Raman Spectroscopy

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A brief article on the Raman effect. We explore the theory behind predicting when Raman transitions occur, as well as how intense the signal from these transitions will be. We then compare this theory to various experimental results.

1. INTRODUCTION

The Raman effect is a light-scattering phenomenon used to gain understanding of the vibrational and rotational modes of a material. When light strikes a material, at a frequency $\nu_{incident}$, it can be scattered at its original frequency (Rayleigh scattering) or at a shifted frequency, due internal transitions within the molecule, $\nu_{molecular}$. This shifted scattering is called Raman scattering, and is classified as either Stokes scattering, $\nu_{scattered} = \nu_{incident} + \nu_{molecular}$, or anti-Stokes scattering, $\nu_{scattered} = \nu_{incident} - \nu_{molecular}$. The shift in frequency is called the Raman shift: $\Delta\nu = |\nu_{incident} - \nu_{scattered}|$. Section 2.1 describes the theory behind predicting when Raman transitions occur, section 2.2 describes the theory behind predicting the intensity of a Raman signal, and finally section 3 compares this theory to experimental Raman measurements under various conditions.

2. RAMAN THEORY

2.1. Raman Transitions

To model the effect of polarized light hitting a sample consider the application of an oscillating electric field of the form $\vec{E} = \vec{E_0} \cos \omega t$, with a wavelength much larger than the molecular dimensions. For Raman scattering the field is not in resonance, $\omega \neq (E_r - E_k)/\hbar = \omega_{rk}$ for any normal modes $|\Psi_r>$, $|\Psi_k>$ of the sample, however it will induce an oscillating dipole moment that will re-radiate. Therefore transitions between normal modes in the system are found by solving the transition dipole moment: $M_{r,k}(t) = \langle \Psi_r | \mu | \Psi_k \rangle$. The normal modes are found by perturbatively solving the time-dependent multi-particle Schrodinger equation with the with the electronic-dipole interaction perturbation, $\hat{H}' = -\mu \cdot E_0 \cos \omega t$, resulting from the applied electric field and induced dipole moment. The first order correction to the wave function is,

$$\Psi_n^1 = \frac{1}{2\hbar} \sum_r \psi_r^0 \left\{ \frac{\mu_{r,n} \cdot E_0}{\omega_{r,n} - \omega} e^{-i(\omega_n + \omega)t} + \frac{\mu_{r,n} \cdot E_0}{\omega_{r,n} + \omega} e^{-i(\omega_n - \omega)t} \right\}. \tag{1}$$

Where the sum is over all of the time independent zeroth-order solutions, $\mu_{rn} = \langle \psi_r^0 | \mu | \psi_n^0 \rangle$, and $\omega_{rn} = (E_r - E_n)/\hbar$. Using this first order correction we can approximate the dipole moment as: $M_{kn} \approx \langle \Psi_k^0 + \Psi_k^1 | \mu | \Psi_n^0 + \Psi_n^1 \rangle \approx \langle \Psi_k^0 | \mu | \Psi_n^0 \rangle + \langle \Psi_k^0 | \mu | \Psi_n^1 \rangle + \langle \Psi_k^1 | \mu | \Psi_n^0 \rangle = M_{kn}^0 + M_{kn}^1$. Where the zeroth order term, $M_{kn}^0 = \mu_{k,n} e^{i\omega_{k,n}t}$, is ignored because it is just a regular transition dipole moment, and therefore doesn't contribute to Raman scattering. Using the first order correction to the wave function in Eqn.1, and orthonormality of the zeroth-order wave functions $\Psi_k^0 = \psi_k^0 e^{-i\omega_k t}$, the dipole moment transition that we are interested in is,

$$M_{kn}^1 = \frac{e^{i(\omega_{k,n} - \omega)t}}{2\hbar} \sum_r \left\{ \frac{\mu_{k,r}(\mu_{r,n} \cdot E_0)}{\omega_{r,n} - \omega} + \frac{\mu_{r,n}(\mu_{k,r} \cdot E_0)}{\omega_{r,n} + \omega} \right\} + \frac{e^{i(\omega_{k,n} + \omega)t}}{2\hbar} \sum_r \left\{ \frac{\mu_{k,r}(\mu_{r,n} \cdot E_0)}{\omega_{r,n} + \omega} + \frac{\mu_{r,n}(\mu_{k,r} \cdot E_0)}{\omega_{r,n} - \omega} \right\}. \tag{2}$$

