

Raman Spectroscopy on Diatomic Molecules

I. INTRODUCTION

Raman spectroscopy is a powerful tool to probe the vibrational and rotational degrees of freedom of molecules [1] as well as characterize structural and electronic properties in solid state samples [2]. Utilizing an absorption to a virtual energy state and an emission at a different frequency, it allows one to access energy differences in the infrared range and does not require materialspecific frequency matching (although driving at a resonant frequency will enhance the Raman signal). The energy differences reveal the spacing between various energy states and hence provide information about bond properties. Since these excitations will be governed by selection rules and will reflect the quantum mechanical nature of molecules, they can also be used to study certain internal properties such as the spin of the nucleus.

Although the Raman effect was first discovered in 1928 [3], it was the appearance of lasers and high resolution spectrometers that made Raman spectroscopy an essential tool for characterizing all kinds of gas, liquid and solid state materials [4]. Narrow emission line width, high intensities and polarization characteristics of lasers improved the precision and enabled certain scattering processes to be probed more specifically. In our setup, we employ laser-excited Raman spectroscopy to observe and analyze the rotational states of O_2 and N_2 and deduce their bond length and nuclear spin configurations. We will then perform similar experiments on air to demonstrate the “remote sensing” capabilities of Raman spectroscopy and explore the effects of other control parameters such as pressure and temperature on the Raman spectrum.

II. THEORY AND BACKGROUND

The structure of a molecule has important implications in its stability and reactivity with other compounds, making its study an important step towards the understanding of molecular dynamics. One way of probing this structure is by the study of the bonds that constitute the molecule, characterizing both their strength and length.

The strength of the bond can be related to vibrational modes in the molecule, as each bond corresponds to a potential well which will contain bound states where the molecules lies. In particular, the strength of the bond can be inferred by the spacing of the energy of the modes, as the potential can be approximated, for low energy excitations, by a harmonic oscillator potential around the minima. The frequency of the corresponding harmonic oscillator is related to the second derivative of the potential at that point by $d^2U(r)/dr^2 = \mu\omega_{osc}^2 = k_{eq}$ with μ the reduced mass of the system, ω_{osc} the natural frequency of oscillation of the bond and k_{eq} the equivalent spring constant of the oscillator. The possible energies E_n associated with a bond are then given by the energy states of a harmonic oscillator:

$$E_n = \hbar\omega_{osc}(n + 1/2),$$

where n is the quantum state occupied by the system and \hbar is the reduced Planck constant.

The length of the bond affects the rotational modes of the molecule, as a greater length in a bond leads to a greater moment of inertia. By measuring the gap between energy levels in the rotational modes of the molecule we can also infer the length of its bonds. The energy E_l is related to the square of the angular momentum by

$$E_l = \frac{\hbar^2}{2I}l(l + 1),$$

where l is the angular momentum quantum number of the system and I is the moment of inertia of the system.

In the case of diatomic molecules studied, such as N_2 and O_2 , the moment of inertia are given by $I = \mu d^2$, where d is the distance between the atoms.

Raman spectroscopy, discussed in [5], allows us to probe these low energy transition in the molecule by shining photons of a frequency ω_0 onto a sample of interest. These photons will excite the molecule to a virtual state, corresponding to an unstable, non-measurable state, which plays the role of the intermediary step in this process. From this state the system decays into a new vibrational state and/or rotational state, emitting a new photon in some direction. The energy difference between the states will be equal to the difference in the

energies of the emitted and the absorbed photon, which can be detected by the difference in the frequencies.

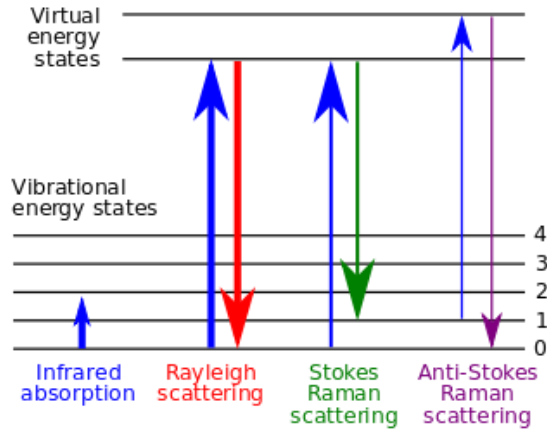


FIG. 1. Much like Rayleigh scattering, in Raman scattering the molecule is excited to a virtual state which then decays to a bound state. However in Raman scattering, the final state is different from the initial state, leading to a change in the frequency of the scattered photon. If the new energy state is of higher energy it is called Stokes Raman scattering, while if it is of lower energy Anti-Stokes Raman scattering. Figure from Wikipedia Raman spectroscopy page.

