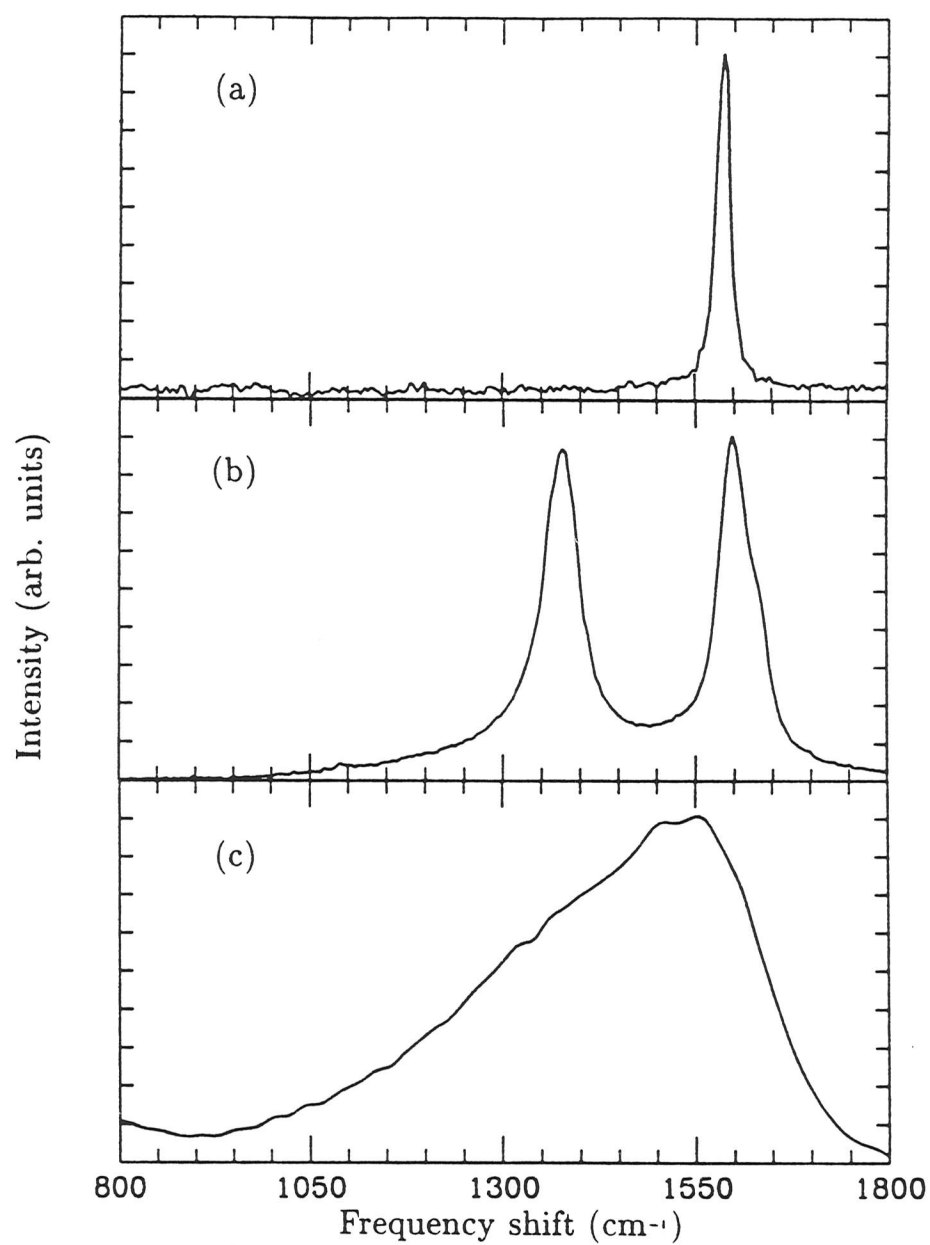


Fig. 6.1 Raman spectrum of (a) single crystal graphite, (b) polycrystalline graphite and (c) a-C.

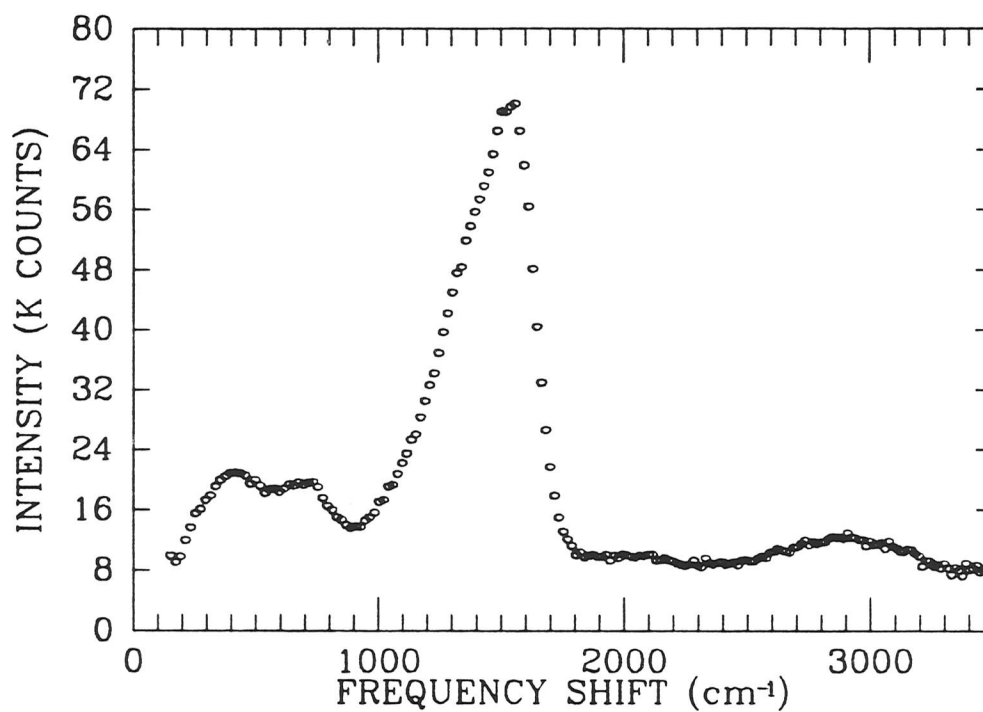


Fig. 6.2 Raman spectrum of an as-deposited sample. The spectrum was cut off at 170 cm^{-1} during the measurement to reduce the Rayleigh scattering intensity. Data points in the region below 400 cm^{-1} were obtained by subtracting the estimated Rayleigh scattering intensity from measured values.

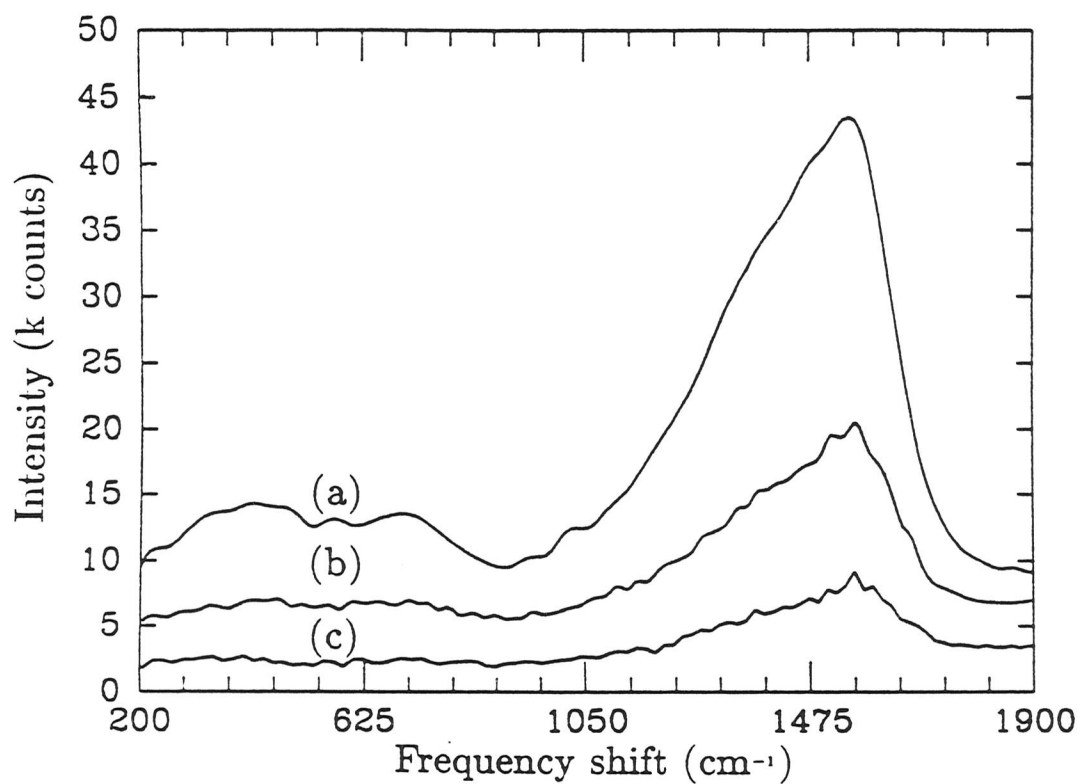


Fig. 6.3 Raman spectrum of W/C multilayers. The multilayers consist of 30 periods. The d_W in each layer pair is nominally a constant of $20 \text{ \AA}$ for all multilayers. The d_C in each layer pair is 80, 40 and $20 \text{ \AA}$ for the curves labeled (a) to (c), respectively.

4 times weaker than the feature centered around 1550 cm^{-1} , but stronger than the second order Raman spectrum around 2900 cm^{-1} . These low frequency features have only been noted previously in a few cases but we could not find any detailed study on them and their behaviour under changing conditions such as annealing.

To learn more about these features we annealed a set of a-C samples in a vacuum chamber at different temperatures for 1 hour with argon gas flowing. The Raman spectra of those samples are presented in Fig. 6.4. As the annealing temperature increases some trends can be clearly seen. First, the low frequency features become less pronounced and the two maxima shift towards higher frequency. They are, however, still visible even for the sample annealed at 1000°C . Second, at the same time the shoulder at about 1360 cm^{-1} gradually grows higher and becomes distinct from the strongest peak at about 1580 cm^{-1} and is resolved as a separate peak. In addition, the 1580 cm^{-1} peak itself seems to shift to higher frequency. Third, the overall intensity of the features in the $1000\text{-}1900\text{ cm}^{-1}$ region do not change much. It is also hard to see any change in the second order spectrum.