The first term in Eq.2 with angular frequency $\omega_{kn} - \omega$ is associated with the Raman effect, and the second term with angular frequency $\omega_{kn} + \omega$ is interpreted as a two-photon transition and therefore ignored when considering the Raman effect. The induced transition from states $\langle \Psi_n |$ to $\langle \Psi_k |$ from the Raman effect can be a transition from high to low frequency, $\omega_{kn} = (E_k - E_n)/\hbar > 0$ (Stokes scattering), or from low to high frequency, $\omega_{kn} = (E_k - E_n)/\hbar < 0$ (anti-Stokes scattering). It is assumed that the incident photon, with frequency ω as sufficient energy to induce the dipole momentum transition: $\omega - \omega_{kn} > 0$. For an applied electric field that is not too strong the induced dipole moment is proportional to the applied field: $\mu_i = \alpha_{ij} E_j$, where the proportionality constant α_{ij} is characteristic of each molecule and is called the polarizability. Looking at the *kn*-matrix element of this expression using the first order wave functions $\Psi_k^0 = \psi_k^0 e^{-i\omega_k t}$ and subbing in our oscillating electric field $\vec{E} = \vec{E_0} \cos \omega t$ then the expression becomes $M_{i,kn} = \langle \Psi_k^0 | \mu_i | \Psi_n^0 \rangle = 1/2 \langle \psi_k^0 | \hat{\alpha}_{i,j} | \psi_n^0 \rangle E_{0j} (e^{i(\omega_{kn} - \omega)t} + e^{i(\omega_{kn} + \omega)t})$. As before the term with frequency $\omega_{kn} + \omega$ is ignored and we're left with:

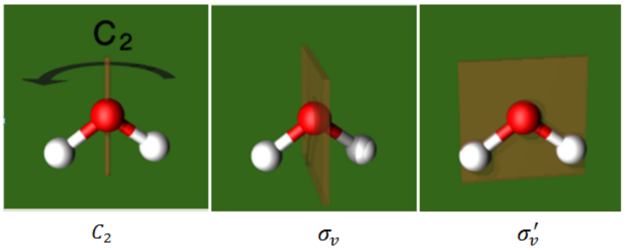
$$M_{i,kn} = 1/2 \langle \psi_k^0 | \hat{\alpha}_{i,j} | \psi_n^0 \rangle E_{0j} e^{i(\omega_{kn} - \omega t)} \tag{3}$$

Comparing Eqn. 3 with the *kn*-component of the Raman part of Eqn. 2,

$$M_{i,kn} = \frac{e^{i(\omega_{k,n} - \omega)t}}{2\hbar} \sum_r \left\{ \frac{\mu_{i,kr}\mu_{j,rn}}{\omega_{rn} - \omega} + \frac{\mu_{i,rn}\mu_{j,kr}}{\omega_{rn} + \omega} \right\} E_j, \tag{4}$$

we find that the *kn*-polarizability matrix elements are:

$$\alpha_{ij,kn} = \frac{1}{\hbar} \sum_r \left\{ \frac{\hat{\mu}_{i,kr}\hat{\mu}_{j,rn}}{\omega_{rn} - \omega} + \frac{\hat{\mu}_{i,rn}\hat{\mu}_{j,kr}}{\omega_{rk} + \omega} \right\} \tag{5}$$



C_2 σ_v σ_v'

FIG. 1: The symmetry operators of H_2O [3]

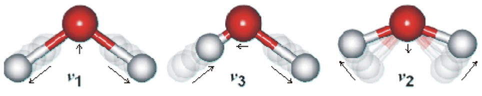
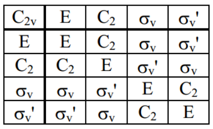


