

Deconvolution of the Raman Spectrum of Amorphous Carbon

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A constrained non-linear deconvolution method was used to analyse the Raman spectrum of amorphous carbon. The method was tested by applying it to a model spectrum. Before the deconvolution the observed Raman spectrum was smoothed by a least-squares convoluting procedure. The proper width of the spread function used in the deconvolution was determined by examining the reversibility of the deconvolution process. The deconvolution result for the Raman spectrum of amorphous carbon has a form very similar to the phonon density of states of graphite. This is taken to be additional evidence for Shuker and Gamon's model for Raman spectra of amorphous materials. Potentially, the deconvolution method can also be used for other aspects of Raman spectrum analysis of amorphous materials, such as finding the relative intensity of each peak of study the structure of the material.

INTRODUCTION

The Raman spectral features of amorphous materials are usually broad,¹ unlike the sharp peaks observed with crystalline materials. This dramatic difference is caused by the structural disorder of amorphous materials. Structural disorder relaxes or breaks down the selection rules which determine the Raman-active modes in crystalline materials. Thus more phonon modes become Raman active for amorphous materials. Disorder also broadens the features associated with each phonon mode, although the total intensity may decrease. These two factors cause Raman spectra of amorphous materials to have a continuous appearance. The fact that amorphous materials possess many Raman-active modes means that the Raman spectra of amorphous materials may carry more information. However, the broad features in the spectra make it difficult to extract the information.

According to the model of Shuker and Gammon,² the reduced Raman spectrum of an amorphous solid is related to its phonon density of states. It is generally believed that for amorphous carbon (a-C) the phonon density of states is similar to that of graphite.³ The outstanding difference is that the features in the phonon density of states of graphite are much sharper than features in the Raman spectrum of a-C. To make a comparison between the two, Wada *et al.*⁴ convoluted the density of states of graphite with a Gaussian function. They showed that such broadened density of states has a qualitatively similar spectral shape to that of the Raman spectrum of certain kinds of a-C.

In this paper, we describe another way to make the comparison. Instead of broadening the phonon density of states, we have deconvoluted the a-C Raman spectrum and then compared the result with the phonon density of states of graphite. An advantage of this method is that after the deconvolution the peaks are sharper than those in the original spectrum. This facili-

tates comparisons between the phonon density of states and the deconvoluted spectrum, because now one is comparing two curves with sharper peaks, not two broad envelopes.

In addition, the deconvolution method has the potential for providing a way of quantitatively describing the differences in the spectra of a-C samples prepared or treated in differing ways. In the analysis of a-C Raman spectra, researchers have often used the decomposition method, which is sometimes also called curve-fitting technique.^{5–8} This method decomposes the continuous spectrum feature in the 1000–1900 cm^{-1} region into two or three individual peaks and fits the combined intensity of these peaks to the spectrum to be analysed. To us, the main problem with this method is that one has to know the number of peaks into which to decompose the spectrum before performing the decomposition. Unfortunately, finding the number of peaks is usually one of the purposes of the spectrum analysis. The decomposition result cannot be taken as the criterion to decide how many peaks should be used in the process. The reason is that, mathematically, the more the peaks used in the decomposition the better the fitting can be achieved. On the other hand, the deconvolution method introduced to the a-C Raman spectrum analysis in this paper does not have this problem. Actually, as shown later, the deconvoluted result may consist of individual peaks in addition to features with complex shapes. Also, knowledge of the number of these peaks and features is not a prerequisite for performing the deconvolution process.

We shall first describe the deconvolution method, then use a model spectrum to test the method and finally apply the deconvolution method to a typical a-C Raman spectrum. The deconvolution result of the a-C Raman spectrum will also be compared with the phonon density of states of graphite.

