The Development of a New Model for the Raman Gain Spectrum in Silica Optical Fibres

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Executive Summary

This report describes the development of a new model for the vibrational and Raman gain spectra of vitreous silica used for optical fibres. The technique requires a limited number of input parameters, is statistical and computationally inexpensive. Model results indicate some correlation with measured spectra that show promise for further development of the technique.

A model such as that reported on here may be of interest to optical fibre manufacturers, since it potentially allows the straight forward modelling of Raman spectra for different fibre core dopants. It may also prove a useful contribution to the understanding of the vitreous state of materials. However, the force constant simplifications made in this investigation should be revised to include long range interactions.

Contents

1 Introduction

The Raman process in optical fibres has been of interest to the telecommunications industry for many years, for its application as a broadband optical amplifier for long-haul signal transmission [1, 2]. However, there is also still much interest in the Raman process and Raman amplification within the research community. Much of this work is focussed on effects on short optical pulses during signal propagation. Inevitably such research involves a great deal of computer simulation. In order that a computer simulation can accurately predict the evolving spectrum of optical pulses propagating along the gain fibre of a Raman amplifier it is essential that the gain spectrum of the amplifier is taken into account. In the case of the Raman amplifier the gain spectrum is not a single featureless curve, as its vibrational origin might suggest, but a series of overlapping peaks resulting in a more complicated structure. The gain spectrum of pure silica core fibres was first measured by Stolen *et al* [3], figure 1.
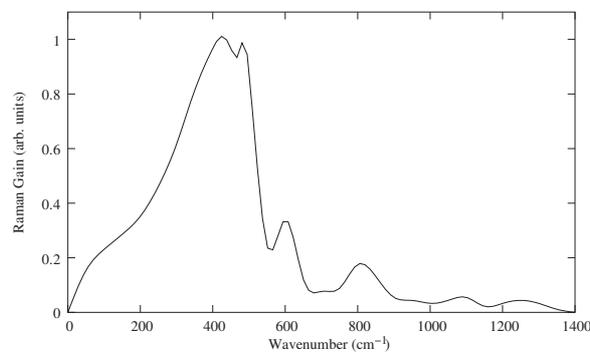

Figure 1:The Raman Gain Spectrum of Pure Silica Fibre [3]

It is precisely this gain spectrum that this project has attempted to model. To date only a limited volume of published work is to be found relating to the modelling of the Raman gain spectrum in optical fibres. Current models are based upon attempting to fit vibrational modes to the pure silica Raman gain profile by varying a set of parameters [4, 5]. This approach is therefore limited to the assumption that the gain fibre core is indeed pure silica. In this report a new approach is taken, based upon previous work, that models the gain spectrum as a collection of harmonic oscillators and a probabilistic distribution of force constants and bond angles. This approach allows dopants to be added to the host material, and thereby determine the expected resultant frequency spectra.

2 Background

Over the past century the structure and properties of vitreous materials has been the topic of much research. The development of the Random Network Theory [6, 7] and studies of its validity [8], has paved the way for much progress in the area. Dean [9] modelled the atomic vibrations of a glass-like structure on a one-dimensional diatomic chain. In this work it was demonstrated that a smooth distribution of force constants between atoms give rise to a broadened frequency spectrum. Further work investigated the effect of disorder upon frequency spectra [10]. A physical model has also been used by Bell and Dean [11] to investigate the vibrational properties of silica. Data from this model has been used to calculate the Raman spectra [12] and investigate the infrared activity [13] of vitreous silica. However, the results fail to resolve some of the structure important to accurately simulate Raman amplification. A useful comparison with the measured Raman spectra is found in [14].