The function of annealing is to provide energy to the annealed material so that some defects and interstitials in the structure can be released. After annealing, the structure of the material becomes more ordered. The observations that the low frequency features do not appear in single crystal and polycrystalline graphite materials,¹³ and gradually disappears when the annealing temperature increases are evidence that they must be characteristic of highly disordered a-C. It is generally believed that the Raman spectrum of a-C is related to the PDOS of graphite.^{8,16,17,18} According to PDOS's calculated by Nicklow *et al.*¹⁹ and by Al-Jishi and G. Dresselhaus²⁰ in the $200\text{-}900\text{ cm}^{-1}$ region of the PDOS of graphite there are three high density peaks.^{19,20} One of them is at about 800 cm^{-1} which is due to the M-point zone-boundary phonon mode with "in-plane" atomic displacement.

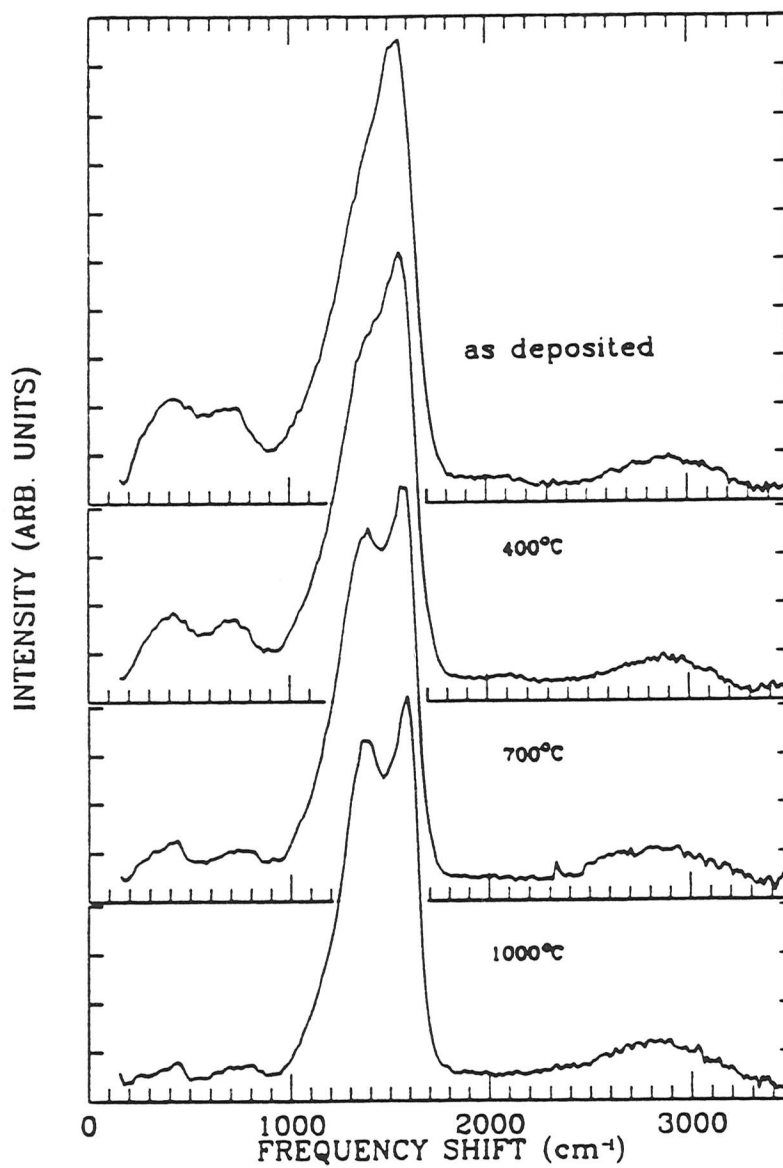


Fig. 6.4 Raman spectra of as-deposited and annealed samples. The annealing was done in a vacuum chamber with argon gas flowing.

Of the other two, one is at about 470 cm^{-1} and another at either about 750 cm^{-1} (Nicklow *et al.*) or about 580 cm^{-1} (Al-Jishi *et al.*) corresponding to the M-point phonon modes with "out-of-plane" displacement. Since the positions of maxima of the low frequency features we observed (one is at about 400 cm^{-1} and another at about 750 cm^{-1}) are in reasonably good agreement with those high density peaks, we attribute these low frequency features to the M-point zone-boundary phonon modes with "in-plane" and "out-of-plane" atomic displacement, respectively.

In the crystal case, symmetry in the structure give selection rules which make most phonon vibration modes Raman inactive. For example, as discussed in Chapter III, for graphite only the two E_{2g} modes are Raman active. This is the reason why the low frequency features in the $200\text{-}900\text{ cm}^{-1}$ can not be seen in Raman spectra of single crystalline and polycrystalline graphite materials. The presence of these features indicate the breakdown of certain selection rules due to the structural disorder. The evolution of these features can be used in the study of the structural changes. On the other hand the study of these low frequency features itself also has theoretical importance. As discussed above, the Raman spectrum of a-C is believed to relate to the PDOS of graphite. Most of PDOS's calculated are based on the neutron-scattering measurement. But until now the experimental data is only available in the region below 500 cm^{-1} .²⁰ This means that the calculated PDOS is more reliable in the low frequency region. So a better way to verify the assumed relationship between a-C Raman spectrum and PDOS of graphite is to compare the two in the low frequency region. Unfortunately, limited by the gratings used in the filter stage of the Raman spectrometer (600 gr/mm) we could not get high quality spectra in this region. The problem is the strong Rayleigh scattering light. To reduce it the spectrum has to be cut off at 170 cm^{-1} . Below 400 cm^{-1} the spectra were obtained by subtracting the estimated Rayleigh scattering from observed data.

This problem could be solved by using two finer gratings, such as 1800 gr/mm ones, in the filter stage.

VII. SPECTRUM ANALYSIS: DECOMPOSITION

The basic assumption of the decomposition method is that the observed spectrum is the envelope of the superimposition of several individual peaks. The number of peaks and the line shape of each peak has to be found through some physical arguments. The decomposition process is to add the n line shape functions together and fit the sum to the observed data. The fitting is done by a modified Levenberg-Marquardt algorithm²¹ which minimizes the sum of the squares of the differences between each observed data point and the corresponding function value by adjusting the parameters of each line shape function. From the basic assumption comes the limitations for this method. First, the spectrum has to be the sum of several peaks which have closed functional form. Second, the number of individual peaks which make up the observed spectrum has to be known before the decomposition process. Unfortunately, sometimes finding the number of the peaks is one of the purposes of the spectrum analysis. The decomposition method and its limitation will be demonstrated through the analysis of a-C Raman spectrum .

In recent studies of the a-C Raman spectrum it becomes almost routine to decompose the continuous spectrum in the 1000-1900 cm^{-1} region into a G-peak at about 1580 cm^{-1} and a D-peak at about 1350 cm^{-1} .^{3,5,16,22} The letter G stands for graphite because this peak is centered roughly at the same position as the sharp Raman peak of the single crystal graphite. The letter D stands for disorder. The reason to call it a disordered peak is that in the spectrum of graphite with very small crystalline size there is a narrow peak at 1355 cm^{-1} which is attributed to the structural disorder or particle size effect. In the polycrystalline graphite case, F. Tuinstra and J. L. Koenig¹² showed that the intensity ratio of the 1355 cm^{-1} and 1575 cm^{-1} lines, I_{1355}/I_{1575} , is inversely proportional to the crystallite size,

L_a . Hoping to use this relation to study the a-C materials is the main reason for making the two-peak decomposition in the a-C Raman spectrum analysis.

Comparing the Raman spectra of polycrystalline graphite and a-C, the features in a-C spectra are so broad that in the 1000-1900 cm^{-1} region it looks like there is only one asymmetrical broad peak with the highest point at about 1550 cm^{-1} and a shoulder at about 1300 cm^{-1} . To decompose the feature in the 1000-1900 cm^{-1} region into two peaks, some researchers use the well known Gaussian line shape without justification³ and others use a damped harmonic oscillator line shape derived by DiDomenico *et al.*²³

$$\frac{\partial I}{\partial \omega} = \frac{N\Gamma\omega_0}{(\omega_0^2 - \omega^2)^2 + 4\Gamma^2\omega_0^2\omega^2} \quad (7.1)$$

where $\partial I/\partial \omega$ is proportional to the detected signal at ω , ω_0 is the undamped mode frequency, ω is the frequency shift from the laser line, Γ is the damping factor and N is a collection of constants proportional to the incident laser power and number of scatterers within the interaction volume. Fig. 7.1(a) shows the decomposition results of a-C Raman spectrum by using the damped harmonic oscillator line shape. The agreement between the fitted curve and observed data gets worse towards the high frequency end. This is caused by the intrinsic property of the line shape which has a long tail. Fig. 7.1(b) and (c) are the results obtained by using the Gaussian line shape. In Fig. 7.1(b) the agreement appears better than that in (a) in the high frequency end but the fitting is not good in the low frequency region. A common procedure to further improve the fitting is to add a third function, "background", which is a straight line, to the two Gaussian functions in the decomposition. Even though the fit is better it makes little sense physically. We have shown how the decomposition method works and we will discuss the validity of using it in the a-C Raman spectrum analysis.

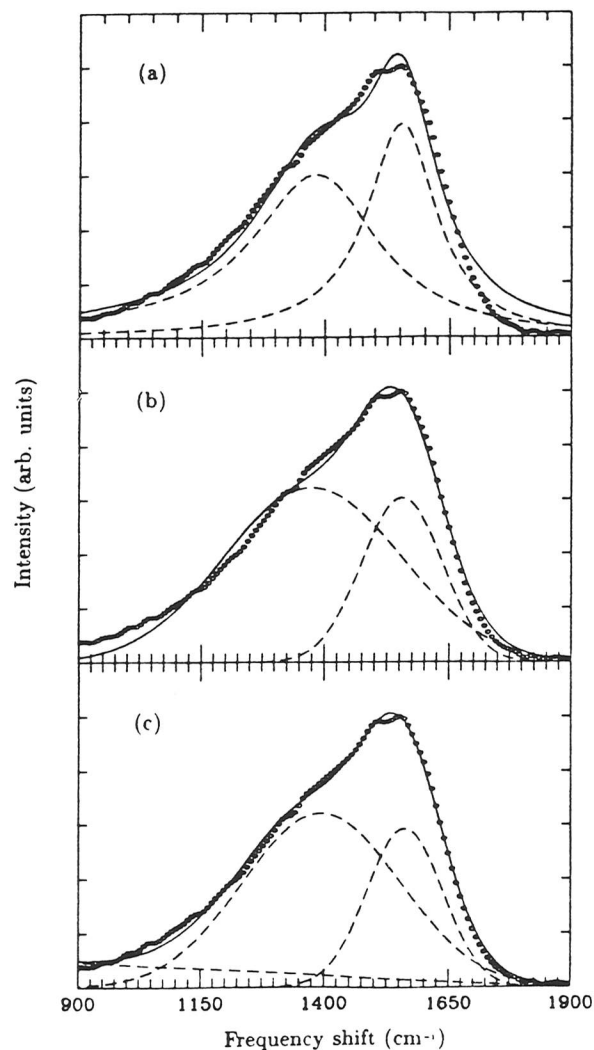


Fig. 7.1 Results of decomposition. Circles are experimental data. Dashed line curves are components from decomposition. Solid line curves are sums of components. The function forms of components used are: two damped oscillator line shapes in (a), two Gaussian line shapes in (b) and two Gaussian line shapes and a straight line in (c).