FIG. 2: The normal modes of H_2O [4]



C2v	E	C2	σv	σv'
E	E	C2	σv	σv'
C2	C2	E	σv'	σv
σv	σv	σv'	E	C2
σv'	σv'	σv	C2	E

FIG. 3: The group table of H_2O [5]

$$\alpha_{ij,kn} = \langle\psi_k^0| \frac{1}{\hbar}\sum_r \left\{ \frac{\hat{\mu}_i\,|r\rangle\,\langle r|\,\hat{\mu}_j}{\omega_{rn}-\omega} + \frac{\hat{\mu}_j\,|r\rangle\,\langle r|\,\hat{\mu}_i}{\omega_{rk}+\omega} \right\} |\psi_n^0\rangle \tag{6}$$

For nonzero dipole moment transitions, $\alpha_{ij,kn} = \langle\psi_k^0|\,\alpha_{ij}\,|\psi_n^0\rangle = \int \psi_k^* \alpha_{ij}\psi_n d\tau$ must be non-zero. In order for this transition to be non-zero, ie Raman active, the direct products of the irreducible representation of ψ_k^*, α_{ij} and ψ_n produces a representation which is or contains the symmetric irreducible representation, then Raman transitions will occur [1]. Group theory must be considered in order to understand this theorem.

In group theory the symmetry of an molecule is described by symmetry operations that leave the molecule unchanged. Some possible symmetry operations are: identity E, rotation C_n (rotation of the molecule around an axis through the molecule by an angle of $2\pi/n$), reflection σ (reflection of the molecule across a plane through the molecule). For an example, H_2O has four symmetry operations, the identity E, and, as illustrated in Fig.1, a C_2 rotation about the axis by π through the hydrogen atom, and two reflections about appropriate planes: σ_v and σ_v'. All of the symmetry operations on a molecule must form a closed group: a symmetry group. A group table can be written up which describes the result of applying two symmetry operations on the molecule. For example, applying the symmetry operation C_2 twice to H_2O is the same as applying the identity E, since two rotations by π is a rotation by 2π, which is the same as doing nothing to the molecule. The other entries of the group table of H_2O can be found in a similar way, by considering how the molecule changes after an application of two symmetry operations and determining which single symmetry operation achieves the same result. The group table for H_2O is listed in Fig.3. This group table isn't unique to H_2O, it describes any molecules with these four symmetry operations, it is called the C_{2v} group.

The symmetry operations can be thought of as matrices. There are many different assignments of matrices to symmetry operators that will satisfy the group table multiplication: each assignment is called a representation. Irreducible representations are the smallest possible matrices that satisfy the group table: they can't be broken into smaller matrices that will also satisfy the group table multiplication. For example, a representation of the C_{2v} group is:

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} C_v = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \sigma_v' = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \sigma_v = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \tag{7}$$

since the matrices satisfy the group table multiplication. However, it isn't irreducible because it can be broken into two irreducible representations: $E = 1$, $C_2 = -1$, $\sigma_v = 1$, and $\sigma_v' = -1$ and $E = 1$, $C_2 = -1$, $\sigma_v = -1$, and $\sigma_v' = 1$ which also satisfy the group table multiplication. All representations of a symmetry group are built from irreducible representations.

A normal mode of a molecule can be thought of as an irreducible representation. The three normal modes of H_2O are illustrated in Fig 2. The symmetric irreducible representation is where nothing is done to the molecule, every symmetry group contains this irreducible representation: it is the one where all symmetry operators are assigned to the constant 1 ($E = 1$, $C_2 = 1$, $\sigma_v = 1$, and $\sigma_v' = 1$).