2.1 A Single Harmonic Oscillator

The Raman response function, from which we may obtain the Raman gain spectrum, has been previously modelled on a single damped harmonic oscillator [15]. In their paper, Blow and Wood approximate the Raman response function by relation 1.

$$h_R(t) \propto \exp\left(-t/\tau_2\right)\sin\left(t/\tau_1\right) \tag{1}$$

Where, $\tau_1 = 1/\omega_v$ and $\tau_2 = 1/\gamma$. These parameters are adjusted to fit the experimental Raman response. In [5] they are taken to be $\tau_1 = 12.2$ fs and $\tau_2 = 32$ fs. Equation (1) is arrived at by solving the differential equation, (2).

$$m\ddot{x} = -m\gamma\dot{x} - kx \tag{2}$$

Using the above values for τ_1 and τ_2 the damping coefficient and the force constant to mass ratio are $\gamma = 3.125 \times 10^{13}$ s^{-1} and $k/m = 6.72 \times 10^{27}$ respectively. The variable x denotes the atomic displacement. It turns out that these values correspond well with those of a single oscillating silicon atom. This leads to the response function and gain spectrum of figure 2.1. The resulting spectrum shows that the general shape of the Raman gain is Lorentzian, however the model includes no indication of the spectral location or structure found in the actual Raman spectrum. This is unsurprising, since the single oscillator model does not simulate the physical structure of vitreous silica.
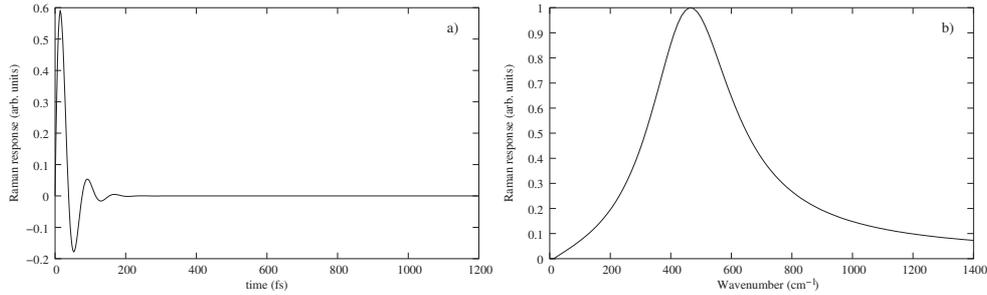
Figure 2: (a) Impulse response function after [15], (b) Impulse gain spectrum from imaginary part of Fourier transform of response function

2.2 Purely Inhomogeneous Broadening

The central limit theorem suggests that the superposition of a large number of Lorentzian peaks from individual atomic vibrations will form a Gaussian profile. The resulting spectrum is then due to inhomogeneous broadening. In this light Walrafen and Krishnan proposed that the Raman spectra of vitreous silica could be deconvolved into a set of ten Gaussians of varying amplitude and width [4]. This work is summarised by a table listing the peak location, height and width of each Gaussian. The resulting frequency spectrum and component Gaussians are shown in figure 3.
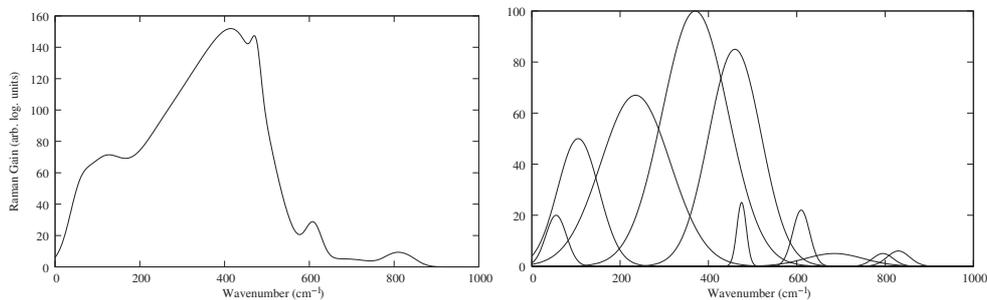

Figure 3:Raman gain spectrum modelled on the convolution of 10 Gaussians [4]