In Tuinstra's plot of $1/L_a$ versus I_{1355}/I_{1575} , the data are well represented by a linear relation only for $L_a \geq 60\text{\AA}$. For smaller L_a the agreement between the data and the fitted line is not satisfactory. A check of the Raman spectra given in the paper for the stress-annealed pyrolytic graphite and the commercial graphite, whose data give good agreement in the plot; shows that the two peaks in each spectrum are narrow, sharp, almost symmetric and well separated one from the other. Under these conditions each peak can be thought of as coming from one or almost one mode and each peak may have an unique physical meaning. The 1575 cm^{-1} peak comes from the graphite structure and the 1355 cm^{-1} peak relates to the disorder in the structure. Under these conditions the ratio I_{1355}/I_{1575} is an indication of the degree of disorder and can be related to the particle size. Thus Tuinstra's relation is justified.

An additional peak in the Raman spectrum becomes evident when the structure of the material becomes even more disordered. For example, in the Raman spectrum of graphite, after a prolonged grinding another peak appears at about 1620 cm^{-1} .²⁴ R. J. Nemanich and S. A. Solin¹³ reported that this peak can be found in the samples with small L_a and it increases with decreasing L_a , exhibiting behavior similar to that of the 1355 cm^{-1} peak. For this kind of material the asymmetric peak centered at about 1600 cm^{-1} includes the contribution from two different modes. Notice that even in these spectra (such as the spectrum in Fig. 6.1(b)), compared with the Raman spectrum of a-C, the peaks are still very sharp and the 1355 cm^{-1} peak is still well separated from the feature at about 1600 cm^{-1} . In the a-C Raman spectrum not only the features are broadened but also some new features appear, for example, the low frequency features in the $200\text{-}900\text{ cm}^{-1}$ region (see Fig. 6.2). So for a-C Raman spectrum it is reasonable to anticipate that more modes participate in the feature in the $1000\text{-}1900\text{ cm}^{-1}$ region and it is not appropriate to attribute

the G peak (which is centered around 1580 cm^{-1}) from the decomposition to a single physical source. Thus it is inappropriate to use Tuinstra's relation in the a-C case or the case of graphite with very small crystalline size L_a .

A few researchers also have recognized this problem. S. A. Solin and R. J. Kobliska²⁵ found that the Raman spectrum of microcrystalline graphite with $L_a=16\text{\AA}$ gives an observed value $I_{1355}/I_{1575}=0.98$. But according to the Tuinstra's relation this value should be 2.70. So they concluded that there is a saturation effect in the I_{1355}/I_{1575} vs. $1/L_a$ curve which is linear only over the range $L_a \geq 40\text{\AA}$. R. O. Dillon *et al.*¹⁶ annealed their a-C film. Their data shows that the value of $I(D)/I(G)$ first increases and then decreases with a maximum for the sample annealed at about 800°C . J. N. Rouzaud and A. Oberlin²² decomposed the spectrum into both two and three bands and they claimed that a visual comparison between the two results obtained by two and three bands decomposition, respectively, shows that the residue, i.e. the difference between the calculated curve and the experimental curve, is negligible only when the spectrum is decomposed into three bands near 1580 , 1500 and 1350 cm^{-1} .

Is it still possible to use the decomposition method in the analysis of a-C Raman spectrum by simply adding more peaks in the process? First, mathematically, the more the peaks used in the decomposition the better the fitting you can achieve potentially. So the decomposition result could not be taken as the criteria to decide how many peaks should be used in the decomposition and without the knowledge of the number of peaks the method could not be used. Second, more basically, the amorphous material Raman spectrum may not consist only of a finite number of peaks with closed function forms. As discussed earlier the Raman spectrum of amorphous materials is related to the phonon density of states which usually has a complex shape. This is contradictory to the basic assumption of the decomposition

method.

In summary, Tuinstra's relation between I_{1355}/I_{1575} and L_a could not be applied directly to a-C material and essentially the decomposition method is not appropriate for the analysis of a-C Raman spectrum .

VIII. SPECTRUM ANALYSIS: DECONVOLUTION

To extract more information from the Raman spectrum of a-C we introduce the deconvolution method into the spectrum analysis. In this chapter we will describe, test the method and then discuss what it can do in the analysis of a-C Raman spectrum .

Deconvolution used in spectrum analysis is based on the assumption that the observed spectrum i is related to the "object" or ideal spectrum o through the convolution

$$i = s \otimes o, \quad (8.1)$$

where s is the spread function caused by certain physical effects such as the details of the atomic or molecular system under study, instrumental response or a combination of several effects. Deconvolution is the process of finding the best estimate of o for the measured spectrum i and an estimate of the spread function, s . Among numerous different methods of deconvolution, we have chosen the "constrained non-linear method" since it has been well developed for the spectrum analysis.

A. Description of the method

The constrained nonlinear deconvolution we used is based on P. A. Jansson's²⁶ modification of Van Cittert's method. It operates in signal space (as opposed to transform or frequency space) because the recovery of o has often been found to be more reliable in this space. Van Cittert's method is essentially an iterative estimation method. The k th estimate can be written

$$\hat{o}^{(k)} = \hat{o}^{(k-1)} + [i - \hat{o}^{(k-1)} \otimes s] \quad (8.2)$$

with the starting assumption that

$$\hat{o}^{(1)} = i$$

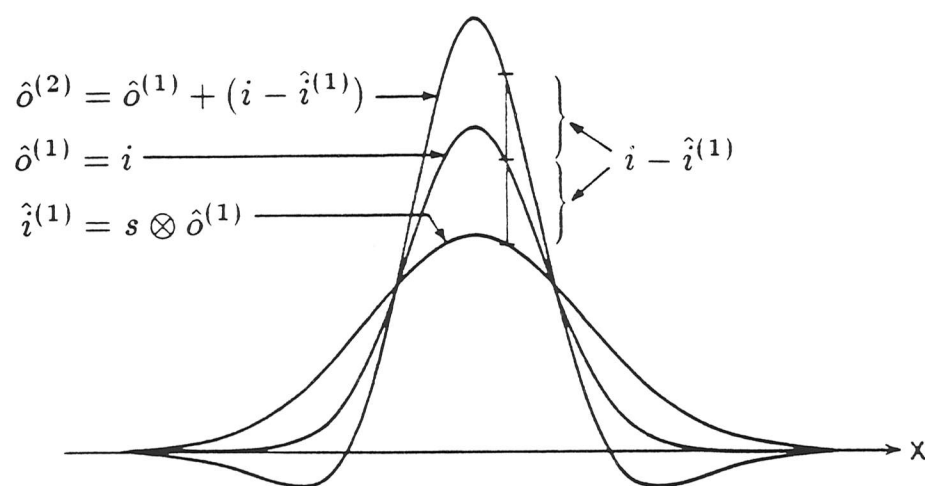


Fig. 8.1 Corrections applied in Van Cittert's method. (Ref. 26)

This is illustrated in Fig. 8.1. P. A. Jansson modified this method by multiplying the correction to the $\hat{o}^{(k-1)}$ iterative estimator of the ideal spectrum by a relaxation parameter $r^{(k)}$ which is a function of $\hat{o}^{(k-1)}$. Then Eq. (8.2) becomes

$$\hat{o}^{(k)} = \hat{o}^{(k-1)} + r^{(k)}(\hat{o}^{(k-1)})[i - \hat{o}^{(k-1)} \otimes s] \quad (8.3)$$

A carefully constructed relaxation function could make the solution to lie in the physical regime by forcing the nonphysical part back toward the bound. For example, Jansson used

$$r^{(k)}(\hat{o}^{(k-1)}) = r_{max}[1 - 2|\hat{o}^{(k-1)} - \frac{1}{2}|] \quad (8.4)$$

for the deconvolution of infrared absorption spectrum. This function assumes full value in the center of the physical region (transmittance=0.5) and falls to zero at the amplitude bounds. The relaxation function we used is

$$r^{(k)}(\hat{o}^{(k-1)}) = r_{max}[\hat{o}^{(k-1)}]^m \quad (8.5)$$

This will suppress the wiggles on the bottom of the spectrum. A detailed discussion will be given later.

B. Test of the method

W. E. Blass and G. W. Halsey²⁷ have tested this method for the spectra consisting of peaks with the same line shape. The spectra we want to deal with, as discussed above, have a complex shape. So we need to learn how this method applies to our situation. To test the method we picked up a known spectrum as o (see Fig. 8.2(a)) and convoluted it with the Gaussian shaped spread function, s , to obtain i (see Fig. 8.2(b)) and then deconvoluted i by using the method described above. Our approach in the deconvolution process is to change one parameter at a time while keeping the others constant. Comparison of the result of the deconvolution, $\hat{o}^{(k)}$, with the known original spectrum, o , gives information about how that parameter effects the deconvolution.

