Chapter 3

Raman spectroscopy

Spectroscopic techniques have been widely used by chemists for the investigations of atoms and molecules for many decades. The molecular spectra give information on molecular dimension, vibrational, rotational and electronic states.

3.1. Theory of Raman scattering

The basic principles of Raman spectroscopy are outlined in Figure 3.1, adapted from Merlin and Dele [1].

When a sample is illuminated with monochromatic light and scattering occurs various processes may take place. The electrons in an atom may be excited to virtual and excited states. When light scattering causes excitation to virtual states ($h\nu_o$, $h(\nu_o - \nu_m)$ and $h(\nu_o + \nu_m)$) there is nearly coincident de-excitation and a change in vibrational energy [2] (Figure 3.1). This process describes normal Raman scattering. In addition to elastic or Rayleigh scattering (scattering without wavenumber change), inelastic scattering occurs resulting in wavenumber change, $h(\nu_o \pm \nu_m)$, where $h(\nu_o - \nu_m)$ represents the Stokes lines and $h(\nu_o + \nu_m)$ the anti-Stokes lines. These lines are situated on either side of the Rayleigh line. The Stokes and anti-Stokes spectra contain the same frequency information, but as the anti-Stokes shifted spectrum is always weaker than the Stokes shifted spectrum, the Stokes spectrum is what is generally used in Raman spectroscopy.

When more energetic lasers are used for excitation a large number of electrons or molecules is excited by absorption of radiation, thus populating the excited state. A spontaneous radiant emission then occurs as the excited species loses all or part of the excess energy and returns to the ground state. The resulting radiant emission is of greater energy than that of light scattered during normal Raman scattering. This process is termed fluorescence and often swamps the Raman bands [3].

