

RAMAN SPECTROSCOPY

Topics :- [Spectroscopy]

1. Classical theories of Raman effect.
2. Quantum theories of Raman effect
3. Pure rotation Raman Spectra
4. Vibrational - rotation Raman Spectra
5. Mutual Exclusion principle
6. Resonance Raman Spectroscopy
7. Coherent anti Stokes Raman Spectroscopy [CARS]
8. Instrumentation [Raman Spectrograph]
9. Application of Raman effect in molecular Structure.
10. Raman activity of molecular Vibration.
11. Structure of CO_2 , N_2O , SO_2 , NO_3 , ClF_3
12. Application of Raman effect in molecular Structure.
13. Advantage of Raman Spectra over IR Spectra.
14. Limitation of Raman Spectra over IR Spectra.

Raman effect :- Raman effect may be defined as a phenomenon due to which scattering of light has a slightly different frequency from that of incident light and there occurs a change in atomic oscillation within the molecule. Raman effect helps in the elucidation of molecular structure, for locating functional group or chemical bonds in the molecules. The origin of Raman effect can be explained by classical and quantum mechanical concepts.

★ Quantum Mechanical theory of Raman effect :-

1. A quantum of radiation $h\nu_{\text{ex}}$ of incident light collide with the molecule. If it is scattered without any energy loss, the scattered light will have the same frequency as the incident light. The phenomenon is called Rayleigh Scattering.
2. If the incident radiation transfer part of its energy to one of the vibrational or rotational energy states of the molecule in the form of quanta $h\nu_m$ then the scattered light will have slightly lower frequency i.e. $\nu_{\text{ex}} - \nu_m$.
3. It may also happen that the molecule is in excited vibrational or rotational state and scattered light may take up some of the excited energy in the form of quanta $h\nu_m$. Hence, the frequency of the emitted radiation will be higher than the incident beam $\nu_{\text{ex}} + \nu_m$.

4. Thus three Raman lines are observed in the spectrum of scattered light; one line at the frequency of incident light ν_{ex} , corresponding to the Rayleigh Scattering and two lines at different frequencies than the incident light. One of these two lines will be at lower frequency ($\nu_{ex} - \nu_m$) than the incident light. This line at lower frequency is referred to as Stokes line in honour of G.G. Stokes. Other line will be at higher frequency ($\nu_{ex} + \nu_m$) than the incident light, it is called Anti-Stokes line.

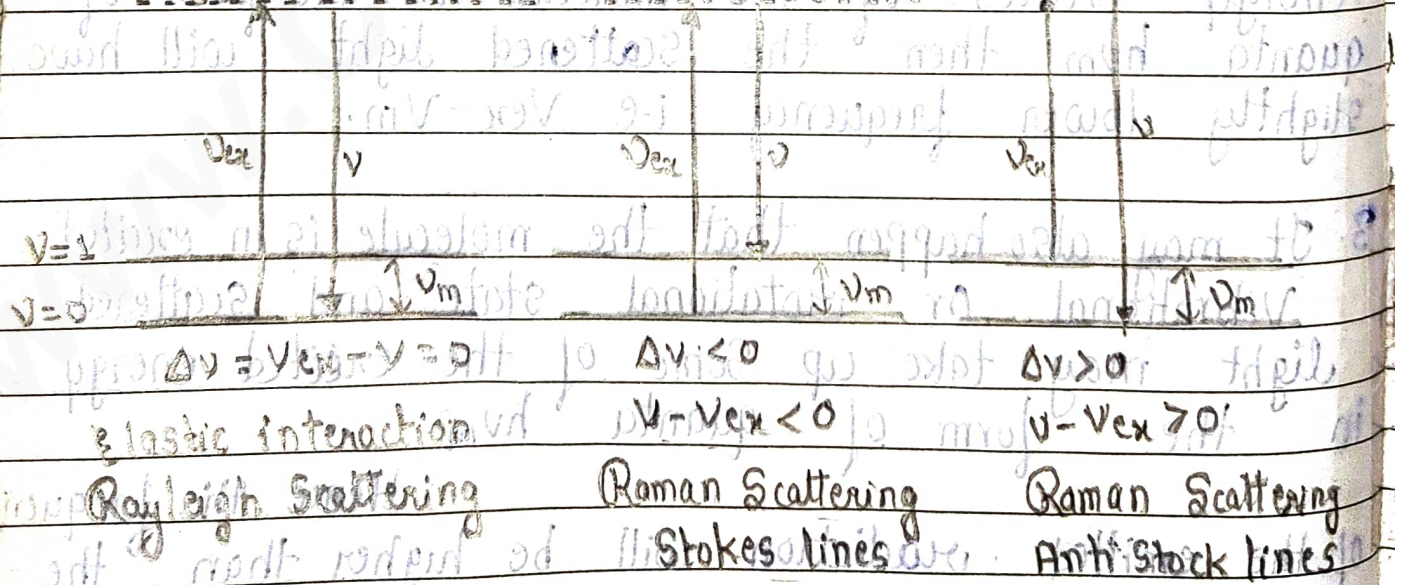
frequency of light undergoing Raman effect is $\nu = \nu_{ex} \pm \nu_m$. Hence the scattered radiation may be classified as:

- (i) $\nu = \nu_{ex}$ ($\Delta\nu = 0$) Rayleigh Scattering
- (ii) $\nu = \nu_{ex} - \nu_m$ ($\Delta\nu < 0$) Stokes lines
- (iii) $\nu = \nu_{ex} + \nu_m$ ($\Delta\nu > 0$) anti-Stokes lines

The latter two are referred to as Raman Scattering.

Lowest excited electronic level

Energy level due to molecule-photon interaction



Quantum mechanical concept of Raman and Rayleigh Scattering

The intensity of Stokes lines is always greater than the antiStokes lines while that of Rayleigh lines is much stronger than that of Stokes lines.

5. Application of the Boltzmann distribution law shows that the ratio of intensities for the Stokes and the antiStokes Raman band is given by :-

$$I_{\text{anti-stokes}} / I_{\text{Stokes}} = \left(\frac{\nu_0 + \Delta\nu}{\nu_0 - \Delta\nu} \right) \exp\left(\frac{-h\Delta\nu}{kT}\right)$$

where $\Delta\nu$ is the magnitude of the Raman shift.

★ Vibrational - Rotational Raman Spectra :-

In gaseous diatomic molecule each vibrational transition consists of a series of closely spaced rotational vibrational lines. When the rotational selection rules are added on to the vibrational selection rule, that is $\Delta\nu = \pm 1$ we get three rotational branches (O, Q, S) of the vibrational Raman spectrum by analogy with P, Q and R branches of the infrared vibration rotation spectrum as follows.

$$\begin{aligned} \Delta J &= +2 && \text{S branch line} \\ \Delta J &= 0 && \text{Q branch line} \\ \Delta J &= -2 && \text{O branch line.} \end{aligned}$$

The energy for $\nu = 0$ to $\nu = 1$ transition.

$$E_{\nu, j} = \left(\nu + \frac{1}{2} \right) h\nu_e + BhcJ(J+1)$$

$$\text{for } \nu = 1 = E_{1R} = \frac{3}{2} h\nu_e + BhcJ(J+1)$$

$$\nu = 0 = E_{0R} = \frac{1}{2} h\nu_e + BhcJ(J+1)$$

If ν_{ex} is the frequency of exciting light used to study the Raman effect for the Stokes line $\Delta\nu = +1$

for Stokes line, S branch = $\Delta J = +2, J \rightarrow J+2, J=0, 1, 2, \dots$
 $\bar{\nu}^S = \bar{\nu}_{\text{ex}} - (\bar{\nu}_e + 6B)$

for Q branch $\Delta J = 0, J \rightarrow J$
 $\bar{\nu}^S = \bar{\nu}_{\text{ex}} - \bar{\nu}_e$

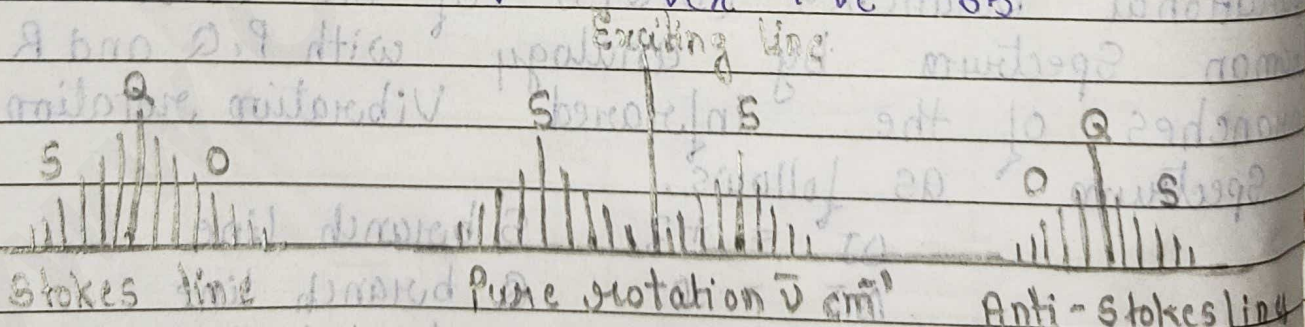
for O branch $\Delta J = -2, J \rightarrow J-2, J=2, 3, 4, \dots$
 $\bar{\nu}^S = \bar{\nu}_{\text{ex}} - (\bar{\nu}_e - 6B)$

