

Chapter 11. Raman Spectroscopy

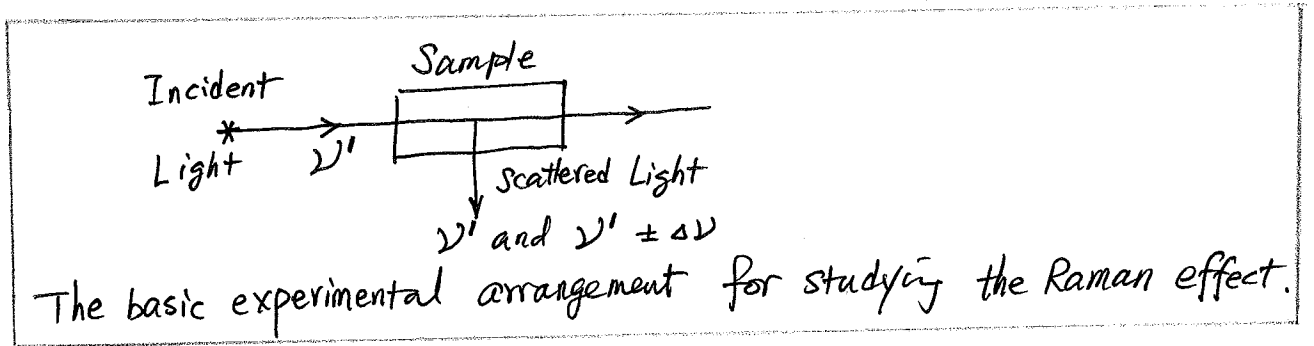
We have seen how it is possible to gain structural information on diatomic molecules from their rotational and rotational-vibrational spectra. In each case, energy is exchanged between the EM radiation and the molecule through the interaction between the oscillating dipole moment and the oscillating electric field in the radiation. These spectra are observed via real electric dipole transitions.

In consequence, there is a requirement, at least for diatomic molecules, that the molecule possess a permanent electric dipole moment, i.e., it must be heteronuclear. Information on the rotational and vibrational levels of a homonuclear diatomic molecule cannot be obtained in this way. Fortunately, there is an alternative way that does not suffer from this restriction. It is called Raman Spectroscopy.

Raman spectroscopy is not based on absorption/emission process, i.e., not real transitions, but rather on a light scattering effect — virtual transition, i.e., two-photon process. It is named after the Indian physicist C. V. Raman, who was the first to observe this phenomenon in 1928 following its theoretical prediction by A. Smekal.

§11.1. Classical Theory of Light Scattering and Raman Effect III 52.

When a parallel beam of light goes through a gas, a liquid, or a transparent solid body, a small fraction of the light is scattered in all directions. The light beam can therefore be seen



from the side (Tyndall effect). The intensity of the scattered light is inversely proportional to the fourth power of the wavelength: blue light is much more strongly scattered than red (which explains the fact that the sky appears blue).

If the incident light has a discrete line spectrum (like a laser) and the spectrum of the scattered light is investigated, it is found that the scattered light contains exactly the same frequencies as the light producing it. This scattering is called Rayleigh scattering. However, if, in taking the spectrogram of the scattered light, the lines that are identical with those of the light source are strongly overexposed, some weak additional lines are found which do not appear in the spectrum of the light source. This phenomenon predicted from theory by Smekal was first discovered by Raman and his collaborators and is now called

the Raman effect. (See the figure below)