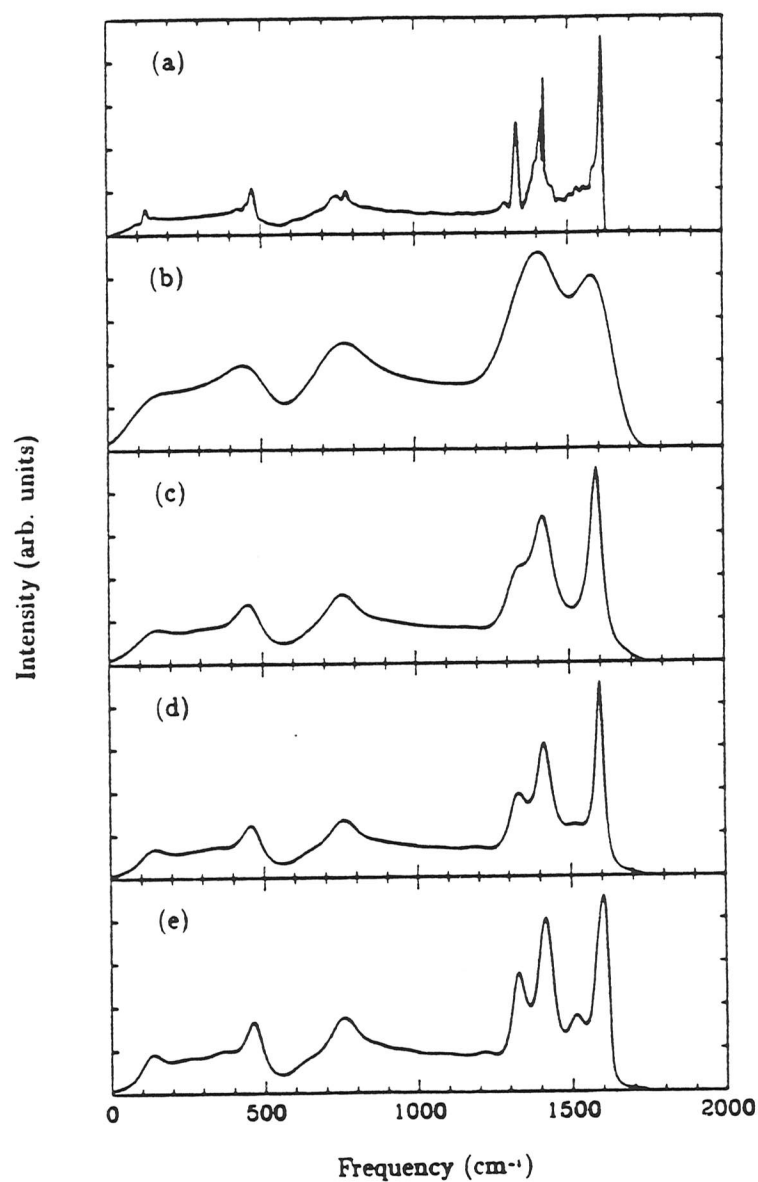


Fig. 8.2 (a): PDOS from Ref. 9. (b): Convolution of the curve in (a) with a Gaussian function of $\Delta=50 \text{ cm}^{-1}$. (c)-(e): Deconvolution results of the spectrum in (b) after 25, 100 and 400 iterations, respectively, with $\Delta=50 \text{ cm}^{-1}$, $m=1$ and $r_{max}=1$.

The first study was to determine the effect of the number of iterations on the deconvolution. The spread function used in this test has a Gaussian shape which can be written

$$s(\omega) = e^{-\frac{(\omega-\omega_0)^2}{2\Delta^2}} \quad (8.6)$$

where ω is the frequency shift from the excitation photon frequency, ω_0 is the center frequency of s and Δ is the half width in cm^{-1} , at which s is about 61% of its maximum value. The same s was used both in the convolution and in the deconvolution processes. Traces (c)-(e) in Fig. 8.2 are the deconvolution results after 25, 100 and 400 iterations, respectively. It seems that higher resolution could be achieved by increasing the number of iterations. For the trace with 400 iterations, however, there appears a side lobe to the left side of the stronger peak at about 1600 cm^{-1} which does not correspond to any feature in the original spectrum. To have good resolution but avoid spurious features, 50-100 iterations seems appropriate.

The next test is to see how the width of the spread function used in the deconvolution affects the result. Fig. 8.3 shows the deconvolution results of the trace in Fig. 8.2(b) with 100 iterations. The widths of the spread function, Δ 's, used in the process are 30, 40, 50, 60 and 70 cm^{-1} for the traces in Fig. 8.3(a)-(e), respectively. The general trend observed is that the wider the s used in the deconvolution, the sharper the peaks seen in the $\hat{o}^{(k)}$. This sharpening, however, is not altogether desirable. A careful examination shows that there is distortion of the spectrum. The peak at about 1330 cm^{-1} nearly disappears in the case (e) where s would have to be 40% wider than that used in the convolution. The distortion is also reflected in the root-mean-square-error between i and $\hat{o}^{(k)} \otimes s$. This value is about 5 times greater in the case (e) than that in case (a). In realistic situations the width of s can only be roughly estimated so it is safer to start from narrower s in the trial and error process.

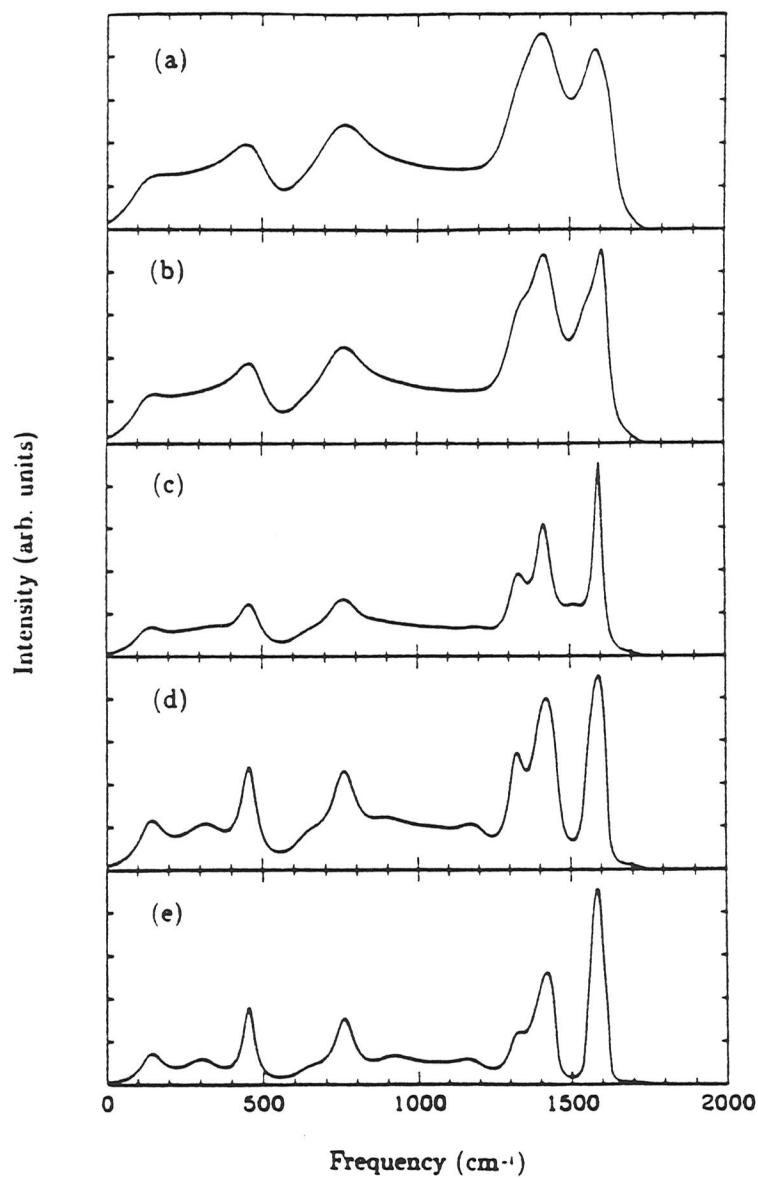


Fig. 8.3 Deconvolution results of the spectrum in Fig. 8.1(b) after 100 iterations with $r_{max}=1$, $m=1$. For traces (a)-(e), the Δ values used in the deconvolution are 30, 40, 50, 60 and 70 cm^{-1} , respectively.

The third test concerns the effect of noise in the measured data. There are always some kinds of noise in measured spectra. The appropriate procedure for dealing with the noise is an important and a difficult issue and has been attacked by many authors. Noise is the primary reason that transform or frequency space deconvolution algorithms do not work well. It is generally the limiting factor in signal space deconvolution, which is the kind of deconvolution performed here. In signal space deconvolution, a noisy spectrum i may cause divergence or generate spurious features. Thus filtering or smoothing the raw data is necessary for successful deconvolution. On the other hand, since noise usually occupies a high frequency region in the power spectrum of frequency space, eliminating the noise will diminish, and in some cases will cause the entire loss of some high frequency components of the true spectrum. This loss will limit the resolution of the deconvoluted spectrum $\delta^{(k)}$. Therefore it is necessary to judiciously choose the high frequency cut off. In this test we add a uniform random noise signal to the spectrum i . The signal to noise ratio is about 50 for the maximum of the signal. Before performing the deconvolution, the spectrum i was transformed to frequency space by using fast Fourier transform (FFT), then high frequency components above a cutoff were deleted from the power spectrum then the data were transformed back to the signal space by using FFT again. Fig. 8.4(a) shows the deconvolution result without any smoothing. Fig. 8.4(b)-(e) are results with different degrees of smoothing before the deconvolution. Among the 300 terms in the power spectrum of the frequency space only the first 30, 20, 15 and 10 lowest terms were kept for traces (b) to (e), respectively. Parameters used in the deconvolution are the same in all cases and their values are: $\Delta=50 \text{ cm}^{-1}$, $r_{max}=2$, $m=2$ and number of iteration=100. There are too many unrealistic details in (b). In the case (e) the smoothing distorts the overall shape of the spectrum. Thus in the rest of the work only the 15-20 lowest