Now consider the theorem again, if the direct products of the irreducible representation of ψ_k^*, α_{ij}, and ψ_n produces a representation which is or contains the symmetric irreducible representation, then Raman transitions will occur. Where the irreducible representations of ψ_k^* and ψ_n will correspond to what normal mode of the molecule they are, and the irreducible representations of α_{ij} are assigned based on how the products of coordinates transform under the symmetry operators (x^2, y^2, z^2, xy, xz, and yz) since, from Eqn. 5, we can see it contains the elements α_{xx}, α_{xy}... which transform like products of coordinates. For a more detailed description of the group theory of molecular structures please see Ref.[5].

2.2. Intensity for Vibrational Raman Scattering

In general the polarizability of a molecule will be given by a 3 by 3 polarizability matrix with components α_{ij}. Since the atoms in the molecule will vibrate about their equilibrium positions one can do a Taylor expansion, assuming the vibrations are sufficiently small, of the components of the polarizability matrix:

$$\alpha_{ij}(Q_k) = \alpha_{ij}(0) + \sum_k \frac{\partial \alpha_{ij}(0)}{\partial Q_k} Q_k + \mathcal{O}(Q^2) \tag{8}$$

In the harmonic approximation we truncate the series to linear order in the displacements. Here Q_k are the normal coordinates for the $k-th$ normal mode (equilibrium positions are at $Q_k = 0$). If we assume that incoming radiation is monochromatic and polarized along the z-direction we get the following equation for the induced dipole moment:

$$\mu_i = \left(\alpha_{iz}(0) + \sum_k \frac{\partial \alpha_{iz}(0)}{\partial Q_k} Q_k \right) E_{0z} cos(\omega_I t) \quad (9)$$

From electromagnetic theory we know that the following proportionality relation holds for the power emitted by an electric dipole with dipole moment $\vec{\mu}$ and ν is the frequency of scattered photons:

$$P \propto \nu^4 \ |\vec{\mu}|^2 = \nu^4 (|\mu_x|^2 + |\mu_y|^2 + |\mu_z|^2) \quad (10)$$

From this point we will treat μ_i as a quantum operator. The normal coordinates will act as position operators in the Hamiltonian. In particular since everything is written in terms of normal coordinates we know that the unperturbed Hamiltonian will be a sum over independent harmonic oscillators vibrating at their respective normal frequencies. As an aside one should note that the number of normal modes for a given molecule with M atoms, which we will denote as N, equals $3M-6$ for non-linear molecules and $3M-5$ for linear molecules [2]. For example a water molecule has three atoms so it has 3 normal modes. The unperturbed states will be products of a harmonic oscillator associated with each normal mode. We will represent these states using the ket notation $|n_1, n_2, ..., n_N\rangle$, where the ket represents a state in which the $k-th$ normal mode is excited to to the n_k level. The state has a total energy of $\sum_{i=1}^{N} [\hbar \omega_i (n_i + 1/2)]$ which is a sum of the collective normal mode energies. Hence from a quantum point of view transitions from one state to another occur due to the time-dependent perturbation caused by the oscillating electric field inducing a dipole moment in the molecule. So to understand intensity of such transitions we should calculate$|\langle n'_1, n'_2, ..., n'_N | \mu_i(\hat{Q}_k) | n_1, n_2, ..., n_N\rangle|^2$. Since we are interested in Raman transitions this would correspond to having the initial state unequal to the state after the interaction so the zeroth order term vanishes due to orthogonality (The zeroth order term actually would represent Rayleigh scattering). So we are left with:

$$\begin{aligned} &\langle n'_1, n'_2, ..., n'_N | \mu_i(\hat{Q}_k) | n_1, n_2, ..., n_N\rangle \\ &= E_{0z} cos(\omega_I t) \sum_k \frac{\partial \alpha_{iz}(0)}{\partial Q_k} \langle n'_1, ..., n'_N | \hat{Q}_k | n_1, ..., n_N\rangle \end{aligned} \quad (11)$$