Correspondingly, for anti-Stokes line $\Delta\nu = -1$

for S branch $\Delta J = 2, J \rightarrow J+2, J=0, 1, 2, \dots$
 $\bar{\nu}^A = \bar{\nu}_{\text{ex}} + \bar{\nu}_e + 6B$

for Q branch $\Delta J = 0, J \rightarrow J$
 $\bar{\nu}^A = \bar{\nu}_{\text{ex}} + \bar{\nu}_e$

for O branch $\Delta J = -2, J \rightarrow J-2, J=2, 3, 4, \dots$
 $\bar{\nu}^A = \bar{\nu}_{\text{ex}} + \bar{\nu}_e - 6B$



Schematic diagram of the vibration-rotation Raman spectrum of a gaseous diatomic molecule.

Since the rotational constant B does not differ greatly for the two vibrational states all the Q branch lines are super-imposed giving a single line at the band centre and it is much intense than the S & O branch

★ classical theory of Raman effect :- The classical or polarizability theory was developed by G. Placzek in 1934. Raman effect may involve absorption or re-emission of light but is actually a scattering phenomenon. Interaction of light in this case depends upon polarizability of the molecule. The stretching vibration of a homonuclear diatomic molecule which do not have a permanent dipole deforms the electronic charge cloud. This alters the polarizability of the molecule and so the Raman effect is observed.

Mathematical Explanation :- In a diatomic molecule, the permanent dipole moment arise from an existing separation between the centre of positive and negative charges, while polarizability measures the induced dipole moment by the action of an electric field. It is known from electrostatics that the electric field E associated with electromagnetic radiation induces a dipole moment μ in the molecule which is given by

$$\mu = \alpha E \quad \text{--- (1)}$$

$$E = E_0 \sin 2\pi \nu t \quad \text{--- (2)}$$

$$\mu = \alpha E_0 \sin 2\pi \nu t \quad \text{--- (3)}$$

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right) q \quad \text{--- (4)}$$

$$q = q_0 \sin 2\pi \nu_m t \quad \text{--- (5)}$$

From equa. (4) and (5) we have :-

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial q}\right) q_0 \sin 2\pi \nu_m t \quad \text{(6)}$$

Substituting the value of α in eq. (3) we get

$$\mu = \alpha_0 E_0 \sin 2\pi \nu t + \left(\frac{\partial \alpha}{\partial q}\right) q_0 E_0 \sin 2\pi \nu t \sin 2\pi \nu_m t$$

Making use of trigonometric relation $\sin x \sin y = \frac{1}{2} [\cos(x-y) - \cos(x+y)]$ (6)