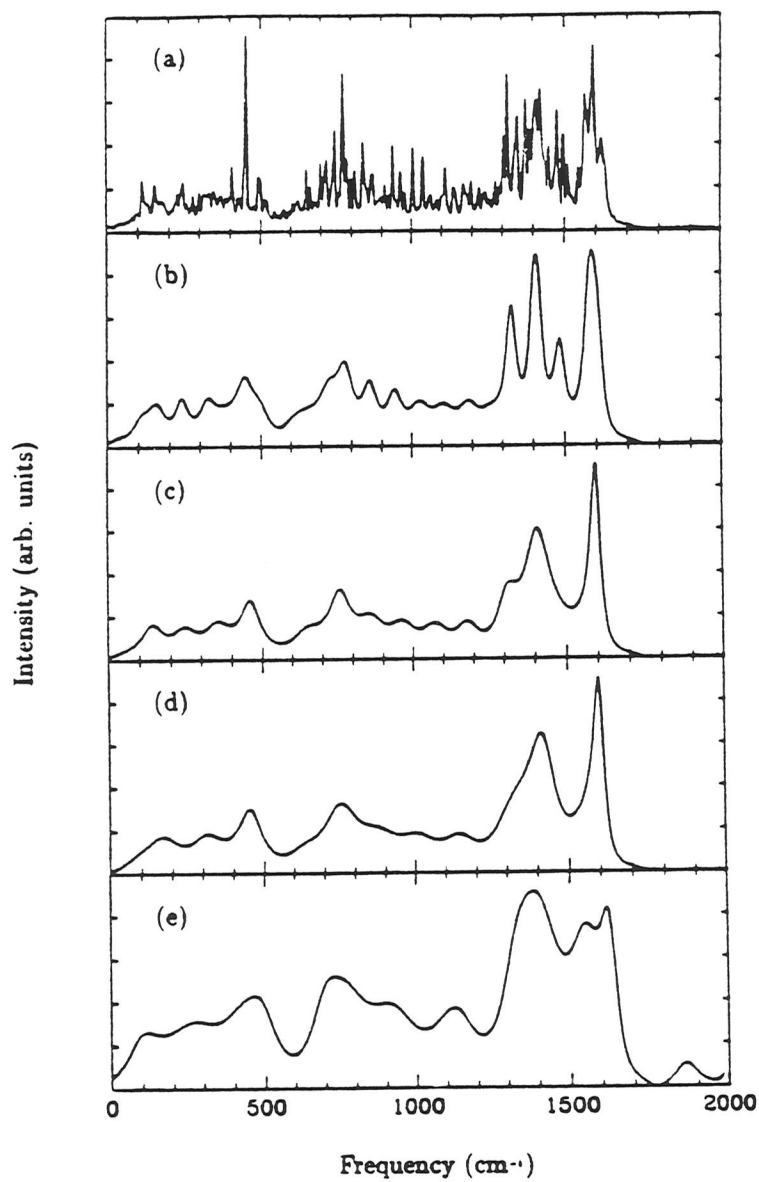


Fig. 8.4 Deconvolution results for simulated noisy spectrum. (a): without smoothing, (b)-(e): smoothed by keeping the lowest 30, 20, 15 and 10 terms, respectively, in the frequency spectrum.

frequency terms will be kept in the filtering process. Notice that all the real features which have corresponding features in the original spectrum can be found in (b)-(d) with relatively stable intensities, but the spurious features decrease quickly when the number of kept terms in the smoothing process reduces.

The final test is to see how the relaxation function works. Fig. 8.5(a)-(e) are deconvolution results with different relaxation functions with all of the other conditions the same as those in Fig. 8.4(c). In Fig. 8.5(a) the deconvolution was done with the relaxation function equals 1. The noise produced wiggling is so strong in the lower intensity portion of the spectrum, that the real features can not be distinguished. Curves (b)-(c) show the results with the exponential, m , to the $\delta^{(k-1)}$ in the relaxation function changes from 1 to 4. It clearly shows how the relaxation function suppresses the spurious features. It also shows that a large m value will reduce the resolution of the portion of the spectrum having higher intensity. For the type of spectrum in the test, $m=2$ is a good choice. Note that in Fig. 8.5 the real features are always in the deconvoluted spectra, but the spurious features disappear while m increases.

We have tested the constrained nonlinear deconvolution method and found the working region for each parameter involved. Generally speaking the method is effective in spectrum analysis. From Fig. 8.2(b) it can be seen that after convolution some of the basic features of the original spectrum are submerged in the broad curve. The number of the peaks in the $1300\text{-}1450\text{ cm}^{-1}$ region and the correct position of the peak at about 1600 cm^{-1} are examples. After deconvolution the two-peak feature in the $1300\text{-}1450\text{ cm}^{-1}$ region is revealed clearly (see Fig. 8.2(d)). The half width of the peak at about 1600 cm^{-1} is narrowed down to less than 50 cm^{-1} . The relative positions of the features in the spectrum remain accurate, but it should be noted that the whole spectrum is shifted toward lower frequency by

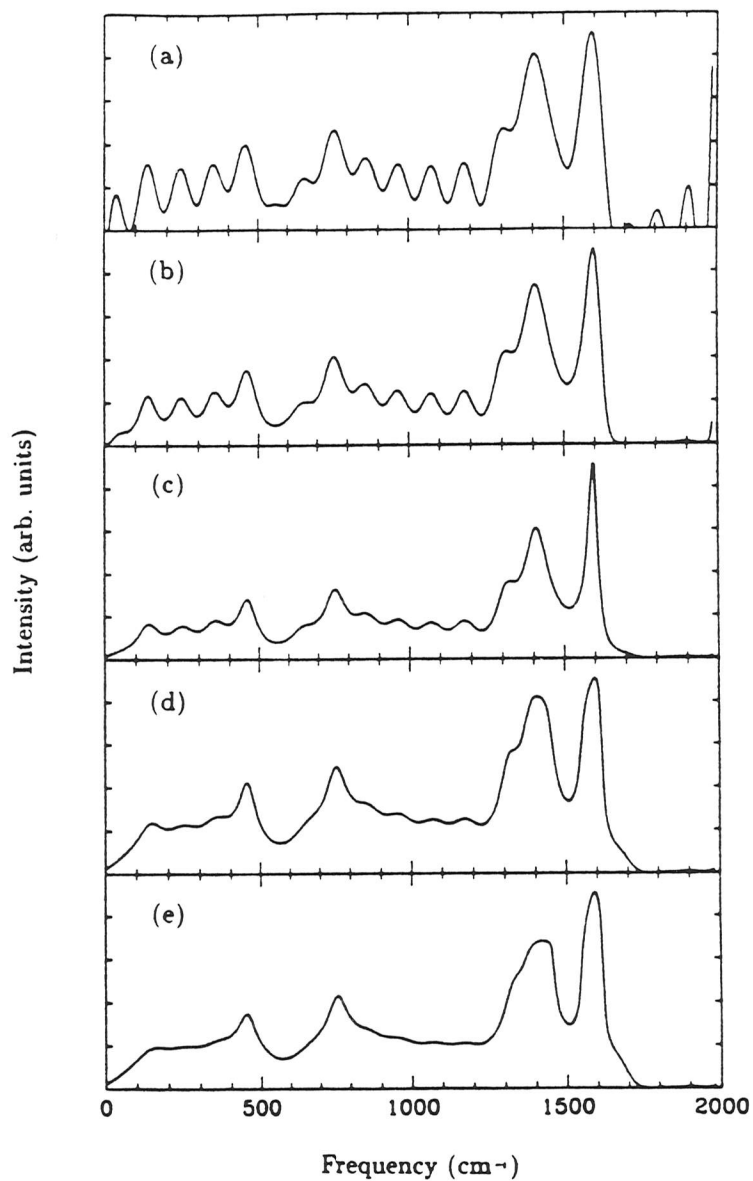


Fig. 8.5 Deconvolution results obtained by using different m values in the relaxation function. For traces (a)-(e) $m=1, 2, 3$ and 4 , respectively. The other deconvolution parameters are: $\Delta=50 \text{ cm}^{-1}$, $r_{max}=2$, number of iterations=100, and the lowest 20 terms in the frequency spectrum were kept in the smoothing process.

about 20 cm^{-1} . Another important thing about the method is that it can preserve the shape of the original spectrum well. That means that it works on spectra with complex shapes. This is in contrast to the decomposition method which works on spectra with finite number of peaks having closed functional forms. Deconvolution is capable of recovering the basic characteristics of the original spectrum.

The limitations of the deconvolution method are as follows.

- First, due to the basic assumption that all the features in the original spectrum are broadened in the same manner and to the same extent, this method can only remove the part of the expansion which is common to all features. For example, if in the deconvoluted spectrum some of the features are wider than others, it can not be concluded exclusively that this is the case in the original spectrum. While this difference may be from the difference in the original spectrum, it may also be due to a different degree of broadening for each feature.
- Second, this method is very sensitive to noise. Even though pre-deconvolution smoothing can improve the quality of the deconvolution result, too drastic smoothing (that is eliminating too many high frequency terms) may cause distortion as shown in Fig. 8.4(e). Obtaining high quality measurements in the first place is critical to the success of the deconvolution method.
- The third limitation concerns the relative intensities of features in the deconvolution result. The relative positions of the features do not change markedly with deconvolution parameters. However, the relative intensities of the features can change with the changes of the parameters in the deconvolution. One should not pay too much attention to the relative intensities when using the deconvolution result.

C. Deconvolution applied to a-C Raman spectrum analysis

The first step is to choose the functional form for the spread function, s , used

in the deconvolution. There are at least two significant possible sources of spread to the spectrum. The first one is the finite widths of the spectrometer slits. The setting of slits used in the experiment produces a triangular function with a half-width of about 20 cm^{-1} at 488 nm. The other spread mechanism is related to the characteristics of Raman scattering in disordered material. To consider explicitly the effect of disorder on the Raman lineshape, P. Lespade and R. Al-Jishi¹⁴ incorporated a bandwidth for the phonon modes into the expression for the Raman intensity of incompletely graphitized carbons. They took the bandwidth as a Gaussian distribution with a width, Δ , which depends on the degree of disorder. We have applied the same idea to the a-C Raman spectrum.

In the case of a crystal, only a few modes in the phonon density of states are Raman active. This is the result of selection rules stemming from the structure symmetry. Imagine that those selection rules were lifted, then all the phonon modes would contribute to the Raman spectrum. Let us call this imaginary spectrum the "core" Raman spectrum. If some kind of disorder is introduced into the system (such as randomly distributed bond angles and/or bond lengths around the values for the crystal) the "core" Raman spectrum would spread in some manner. Due to the statistical nature of the disorder, it is reasonable to assume that the spread takes a Gaussian function form if we have no exact information about it experimentally or theoretically.

In summary the overall spread function used in the deconvolution of a-C Raman spectrum should include two parts: a triangular shaped slit function and a Gaussian function due to the disorder of the scattering structure. Mathematically, the convolution of a narrow triangular function with a broad Gaussian function gives a function which can be satisfactorily approximated as a Gaussian function. Thus for the measurement condition of this work a Gaussian function is an adequate

choice for the spread function.

It is our hope that through deconvolution we can get some information about the components of the a-C Raman spectrum, how many modes are there and where they are. In other words we hope to recover the "core" spectrum. This information may be helpful in the study of the material structure and the relation between the structure of a-C and other forms of carbon such as graphite and diamond.