We know from the the ladder operator formalism for SHO that the matrix element $\langle n'_1, n'_2, ..., n'_N | \hat{Q}_k | n_1, n_2, ..., n_N\rangle$ is non-zero iff $n'_k = n_k \pm 1$ and $n'_{i \neq k} = n_{i \neq k}$. We can only have transitions of the form $|n_1, n_2, .., n_k, .., n_N\rangle \rightarrow |n_1, n_2, .., n_k \pm 1, .., n_N\rangle$, assuming that $\frac{\partial \alpha_{iz}(0)}{\partial Q_k} \neq 0$, if it is zero then a transition through that mode will not occur such modes are called Raman inactive. So we are left with the following type of transition element which is going to correspond to a transition through the $k-th$ mode:

$$|\langle n'_1, ..., n'_N | \mu_i(\hat{Q}_k) | n_1, ..., n_N\rangle|^2 \propto \frac{E_{0z}^2}{\omega_k} \left(\frac{\partial \alpha_{iz}(0)}{\partial Q_k} \right)^2 \quad (12)$$

Where we time averaged over one cycle to get rid of the $cos^2(\omega_I t)$ function, the $1/\omega_k$ comes from evaluating the matrix element using ladder operators for the $k-th$ normal mode:

$$P_k \propto (\omega_I \pm \omega_k)^4 \frac{E_{0z}^2}{\omega_k} \sum_{x,y,z} \left(\frac{\partial \alpha_{iz}(0)}{\partial Q_k} \right)^2 \quad (13)$$

This gives the scattered power for one molecule for undergoing a transition through the $k-th$ normal mode. Here the plus corresponds to Anti-Stokes scattering and the minus corresponds to Stokes scattering. However typical samples in a lab will have many molecules that can scatter the incoming photons. If we assume the sample to be in thermal equilibrium at a temperature T then we know from basic statistical mechanics that the relative probability, compared to the ground state, of finding a molecule in some excited state will be suppressed by by the Boltzmann weight. This implies that at sufficiently low temperatures we expect most of the molecules to be in the ground state. Hence if Raman scattering does occur it is more likely that a photon will excite the vibrational mode to higher energy states and come out with lower energy this is often seen in experiments. This means that the ratio of the intensity of Anti-Stokes scattering and Stokes scattering through some Raman active mode vibrating at ω_k will be roughly given as:

$$\frac{I_{Anti-Stokes}}{I_{Stokes}} = \frac{(\omega_I + \omega_k)^4}{(\omega_I - \omega_k)^4} e^{-\beta \hbar \omega_k} \quad (14)$$

where $\beta = (k_b T)^{-1}$. For a more precise treatment for calculating intensity please see Ref.[1].

3. RAMAN EXPERIMENT

3.1. Experimental Set-up

Fig.4 illustrates a typical Raman system. The system is mainly composed of three parts: incident light part, sample part and scattered light part [6]. Fig.5 corresponds to the sample part of a Raman system, where the red arrow stands for the direction of incident light, and the blue arrow stands for the scattered light, this picture was taken from Dr. Guangrui Xia's lab, located in the department of materials engineering at UBC. In Dr. Guangrui Xia's lab Raman spectra are collected on a backscattered Horiba Jobin Yvon HR800 Raman system with 442nm (2.81 eV) line from a He-Cd laser. The 442 nm incident laser beam is polarized.

To measure the Raman spectra, we first use the microscope to focus on the sample, then turn on the laser. The scattered light goes through various optical devices and finally the signal is collected by a CCD. Thus, Raman

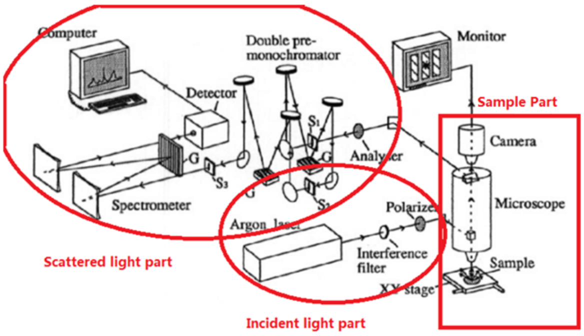


FIG. 4: Typical experimental set-up of a micro-Raman spectrometer

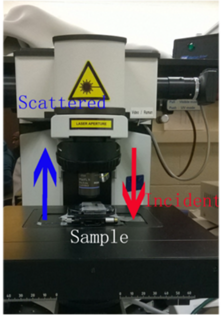


FIG. 5: Sample part of a Horiba Jobin Yvon HR800 Raman system

spectra will appear in the computer. A heating stage can be used to create a higher temperature environment for the sample.