DESCRIPTION OF THE METHOD

The basic assumption of the deconvolution used in the spectrum analysis is that the observed spectrum i is

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related to the 'object' or ideal spectrum o through the convolution which mathematically is

$$i(\tilde{\nu}) = \int s(\tilde{\nu} - \tilde{\nu}')o(\tilde{\nu}') d\tilde{\nu}'$$

or written symbolically as

$$i = s \otimes o \quad (1)$$

where s is the spread function. The spread function, s , arises from certain physical processes. We assume that it has the same form in the whole spectrum range. Deconvolution is the process of finding the best estimate of o for the measured spectrum i and the spread function s . Among numerous different deconvolution methods available, we have chosen the 'constrained nonlinear method', which has been well developed for, in particular, infrared spectrum analysis. The method is based on Jansson's modification of Van Cittert's method, which is essentially an iterative estimation method.⁹ The k th estimate in Van Cittert's method can be written as

$$\hat{o}^{(k)} = \hat{o}^{(k-1)} + [i - \hat{o}^{(k-1)} \otimes s] \quad (2)$$

with the starting assumption that

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

Jansson modified this method by multiplying a correction, r^k , to $[i - \hat{o}^{(k-1)} \otimes s]$. r^k is also called the relaxation parameter and is a function of $\hat{o}^{(k-1)}$. A carefully constructed relaxation function may help constrain the solution to lie in a physically meaningful regime. Then Eqn (2) becomes

$$\hat{o}^{(k)} = \hat{o}^{(k-1)} + r^k [i - \hat{o}^{(k-1)} \otimes s] \quad (3)$$

The relaxation function we used is

$$r^k [\hat{o}^{(k-1)}] = r_{\max} [\hat{o}^{(k-1)}]^m \quad (4)$$

with the purpose of suppressing the high-frequency 'jitter' in the low-intensity portion of deconvoluted spectra.

The spread function s used in our deconvolution process is Gaussian:

$$s(\tilde{\nu}) = \exp\left(-\frac{(\tilde{\nu} - \tilde{\nu}_0)^2}{2\Delta^2}\right) \quad (5)$$

where $\tilde{\nu}_0$ is the centre wavenumber and Δ , which in statistics is denoted by σ , is the standard deviation. The relation between Δ and the full width at half-maximum (FWHM) of the function is

$$W_{1/2} = 2.35\Delta \quad (6)$$

To emphasize the physical meaning of Δ in our work, we shall call it the width factor later in this paper. Two different spread function forms were used in the analysis of a-C Raman spectrum. One is called a damped harmonic oscillator function. It was initially introduced to fit the soft mode in the Raman spectra of BaTiO₃ crystals.¹⁰ Later, some researchers used it for the curve fitting of a-C Raman spectra.^{8,11} Our early experience showed that because of the slowly declining tails of the function form, the curve-fitting results obtained by using damped harmonic oscillator function are unacceptable. The other form used in the analysis is Gaussian.^{4,5} We could not find a strict justification for using

Gaussians in the analysis of a-C Raman spectrum. However, since it is known that the broad features in the Raman spectra of amorphous materials stem from the variations in bond length and angle and these variations have a statistical nature, it can be argued that a Gaussian is a justifiable choice for the spread function.

TESTING OF THE METHOD

Blass and Halsey¹² tested the deconvolution method for infrared absorption spectra which consist of broadened single lines. Since the spectra we deal with have a more complicated shape, we conducted our own test. To do that we began with a known spectrum o and convoluted it with a Gaussian spread function s to obtain i and then deconvoluted the i by using the method described above. In Fig. 1, curve (a) is the chosen spectrum, (b) is the result of convolution of that spectrum with a Gaussian spread function and (c) is the deconvolution of (b).

To understand and optimize the deconvolution process, we changed one parameter at a time, keeping the others constant. The deconvolution parameters which proved to be more important and which we shall consider are first Δ , the width factor in the spread function used in deconvolution, and second the number of iterations. Comparison of the result of the deconvolution, $\hat{o}^{(k)}$, with the original spectrum o can provide information about how each parameter in the deconvolution process affects the deconvolution.

