Rotational Raman Spectroscopy

If EM radiation falls upon an atom or molecule, it may be absorbed if the energy of the radiation corresponds to the separation of two energy levels of the atoms or molecules. If the EM radiation is not observed, it may be either transmitted or scattered by the molecule.

Most of the scattered radiation has an unchanged wavelength and is the Rayleigh scattering (elastic scattering). The intensity of the scattered light is $I \propto \lambda^{-4}$. Blue radiation is scattered preferentially by particles in the atmosphere, resulting in a blue sky.

It was shown theoretically by Smekal in 1923 and by Raman and Krishnan in 1928 that a small amount of the radiation scattered by all phases of matter is slightly increased or decreased in wavelength. This is called the Raman effect, and the decreased or increased frequencies (energies) are referred to as Stokes and anti-Stokes Raman scattering (inelastic scattering), respectively.
Raman spectra

The generalized form of a Raman spectrum is sketched below, complete with vibrational and rotational Raman effects.

The Raman effect is a two-photon process (as we shall see) involving excitation to a virtual excited state followed by return to a lower energy state. The processes are similar to vibrations and rotations (just different energies).

The peaks in Stokes and anti-Stokes rotational spectra generally have similar intensities, since the levels are similarly populated.

However, for Stokes and anti-Stokes vibrational peaks, the latter are of lesser intensity at standard temperatures, since the excited states are generally much less populated than the ground states (we will deal with the vibrational peaks in a later lecture).
Experimental Set Up

Scattered radiation is ideally collected at right angles to the incident light and sample holder.

Incident monochromatic radiation is passed through a sample cell, and must be very intense, since the Raman scattering is very weak (multiple reflection gas cells used).

This makes lasers the ideal source of incident radiation. Interestingly, lasers are usually in the optical or UV range, but rotational Raman spectra are observed in the μ-wave region - in some cases fluorescence can overwhelm the weak Raman signal.

IR lasers are also used, which overcomes the problem of fluorescence, but then a grating cannot be used to disperse the radiation. Interferometry and FT-IR techniques revolutionized Raman spectroscopy, so a FT-Raman spectrometer is an FT-IR spectrometer adapted to accomodate a laser, filters to remove laser radiation during detection, and a variety of IR detectors. The Nd-YAG laser, operating at 1064 nm, is the most common.
Rotational Raman Scattering

Electronic, vibrational or rotational transitions may be involved in Raman scattering, but here we consider only rotational Raman scattering.

The polarizability, \( \alpha \), of a molecule determines the degree of scattering of incident radiation, and when the radiation is in the uv or visible region, it is a measure of the degree to which electrons in the molecule can be displaced or distorted relative to the nuclei.

When monochromatic radiation falls upon a molecular sample and is not absorbed by it, the oscillating electric field, \( E \), of the EM radiation induces an electric dipole, \( \mu \), which is related to \( E \) by the polarizability:

\[
\mu = \alpha E
\]

where \( \mu \) and \( E \) are both vector quantities, and the magnitude of the vector \( E \) can be written as:

\[
E = A \sin 2\pi c \bar{v} t
\]

where \( A \) is the amplitude and \( \bar{v} \) is the EMR wavenumber.

The polarizability is not a scalar, but actually an anisotropic property, which means that at equal distances from the centre of the molecule, \( \alpha \) may have different magnitudes when measured in different directions.

Atoms and spherical rotors are isotropically polarizable, meaning that the same distortion is induced regardless of the direction of the applied field.
Anisotropic Polarizability

Non-spherical molecules are **anisotropically polarizable**, meaning that the magnitude of polarization at different positions in the molecule equidistant from the centre are different (**orientation dependent polarizability**).

A surface drawn so that the distance from the origin to a point on the surface is $\alpha^{-1/2}$, where $\alpha$ is the polarizability in that direction, forms an **ellipsoid**. The most common way to mathematically describe such an anisotropic property (including moments of inertia, electrical conductivity in crystals, chemical shielding in NMR and anisotropic stress and strain in solid materials) is using a **second-rank tensor**

$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

where $\alpha_{xx}$, $\alpha_{yy}$ and $\alpha_{zz}$ are the **principal components** along the $x$, $y$ and $z$ axes of the molecule. The tensor is symmetric in the sense that $\alpha_{xz} = \alpha_{zx}$, $\alpha_{yz} = \alpha_{zy}$ and $\alpha_{xy} = \alpha_{yx}$.