$$\frac{1}{2} [\cos(x-y) - \cos(x+y)]$$

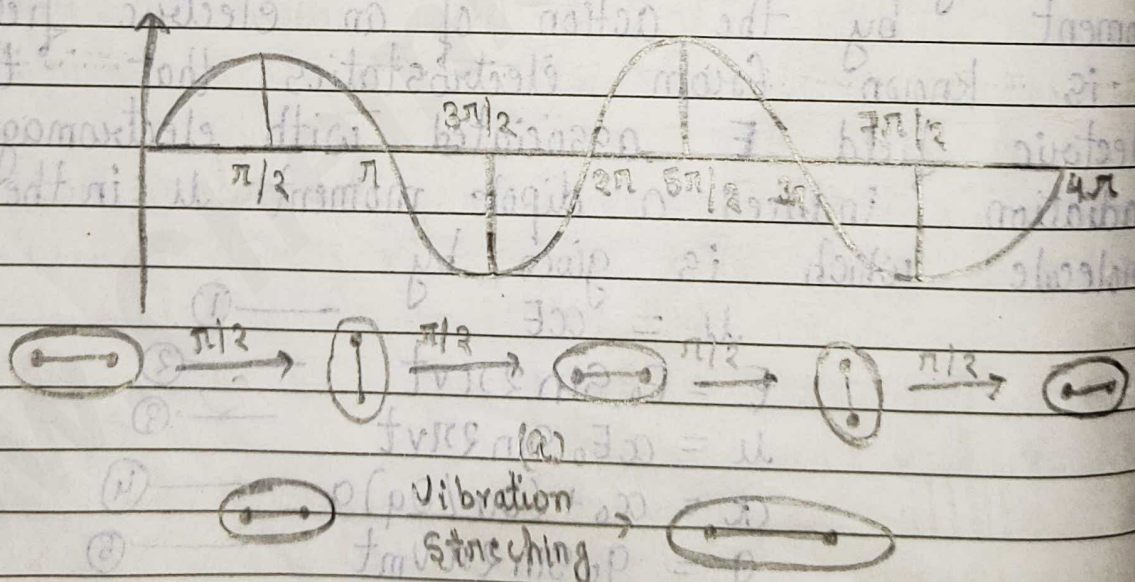
Equation (6) is transformed into :-

$$\mu = \alpha_0 E_0 \sin 2\pi \nu t + \frac{1}{2} \left(\frac{\partial \alpha}{\partial q}\right) q_0 E_0 \times [\cos 2\pi(\nu - \nu_m)t - \cos 2\pi(\nu + \nu_m)t] \quad (7)$$

Thus the oscillating dipole has three distinct frequency components.

(1) the exciting frequency ν with amplitude $\alpha_0 E_0$

(2) $\nu - \nu_m$ and (3) $\nu + \nu_m$ with very small amplitude $\frac{1}{2} \left(\frac{\partial \alpha}{\partial q}\right) q_0 E_0$.



Change in polarizability^(b) of H_2 molecule during
(a) Rotation and (b) Vibration along bond axis

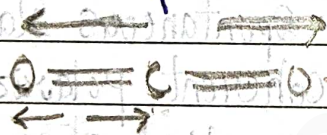
Thus, classical E.M. theory predicts that a beam of E.M. radiation induces an alternating dipole moment in the molecular system or polarizes the molecules.

*** Rule of Mutual Exclusion :-** The mutual exclusion rule states that if a molecule has a centre of symmetry, then only those vibrations which are antisymmetric with respect to the centre of symmetry can be Raman infrared active and only those vibrations which are symmetric with respect to the centre of symmetry can be Raman active.

The rule also states that if a molecule has a centre of symmetry, then Raman active vibrations are infrared inactive and vice-versa. If there is no centre of symmetry then some (but not all) vibrations may be both Raman and infrared active.

Distinction Between Raman & Infrared Activity :-

Consider CO_2 molecule with a centre of symmetry.
 Vibrations of CO_2 are illustrated below :-



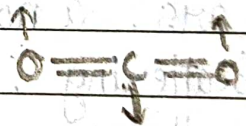
Symmetric stretching

(a) Raman active



Asymmetric stretching

(b) IR active (PR)



Degenerate bending vib.

(c) IR active (PR)

★ Application of Resonance Raman Spectroscopy (RRS):-

1. RRS offers an accurate method for the determination of anharmonicity constants of resonance enhanced vibrational modes.
2. RRS is well suited for the study of free radicals and transient species.
3. RRS is not affected by line broadening and other interferences which limit the applicability of electron spin resonance spectroscopy.
4. RRS is highly specific to the absorbing species.
5. RRS is used for studying biostuctural problems and complex biological materials.

★ Coherent Anti-Stokes Raman Scattering (CARS)

CARS, a non-linear analogue of spontaneous Raman scattering, arises due to the coherent polarizability of the molecule. This technique was first observed by Maker and Terhune in 1965.

① When two laser beams of sufficiently high intensity and of frequency ν_0 and ν_t coincide in space in a molecular medium, new frequencies of low intensity are generated of the following type $\nu_0 + \nu_0 - \nu_t$.

② If the ~~exc~~ frequency ν_t is varied such that $\nu_0 - \nu_t = \nu_m$, then the scattered radiation occurs at $\nu_0 + \nu_m = \nu_a$.

③ The radiation frequency ν_a is anti-Stokes Raman radiation relative to ν_0 . It is very intense, directional and coherent. It is known as Coherent anti-Stokes Raman Scattering or CARS.