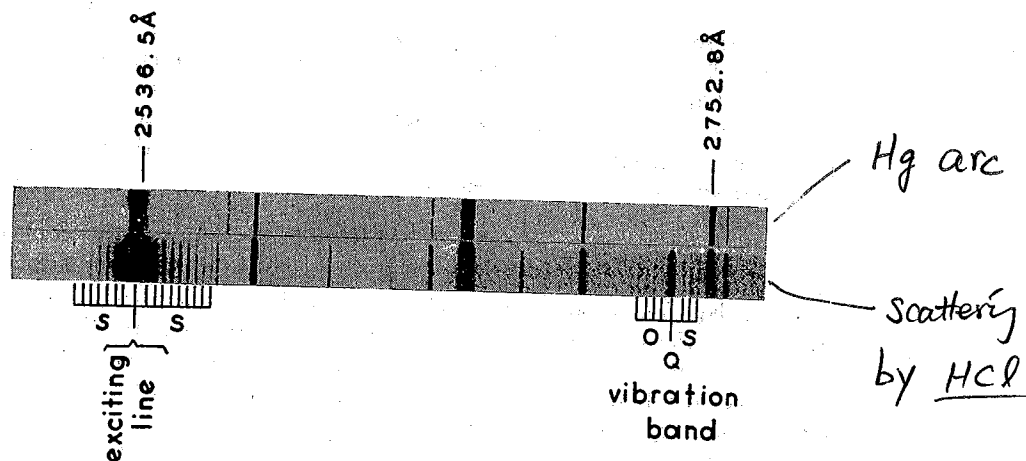


Fig. 36. Raman Spectrum of HCl [after Andrychuk (752a)].* Above is the spectrum of the Hg arc, below the Hg spectrum scattered by HCl gas (5 atm.). The exciting line of the Raman spectrum is the Hg line 2536.5 Å. With lower resolution and less exposure time only the Raman line at 2737 Å (marked Q) corresponding to a shift of 2886 cm^{-1} appears. The spectrogram shows in addition Raman lines of small displacement on both sides of the exciting line (rotational Raman spectrum; see p. 88) and, very weakly, a fine structure accompanying the Raman line 2737 Å (rotation-vibration band; see p. 114).

A comparison of the wave numbers of these additional lines with those of the most intense lines of the incident light (or the Rayleigh lines) shows that each one of the original lines is accompanied, in the Raman Spectrum, by one or more weak lines such that the displacements (in cm^{-1}) of the Raman lines from the exciting lines are independent of the frequencies of the latter. In other words, if another light source with a different spectrum is used, other Raman lines are obtained for the same scattering substance. However, the displacements from the exciting lines are the same. For different scattering substances, the displacements have different magnitudes. Thus, the Raman displacements are characteristic of the scattering substance under consideration.

TABLE 11. LARGE RAMAN DISPLACEMENTS AND INFRARED FREQUENCIES OF DIATOMIC GASES

| Gas | Raman Displacement $\Delta\nu$ (cm ⁻¹) | Infrared Frequency ν_0 (cm ⁻¹) | References |
|-----------------|--|--|-------------|
| HCl | 2886.0 | 2885.9 | (720) |
| HBr | 2558 | 2559.3 | (611) (563) |
| HI | 2233 | 2230.1 | (611) (531) |
| NO | 1877 | 1875.9 | (101) |
| CO | 2145 | 2143.2 | (68) |
| H ₂ | 4160.2* | | (662) |
| N ₂ | 2330.7 | | (578) |
| O ₂ | 1554.7 | | (578) |
| F ₂ | 892 | | (752b) |
| Cl ₂ | 556 | | (800) |

* Refers to the transition $J = 0 \rightarrow J = 0$ (see page 114).

} Homonuclear diatomic molecules do not have IR transitions

TABLE 12. SMALL RAMAN DISPLACEMENTS FOR HCl

[After Wood and Dieke (720)]

| m | $\Delta\nu_{\text{obs.}}$ | $\Delta(\Delta\nu)$ | $\Delta\nu_{\text{calc.}}$ |
|-----|---------------------------|---------------------|----------------------------|
| 2 | +143.8 | | 145.7 |
| 3 | +183.3 | 39.5 | 187.4 |
| 4 | +232.2 | 38.9 | 229.0 |
| 1 | -101.1 | | 104.1 |
| 2 | -142.7 | 41.6 | 145.7 |
| 3 | -187.5 | 44.8 | 187.4 |
| 4 | -229.4 | 41.9 | 229.0 |
| 5 | -271.0 | 41.6 | 270.7 |
| 6 | -312.9 | 41.9 | 312.3 |
| 7 | -353.0 | 40.0 | 353.9 |

There are two main types of Raman displacements — one is the large Raman displacements corresponding to the vibrational (infrared) frequencies of molecules (Table 11) and another is the small Raman displacements corresponding to the rotational frequencies (far IR or microwave) of molecules (Table 12).