So there are six different components of $\alpha$: $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$, $\alpha_{xz}$, $\alpha_{yz}$ and $\alpha_{xy}$, each of which can be assigned to one of the symmetry species of the point group to which the molecule belongs.
The polarizability ellipsoid rotates with the molecule at a frequency of \( \nu_{\text{rot}} \). The polarizability appears to change at \textbf{twice the frequency of rotation} since the ellipsoid is symmetric to a rotation by \( \pi \) about any Cartesian axis.

The variation of \( \alpha \) with rotation is given by:

\[
\alpha = \alpha_{0,r} + \alpha_{1,r} \sin 2\pi c (2\overline{\nu}_{\text{rot}}) t
\]

where \( \alpha_{0,r} \) is the average polarizability and \( \alpha_{1,r} \) is the amplitude of the change of the polarizability during rotation. Using the relations \( \mu = \alpha E \) and \( E = A \sin 2\pi c \overline{\nu} t \), the magnitude of the induced dipole moment is:

\[
\mu = \alpha_{0,r} A \sin 2\pi c \overline{\nu} t - \frac{1}{2} \alpha_{1,r} A \cos 2\pi c (\overline{\nu} + 2\overline{\nu}_{rot}) t \\
\quad + \frac{1}{2} \alpha_{1,r} A \cos 2\pi c (\overline{\nu} - 2\overline{\nu}_{rot}) t
\]

1st term: \textbf{Rayleigh} scattering of unchanged \( \overline{\nu} \)
2nd term: \textbf{anti-Stokes} scattering \((\overline{\nu} + 2\overline{\nu}_{rot})\)
3rd term: \textbf{Stokes} scattering \((\overline{\nu} - 2\overline{\nu}_{rot})\)
Rotational Raman: Linear Molecules

Since the polarizability ellipsoid returns to its initial value after rotating only 180°, the selection rule for rotational Raman spectroscopy of a linear molecule is:

$$\Delta J = 0, \pm 2$$

The $\Delta J = 0$ transitions correspond to Rayleigh scattering and are very intense - however, this scattering is unimportant in considering Raman spectroscopy.

Another selection rule is that the molecule must have anisotropic polarizability (i.e., $\alpha$ not the same in all directions) - just atoms and spherical rotors do not meet this requirement while all other molecules do.

This means that all linear molecules, whether or not they have a centre of inversion, will be Raman active.

The rotating molecule modulates the scattering of the light via rotation of the polarizability ellipsoid.

Molecules initially in the $J = 0$ state encounter intense, monochromatic radiation of frequency $\nu$. If $h\nu$ does not correspond to a difference in energy between $J = 0$ and any other state (rotational, vibrational or electronic), it is not absorbed by the molecule. Rather, it produces an induced dipole $\mu = \alpha E$. 
Origin of Rotational Raman Spectra

The molecule with the induced dipole resulting from EM irradiation is said to be in a **virtual state**, $V_0$, and when scattering occurs the molecule returns to $J = 0$ (Rayleigh) or $J = 2$ (Stokes).

A molecule initially in the $J = 2$ state goes to the virtual state $V_1$ and returns to $J = 2$ (Rayleigh) and $J = 4$ (Stokes) or $J = 0$ (anti-Stokes). The overall transitions are indicated by the solid lines below.

For a symmetric rotor molecule the selection rules for rotational Raman spectroscopy are:

\[ \Delta J = 0, \pm 1, \pm 2; \quad \Delta K = 0 \]

resulting in $R$ and $S$ branches for each value of $K$ (as well as Rayleigh scattering). For asymmetric rotors, $\Delta J = 0, \pm 1, \pm 2$, but since $K$ is not a good quantum number, spectra become quite complicated.

Raman spectroscopy is therefore a **two-photon process**, unlike other techniques discussed so far.
Origin of Rotational Raman Spectra, 2

More overall transitions are shown in the figure below, with overall transitions pointing downwards indicating anti-Stokes lines (positive frequency shift) and those pointing upwards indicating Stokes lines (negative frequency shift).