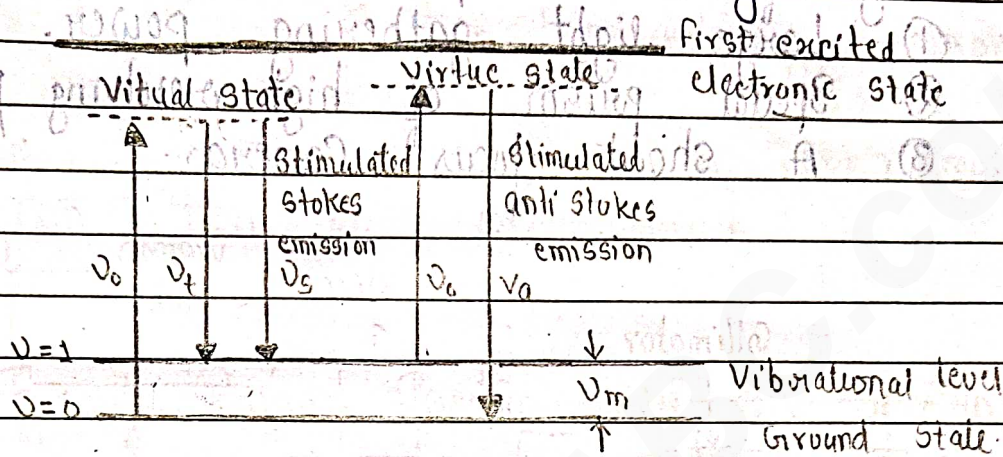


Diagram of CARS and CSRS processes.

Advantages of CARS :- CARS signals are stronger than normal Raman lines by 8 to 10 orders of magnitude. Thus detection problem is much improved in CARS technique. CARS signals can be easily visualised compared to fluorescence.

Limitations of CARS :- CARS requires complicated set up with difficult adjustment and costly equipment. Spectral evaluation is non-trivial.

Applications of CARS :- # The CARS is an important tool for molecular structure determinations.

CARS has been used for the study of rotational spectra of gases.

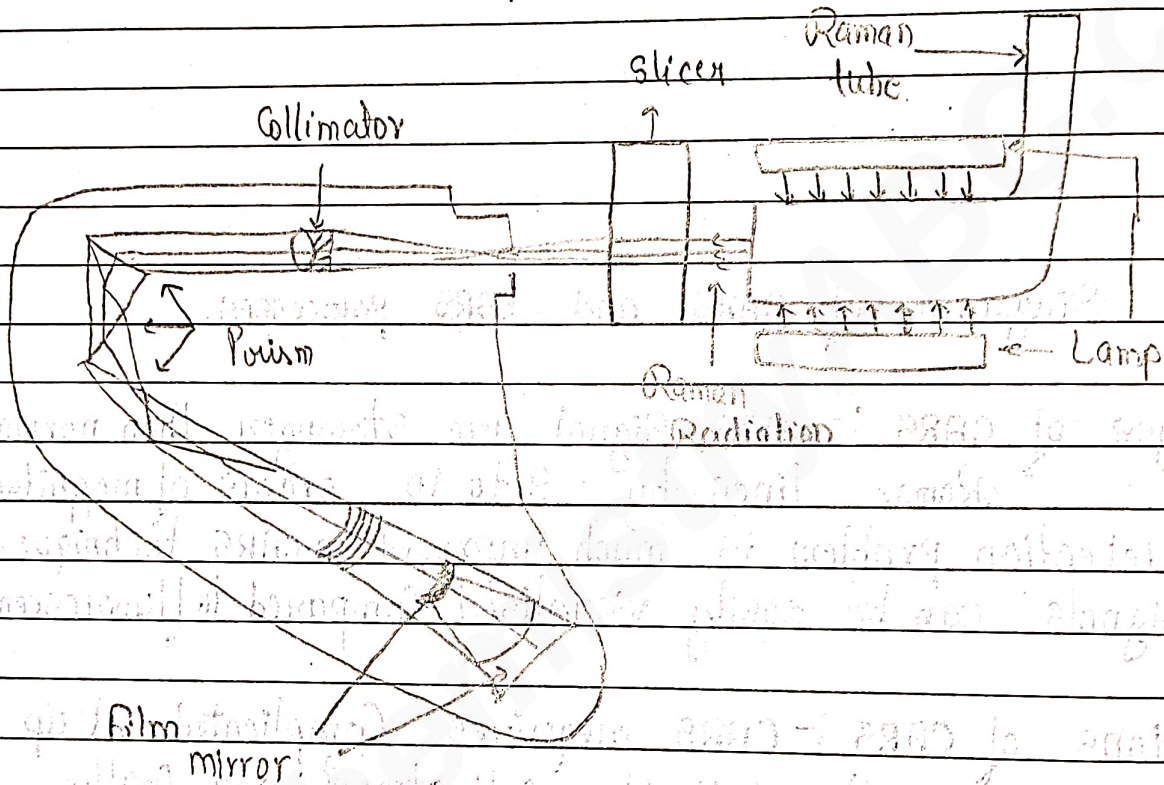
CARS is well suited for single point temperature measurements.