2.3 Intermediate Broadening

More recently Hollenbeck *et al* has extended Walrafens work to an intermediate broadening model of the Raman gain spectrum [5]. In Hollenbeck's paper it is suggested that the width of the individual Lorentzian peaks contributing to the Raman gain spectrum are too wide for their superposition to be truly Gaussian. In this case the broadening of the Gain spectrum is not purely inhomogeneous, but involves the convolution of Gaussian and Lorentzian curves. The gain spectrum according to this model is obtained from the response function by taking the imaginary part of its Fourier transform. Hollenbeck gives the analytical form of the response function as equation (3)

$$h_R(t) = \sum_{i=1}^{13} \frac{A'_i}{\omega_{v,i}} \exp\left(-\gamma_i t\right) \exp\left(-\Gamma_i^2 t^2/4\right) \sin\left(\omega_{v,i} t\right) \theta(t) \tag{3}$$

where A'_i is the amplitude of the ith vibrational mode, $\omega_{v,i}$ is the centre vibrational frequency for the mode i, γ_i is the Loretzian linewidth for mode i, Γ_i is the Gaussian linewidth for mode i, and $\theta(t)$ is the unit step function. The Raman response function is computed using equation (3) from data tabulated in [5], figure 4.
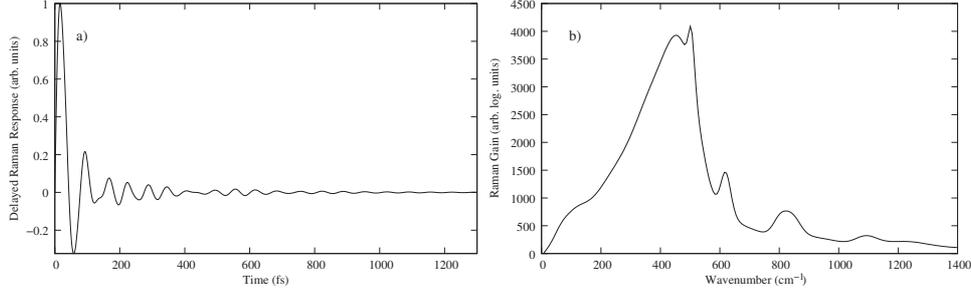

Figure 4: (a) Raman response function after [5], (b) Raman gain spectrum from imaginary part of Fourier transform of response function

Both the inhomogeneous and intermediate broadening models show good agreement with the features of the Raman gain spectrum. Indeed the work of Hollenbeck is useful in that it models the Raman response function, this being beneficial for simulations of fast pulses in the time domain.

3 The Structure and Vibrational Spectra of Silica

To re-examine the problem of modelling the Raman gain spectrum it is first useful to look at the origin its features, i.e. the structure of vitreous silica, and the resulting vibrational spectrum.

In bulk silica the component SiO_2 molecules are arranged into SiO_4 tetrahedral unit cells, figure 5, comprising one silicon atom at the centre and four radially connected oxygens.
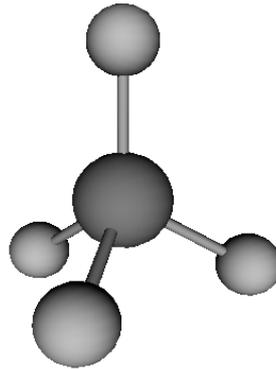

Figure 5: The SiO_4 unit cell of bulk silica. The central silicon atom is attached to 4 radially extending oxygens.

Each unit cell connects to another via the radial oxygen atoms, with the bond angle between each SiO_4 cell varying from approximately 100° to 180°. Analysis of some of the early work by Bell and Dean on Random Network Theory [11], reveals the distribution of Si-O-Si bond angles to be Lorentzian with a mean of 140°. The mean bond length is approximately 1.6 Å and also varies according to a Lorentzian distribution. The bond angle and length distributions are shown in figure 6.
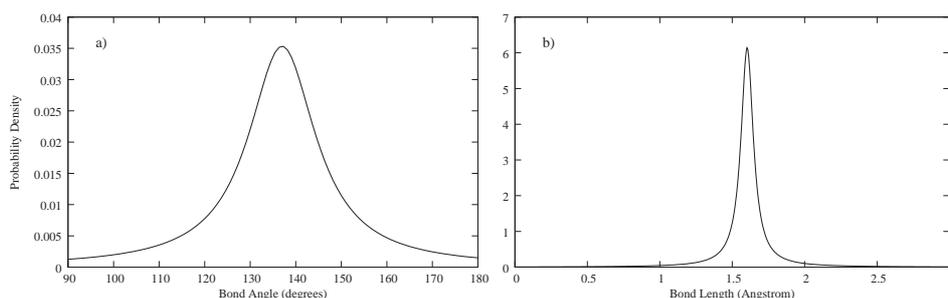