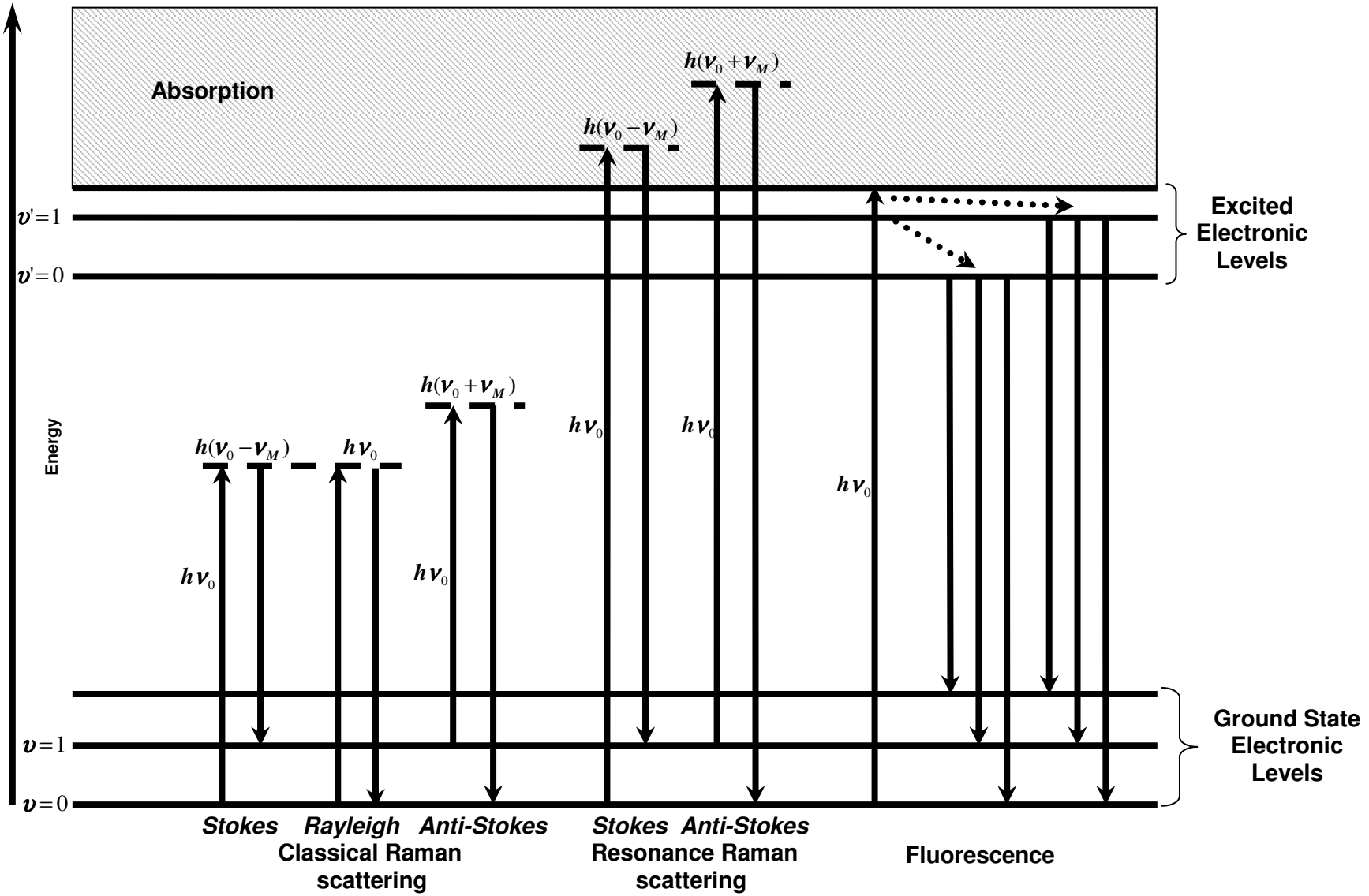

Figure 3.1: Energy levels and transition spectra originating from classical Raman and resonance Raman effect.

When the wavelength of the exciting visible radiation is close to or coincident with that of an electronic transition of the scattering species then a very large enhancement of the intensities of particular Raman bands, sometimes with the appearance of overtones and combination bands, occurs. This process is called resonance Raman spectroscopy (RRS) [4].

The energy difference between initial and final vibrational levels (ΔE) is calculated as follows [2]:

$$\Delta E = hc\left(\frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}}\right) \qquad 3.1$$

where *h* is Planck's constant, *c* is the speed of light and *λ* is the wavelength [3]. The Raman shifts are normally expressed in wavenumber (cm^{-1}) and the wavenumber of the normal vibration ($\tilde{\nu}$) is then:

$$\tilde{\nu} = \frac{1}{\lambda_{incident}} - \frac{1}{\lambda_{scattered}} \qquad 3.2$$

where *λ* is the wavelength in cm.

When the energetics of the equation 3.1 are satisfied during light scattering, a spectrum unique to the molecule under investigation is obtained. The spectrum is usually represented as a plot of the Raman intensity against the wavenumber shift and a peak occurs whenever the conditions of equation 3.1 are satisfied.

3.2. Raman activity of vibration

Raman spectroscopy is a vibrational technique and thus each molecule has 3N-6 (3N-5 for linear molecules) potential vibrational motions, where N represents the number of atoms in the molecule, each band having a particular wavenumber, intensity and width [2]. Not all

normal modes of vibration will be observable as bands in the Raman spectrum. When a molecule is exposed to an electric field, a dipole moment is induced which is proportional to the electric field strength and to the molecular polarisability, α. A molecular vibration can only be observed in the Raman spectrum if it alters the molecular polarisability [5].

$$\frac{\partial \alpha}{\partial Q} \neq 0 \qquad 3.3$$

where *α* is the molecular polarisability and Q stands for the normal coordinate describing the motion of the atoms during a normal vibration. If the conditions of equation 3.3 above are fulfilled by symmetry, then vibrations are allowed or active in Raman spectra; if they are not fulfilled by the symmetry, they are forbidden or inactive. Group theoretical methods are used to determine the symmetries of the normal modes of vibration of molecules and crystal lattices [6, 7]. Character tables have been compiled to assist in determining the number of fundamental vibrations and the selection rules that govern Raman activity. The energy of a vibrational mode depends on molecular structure and environment.

The intensities of bands in the Raman spectrum of a compound are determined by the changes in polarisability, α, that occur during the vibrations. The intensity of a band in the Raman spectrum is given by the equation 3.4

$$I_{Raman} = KI_L(\tilde{\nu}_o - \tilde{\nu}_i)^4 (\frac{\partial \alpha}{\partial Q})^2 \qquad 3.4$$

where I_L is the power of the laser at the sample, $\tilde{\nu}_o - \tilde{\nu}_i$ is the wavenumber at which the band is measured and $\frac{\partial \alpha}{\partial Q}$ is the change in polarisability with the normal coordinate of the vibration [8]. The value of the constant of proportionality, *K*, is dependent on the efficiency at which Raman scattered light may be collected.