3.2. Raman vs. Temperature

From the equation of intensity from Ref.[7] it is clear that the Stokes Raman Intensity $I_s \propto (\omega_I - \omega_k)e^{\frac{\hbar\nu}{kT}}$, differs from the Anti-Stokes Raman intensity, $I_{as} \propto (\omega_I + \omega_k)(1 - e^{-\frac{\hbar\nu}{kT}})^{-1}$. At low temperatures these intensity proportionalities match what was derived in section 2.2. Fig.6 shows the Anti-Stokes (AS) (left) and Stokes (S) (right) spectra for the 610 cm^{-1} mode of Rhodamine 6G (RH6G) under different temperatures. The x-axis is the differences between the frequency of the incident light and the scattered light, which is in the units of wave-number (cm^{-1}). The y-axis stands for the relative intensity of the scattered light. Since the intensity depends of the parameters of the set-up, the units differ for each experiment, and therefore are given the general label "arbitrary units". Note the change in scale between the AS and S spectra. Panels a and b show the AS and S modes respectively at 300 K (dark gray) and 170 K (light gray). It is clear that while there is little effect on the intensity on the Stokes side there is a significant decrease in the intensity of the AS signal as the temperature is decreased, as is expected from a decrease in thermal population [7]. This result is expected from the theory described in section 2.2.

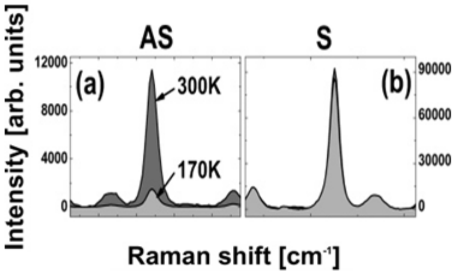


FIG. 6: The stokes and anti-stokes Raman spectra of Rhodamine 6G (RH6G) under different temperatures

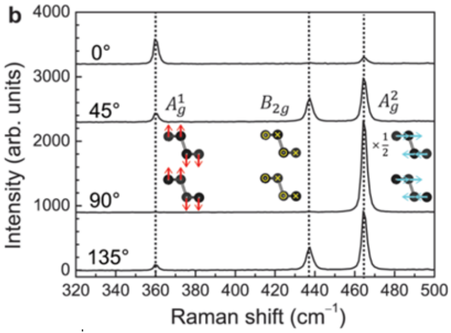


FIG. 7: The Raman spectra of BP in 4 different crystal orientations. The 3 peaks correspond to the 3 different normal modes.

3.3. Raman vs. Crystal Orientation

Fig.7 shows three typical Raman Modes in Black Phosphorus (BP):A_g^1, A_g^2, B_g^2 [8]. In this example, for the A_g mode only has diagonal parts,

$$\frac{\partial\vec{\alpha_{ij}}}{\partial Q_k} = \begin{bmatrix} ae^{i\sigma_a} & 0 & 0 \\ 0 & be^{i\sigma_b} & 0 \\ 0 & 0 & ce^{i\sigma_c} \end{bmatrix} \tag{15}$$

From Eqn.13 in section 2.2, we can see that the intensity of the scattered light, and therefore the electric field of the scattered light, satisfies,

$$\vec{E}_{scattered} \propto \frac{\partial\vec{\alpha_{ij}}}{\partial Q_k} \cdot \vec{E}_{incident}, \tag{16}$$