The intensities along the branches show a maximum because the populations of the initial levels of the transitions quickly rise to a maximum and then fall off. In practice, the anti-Stokes lines are less intense than the Stokes lines, since the former have their origin in an excited rotational state.
Rotational Raman Spectra

Conventionally, $\Delta J = J(\text{upper}) - J(\text{lower})$, so the real selection rule is just $\Delta J = +2$. The magnitude of the Raman displacement from exciting radiation $\bar{v}$ is

$$|\Delta \bar{v}| = F(J + 2) - F(J)$$

where $\Delta \bar{v} = \bar{v} - \bar{v}_L$ and $\bar{v}_L$ is the wavenumber of exciting laser radiation. The term symbol for rotation is the same as before:

$$F(J) = \frac{E_r}{hc} = \frac{h}{8\pi^2 c I} J(J + 1) = BJ(J + 1)$$

so substitution yields

$$|\Delta \bar{v}| = 4B_0 J + 6B_0$$

where the subscript “0” indicates the ground vibrational state. So lines will be evenly spaced by $4B_0$, and the first anti-Stokes and Stokes lines are separated by $12B_0$.

As for rotational spectroscopy, centrifugal distortion may be taken into account, resulting in additional terms:

$$|\Delta \bar{v}| = (4B_0 J - 6D_0) \left( J + \frac{3}{2} \right) - 8D_0 \left( J + \frac{3}{2} \right)^3$$

Series of rotational transitions are referred to as branches:

$\Delta J$ ..., -2, -1, 0, +1, +2, ...

Branch ..., $O$, $P$, $Q$, $R$, $S$, ...

Stokes and anti-Stokes are both $S$ branches, though they are sometimes referred to as $O$ and $S$ branches, respectively.
Rotational Raman Spectrum of $^{15}$N$_2$

The rotational Raman spectrum of $^{15}$N$_2$ is shown below, which was obtained with 476.5 nm radiation from an argon ion laser.

From this spectrum a very accurate value of $B_0$ is obtained: $B_0 = 1.857672 \pm 0.000027$ cm$^{-1}$, from which a bond length of $r_0 = 1.099985 \pm 0.000010$ Å is calculated.

One unusual feature of this spectrum is the intensity alternation of 1:3 when the $J$ value of the transitions that have even:odd - this is due to the nuclear spin of the $^{15}$N$_2$ nuclei (we will discuss this shortly).

Another feature (marked with crosses) are grating ghosts, which are spectral artifacts resulting from dispersal of the radiation from the sample using a grating. Spectral artifacts occur in all forms of spectroscopy and do not correspond to any real features of the spectrum of the molecule (sometimes can severely hamper analysis!).
Nuclear Spin Statistical Weights

The nuclear spin can be included in the total wavefunction for a molecule:

\[ \Psi = \Psi_e \Psi_v \Psi_r \Psi_{ns} \]

We focus upon the symmetry properties of \( \Psi_r \) and \( \Psi_{ns} \) here.

The parity of the rotational state = \((-1)^J\), \(J = 0, 1, 2, \ldots\)
Thus, for even values of \(J\), \(\Psi_r\) is symmetric to exchange, and for odd values of \(J\), \(\Psi_r\) is antisymmetric to exchange.

For a symmetrical \(D_{sh}\) diatomic or linear polyatomic molecule with any number of identical nuclei having the same nuclear spin quantum number, \(I = n + \frac{1}{2}\), where \(n\) is zero or an integer, exchange of any two nuclei results in a change of sign of \(\Psi\) which is said to be antisymmetric to nuclear exchange. The nuclei are said to be fermions (or Fermi particles), obeying Fermi-Dirac statistics.

If \(I = n\), where \(n\) is an integer, \(\Psi\) is symmetric to nuclear exchange and the nuclei are said to be bosons (Bose particles) obeying Bose-Einstein statistics.