We found that the most important parameter, and yet the most difficult with which to deal, is the width of

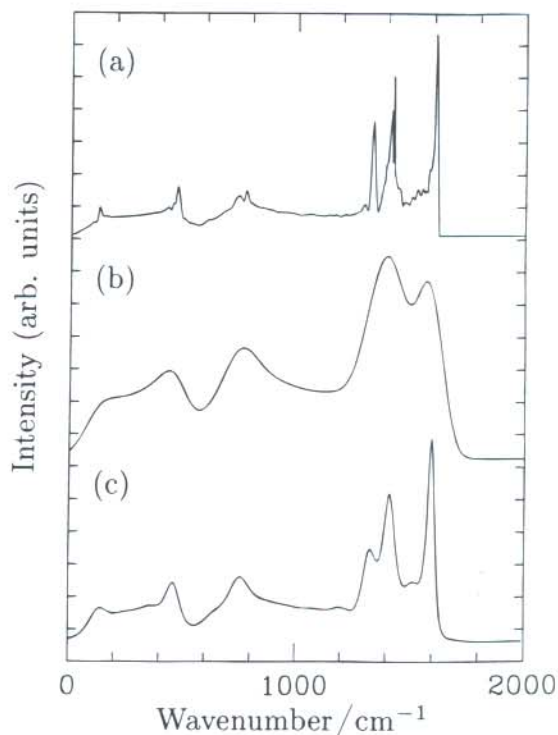


Figure 1. (a) The known spectrum taken as o . (b) The convolution of the spectrum in (a) with a Gaussian function with a width factor of 50 cm⁻¹. (c) The deconvolution of (b) using a Gaussian-shaped spread function with a width factor of 50 cm⁻¹. The iteration number is 200.

the spread function. To study the effect of the width of the spread function, a model or 'pseudo-observed' spectrum i was first generated by convoluting the known model spectrum o with a Gaussian-shaped spread function s where the width factor is 50 cm^{-1} [see Eqns (1) and (5)]. The spectrum i was then deconvoluted. The deconvolution result, $\hat{o}^{(k)}$, can be taken as an approximation of o . Different $\hat{o}^{(k)}$ s were obtained by changing the width of the spread function used in the deconvolution process. The measure of the appropriateness of the spread function is the degree to which the $\hat{o}^{(k)}$ approximates o .

Figure 2 shows $\hat{o}^{(k)}$ s obtained by using the spread functions with width factors of 30, 50 and 80 cm^{-1} in deconvoluting i . Note that the original spectrum o cannot be completely recovered even with the same spread function as used in the convolution. As the width of the spread function used in the deconvolution increases, the peaks in the resulting spectrum became narrower. However, the narrowing is at a cost; when the width factor is 80 cm^{-1} the peak at 1330 cm^{-1} is almost lost.

In the above case, a model pseudo-observed spectrum i was generated using a known spread function. Hence the proper width to use in deconvolution is known. However, how can the proper spread function be determined when working on a real-world deconvolution problem? One way is to check the reversibility of the deconvolution process. To do this, after the deconvolution, we reconvoluted the deconvolution result $\hat{o}^{(k)}$ using the same width of the spread function as used in the deconvolution. Let us call the result of reconvolution \hat{i} . The root-mean-square (RMS) difference between the spectrum \hat{i} and the model spectrum i was then calculated. The size of this difference is taken as an indication of the reversibility of the deconvolution process.

The size of the RMS difference, which is also termed RMS error, vs. the number of iterations is shown in Fig. 3. Generally, the error decreases exponentially as the number of iterations used in the deconvolution process increases. It can also be seen that at a given number of