(in section 1.2 the specific case of $\vec{E}_{incident} = E_{incident}\hat{z}$ was used).Usually we add a polarizer with the parallel polarization of the incident light when measuring the scattered light. If we assume the parallel polarization of the incident light as $\vec{E}_{incident} = (\sin\theta \;\; 0 \;\; \cos\theta)$, the intensity is,

$$I_{A_g}^{\parallel} \propto |(\sin\theta \;\; 0 \;\; \cos\theta)\frac{\partial\vec{\alpha_{ij}}}{\partial Q_k}(\sin\theta \;\; 0 \;\; \cos\theta)^T|^2$$
$$= |a|^2[(\sin\theta^2 + |\frac{c}{a}|\cos\phi_{ca}\cos\theta^2)^2 + |\frac{c}{a}|^2\sin\phi_{ca}{}^2\cos\theta^2]. \tag{17}$$

Since the intensity is angularly resolved, we see the results in Fig.7, where intensity changes with changing angles [9].

3.4. Raman Strain vs. Stress

The Raman scattering spectrum is a useful tool to resolve internal strains and stresses in materials through the high resolution of determining normal mode frequencies, and it represents an effective and nondestructive technique. Tensile or compressive stress can induce the redshift or blueshift of each Raman peak. Once the strain/stress relationship is known for a specific material, it offers a convenient way, by Raman scattering, to detect the strain/stress distribution on a sample of that material.

Silicon (Si) and Gallium Nitride (GaN) were used as the examples to illustrate the relationship between stress and Raman spectroscopy. Fig.8 shows typical Raman spectra measured from Si under tensile, free, and compressive stresses. According to the result, for silicon, a compressive stress will lead to a blueshift in spectra, while a tensile strain will lead to a redshift. And the response is almost linear in certain range of stress[10]. Fig.9 illustrates the Raman spectra of Si and GaN under increasing compressive stress [11]. Curves "a"-"f" stand for one Raman spectra under increasing compressive stress. Each curve, except curve "a", have been moved up in parallel for comparison. Both the materials show a blueshift, and the shift almost increases linearly with the stress.

4. CONCLUSION

In this article we explored the experimental technique of the Raman effect. We began by describing the theory that predicts when Raman transitions will occur, as well as how intense the signal from those transitions should be. Then we looked into the experimental side of the Raman effect. We described how Raman spectra are measured, and analyzed various spectra from different experimental conditions, noticing how the theory tied in with what was experimentally observed.

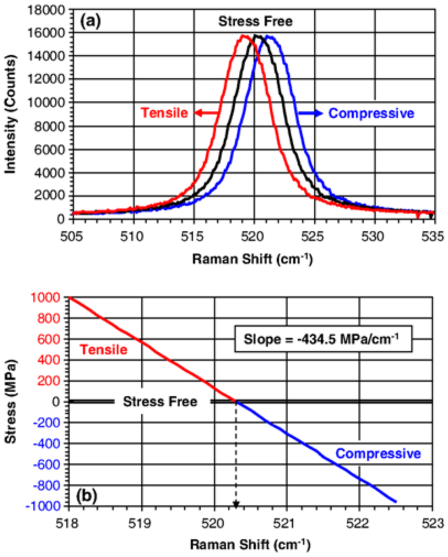


FIG. 8: (a) Typical Raman spectra measured from Si under tensile, free, and compressive stresses (b) Relation between Si stress and measured Raman shift (peak position)

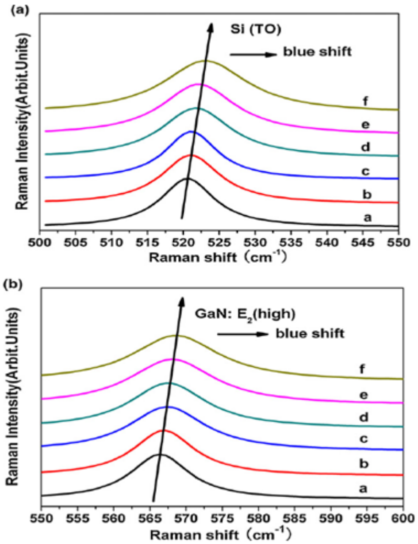


FIG. 9: (a) The Raman peaks shift of Si under applying increasing compressive stress loadings (b) The Raman peaks shift of GaN under the same condition

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