3.3. Raman instrumentation

The instrument type used in this study was a dispersive Raman spectrometer. The basic components of the Raman spectrometer include the light source, optical system, detector and signal amplifier. Figure 3.2 shows the organisation of components in relation to each other.

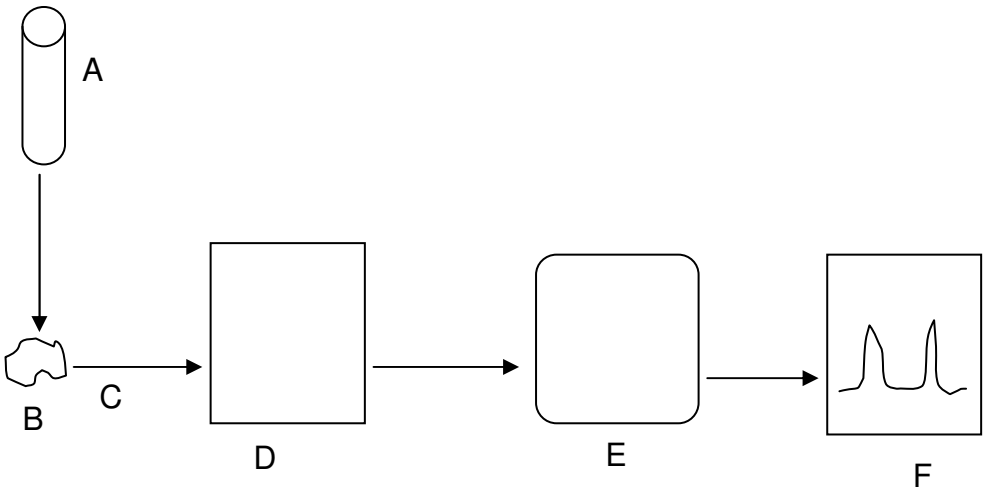

Figure 3.2: Schematic representation of the organisation of Raman components showing the path of the scattered light during recording. A, laser source; B, sample; C, scattered light; D, optical system (e.g. monochromator); E, detector (e.g. charge coupled detector) and F, signal amplifier.

Laser radiation is brought to focus on each grain in the sample via the microscope objective (x50 or x100). The scattered light is then collected and directed to the optical system (e.g. monochromator) and then to the detector. The data may then be processed and displayed on screen or a hard copy (Figure 3.2).

3.3.1. Light source

Due to the inherent weakness of the Raman scattering signal, the sources most often used are lasers. Lasers are high in intensity and are thus able to produce Raman scattering of sufficient intensity to be measured with reasonable signal-to-noise ratio. There are three types of lasers that operate in the ultraviolet (UV), visible and near-infrared regions. The

intensity of Raman scattering varies as the fourth power of the frequency of radiation [5]. Therefore, the order of sensitivity of lasers follows this trend: ultraviolet > visible > near-infrared. However, UV lasers are not commonly used.

The common lasers operating in the visible region are gas lasers, e.g. He-Ne (632.8 nm), Kr^+ (647.0 nm or 530.9 nm) and Ar^+ (488.0 or 514.5 nm). The use of short wavelength visible lasers for excitation of Raman spectra results in the high-energy photons inducing photon fluorescence. To reduce the problem of fluorescence, near-infrared (NIR) lasers are used to illuminate the sample [3]. The most commonly used NIR lasers are the diode lasers (782 or 830 nm) and the Nd/YAG laser (1074 nm). The light source for Fourier Transform Raman spectroscopy (FT-Raman) is the Nd/YAG laser. This technique was developed mainly to overcome fluorescence. However, the use of this type of laser results in weaker bands compared with visible lasers at the same power [8].

3.3.2. Optical system

Light collected from a sample needs to be processed in some way that wavenumbers and intensity information can be extracted from the detected signal. The component used for this purpose is the optical system. This component consists of filters, gratings and mirrors, which collectively select wavelength information to be sent to the detector. The optical system of the Raman spectrometer may be monochromators, polychromators and interferometers. Monochromators block all but a narrow spectral region from reaching the detector. Polychromators separate different wavelengths of light and deliver them to different detectors for simultaneous measurements. Spectra can be built up by measuring the transmitted intensity as the spectral region transmitted by the monochromator changes with time. Spectra from the polychromators can be built by making a histogram for signals from different detectors. Spectrometers (which include monochromators and polychromators) can be classified as dispersive and non-dispersive. Dispersive spectrometers deliver light to a position that varies continuously with wavelength. A dispersive polychromator is called a spectrograph. Non-dispersive spectrometers include anything else such as interferometers, dichroic beam splitters, optical filters and energy

selective detectors. The most common non-dispersive spectrometers use interferometers as their optical system and are called FT-Raman spectrometers [9].