Figure 6: The distribution of Si-O-Si bond angles (a), and bond lengths (b) in vitreous silica after Bell and Dean [11]

From these distributions we can deduce at least two sources of vibrational spectra, bond bending and bond stretching. Indeed the peak of the Raman spectrum is attributed to the bending of the Si-O-Si bond [16].

The vibrational spectrum of vitreous Silica is itself is not directly equivalent to the Raman or infrared spectra. However, a useful comparison between these spectra and the results

from neutron scattering experiments is given by Galeener *et al* [17]. A comparison is also drawn between experimental data and the models of Bell and Dean. Further analysis of the vibrational density of states in vitreous SiO_2 by inelastic neutron scattering has been carried out by Carpenter and Price [18]. Their reduced neutron spectrum for vitreous silica is shown in figure 7.
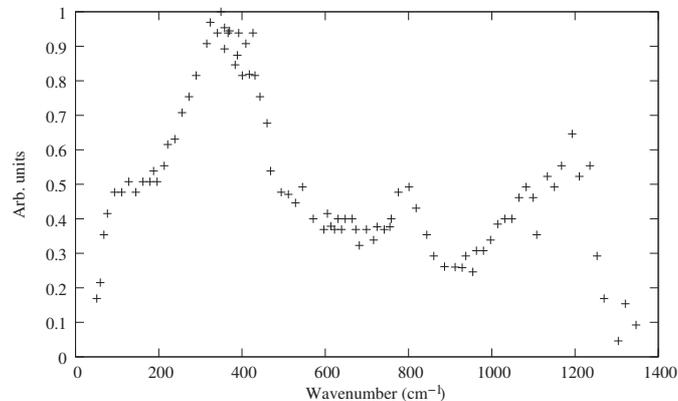

Figure 7: The reduced neutron spectrum of vitrous SiO_2 after Carpenter *et al* [18], from inelastic neutron scattering experiments

The Raman spectrum of vitreous silica can be obtained from its vibrational spectrum as discussed in section 6. This relationship has been shown previously by Bell *et al* [12] and more recently, using a similar method, by Umari *et al* [19]. The result of this previous work shows general agreement with the feature locations of the measured spectra, however these models must be built upon to improve the agreement between experimental and modelled data. A comparison of different techniques for the generation of vibrational spectra has been made by Benoit and Kob [20]. In their paper the comparison is made between molecular dynamics and a first principles approach based upon that of Bell and Dean.
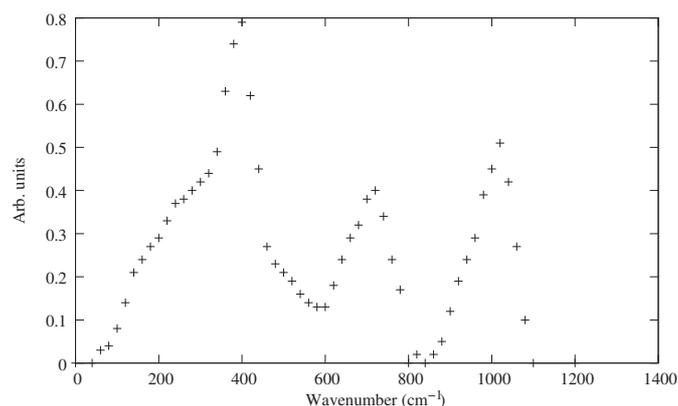