Since the experiment is conducted on a macroscopic sample in equilibrium before the excitation, the various molecules will be in a distribution of the many available rotation and vibrational states. This distribution will be proportional to the Boltzmann weight, which suppresses higher energy states, and the degeneracy, which increases with l . This will have an observable effect, since the higher the population of a state, the higher the probability of that state undergoing Raman scattering, hence leading to an increase in the intensity of a particular line. The population can then be characterized by the difference in intensities of the scattered light.

To calculate the degeneracy of the energy states the nuclei spins need to be taken into account [6]. For a homonuclear diatomic molecule, the wave function of the nuclei can be written by the product of a spin part and a rotation part, $\psi_{nuc} = \psi_{rot}(\sim r)\psi_{spin}(\vec{I}_1, \vec{I}_2)$, where $\sim r$ is the vector from one nucleus to the other, \vec{I}_1 is the spin vector of atom 1 and \vec{I}_2 is the spin vector of atom 2.

However, due to quantum statistics, the wavefunction must be anti-symmetric for Fermionic systems and symmetric for Bosonic systems under exchange of indistinguishable particles. This imposes a relationship between the rotational modes and the spin states that each atom can occupy. Let I denote the spin value of the

nucleus. Choosing one value of m_I there are $2I + 1$ choices for each atom. However if both m_I are equal, the functions cannot be anti-symmetrized so ψ_{spin} will be symmetric corresponding to $2I + 1$ states. For any other combination the wavefunction can be made symmetric or antisymmetric, corresponding to $(2I + 1)I$ states, as order is irrelevant.

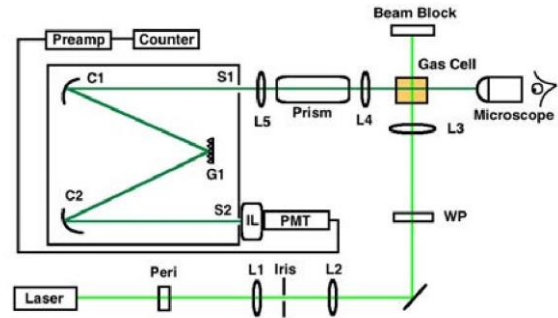


FIG. 2. Schematic of our experimental setup. Peri: periscope to raise beam height; L: lenses, L1 has a focal length half that of L2, L3 focuses the beam down to the gas cell, L4 makes the scattered beam collinear, L5 images the beam onto the spectrometer slit; WP: half wave plate to rotate beam polarization; S: spectrometer input and output slits; C: curved mirrors for focusing; G1: spectrometer grating; IL: imaging lens to map slit to photomultiplier (PMT) cathode.

The spatial part will also be either symmetric or antisymmetric under the transformation $\sim r$ to $-\sim r$ when the angular momentum state l is even or odd respectively. Moreover, each angular momentum state l will have degeneracy $2l + 1$.

If I is an integer, it obeys Bosonic statistics, so we require the wavefunction to be symmetric, hence both spin and spatial parts need to have the same parity. This means that for l even, there is a $(2l + 1)(2l + 1)(l + 1)$ degeneracy while for l odd the degeneracy is $(2l + 1)(2l + 1)l$. Analogous to this, for I half-integer, l even gives rise to a $(2l + 1)(2l + 1)l$ degeneracy while l odd gives rise to $(2l + 1)(2l + 1)(l + 1)$ degeneracy.

The resulting effect is a difference in the intensities of the transitions corresponding to l even and odd states, proportional to the difference in the degeneracy. The height ratio will thus be given by $l/(l + 1)$, which in the case of ^{14}N with $l = 1$ corresponds to $1/2$.