3.3.3. Detector

Multichannel detectors are commonly used in Raman spectroscopy. These are transducers detecting multiple resolution elements at a time allowing spatial resolution in one or two dimensions [10]. The liquid N_2-cooled charged coupled device (CCD) was used in this study. The multichannel detectors are photodiode arrays, charge coupled devices (CCD), charge injection devices and non-silicate devices. An array detector is composed of an array of pixels, where each pixel is one resolution element of the array. The maximum amount of charge a pixel can hold is defined as a full well capacity (FWC), see Figure 3.3. Array detectors are integrative devices, collecting electrons as long as the detector is exposed to light. After exposure the device is sampled to read the signal. For instance, the CCD array is read by shifting the electrons from pixel to pixel across the chip into a register consisting of an analog amplifier and an analog-to-digital converter (ADC) converts the signal from the chip into a computer readable format [10], see Figure 3.4.

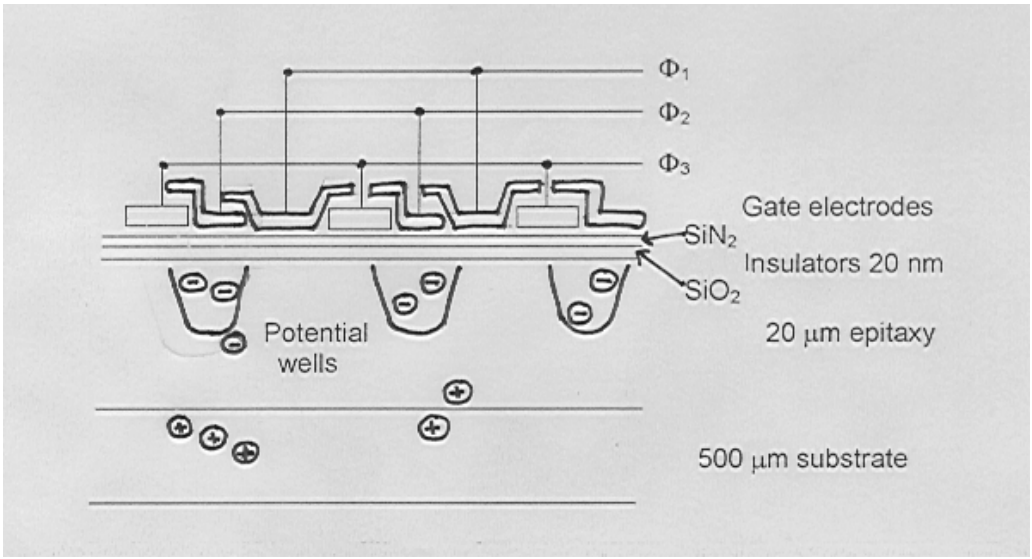

Figure 3.3: Cross-section of charge coupled detector (CCD), demonstrating the location of electrodes and the formation of potential wells. The locations of the electrons and holes in the diagram show where charge is collected.