Figure 8: The vibrational spectrum of vitreous SiO_2 after Bell and Dean [11], its features follow the general shape of figure 7

4 Modelling Atomic Vibrations in Vitreous Silica

Historically, atomic vibrational spectra have been obtained from computer models by calculation and diagonalisation of the mass-weighted force constant matrix, the Hessian. The limitations of this approach have been demonstrated [20, 19, 17] by comparison with neutron scattering data. In this section the method of Driven Molecular Dynamics, attributable to Bowman *et al* [21], is applied to a new statistical model of vitreous silica based upon results obtained from the Random Network Theory.

4.1 Driven Molecular Dynamics

Bowman has demonstrated a different method for determining the normal mode vibrational frequency spectrum of a molecular system, Driven Molecular Dynamics (DMD). A molecule is driven by a weakly coupled harmonic force field, the force field frequency is scanned over a range of frequencies, and the absorption of energy due to vibrations of the molecule is monitored. Strong absorption indicates resonance, and hence a normal mode. Here the DMD technique is applied to glass-like chains, in preference to the eigenvalue counting technique of Bell [22].

The equations of motion can be formulated for a chain of coupled oscillators, equation (4).

$$m_i\ddot{x}_i = -m_i\gamma\dot{x}_i - k_i[x_{i-1} - x_i] + k_{i+1}[x_{i+1} - x_i] \tag{4}$$

The mass of the ith atom in the chain is represented by m_i, k_i is the force constant connecting atom $i - 1$ and i, γ is the damping coefficient and x_i is the displacement of the ith atom from equilibrium.

The DMD approach modifies the set of coupled equations by applying a weak sinusiodal driving force to the first atom in the chain. Equations (5) show this explicitly for a chain of 3 atoms. F_0 and ω are the magnitude and frequency of the driving force respectively.

$$\begin{aligned}
m_1\ddot{x}_1 &= -m_1\gamma\dot{x}_1 - k_1x_1 + k_2[x_2 - x_1] + F_0\sin(\omega t) \\
m_2\ddot{x}_2 &= -m_2\gamma\dot{x}_2 - k_2[x_1 - x_2] + k_3[x_3 - x2] \\
m_3\ddot{x}_3 &= -m_3\gamma\dot{x}_3 - k_3[x_2 - x_3] + k_4[-x3]
\end{aligned} \tag{5}$$

This set of coupled differential equations is solved for a range of sinusoidal driving force frequencies ω. Here the measure of energy absorption adopted is the average kinetic energy of the molecule over time, and is calculated using equation (6).

$$E = \frac{1}{2nl} \sum_{i=1}^{n} \left(m_i \sum_{j=1}^{l} v_i(j\delta t)^2 \right) \qquad (6)$$

Where the second summation represents the time-averaged velocity of the ith atom at time $t = j\delta t$, δt is a small step in time, and l the total number of steps. n is the total number of atoms and m_i is the mass of the ith atom.

4.2 A Diatomic Chain

To accurately model silica, oscillations from the two atomic types (Silicon and Oxygen) must be present. This can be modelled by constructing a diatomic chain of alternating Silicon and Oxygen atoms. A chain of this type is shown for five atoms in figure 9.

Figure 9:A diatomic chain of 5 atoms.

Bond Stretching in One Dimension

A solution to the system of coupled differential equations (4) is obtained numerically by using a fourth order Rungé Kutta method. Here the DMD technique is applied to 1-dimensional atomic chains to investigate resonant bond stretching frequencies. Results for diatomic chains consisting of three, four, five and six atoms are shown in figure 10. The force constant has been taken as equal between each atom.
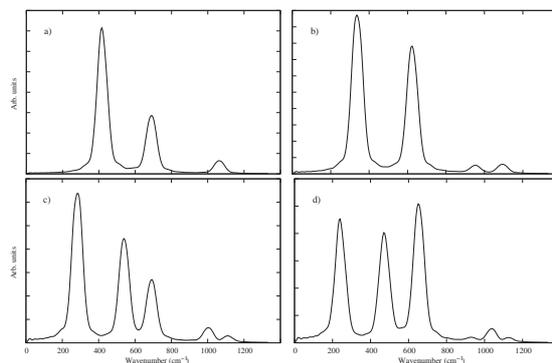