If 2 fermions are exchanged: \(\Psi_r \Psi_{ns}\) must be antisymmetric
If 2 bosons are exchanged: \(\Psi_r \Psi_{ns}\) must be symmetric

Consider the molecule \(^1\text{H}_2\), for which the ground state of \(\Psi_e\) and \(\Psi_v\) for any vibrational state are symmetric with respect to nuclear exchange. Since \(I = \frac{1}{2}\), then \(\Psi_r \Psi_{ns}\) must be anti-symmetric w.r.t. nuclear exchange.
Nuclear Spin Statistical Weights, 2

For $I = \frac{1}{2}$, space quantization gives $m_I = +1/2$ or -1/2. The nuclear spin wavefunction is normally written as $\alpha$ or $\beta$ to correspond to these values, respectively. Both $^1$H nuclei, labelled 1 and 2, can have either $\alpha$ or $\beta$ spin wave functions, so there are four possible forms of $\psi_{ns}$:

$$\psi_{ns} = \alpha(1)\alpha(2); \quad \beta(1)\beta(2); \quad \alpha(1)\beta(2); \quad \text{or} \quad \beta(1)\alpha(2)$$

The first two functions are symmetric w.r.t. exchange of labels, but the other functions are neither symmetric nor antisymmetric. So it is necessary to use the linear combinations of the spin wave functions shown below:

$$(s) \quad \psi_{ns} = \begin{cases} 
\alpha(1)\alpha(2) \\
2^{1/2}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] \\
\beta(1)\beta(2)
\end{cases}$$

$$(a) \quad \psi_{ns} = 2^{1/2}[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

So 3 of the spin wave functions are symmetric ($s$) w.r.t. nuclear exchange and 1 is antisymmetric ($a$).

For a homonuclear diatomic molecule, there are $(2I+1)(I+1)$ symmetric and $(2I+1)I$ antisymmetric spin wave functions, so:

$$\frac{\text{Number of (s) functions}}{\text{Number of (a) functions}} = \frac{I + 1}{I}$$
In order for $\psi_r \psi_{ns}$ to be antisymmetric for $^1\text{H}_2$, the antisymmetric $\psi_{ns}$ are associated with even $J$ states and the symmetric $\psi_{ns}$ are associated with the odd $J$ states.

So $^1\text{H}_2$ is regarded as existing in two distinct forms:

(1) \textit{para-hydrogen} with $\psi_{ns}$ antisymmetric and anti-parallel nuclear spins
(2) \textit{ortho-hydrogen} with $\psi_{ns}$ symmetric and parallel nuclear spins

The interchange of two identical fermion nuclei results in a change in the sign of the overall wavefunction. Re-labelling can be though of in two steps: (1) a rotation of the molecule, (2) interchange of the unlike spins (differently coloured nuclei).

If the nuclei have anti-parallel spins, the wavefunction changes sign.

\textit{para}-$^1\text{H}_2$ can only exist in even $J$ states and \textit{ortho}-$^1\text{H}_2$ in odd $J$ states. At temperatures where there are populations up to fairly high values of $J$, there will be roughly 3 times as much \textit{ortho}- as there is \textit{para}-$^1\text{H}_2$. If $J$ is small, there is mostly \textit{para}-$^1\text{H}_2$. All other homonuclear diatomic molecules with $I = \frac{1}{2}$ for each nucleus (e.g., $^{19}\text{F}_2$) also have \textit{ortho} and \textit{para} forms (see the diagram on the next page)
Nuclear Statistical Spin Weights, 4

For $I = 1$ for each nucleus (e.g., $^2\text{H}_2$ and $^{14}\text{N}_2$) the total wavefunction must be symmetric w.r.t. nuclear exchange. There are 9 nuclear spin wave functions, 6 of which are symmetric and 3 of which are anti-symmetric.

This means that molecules like $^2\text{H}_2$ and $^{14}\text{N}_2$ have ortho forms only when $J$ is even and para forms only when $J$ is odd, and there is roughly two times as much ortho as there is para at normal temperatures. At low temperatures, there is an excess of the ortho form.

Nuclear spin statistical weights of rotational states for various diatomic molecules are shown below:

<table>
<thead>
<tr>
<th></th>
<th>$^1\text{H}_2$ or $^{19}\text{F}_2$</th>
<th>$^2\text{H}_2$ or $^{14}\text{N}_2$</th>
<th>$^{16}\text{O}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_r$</td>
<td>$\psi_{ns}$</td>
<td>$o/p$</td>
<td>$ns$ stat wt.</td>
</tr>
<tr>
<td>5</td>
<td>a</td>
<td>s</td>
<td>o</td>
</tr>
<tr>
<td>4</td>
<td>s</td>
<td>a</td>
<td>p</td>
</tr>
<tr>
<td>3</td>
<td>a</td>
<td>s</td>
<td>o</td>
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<tr>
<td>2</td>
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<tr>
<td>1</td>
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<td>o</td>
</tr>
<tr>
<td>0</td>
<td>s</td>
<td>a</td>
<td>p</td>
</tr>
</tbody>
</table>
Nuclear Spin Statistic Weights, 5