Using insights from the previous section, the deconvolution results for as-deposited a-C sample are displayed in Fig. 8.6 and 8.7. The deconvolution parameter varied in Fig. 8.6 is the half width of the spread function, Δ which takes values of 60, 65, 70 and 75 cm^{-1} for (a)-(d), respectively. In Fig. 8.7(a)-(c) the only parameter changed is the number of iterations which is 400, 200, 100 and 25 for (a)-(c), respectively. The high peak at about 1580 cm^{-1} and the protrusions at about 1390, 1290, 740 and 390 can be seen in every deconvoluted spectrum and their intensities are relatively stable. The feature at about 1500 cm^{-1} seems sensitive to the changes of the parameters. Recalling that in the test spurious features are also sensitive to small changes of the deconvolution parameters we suspect that the 1500 cm^{-1} feature appearing in some of the deconvoluted spectra may not be a real peak, at least it is not a strong peak in this case.

As a test of the hypothesis that the Raman spectrum of a-C is a broadened version of the phonon density of states of graphite, the PDOS data from R. Nicklow *et al.*¹⁹ and from R. Al-Jishi and G. Dresselhaus²⁰ are displayed in Fig. 8.8 together with our deconvolution result of the a-C Raman spectrum. The agreement of our results, particularly with Nicklow's data, is noteworthy. If the 20 cm^{-1} down frequency shift of the features due to the deconvolution process is taken into account, the reliable features in the deconvoluted spectra are at about 410, 760, 1310, 1410 and 1600 cm^{-1} , respectively. These positions are in fairly good agreement with the

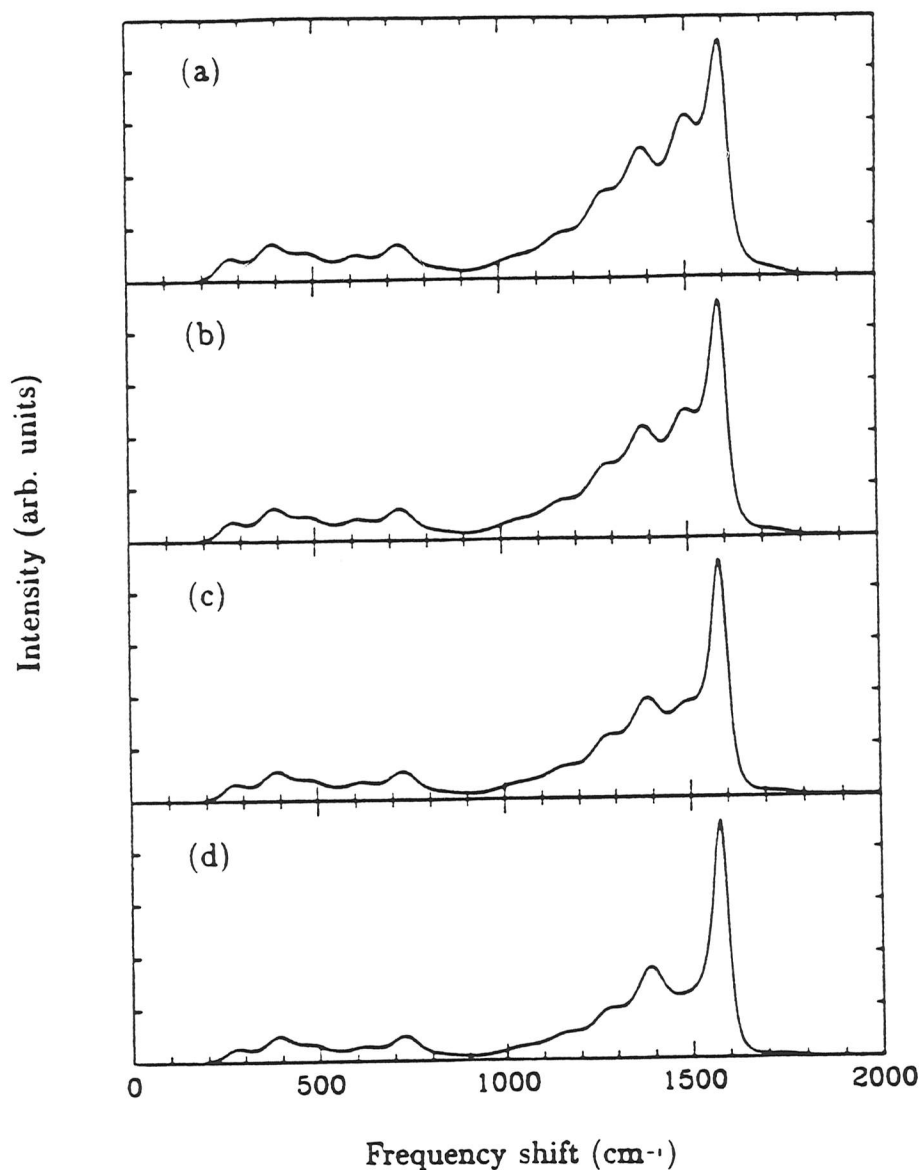


Fig. 8.6 Deconvolution results for the as-deposited carbon sample. Before deconvolution the spectrum was smoothed by keeping the 18 lowest terms in the frequency spectrum. For traces (a)-(d) deconvolution parameters are: number of iterations=100, $r_{max}=1$, $m=1.5$ and $\Delta=60, 65, 70$ and 75 cm^{-1} , respectively.

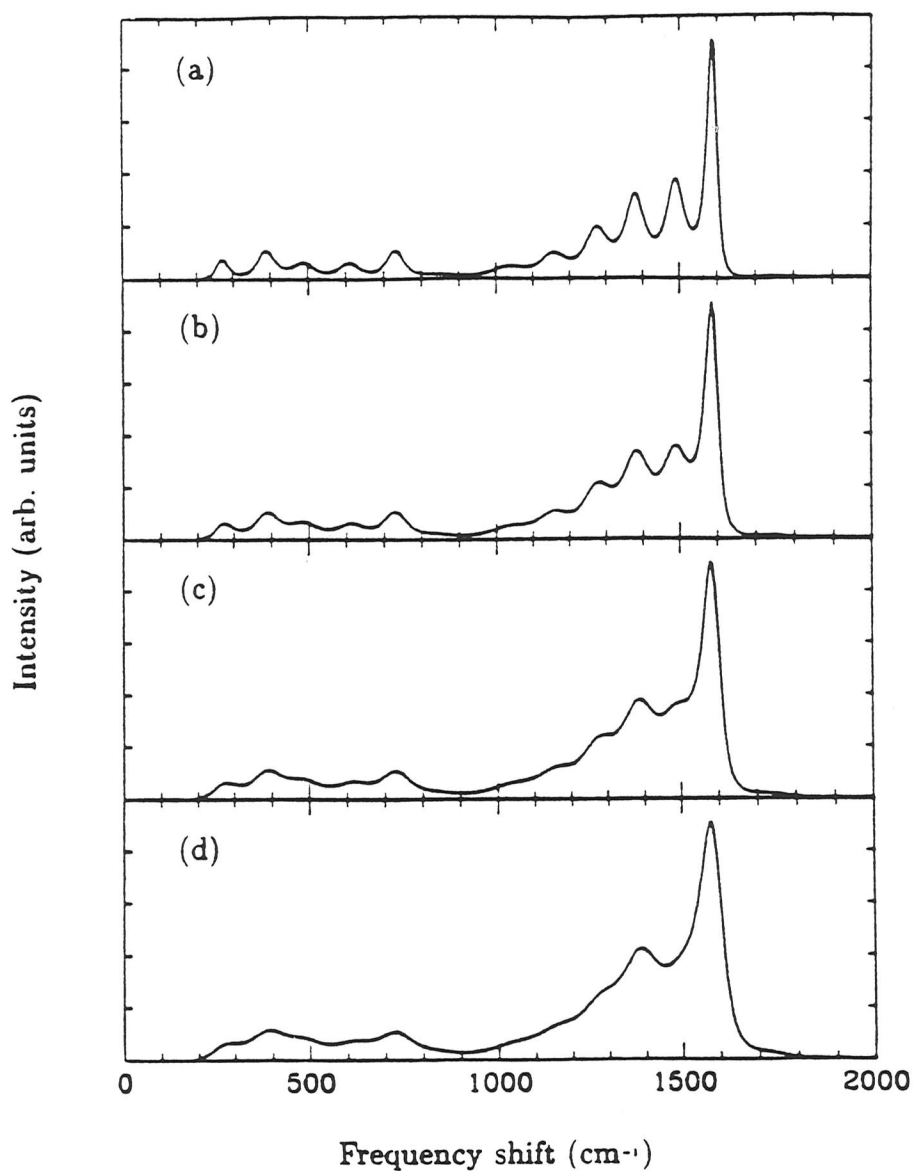


Fig. 8.7 Deconvolution results for the as-deposited carbon sample. Before deconvolution the spectrum was smoothed by keeping the 18 lowest terms in the frequency spectrum. For traces (a)-(d) deconvolution parameters are: $r_{max}=1$, $m=1.5$, $\Delta=70$ cm⁻¹ and number of iterations=400, 200, 100 and 50, respectively.

high density peaks in Nicklow's PDOS of graphite at about 468, 773, 1335, 1425 and 1610 cm^{-1} , respectively. The overall shape of the deconvoluted spectrum is also similar to Al-Jishi's calculation of PDOS of graphite but the correlation is not as good as with Nicklow's.

We take the deconvoluted result of the Raman spectrum of a-C as further evidence of the close relationship between Raman spectrum of a-C and PDOS of graphite. The result also shows that the highly disordered a-C Raman spectrum can not be obtained by simple expansion of the Raman lines of polycrystalline graphite. There are many more modes which contribute to the Raman spectrum of a-C than to that of polycrystalline graphite. We feel that for this kind of a-C material it is no longer appropriate to analyse the first order Raman spectrum by decomposing the high frequency features into a G-peak and a D-peak. We believe that the deconvolution method is a better choice for spectrum analysis in this area. P. Lespade and R. Al-Jishi¹⁴ used a two dimensional model and expanded only "in-plane" modes to calculate the Raman spectrum of incompletely graphitized carbon. Comparing our observed Raman spectrum of a-C with their calculations, we find that features in our observed spectrum are broader; in addition there are low frequency features in the observed spectrum as discussed above, which are not seen in theirs. We suspect that the "out-of-plane" modes play a role in the observed spectrum.

The above observation suggests that there are four stages in the transformation of amorphous carbon to crystal graphite. In the first stage the material has a truly amorphous structure. This kind of material is usually prepared in the form of thin films by near room-temperature sputtering, evaporation or chemical vapor deposition. In these processes the adatom mobility is sufficiently low and crystallization is prevented. This is due to the relatively low temperature of the substrate.