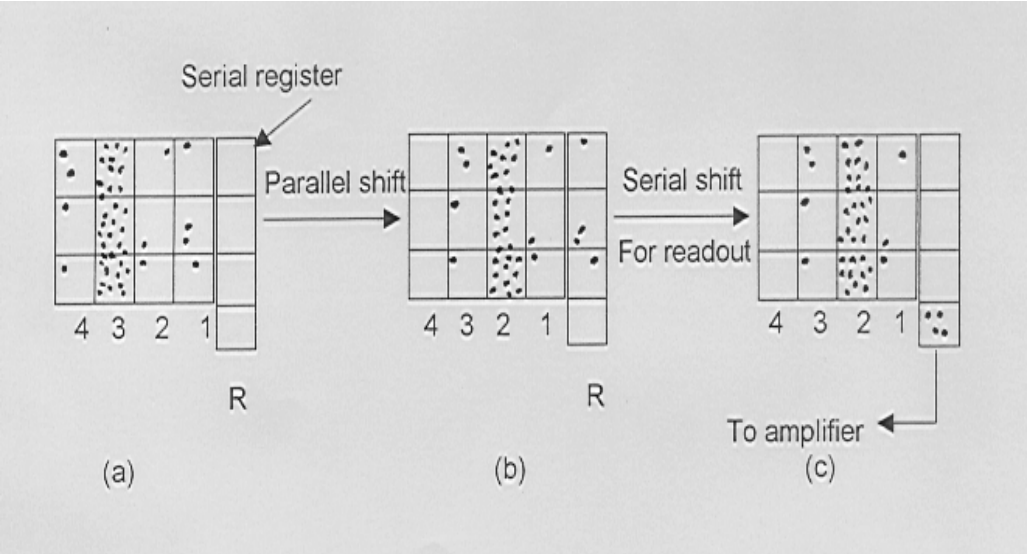

Figure 3.4: Illustration of charge readout on a CCD. (a) Charge collected on the CCD immediately following integration. (b) Readout begins - charge from columns in (a) are shifted one column towards the readout such that the charge from column 1 in (a) is moved to the readout in (b). (c) Charge in the readout is measured and the process is repeated until all columns have been read.

For more details on Raman instrumentation and its operations see ref. [9].

3.4. Operational parameters

There are a number of operational parameters that influence the quality of the Raman spectrum obtained from the sample which have been significant in the current study. These parameters include laser power, sample form, recording time, number of accumulations and confocal microscope.

3.4.1. Laser power

This parameter affects the shapes and intensities of the bands resulting from the sample under investigation. The increase in laser power may result in band broadening and shifts. These effects arise from local heating due to relatively high laser power, which enhances anharmonic interactions [11]. The increase in laser power may destroy the sample or

transform it into a different chemical phase. The laser power may range from a few milliwatts (0.1 mW) to several hundreds. For the heat sensitive compounds e.g. pigments, low laser powers (≤ 5 mW) are desirable in order to minimise the possibility of sample degradation [4]. Coloured molecules can be so strongly absorbing that they thermally degrade [12]. At lower laser power, no sample heating is observed but the spectrum is very weak. As the laser power is increased the Raman band intensities may increase but the baseline starts to increase at high Raman shift because of the effect of sample heating.

When laser power is increased to even higher values (several hundred milliwatts) the black body radiation may cause severe degradation of the spectrum. Black body radiation is continuum radiation produced when solids are so hot that they glow with heat [3]. It is produced by the innumerable atomic and molecular oscillations excited in the condensed solid by the thermal energy. The heat due to the increased laser power slowly changes the structure of the sample. Therefore, the operator must be careful to select the appropriate laser power to maximise the signal-to-noise ratio and minimise black-body radiation caused by the sample heating.

3.4.2. Sample form

Ways of diminishing sample heating include spinning the sample or diluting the sample in some matrix, e.g. oil, KBr, KCl, etc. The low concentration of the sample (often 2%) has the effect of diluting the colour and reducing thermal degradation [12]. This enables strong Raman spectra to be recorded where the bands due to the coloured component could predominate. The strong bands occur due to the molecule generating colour, most likely due to resonance Raman spectroscopy. Thermally stable samples can be analysed in their original form.

3.4.3. Sample recording time

Some compounds, e.g. silicates, are weak Raman scatterers and short time recordings may not yield any peaks. However, with longer recording times the results improve [13]. Therefore, the extension of recording time increases the efficiency and sensitivity of Raman spectroscopy. However, for heat sensitive samples degradation may occur as the recording time is lengthened.

3.4.4. Number of scan accumulations

The number of scan accumulations is closely linked to the recording time. When the sample recording is accompanied by more accumulations, there is an increase in efficiency and sensitivity. One distinct advantage that stems from the increased accumulations is the increase in the signal-to-noise ratio. The recordings using more accumulations result in more pronounced Raman peaks. However, increasing the number of accumulations can result in a different spectrum. This is a direct result of sample heating capacity and/or the heat capacity of its surroundings [14].

3.4.5. Confocal microscope

The use of Raman microscopy (Raman spectrometer coupled to a microscope) gives information on the microstructure of samples analysed and also improves the spatial resolution, the smallest physical distance between measured positions on the sample in single point mapping. When coupled to a confocally optical feature the samples buried in a matrix and at various depths can be analysed. A confocal optical set up occurs when an aperture is placed at the back-focal image plane, where only the radiation emitted laser focal volume will be collected [14]. A suitable choice of optical objectives and the hole for confocal microscope will enable the detection of structural phases existing in micrometre size and along with the depth of the sample, while reducing fluorescence. The use of a confocal hole of several tens of micrometres could give results on a volume < 1 μm^3 [15].

3.5 References

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