The effects of low temperatures on ortho:para ratio is more important for light molecules (e.g., $^1$H$_2$ and $^2$H$_2$) than for heavy molecules (e.g., $^{19}$F$_2$ and $^{14}$N$_2$), since the separation of $J = 0$ and $J = 1$ energy levels is smaller for heavier molecules than for light molecules.

The symmetrical linear polyatomic molecule acetylene, $^1$H - $^{12}$C $\equiv$ $^{12}$C - $^1$H is very similar to $^1$H$_2$, since the nuclear spin of $^{12}$C is $I = 0$. However, since the rotational energy levels are more closely spaced in acetylene, a very low temperature is required to produce the para form predominantly, in comparison to $^1$H$_2$.

For $^{16}$O$_2$, $I = 0$, and there are no antisymmetric nuclear spin wave functions. Since each $^{16}$O nucleus is a boson, the total wavefunction must be symmetric to nuclear exchange. Since this molecule has two unpaired electrons in its ground state (triplet state), $\psi_e$ is antisymmetric, so $\psi_{ns}$ is symmetric w.r.t. nuclear exchange.

So $^{16}$O$_2$ only has levels with odd values of $J$. In the rotational Raman spectrum, alternate lines with even values of $N''$ are missing. (For molecules with unpaired electrons, the quantum number $N$, rather than $J$, distinguishes the rotational energy levels).
Structure Determination

Measurement of the rotational constants of the zero point vibrational state, $B_0$, and one or more vibrational states, $B_v$, may allow for the determination of the rotational constant of the hypothetical equilibrium state, $B_e$.

$$B_v = B_e - \alpha(v + 1/2)$$

These rotational constants can be used to determine $r_0$ and $r_e$. $r_e$ will be independent of the isotopic species whereas $r_0$ will not, so $r_e$ is typically used in discussing bond lengths of the highest accuracies.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$r_0$(Å)</th>
<th>$r_e$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{14}\text{N}_2$</td>
<td>1.100 105 ± 0.000 010</td>
<td>1.097 651 ± 0.000 030</td>
</tr>
<tr>
<td>$^{15}\text{N}_2$</td>
<td>1.099 985 ± 0.000 010</td>
<td>1.097 614 ± 0.000 030</td>
</tr>
</tbody>
</table>

Note that $r_e$ does not change with isotopic substitution since it refers to bond length at the minimum of the potential energy curve (which does not change for either harmonic or anharmonic oscillators).

On the other hand, vibrational energy levels within the potential energy curve change, thereby resulting in changes in $r_0$ with isotopic substitution.

For non-linear molecules, determination of rotational constants becomes increasingly difficult - substitution structures and isotropic substitution are used for larger molecules (e.g., aniline, formaldehyde, etc.).
Key Concepts

1. EM radiation that is not absorbed by the molecule is scattered. Most of the scattered radiation is unchanged in wavelength (Rayleigh scattering) and a small percentage of the light is increased and decreased in wavelength (referred to as Stokes and anti-Stokes Raman scattering, respectively).

2. The polarizability, $\alpha$, of the molecule determines the degree of scattering of the incident radiation. Polarizability is an anisotropic property, which means that $\alpha$ may have different magnitudes when measured in different directions. The polarizability ellipsoid is described by a second-rank tensor.

3. Due to the symmetry of the polarizability ellipsoid, when a molecule rotates the frequency of rotation of the ellipsoid appears to proceed at twice the frequency of rotation.

4. The selection rule for rotational Raman spectroscopy of a linear molecule is $\Delta J = 0, \pm 2$. Only atoms and spherical rotors are Raman inactive, all other molecules are Raman active.

5. The Rayleigh line is in the centre and intense, the weaker Stokes and anti-Stokes lines occur at lower and higher frequencies, respectively.

6. Nuclei which are fermions or bosons result in different peak intensities in rotational Raman spectra. Nuclear spin statistics change with temperature and may alter the appearance of the spectrum.