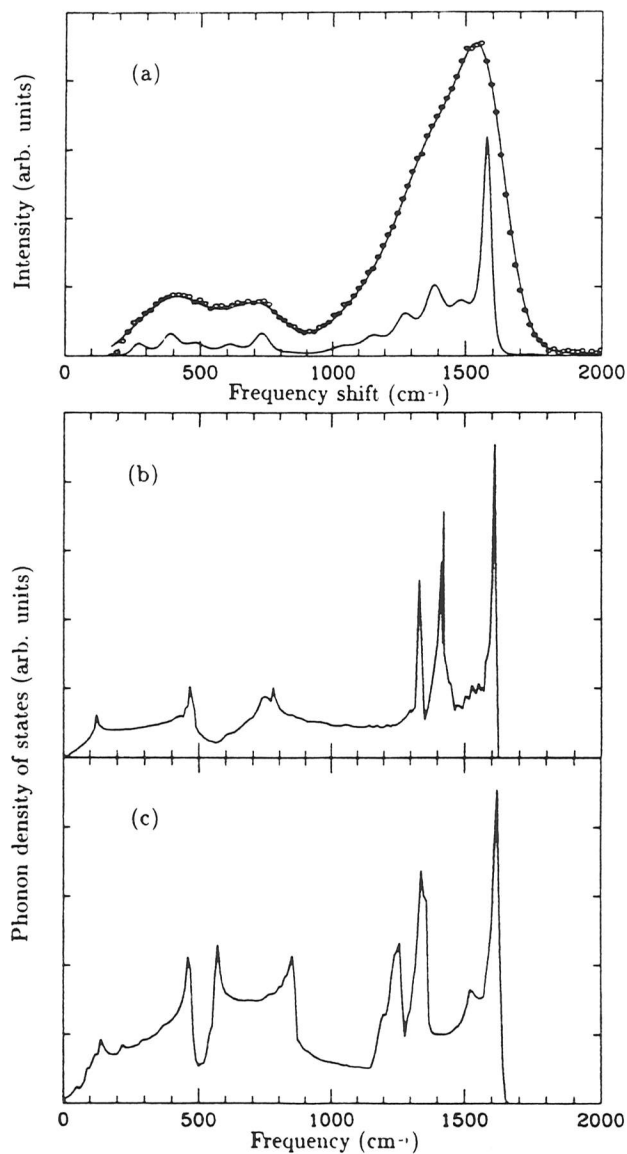


Fig. 8.8 (a): The lower curve is the deconvolution result for the as-deposited carbon sample. Circles are experiment data. The upper curve is the convolution result of the lower curve with the same Δ value used in the deconvolution. (b) and (c): PDOS's of graphite calculated by Nicklow *et al.* and Al-Jishi *et al.*, respectively.

There is no long range order and there is considerable short range disorder in the material. We term this stage the "highly disordered state" with respect to Raman scattering. As a result of this structural disorder the selection rules are completely relaxed for Raman scattering and all possible phonon modes are Raman active. A very important distinction in the Raman spectra of this stage is the low frequency feature in the $200\text{-}900\text{ cm}^{-1}$ region. Also, due to the disorder, each phonon mode gives - instead of a spectral line - a broad peak. These peaks are so broad that they are smeared out and form a typical continuous spectrum as seen above.

The second stage is produced by annealing the as-deposited amorphous carbon samples or by supplying sufficient energy, such as by heating the substrate to the material during deposition. We term this stage the "anneal stable state" in analogy with traditional amorphous semiconductors. And in analogy with what is observed with traditional amorphous semiconductors there is no sharp distinction (phase change) between the "highly disordered state" and "anneal stable state". Instead the changes happen gradually. In the Raman spectra, the low frequency features in the $200\text{-}900\text{ cm}^{-1}$ become lower and lower and the shoulder at about 1360 cm^{-1} progressively grows and narrows into a separated peak when the material transfers from the first to the second stage.

The next stage is the formation of polycrystalline graphite. The structure is a collection of graphite crystallites of finite size. This kind of material is obtained by annealing the a-C material sufficiently to nucleate and grow crystals or by grinding up crystalline graphite.²⁴ For polycrystalline graphite materials the crystallite size, L_a , is an important structural parameter and is often used in the discussion of the Raman spectrum.^{12,14} In the first order Raman spectrum of polycrystalline graphite the low frequency features are essentially totally gone. The high frequency features consist of two individual peaks. One is at about 1360 cm^{-1} and the other is centered

around 1600 cm^{-1} . The latter itself can be decomposed into two peaks. The one at about 1580 cm^{-1} is the broadened version of single crystal graphite Raman line. The other at about 1620 cm^{-1} like the peak at about 1360 cm^{-1} is induced by the structure disorder which causes the breakdown of the full translational symmetry and in turn relaxes the wave-vector selection rule.

The last stage is single crystal graphite. The first order Raman spectrum of single crystal graphite is the well known sharp line at 1580 cm^{-1} .

These four stages can be further divided into two categories. Materials in the first two stages, "highly disordered" and "anneal stable", are in amorphous state. Materials in the last two stages are crystal kind of materials. That means that for the crystalline material you can always find certain areas, albeit very small but much larger than that of unit cell of crystal, which have order structure. In contrast, for amorphous materials disorder exists everywhere, though the degree may vary. The crossing from one kind of material to another requires a phase transition.

IX. RAMAN STUDY OF ANNEALED a-C FILMS

In chapter VI we discussed some Raman spectra of annealed a-C samples. As the annealing temperature is increasing the low frequency features become less pronounced and the shoulder at about 1360 cm^{-1} gradually grows and becomes more distinct from the peak at about 1580 cm^{-1} . Fig. 9.1 and 9.2 show the result of applying the deconvolution method to the Raman spectrum of a sample annealed at 1000°C for one hour with argon gas flowing. The half width of the response function, Δ , which is best suited for the deconvolution is about 45 cm^{-1} , which is much narrower than the value of about 75 cm^{-1} used for the as-deposited sample. As discussed in chapter VIII, a narrower Δ implies the material structure is more ordered after annealing. The feature at about 1370 cm^{-1} also becomes stronger.

Another important thing to note is the feature at about 1480 cm^{-1} . As discussed in Chapter VIII, for the as-deposited sample the intensity of the feature at about 1500 cm^{-1} is sensitive to the changes of the deconvolution parameters (see Fig. 8.6 and 8.7). But for the annealed sample the intensity of the feature at about 1480 cm^{-1} is more stable when the parameters vary. This provides evidence that there is a real peak at about 1480 cm^{-1} . It is interesting to note that there is a second order Raman feature at 2950 cm^{-1} .⁵ All the observed second order Raman features are clearly overtones of the first order features with the exception at 2950 cm^{-1} . This is attributed to a combination of two different first order features (the 1370 and 1580 cm^{-1} peaks). There is a possibility that the 2950 cm^{-1} feature also is the overtone of the 1480 cm^{-1} feature.

To study the effect of annealing on the a-C structure, we annealed two sets of a-C samples under different annealing conditions. One set was annealed in atmosphere for two hours at 200 , 300 and 400°C , respectively. The samples of the comparison

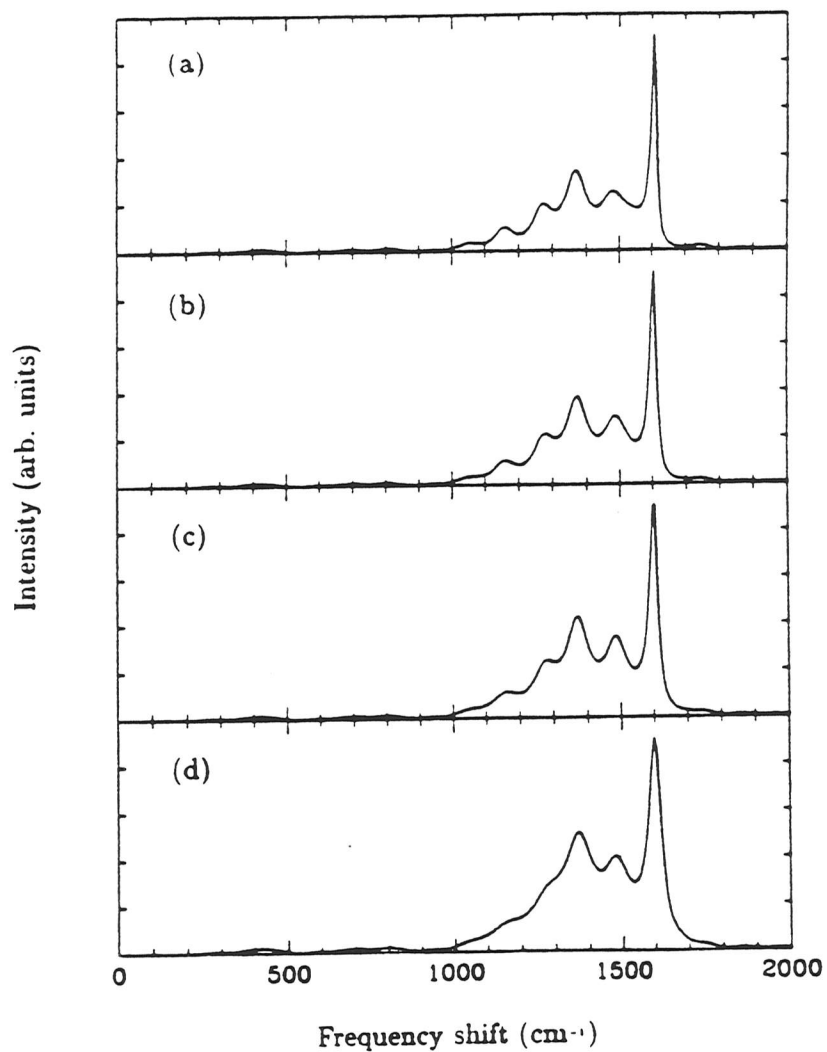


Fig. 9.1 Deconvoluted results for the sample annealed in a vacuum chamber for 1 hour at 1000°C with Ar flowing. For traces (a)-(d) deconvolution parameters are $\Delta=45 \text{ cm}^{-1}$, $r_{max}=1$, $m=2$ and number of iterations=400, 200, 100 and 25, respectively. In the smoothing process the 18 lowest terms in the frequency spectrum were kept.