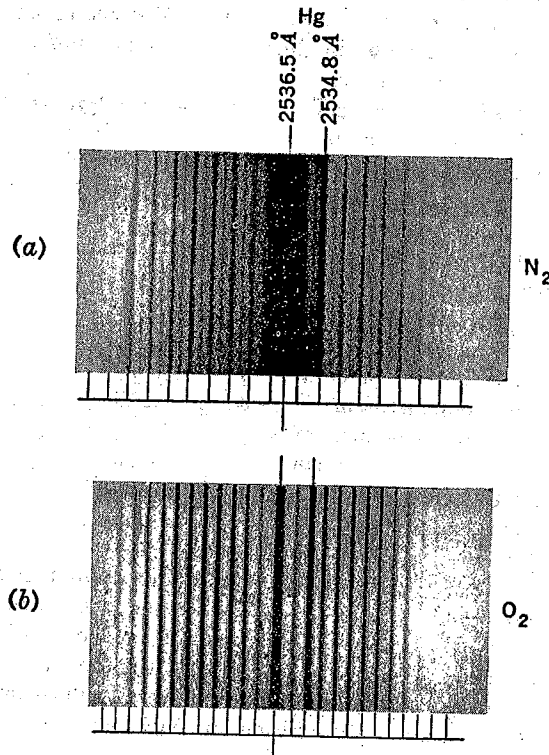


FIG. 37. Raman Spectrum of (a) N₂ and (b) O₂: Small Raman Shifts, Excited by the Hg Line 2536.5 Å [after Rasetti (579)].* The exciting line (longer leading line) is not so strongly overexposed in (b), since it has been almost completely absorbed by Hg vapor before falling on the plate. The relatively strong line to the right of the exciting line, which is superimposed on a Raman line, is the Hg line 2534.8 Å. The dispersion of the enlarged spectrogram is about 0.37 Å/mm.

Next we describe how to explain Raman effect in classical and quantum theories.

If an atom or molecule is brought into an electric field \vec{E} , an electric dipole moment \vec{P} is induced in the system. The center of the positive charge is moved a small distance in one direction, and that of the negative charges is moved in the opposite direction. The magnitude of the resulting dipole moment is proportional to that of the field, i.e.,

$$|\vec{P}| = \alpha |\vec{E}| \quad (1)$$

where α is called the polarizability.

Except in the case of spherical symmetry, the magnitude of the induced dipole moment depends on the orientation of the system to the field. For a diatomic molecule, for example, a field lying along the internuclear axis obviously induces a dipole moment of different magnitude from that induced by a field at right angles to the axis. In general, the direction of \vec{P} does not coincide with the direction of \vec{E} . However, for reasons of symmetry, these two directions do coincide if \vec{E} has the direction of one of the axes of symmetry of the system.

Choosing these axes as coordinate axes, we have

$$P_x = \alpha_{xx} E_x, \quad P_y = \alpha_{yy} E_y, \quad P_z = \alpha_{zz} E_z \quad (2)$$

where α_{xx} , α_{yy} , α_{zz} are the components of the polarizability which in the most general case are all different. However, for a diatomic molecule, taking the z-axis in the internuclear axis,

it is clear that $\alpha_{xx} = \alpha_{yy}$, since the x direction is in no way distinguished from the y direction. In any case, the magnitude of \vec{p} is proportional to the magnitude of \vec{E} , given by Eq. (1).

If a light with frequency ν' falls on an atom or molecule, there is a varying electric field:

$$\vec{E} = \vec{E}_0 \sin 2\pi\nu't \quad (3)$$

where t is the time and E_0 is the amplitude of the oscillating electric field. This field induces a varying dipole moment, which in turn causes an emission of light of the same frequency as the incident light. Thus arises the so-called Rayleigh scattering, which is responsible for the phenomena of refraction and of the Tyndall effect. For visible and UV incident light, essentially only the electrons move under the influence of the alternating electric field and produce the dipole moment thus emission of the photons with the same frequency as the incident light, since the nuclei cannot follow the rapid oscillations. Both atoms and molecules (free, in gas phase) have Rayleigh scattering.