Figure 10: Vibrational spectra for a linear diatomic chain of alternating silicon and oxygen atoms, (a) 3 atoms (Si-O-Si), (b) 4 atoms (Si-O-Si-O), (c) 5 atoms (Si-O-Si-O-Si), (d) 6 atoms (Si-O-Si-O-Si-O)

The resonant vibrational frequencies are shown by sharp Lorentzian peaks. These spectra can be compared to the inelastic neutron scattering spectrum of figure 7. Peak locations do not exactly match, however there is some interesting correlation.

The glass-like properties of diatomic chains have previously been investigated by Dean [9]. The inter-atomic force constant was varied according to a probability distribution similar to that of figure 6b. It was shown that this led to broadening of the vibrational spectra and was used to investigate the 'glass-like' properties of a diatomic chain.

Bond Bending in Two Dimensions

A one dimensional chain is a useful tool for extracting general properties of a disordered system. However, it cannot describe properties that are intrinsically two or three dimensional. An example of this is bond bending and associated bending modes.

Here the one dimensional model is extended into two dimensions to investigate the effect of bond bending on the vibrational spectrum. To do this a non-central force constant is introduced, that acts perpendicularly to the inter-nuclear line. The ratio of central and non-central force constants is taken to be 0.15 [11]. For a linear chain of three atoms, the inclusion of a non-central force constant introduces a new peak into the vibrational spectrum, figure 11.
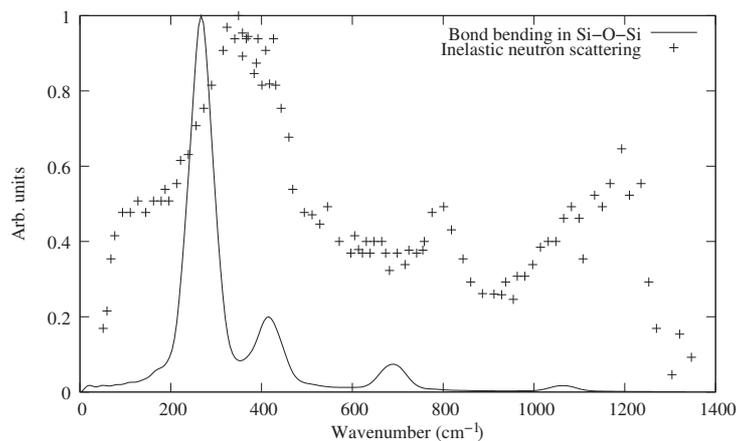

Figure 11: Vibrational spectra for a linear diatomic chain of alternating silicon and oxygen atoms compared with the vibrational spectrum of vitreous silica obtained by inelastic neutron scattering.

Figure 6 shows that in vitreous Silica we may reasonably expect the Si-O-Si bond angle to be in the region 100° to 180°. The resulting spectra obtained from a range of bond angles is shown in figure 12.