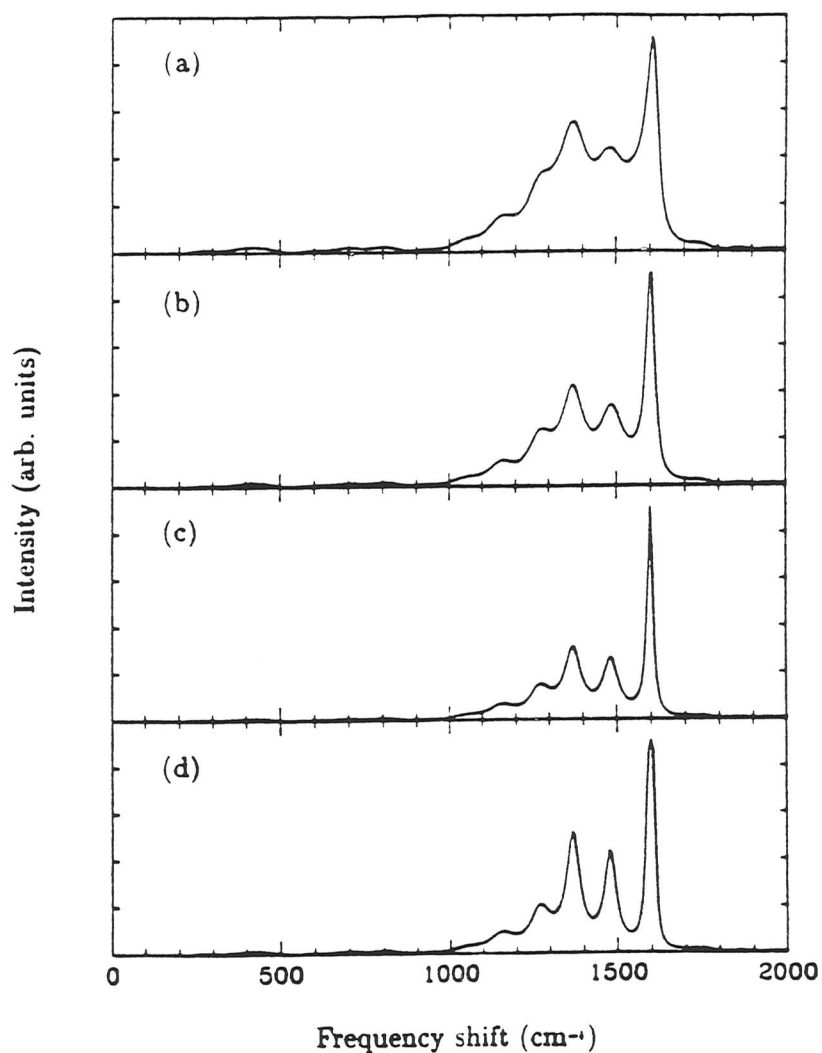


Fig. 9.2 Deconvoluted results for the sample annealed in a vacuum chamber for 1 hour at 1000°C with Ar flowing. For traces (a)-(d) deconvolution parameters are $r_{max}=1$, $m=2$, number of iterations=100 and $\Delta=40, 45, 50$ and 55 cm^{-1} , respectively. In the smoothing process the 18 lowest terms in the frequency spectrum were kept.

set were annealed in a vacuum chamber with argon gas flowing for two hours at 400, 600 and 1000°C, respectively. Fig. 9.3 shows the Raman spectra taken from the two sets of samples. There are some remarkable differences between the two sets of spectra.

For samples annealed in the air the overall intensity of the feature at about 1560 cm^{-1} increases dramatically when the annealing temperature increases. Compare the spectrum in Fig. 9.3(a) with that in 9.3(c) when the annealing temperature increases from 200°C to 400°C the overall intensity increases by more than a factor of two. On the other hand for the sample annealed in the inert gas at low pressure the overall intensity of the 1560 cm^{-1} feature changes only slightly even when the annealing temperature gets as high as 1000°C (see Fig. 9.3(f)). It is not clear at the moment why the intensity change rate is so different for samples annealed in air than those annealed in inert gas.

Another obvious contrast between the two sets of spectra is that for the sample annealed at 400°C in air the peak at about 1600 cm^{-1} is much higher and sharper than that for the sample annealed at 1000°C with inert gas flowing. The development of the 1580 cm^{-1} is usually taken as an indication of the graphitization. J. N. Rouzaud and A. Oberlin²² used optical and electron microscopy and Raman spectroscopy to study carbon films. They reported that carbon films are constructed of polyaromatic molecules less than twelve rings in diameter, single or piled up in parallel in twos or threes and forming basic structure units. Below 1600°C, such units show a noticeable mutual misorientation but are nearly parallel to the film plane. Adjacent structural units are associated with tilt and twist boundaries to form larger distorted layers with a characteristic zigzag texture. Upon annealing the interstitials and defects are removed from the structure in several stages corresponding to the annealing temperature. Annealing was done under argon flow.

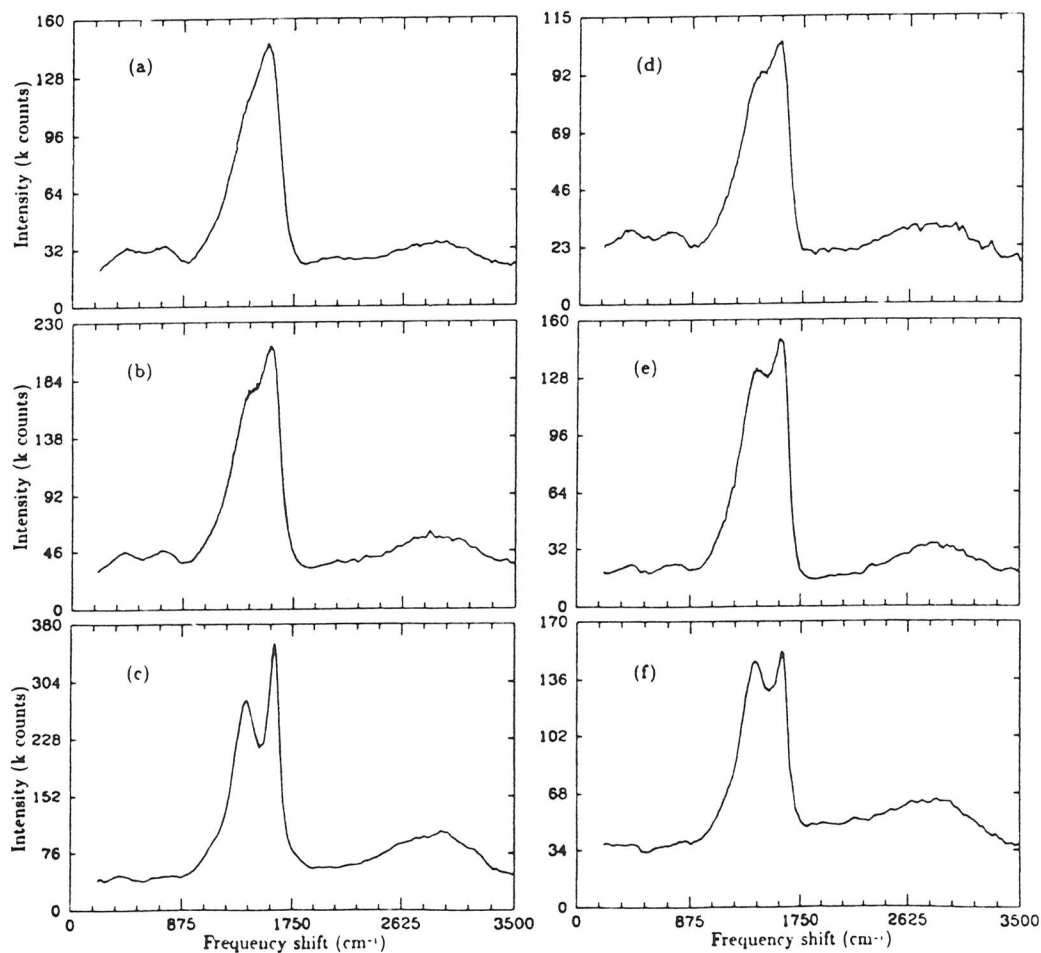


Fig. 9.3 Raman spectra of annealed carbon film. For traces (a)-(c) the samples were annealed in the atmosphere for 2 hours at 200, 300 and 400°C, respectively. For traces (d)-(f) the samples were annealed in a vacuum chamber for two hours with Ar flowing at 400, 600 and 1000°C, respectively.

The spectrum in Fig. 9.3(c) is approximately equivalent to their spectrum for the sample annealed at about 1400°C. The questions - "what is the mechanism which speeds up the structure reorganization process with annealing in the air?" And "which components in air play the key role in this process?" - possess theoretical importance and have practical value. Some more experiments must be performed to answer these questions.

X. SUMMARY

We have studied the low frequency features in the 200-900 cm^{-1} region of the Raman spectrum of a-C. They may be related to the M-point zone-boundary modes of graphite. The experiments show that these features are an important characteristic of the disordered carbon structure.

The Raman study of annealed a-C samples reveals that different annealing environments cause dramatic differences in the crystallization process. The Raman spectra show that the sample annealed at 400°C in the air has similar structure like that of the sample annealed at about 1400°C in argon gas.

The improperness of using decomposition in the analysis of a-C Raman spectrum has been discussed. We have introduced the constrained deconvolution technique in the Raman spectrum analysis for amorphous materials. The method has been tested and then applied to the case of a-C. The deconvolution result of a-C Raman spectrum has been used to verify the assumed relation between the a-C Raman spectrum and phonon density of states of graphite. The comparison clearly shows the close relation between the two. The deconvolution method has also been used to study the structure change of a-C sample upon annealing.

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Raman Study of Amorphous Carbon

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Ph.D. Degree, December 1990

ABSTRACT

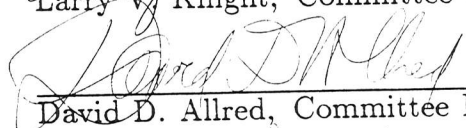
In the Raman spectrum of amorphous carbon (a-C) the low frequency features, in the $200\text{-}900\text{ cm}^{-1}$ region, are an important indication of structural disorder. They may be related to the M-point zone-boundary phonon modes of graphite.

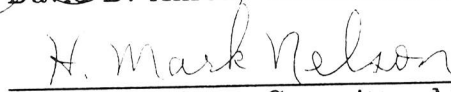
The Raman study of annealed a-C samples reveals that there are dramatic differences in the crystallization process depending upon whether the sample was annealed in air or in an inert gas.

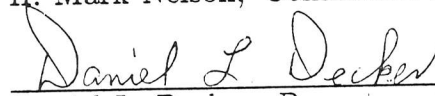
The constrained deconvolution method has been introduced in the analysis of a-C Raman spectrum. The result has been used to verify the assumed relationship between Raman spectrum of a-C and phonon density of states of graphite. This method can also be used in the study of a-C structure and structural changes.

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