If the internuclear distance changes, obviously the polarizability must also change, even if slightly. Furthermore, according to the above discussion, the polarizability depends on the orientation of the molecule to the field. Thus, a change in polarizability, i.e., a change in the amplitude of the induced dipole moment,

is associated with both the vibration and the rotation of the molecule. For the vibration, to the first good approximation,

$$\alpha = \alpha_{0v} + \alpha_{1v} \sin 2\pi \nu_{\text{vib}} t \quad (4)$$

where α_{0v} is the polarizability in the equilibrium position and α_{1v} is the amplitude of the change in polarizability during the vibration ($\alpha_{1v} \ll \alpha_{0v}$). Correspondingly, for the rotation,

$$\alpha = \alpha_{0r} + \alpha_{1r} \sin 2\pi \cdot 2\nu_{\text{rot}} t \quad (5)$$

where α_{0r} is an average polarizability and α_{1r} is the amplitude of the change in polarizability for rotation about the rotational axis considered. The frequency with which the polarizability changes during the rotation is twice the rotational frequency, since the polarizability is the same for opposite directions of the applied field.

Substituting Eqs. (3) and (4) into (1), we obtain for the induced dipole moment in the case of a vibrating molecule:

$$\vec{P}_v = \alpha_{0v} \vec{E}_0 \sin 2\pi \nu' t + \alpha_{1v} \vec{E}_0 \sin 2\pi \nu' t \sin 2\pi \nu_{\text{vib}} t \quad (6)$$

Similarly substitute Eq. (3) and (5) into (1), we obtain for a rotating molecule:

$$\vec{P}_r = \alpha_{0r} \vec{E}_0 \sin 2\pi \nu' t + \alpha_{1r} \vec{E}_0 \sin 2\pi \nu' t \sin 2\pi 2\nu_{\text{rot}} t \quad (7)$$

From trigonometrical formulae, we obtain

$$\vec{P}_v = \alpha_{0v} \vec{E}_0 \sin 2\pi \nu' t + \frac{1}{2} \alpha_{1v} E_0 [\cos 2\pi (\nu' - \nu_{\text{vib}}) t - \cos 2\pi (\nu' + \nu_{\text{vib}}) t] \quad (8)$$

$$\vec{P}_r = \alpha_{or} \vec{E}_0 \sin 2\pi\nu't + \frac{1}{2} \alpha_{ir} \vec{E}_0 [\cos 2\pi(\nu' - 2\nu_{rot})t - \cos 2\pi(\nu' + 2\nu_{rot})t]. \quad (9)$$

Thus we see that on account of the small alteration of α during the vibration or rotation of the molecule, the induced dipole moment changes not only with the frequency ν' of the incident light, but also with the frequencies $\nu' - \nu_{vib}$ and $\nu' + \nu_{vib}$, or with the frequencies $\nu' - 2\nu_{rot}$ and $\nu' + 2\nu_{rot}$.

So, according to classical theory, in the spectrum of the scattered light, we have to expect displaced lines on both sides of the undisplaced line — in the case of an oscillator, at a distance ν_{vib} , and in the case of a rotator, at a distance $2\nu_{rot}$.

Thus, qualitatively, even classical considerations lead to the Raman effect — displaced frequencies in the spectrum of the scattered light. However, quantitatively there is no agreement. Empirically, there is no continuous Raman spectrum present for diatomic molecules (classical theory would predict continuous spectrum of Raman for a rotator), and in general only the longer wavelength components (Stokes) are found for the larger displacements (vibrational effect) but not the correspondingly short wavelength components. The quantitative agreements can only be achieved by quantum theory.

§11.2. Quantum Theory of the Raman Effect.

The quantum theoretical explanation of the Raman effect is as follows: When the incident light quantum $h\nu'$ collides with a molecule, it can either be scattered elastically, in which case its energy (and therefore its frequency), remains unaltered (Rayleigh scattering), or it can be scattered inelastically, in which case it either gives up part of its energy to the scattering system or takes energy from it. Naturally, the light quantum can give to or take from the system only amounts of energy that are equal to the energy differences between the stationary states of the system. Let $\Delta E = E' - E''$ be such an energy difference. Then