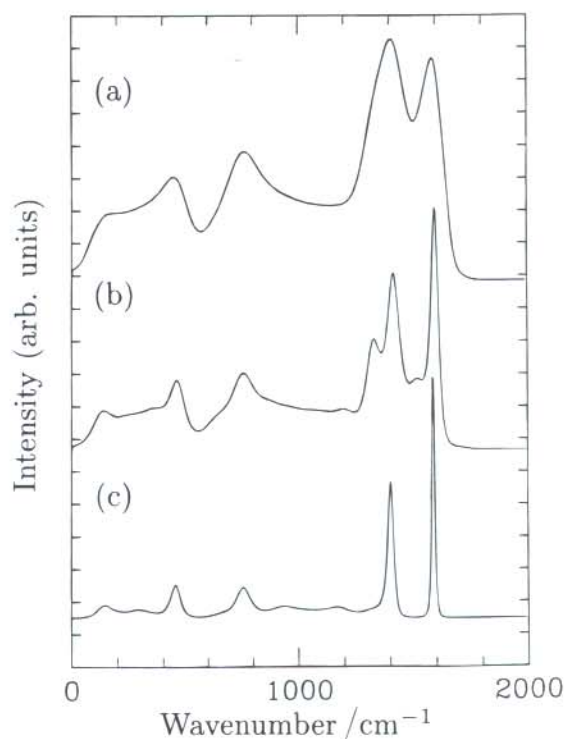


Figure 2. Deconvolution results of the curve in Fig. 1(b). The width factors of the spread functions used in the deconvolutions are (a) 30, (b) 50 and (c) 80 cm^{-1} .

iterations, the wider the spread function used in the deconvolution the larger is the RMS error. One interesting phenomenon is that when the width factor is 70 cm^{-1} or wider the RMS error vs. iteration number curve is no longer smooth. Strong oscillation occurs at large iteration numbers. We take this last phenomenon as an indication that the spread function used in the deconvolution is too wide. Deconvolution performed on actual spectra, as reported later, shows that the smallest width for which such oscillation occurs also depends to some degree on the amount of noise in the spectra

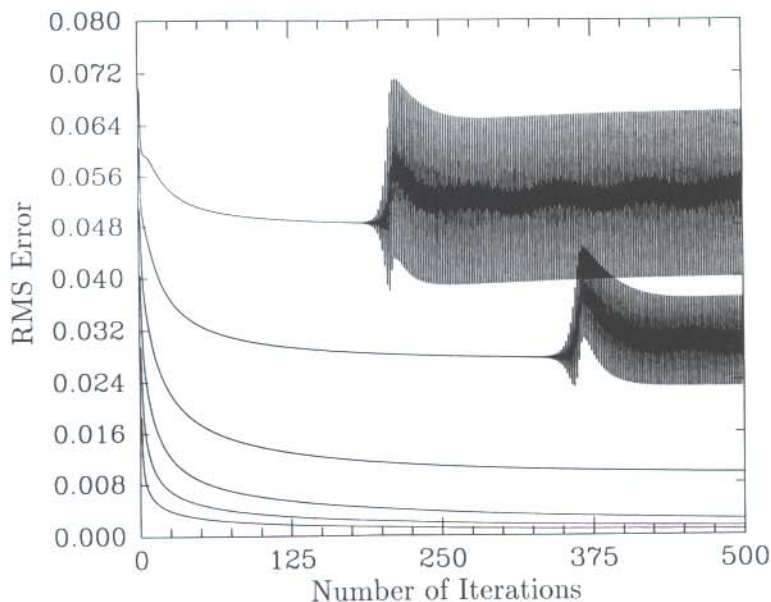


Figure 3. RMS error vs. the number of iterations used in the deconvolution. The curves, from top to bottom, are results obtained by using the spread functions with width factors of 80, 70, 60, 50, 40 and 30 cm^{-1} .

which are to be deconvoluted and other deconvolution parameters.

The next study focused on the effect of the number of iterations on deconvolution. In general, $\hat{o}^{(k)}$ possesses sharper peaks for a larger number of iterations. When the number is larger than 300, however, there appears a side lobe at the left side of the strong peak at about 1600 cm^{-1} . This does not correspond to any feature in the original spectrum. To have good resolution but avoid spurious features, then the number of iterations should be limited; 100–200 iterations seem appropriate.

