Quantized Oscillations Lab Report

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December 2024
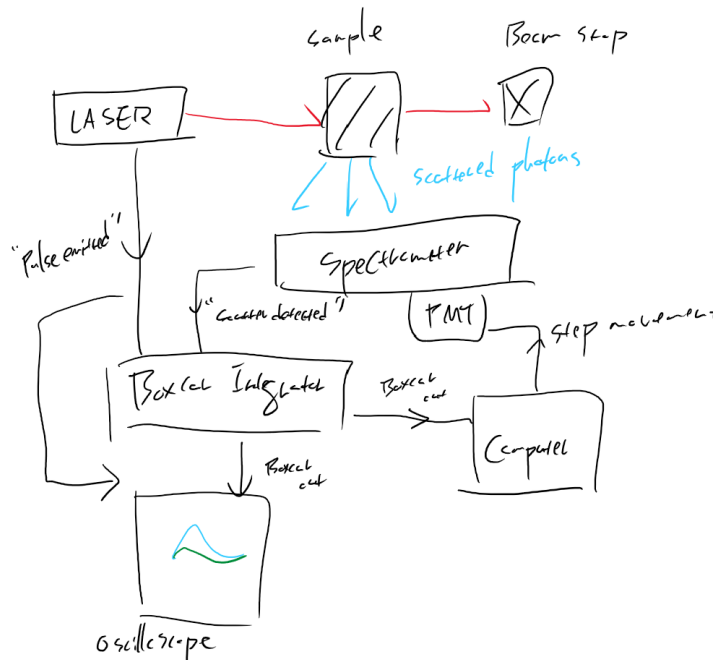
1 Setup and Methods

Figure 1: Figure of the setup

In this lab, we observe the interactions between photons and molecules. When a photon collides a molecule, the molecule is exciteted to a virtual state. Then, as the molecule exits the virtual state and collapses to one of the stable energy states it emits a photon. This process of photon emission related to change of a molecule's vibrational mode is called **Raman Scattering**.

1.1 General Setup

Pulses of Nitrogen lazers are shot at the sample. As Raman Scattering occurs within the sample, the sample emits photons. These photons are emitted towards the spectrometer. A computer system drives the PMT motor in order to collect the emission around diverse range of spectra.

Since the laser is emitted in form of pulses, it is imperitive to take measurements exactly at the point of the time when the pulse is emitted. In order to guarantee that the collected data has the hightest intensity originating from the pulse, we use the **Boxcar Integrator**.

The Boxcar integrater accepts two inputs. The first is the signal input, and the second is the gate input. The gate input triggers the Boxcar integrator to set up a square pulse after a event. Then, the boxcar integrates the product of the generated square pulse and the signal input. The integrated value is proportional to the average sequence intensity in a short time period after the trigger.

The Spectrometer consists of two slits. Narrowing down the distance between the slits guarantee better resolution of the data. However, as the slit is narrowed, less photons enter the detector, and a greater gain is required to amp up the spectrometer output signal.

1.2 Week 1: Vibrational Modes of Water and Benzene

We explore the vibrational modes of Water(H_2O) and Benzene (C_6H_6). The former has three vibrational modes and the latter has 30. Around the vibrational modes, we expect to observe a peak of measured intensity.

1.3 Week 2: Dye lasers and the Iodine molecule

The molecules observed in week 1 have a complicated structure. We explore a simpler moleclue, Iodine(I_2). The potential of this molecule can be losely considered as a simple harmonic oscillator. Since the energy eigenstates of a harmonic oscillator potential have equal spacings, we expect the measured intensity peaks to be equidistant for the iodine molecule.

2 Overview of Vibrational Peaks

We first demonstrate the advantages of Raman Spectroscopy. The two close vibrational modes of the water molecule are at $3650cm^{-1}$ and $3750cm^{-1}$ which correspond to symmetric and asymmetric stretch. Suppose we wish to induce a vibrational mode change using classical absorbtion tecnhiques. The required wavelength of the driver photon can be computed by considering the energy difference between the two modes.

$$\Delta E = \Delta k \hbar c = \frac{c}{\lambda} \tag{2.1}$$

$$\lambda = \frac{1}{\Delta k} = \frac{1}{100 cm^{-1}} = 10^{-4} m \tag{2.2}$$

Such lambda in the magnitude of -4 is in the borderline of IR rays and radars. Therefore, it is impossible to drive a water molecule using a N^2 laser that has a wavelength of $\lambda_N = 535nm$.