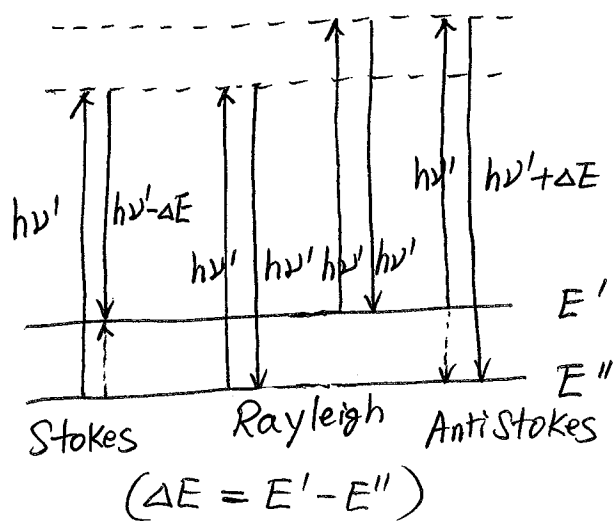
(1) If the system is initially in the lower state E'' , it may be brought to the upper state E' by the scattering of a light quantum, the energy ΔE being taken from the light quantum. Thus, after the scattering, the energy of the light quantum is only $h\nu' - \Delta E$, i.e., lower frequency (longer wavelength).

(2) If, on the other hand, the system was initially in the state E' and is transferred to E'' by scattering, the energy of the light quantum after the scattering is equal to $h\nu' + \Delta E$, i.e., higher frequency (shorter wavelength).

The frequency of the scattered light quantum is equal to the energy divided by h , i.e., the frequencies $\nu' - (\Delta E/h)$ and $\nu' + (\Delta E/h)$ appear in the scattered light as well as the undisplaced frequency ν' , i.e., we have the Raman effect.

In most cases, ΔE may take a number of different values. If frequencies and energies are measured in wavenumber units, it is clear that the Raman shifts give directly the energy differences of the system in cm^{-1} .

The Raman lines displaced toward longer wavelengths are called Stokes lines, and those displaced toward shorter wavelengths are called anti-Stokes lines.



The relationships for light scattering are shown in an energy level diagram.

The levels indicated by broken lines do not correspond to any possible energy states of the system but only give

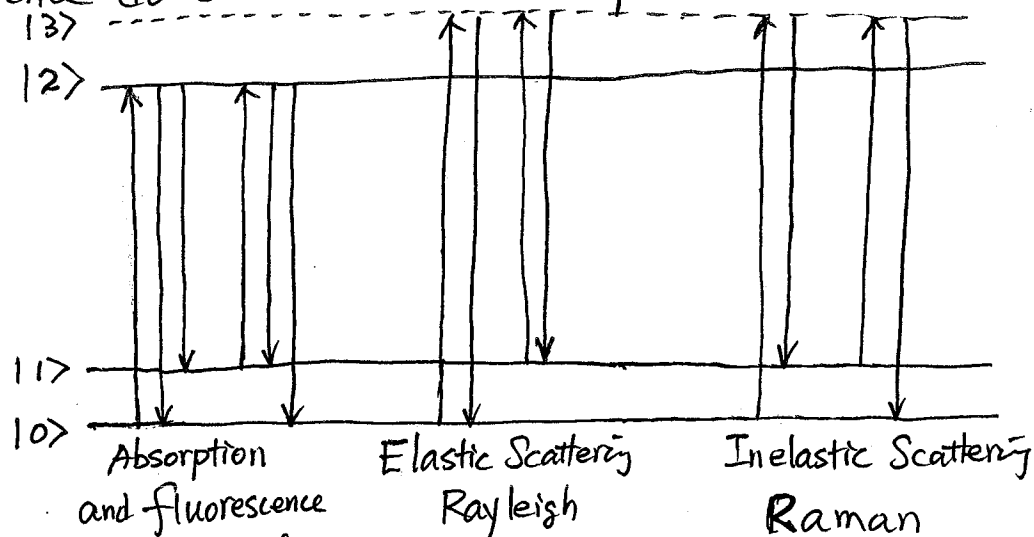
the energy of the light quantum above the initial states.

In the view of Quantum theory of light, the scattering process involves the destruction (annihilation) of a photon of energy $h\nu_i$ from the incident beam and the creation of

a photon of energy $h\nu_s$ in the scattered beam. The scattering is a two-photon process, as two photons are involved simultaneously and we cannot divide the annihilation of photon $h\nu_i$ from the creation of photon $h\nu_s$ into two separate steps. The annihilation and creation of photons happen at the same time!

This is very different from resonance fluorescence process.