From Fig. 1, it can be seen that all the main features in the original spectrum o have been recovered in $\hat{o}^{(k)}$. The peaks in the deconvolution spectrum are broader and the peak position differences between the original and deconvolution spectrum are within 16 cm^{-1} .

In real spectra there is always some noise superimposed on them. The presence of noise in the spectrum i may cause the deconvolution process to diverge and may generate spurious features in the deconvoluted spectrum. Thus, finding an appropriate method for 'cleaning' the measured spectra before deconvolution could be very important.

Instrument-related noise usually has higher spectral frequency than the features we are trying to examine in the spectrum. High-frequency filtering is thus the proper way to smooth the measured data before deconvolution. We wish to use the most extensive filter possible to eliminate noise. It is clear that if the filtering is too severe, however, some information which otherwise should be extracted from the measured spectra might be lost. The way we chose to examine whether high-frequency filtering is appropriate is to apply the filtering technique to a noise-free spectrum which approximates measured spectra. If the spectra before and after the smoothing have no significant difference, then the smoothing process is defensible.

Following Blass and Halsey,¹² we used a smooth procedure introduced by Savitzky and Golay.¹³ The method is a least-squares convoluting procedure and consists of convoluting a set of integers, called least-squares smooth filter, with the data to be smoothed. One filter can filter out certain wavenumber range. To cover the entire high-wavenumber range to be smoothed, several filters may be used. In our case they are 7-, 15- and 23-point quartic filters. The interval between adjacent data points in the Raman spectra is 8 cm^{-1} .

DECONVOLUTION OF AN a-C RAMAN SPECTRUM

Figure 4(a) is an optimized deconvolution result of a first-order a-C Raman spectrum. The circles are the raw data of the spectrum. The deconvoluted result of the spectrum is indicated by the solid line below it. The carbon sample was a 300 nm carbon film made by d.c. magnetron sputtering.¹⁴ The Raman system used to obtain the spectrum consisted of a SPEX 1877 Triplemate, a photomultiplier and a photon counter. The light source was 488 nm radiation from an argon ion laser. The system was calibrated using a standard tungsten-halogen lamp. Limited by the resolution of the spectrometer, the spectrum below 250 cm^{-1} was lost in

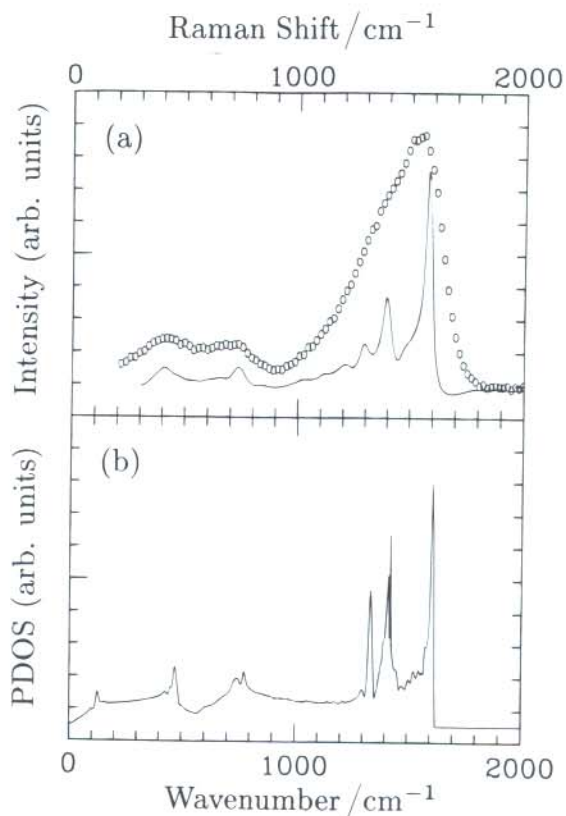


Figure 4. (a) Deconvolution of an a-C Raman spectrum. The circles are the raw data of the a-C Raman spectrum and the solid line is the result of deconvoluting the raw spectrum. The width factor of the spread function used in the deconvolution is 80 cm^{-1} and the iteration number is 100. The curve in (b) is the phonon density of states of graphite calculated by Nicklow *et al.*¹⁵