Figure 12 shows how the relative intensities of the peaks change with angle, and that there is a shift in each peak position. In figure 13 the spectra for Si-O-Si bonds with different bond angles are summed to generate a combined spectrum. These results suggest some similarity with the inelastic neutron scattering spectra, with the generation of a broader peak at high frequencies. It is therefore implied that bond bending may have a significant contribution at low frequencies. Inclusion of vibrational interactions beyond nearest neighbours would perhaps introduce further structure into the spectrum.
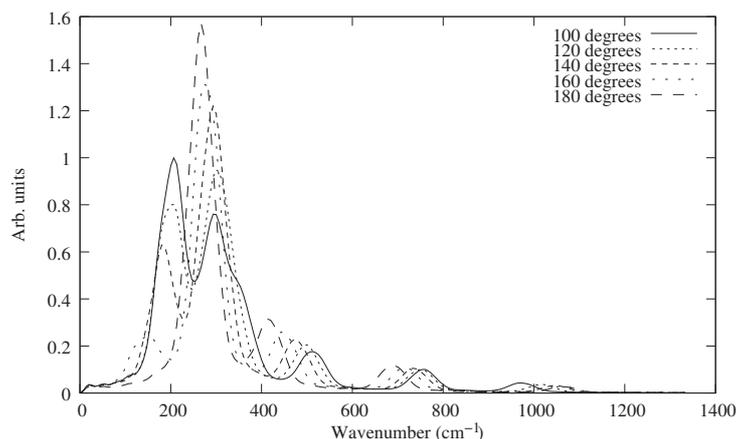
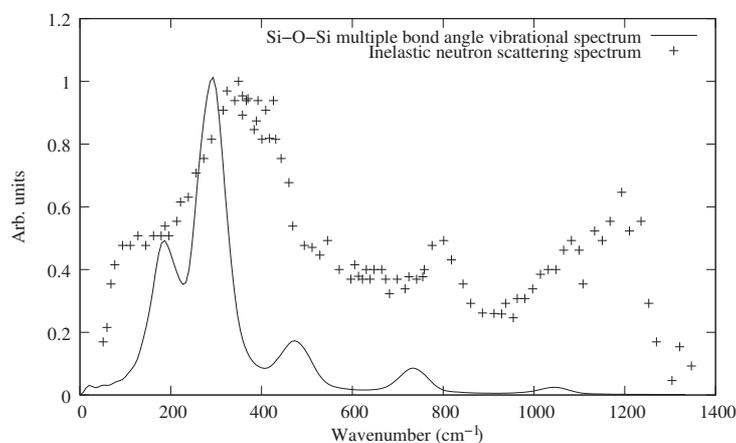Figure 12:Vibrational spectra of a diatomic chain in two dimensions, for a range of equilibrium angles.

Figure 13: Sum of spectra for bond angles of 100°, 120°, 140°, 160° and 180°, weighting each according to the bond angle distribution, figure 6. Results are compared with measured inelastic Neutron scattering spectra of vitreous silica

Ring Structure in Vitreous Silica

Dean has suggested that the Si-O-Si bonds in vitreous silica may form a local ring structure [23]. In their physical model Bell and Dean [11] have reported the number of rings of different sizes, table 1.

Length of Ring (No. Atoms)	3	4	5	6	7	8
Number of Rings	13	16	21	31	69	112

Table 1:The size and number of atomic rings in vitreous Silica

However, in the work reported on here no ring structure has been incorporated.

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5 Modelling a Collection of Si-O-Si Bonds

The present work has attempted to model vitreous silica as a collection of Si-O-Si bonds. The force constants and bond angles are determined for each Si-O-Si bond by the statistical distributions shown in figures 6a and 6b. Hence, the vibrational spectra of the collection is a linear sum over contributions from each SiO_2 molecule. By using this method a vibrational spectra was determined as shown in figure 14.
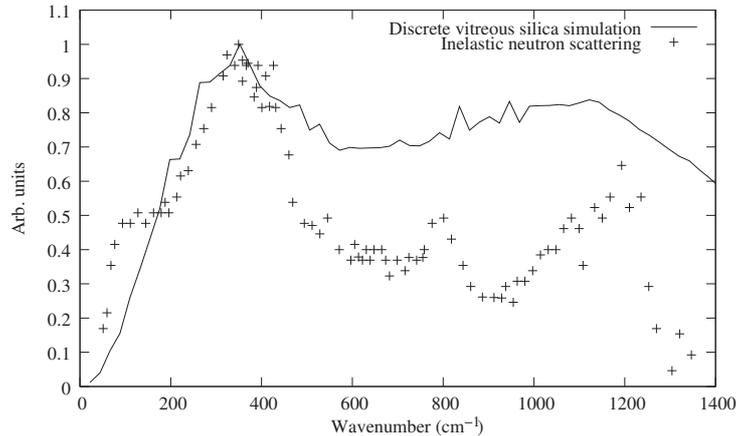

Figure 14: The full Si-O-Si collection vibrational spectrum simulation compared to that obtained by inelastic neatron scattering.