Raman Spectroscopy drives the molecule to a virtual energy state that is unstable. From the unstable state, the molecule might either fall to a higher or a lower energy eigenstate that it used to be. If after the scattering, the molecule gains energy, the wavelength shift in the incident and emitted photon is called **Stokes Shift**. If the molecule loses energy, the phenomenon is called a **anti-Stokes Shift**. In the perspective of the photon, the stokes shift are red since the photon loses energy. On the contrary, anti-stokes shifts are blue. The peaks in spectrum induced by these shifts are called **Stokes and anti-Stokes peaks** or **Raman peaks**.

If the temperature of the system is low, then most of the molecules will be in the lowest vibrational mode. If a photon is scattered upon a low-temperature sample, the molecule will always take energy from the photon, resulting in a stokes shift. Therefore, all the Raman peaks will be red.

The distribution of molecules over the vibrational modes can be characterized by the boltzman distribution. The measured intensity corresponds to the population of the molecule. The intensity ratio can be quantified theoretically as follows.

$$\frac{I}{I_{gr}} = \exp\left(-\frac{\Delta E}{k_B T}\right) \tag{2.3}$$

Here, ΔE corresponds to the energy difference between the vibrational mode in question and the ground state.

Question 2.1. *At what temperature will a blue Raman peak will occur in a $1/e$ intensity of the largest red Raman peak?*

Solution. If we assume that the probability of occurence of the stokes shifts are proportional to the population density of molecules in each vibrational mode, we can compute the temperature where a change in energy between the two peaks leads the argument of the boltzman exponential to evaluate to -1. At the desired temperature T, in Kelvins,

$$\frac{\Delta E}{k_B T} = \frac{\Delta k \hbar c}{k_B T} = 1 \tag{2.4}$$

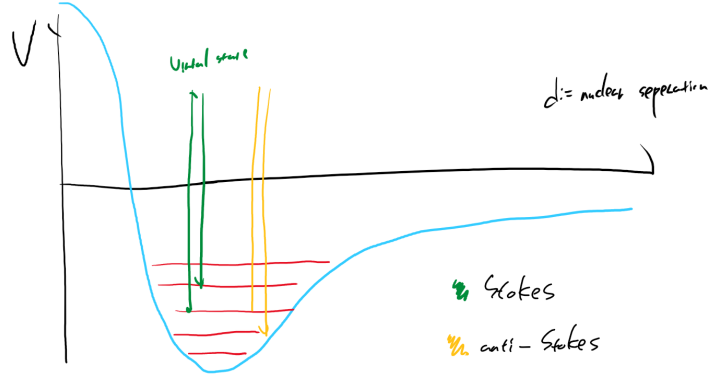$$T = \frac{(\Delta k)\hbar c}{k_B} = \boxed{469.7K} \tag{2.5}$$

$\square$

Figure 2: Raman Shifting in an Iodine molecule

We continue our discourse of vibrational peaks in an Iodine molecue. The potential of a two atom system diverges to infinity around $r = 0$ and asymptotes to zero at $r \to \infty$. In between the two limits exists a well. At the global minimum of the potential well, Taylor series approximations reveal the well to be approximately a simple harmonic oscillator. Let ω be the resonant frequency of the approximated potential. Then,

$$E_n = (\frac{1}{2} + n)\hbar\omega \quad (n = 0, 1, 2, \dots) \tag{2.6}$$

$$\Delta E = \hbar\omega \tag{2.7}$$

Question 2.2. *What is the approximated "spring constant" at the bottom of the well?*

Solution. The frequency of the oscillator is related to the spring constant.

$$\omega = \frac{\Delta E}{\hbar} = \sqrt{\frac{k}{\mu}} \tag{2.8}$$

Instead of mass, we use the reduced mass of the Iodine atom, $\mu = m_I/2$. After algebraic manipulations, we deduce the following.

$$k = \frac{m_I}{2}\left(\frac{\Delta E}{\hbar}\right)^2 \tag{2.9}$$

$\square$

As the vibrational energy of the molecule increases, the well width of the approximated SHO increases too. The increase in well width leads to a smaller spring constant. The square root of the spring constant is proportional to the frequency, which is proportional to the energy difference between two consecutive vibrational modes. Therefore, around the top of the well where the well width approaches infinity, the spacings between the vibrational modes vanish.

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3 Data and Analysis

Plesae plot

1. (week 1) Intensity vs wavelength/vibrational spacing for Benzene and water

2. (week 2) Plot vibrational spacing (in cm^-1) vs vibrational quantum number.

4 Frank-Condon factors and Overlap Integrals

Question 4.1. *Explain the observed 'long vibrational progression' of a single vibrational level*

This part refers to the last problem in the lab handout. Please check glow for details.