For the case of $l = 0$, as in O_2 , the spin part of the wavefunction will always be symmetric, meaning that the spatial part must also be symmetric. The molecule can only occupy l even states, making the spectra lines further

apart from one another and the spectra lines corresponding to l odd disappear.

III. APPARATUS

We shall use an apparatus built by Prof. Greytak and located in building 13 to perform Raman spectroscopy on systems of interest. The apparatus is shown schematically in Fig. 2. A green laser beam with a power of up to 2 W is emitted from a commercial laser, which is then raised by a periscope to be at the same height as the spectrometer. A collimating lens system expands the beam diameter by a factor of 2 and sends the light through a half-wave plate which rotates the polarization of the laser beam from vertical to horizontal. Since detection of Raman-scattered photons is in the horizontal plane, this choice of polarization reduces Rayleigh scattering and improves the signal to noise ratio of our experiment.

This laser beam with the appropriate polarization is then focused onto a gas cell which can be filled with nitrogen, oxygen, or other gas phase samples of interest. Rayleigh scattering and Raman scattering occur and light scattered in the orthogonal direction is sent into the spectrometer. To match the spectrometer slit orientation and the laser emission direction, a trapezoidal prism is employed. Both images are observed with a microscope to ensure that the Raman scattering direction is well aligned with the spectrometer input.

The spectrometer we use is a grating spectrometer that is capable of scanning across a range of wavelengths encompassing the Raman scattered light frequency. The scattered light intensity at each wavelength is monitored by a photomultiplier tube at the end of the spectrometer (there is an optical assembly here to ensure efficient coupling), which is then sent to a pre-amplifier and discriminator for signal separation. By recording the number of counts at each scanned wavelength, we can then reconstruct the Raman scattering signal and obtain information about the molecular structure.

All of the equipment required for this experiment has been set up in building 13. The main part which requires improvement is the counter output; there have been some issues with correctly setting up the Agilent 5321A counter which would provide easier data acquisition, digitization and analysis, but for the moment we can use an older counter which gives reasonable readings. For further experiments, if we would like to perform Raman spectroscopy on solid state materials, we might also need to make a new sample mount.

IV. PROPOSED EXPERIMENT AND EXPECTED RESULTS

The main goal for this project is to verify experimentally the Raman scattering effect. For this purpose, samples of nitrogen and oxygen molecules will be primarily used, as they provide an experimental calibration al3

lowing us to demonstrate the validity of the technique against current literature. Since the spin of ^{14}N is 1 and of ^{16}O is 0, they will exhibit different intensities at different spectral lines arising from quantum statistics. In particular, we shall see lines of alternating intensity in nitrogen and the vanishing of one set of lines for l odd in oxygen (see Fig. 3 for the expected spectra for N_2). We will also be able to calculate bond properties from the spacing of Raman scattered lines.

The data obtained from the two previous experiments will then allow us to perform Raman Spectroscopy in air and from the spectrum infer the quantities of O_2 and N_2

ROTATIONAL RAMAN SPECTRUM OF N_2

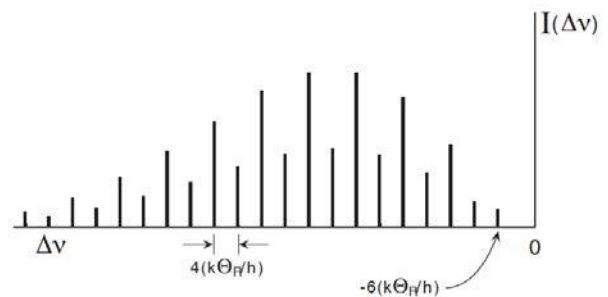


FIG. 3. Expected Raman spectrum for $^{14}\text{N}_2$. Apart from the overall intensity envelope caused by level degeneracy and Boltzmann distributions, we also observe alternating intensities in adjacent peaks caused by quantum statistics. For O_2 , we expect to see only the outside envelope, although the peak spacings will be doubled. Figure from Prof. Greytak's 8.044 lecture notes [6].

based on the strength of the observed spectra.

Time permitting, we would also like to perform Raman spectroscopy on other gases such as CO_2 and observe the Raman spectrum of graphene. It would also be interesting to observe the effects of pressure and temperature on the Boltzmann distribution of energy states.