Resonance fluorescence is a single-photon process with two steps: the incident light quantum is completely absorbed and the system (an atom or a molecule) is transferred to an excited state. After a certain time (effective lifetime), the system decays to one of various lower states by emitting a photon whose frequency can be the same as the incident photon if the system returns to its initial state, or be different than the incident photon if the system goes to a different state. Each step is a single-photon process, and the resonance fluorescence does contain two steps.



$|0\rangle$, $|1\rangle$ and $|2\rangle$ are real states, while $|3\rangle$ is virtual state.

§11.3. Raman Scattering: Selection Rules.

(1) Rotational selection rules for Raman transitions

For a molecule to show a rotational Raman spectrum (where the scattering excites or deactivates rotational motion), the polarizability α must depend on its orientation. Thus, any rotating diatomic molecule is Raman active because it has a different polarizability parallel and perpendicular to the bond. This is simply a result of its cylindrical symmetry.

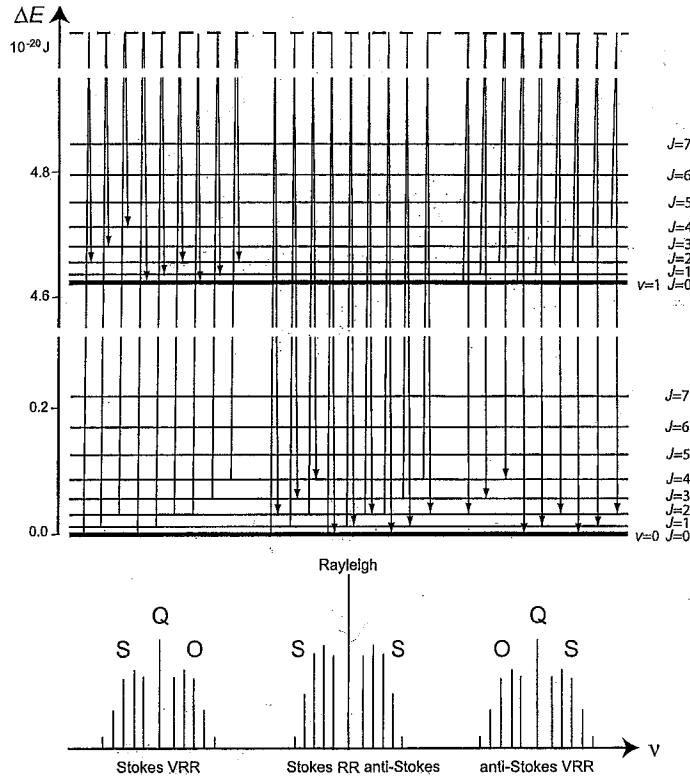
On the other hand, any spherically symmetric molecule, such as CH_4 , is not Raman active because its polarizability is independent of orientation. The oscillating electric field in the light wave cannot couple differently with the molecule, so only Rayleigh scattering is observed.

Considering the fact that the Raman transition is a two-photon process and involves two successive electric dipole transitions (Each of which obeys $\Delta J = \pm 1$ and parity $+\leftrightarrow -$) for a molecule in a non-degenerate, closed-shell state, photon 1 deposits the molecule in an intermediate state with $J' = J \pm 1$ and opposite parity, and then photon 2 picks up from there and takes the molecule to the final state with $J'' = J, J \pm 2$ and the same parity as the original state.

Therefore, the overall rotational selection rule for Raman Spectroscopy (in rotational consideration) is

$$\left\{ \begin{array}{l} \Delta J = 0, \pm 2 \\ \text{Parity } + \leftrightarrow + \text{ and } - \leftrightarrow - \end{array} \right.$$

(10)



Example shows selection rules for both rotational Raman and Vibration-rotational Raman transitions.

RR

VRR

Fig. 9.1. Vibration-rotation energy levels of the N₂ molecule, Raman transitions, and resulting spectrum.

(2) Vibrational selection Rules for Raman Transitions:

The overall selection rules for Vibration-Rotational Raman spectrum are

$$\left\{ \begin{array}{l} \Delta v = \pm 1, \pm 2, \pm 3, \dots \\ \Delta J = 0, \pm 2 \\ \text{parity unchanged } (+ \leftrightarrow + \text{ and } - \leftrightarrow -) \end{array} \right.$$

However, $\Delta v = \pm 1$ is the strongest band.