The resulting spectrum has some correlation with the corresponding measured spectra. The best agreement is found at low frequencies, notably the first peak in the spectrum is located in the correct position. Other peaks and troughs cannot be resolved, this is probably due to the lack of complex structure in this model. The atmoic interactions of this model are relatively simple, and neglect long range interactions that are evidently important.

6   Relationship between Vibrational and Raman Spectra

The spontaneous Raman spectrum, figure (1), is related to the vibrational spectrum of a material and the corresponding normal modes [12, 13]. In the semi-classical description of Raman scattering [24, 25] a polarised light beam of frequency Ω is scattered by a solid with fundamental vibrational frequencies ω. The light beam therefore acquires components of up and down shifted frequencies $\Omega \pm \omega$ and polarisation p. The resulting component intensities are given by

$$I_p^{\pm}(\omega) = \left[\left(\bar{n} + \frac{1}{2} \mp \frac{1}{2}\right)/2\omega\right] I_p^{\mathrm{RED}}(\omega). \tag{7}$$

The temperature independent factor $\bar{n} = [exp(\omega/kT) - 1]^{-1}$ is the mean normal mode occupation number at temperature T and frequency ω, k is the Boltzman constant. The reduced scattering intensity $I_p^{\mathrm{RED}}(\omega)$ is determined from the vibrational frequency spectrum, normal mode displacement amplitudes and polarisability change amplitudes defined by Bell and Hibbins-Butler [12]. The first two of this quantities can be determined numerically from the computer model. The determination of polarisability change amplitudes requires a suitable model, the simplest of which is the bond polarisability approximation also described by Bell and Hibbins-Butler. This model has been successfully applied to infrared activity in α-quartz [26] and is therefore assumed reasonable for vitreous silica also.

The resulting Raman spectrum of the model described in this report has not yet been fully evaluated or analysed. This important step has been left to later publications. However, comparison of the computed and experimental vibrational spectra indicate that the present approach to modelling Raman gain in vitreous silica will be partially successful, showing promise for further development.

7 Conclusions

This investigation has attempted to create a computational model of vitreous silica used for optical telcommunication fibres. A statistical approach was used that has the potential to allow dopants to be easily added to the model. Although not investigated here, the expected result is the enhancement of particular peaks and the introduction of new frequencies into the observed Raman spectrum. As previously cited, such observations have been made experimentally in optical fibres using Raman spectroscopy.

Based on the results from previous work the core of this investigation has been concentrated on simulating the vibrational frequency spectrum of vitreous silica. Early simulations have demonstrated good correlation between the molecular oscillations and Raman spectra as expected from experimental investigations. However, the full simulation has yielded a broad vibrational response that is lacking in structure. It is believed that this is due to over-simplification of the underlying model. In future work account should be taken of the long range force field interactions between non-adjacent atoms. Such inclusion will increase computation times, but should require no extra input parameters. The full Raman spectrum due to this model should also be calculated and analysed, as should the radial density function for the modelled silica. The latter of these may provide insight into the resulting structure from this approach.

A suggested route for future research is to use a combination of force field models to link SiO_4 unit cells, and allow the system to relax slowly into a structure. This structure could then be driven at a range of frequencies as in the present investigation. Aside from the long range force interactions, this approach would implicitly include multiple molecular orientations in three-dimensions. The atomic and molecular force fields should be expressed as three-dimensional potentials, this could be determined quantum mechanically by numerical techniques.

In summary, this work has demonstrated a new technique for modelling vibrational interactions within vitreous silica. The technique is simple and computationally inexpensive. This new approach has implications for both the design of optical fibres for Raman amplification and for the fundamental understanding of the vitreous state of materials.

Acknowledgement

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