the strong Rayleigh scattering light. The first step in deconvolution was to smooth the spectrum by the three-stage least-squares procedure described above. The curves of RMS error *vs.* iteration number discussed earlier were calculated. For $m = 1.5$ [see Eqn (4)] when the width factor of the spread function used in deconvolution is 100 cm^{-1} , the curve oscillates after about 400 iterations. As we have shown, oscillations occur when the spread function is too wide. We therefore chose 80 cm^{-1} as the width factor of the spread function and 100 iterations for the final deconvolution shown in Fig. 4(a).

Shuker and Gammon's model² is that the measured Raman spectrum of an amorphous solid includes three parts. The first part consists of the Bose-Einstein factor, the $1/\tilde{\nu}$ harmonic oscillator factor and the radiation factor $(\tilde{\nu}_L \pm \tilde{\nu})$,⁴ where $\tilde{\nu}_L$ is the incident photon wavenumber and $\tilde{\nu}$ is the Raman shift. Within the wavenumber region of interest, this part is a monotonically increasing function of the Raman shift. The second part is a wavenumber-dependent matrix element factor, which is usually presumed to be smooth and slowly varying. The third part is the vibrational density of states, which gives the spectrum its peaks and valleys. Thus, a comparison of the peak positions in the measured Raman spectrum of the amorphous material with the calculated phonon density of states is a test of this approach.

Because of the similarity between the phonon density of states of a-C and that of graphite,^{3,4} a comparison

may be made between the Raman spectrum of a-C and the phonon density of states of graphite. Figure 4(b) is the phonon density of states of graphite calculated by Nicklow *et al.*¹⁵ It is clear that there is good agreement in peak position and intensity between it and the deconvoluted Raman spectrum of a-C in Fig. 4(a). The differences between corresponding peak positions are less than 40 cm^{-1} for all features except the peak in the $400\text{--}500\text{ cm}^{-1}$ region. The difference in this case is about 65 cm^{-1} . The similarity of the spectra provides clear evidence of the utility of Shuker and Gammon's model.

The deconvolution result of a-C Raman spectrum also clearly shows that the broad feature in the $1000\text{--}1900\text{ cm}^{-1}$ region is the envelope of the superimposition of three peaks at about 1295, 1392 and 1585 cm^{-1} . This observation is different from the common belief that the feature is the combination of two peaks at about 1350 and 1580 cm^{-1} .^{5,8} We shall discuss this issue in another paper.

Potentially, the deconvolution method described above can also be used on other aspects of Raman spectrum analysis of amorphous materials. For example, it can be used to find the relative intensity of each phonon mode to determine the structure of the material and to monitor how each mode changes when the material is under heat treatment.

CONCLUSION

We have explored the deconvolution of a-C Raman spectra using a method based on Jansson's modification

of Van Cittert's method. A model spectrum produced by convoluting a known spectrum with a known spread function was used to test the deconvolution method. The result showed that the deconvolution of the model spectrum can recover all the main features of the original spectrum, although peaks are broadened. We found that the reversibility of the deconvolution process could be used in determining the proper width of the spread function. The optimum iteration number for deconvolution is 100–200.

The deconvolution of an actual a-C Raman spectrum produces an image spectrum which is very similar to the phonon density of states of graphite. Before deconvolution the Raman spectrum needs to be smoothed, in our case, by using several different high-frequency numerical filters. The peak position differences between the image spectrum and the phonon density of states of graphite are less than 40 cm^{-1} for all peaks except that in the $400\text{--}500\text{ cm}^{-1}$ region. The difference is about 65 cm^{-1} for that peak. The similarity of the spectra provides striking evidence of Shuker and Gammon's model for Raman spectra of amorphous materials. Deconvolution of Raman spectra also has potential for comparing various a-C samples.

The deconvolution method is a useful tool in the analysis of Raman spectrum of amorphous materials.

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