Instrumentation

Raman Spectrograph :- The important features of a Spectrograph suitable for the

Study of Raman Spectra are :-

- ① Large light gathering power.
- ② Special prism of high resolving power and.
- ③ A short focus camera.



Diagrammatic assembly of Raman Spectrograph

* Application of Raman effect in molecular structure:-

- 1) Structure determination using depolarisation ratio. Consider X_2Z_2 type systems.
- 2) Structural elucidation by the activity selection.
- 3) If one can extract all of the vibrational information corresponds a molecule, its molecular structure can then be determined.

* Advantage of Raman Spectroscopy over IR Spectroscopy:-

- 1) Raman Spectra can be obtained not only for gases but even for liquids and solids. IR Spectra for liquids and solids are quite diffuse.
- 2) Raman Spectra can be used to analyse homonuclear diatomic molecules which have no permanent dipole moment. Such a study is not possible with IR Spectroscopy.
- 3) Overtone and combination bands are weak in Raman Spectrum whereas these bands tend to complicate the IR Spectrum.

* Limitation of Raman Spectroscopy over IR Spectroscopy:-

- 1) Raman Spectroscopy is restricted to weakly absorbing non-fluorescent materials.
- 2) Large amount of sample was required in Raman Spectrum compare to the IR Spectroscopy.
- 3) Both solid and liquid samples must be free from dust particles. Otherwise the Raman Spectrum may be masked by Tyndall Scattering.

★ Raman activity in molecular Vibration :-

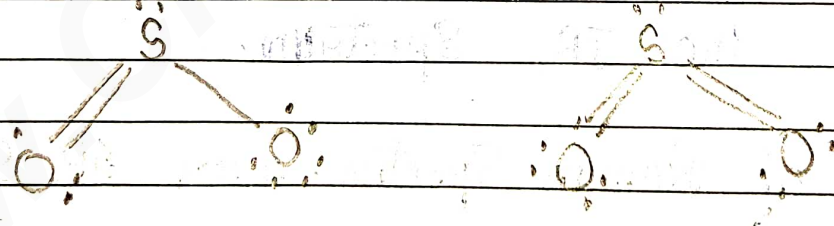
Raman Spectroscopy depends on the change in polarizability. Therefore it is possible to get Raman Spectra for molecules which do not show IR Spectra. e.g. The change in polarizability during rotation & vibration is shown below.

diagram - from Page No. 36.

★ Rule for drawing Lewis dot structure :-

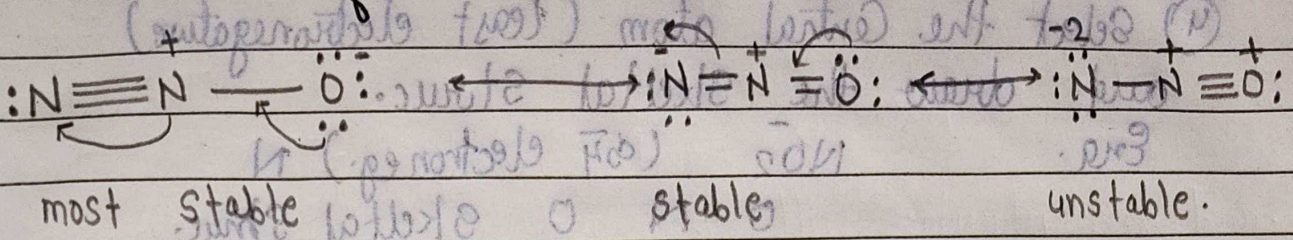
- Count the number of valence e^- each atom brings into the molecule.
- Put electron pairs about each atom such that there are 8 elec. around each atom (Octet rule), with the exception of H, which is only surrounded by 2 electrons.

★ Structure of SO_2 :- Two different ways to Lewis dot structure written.



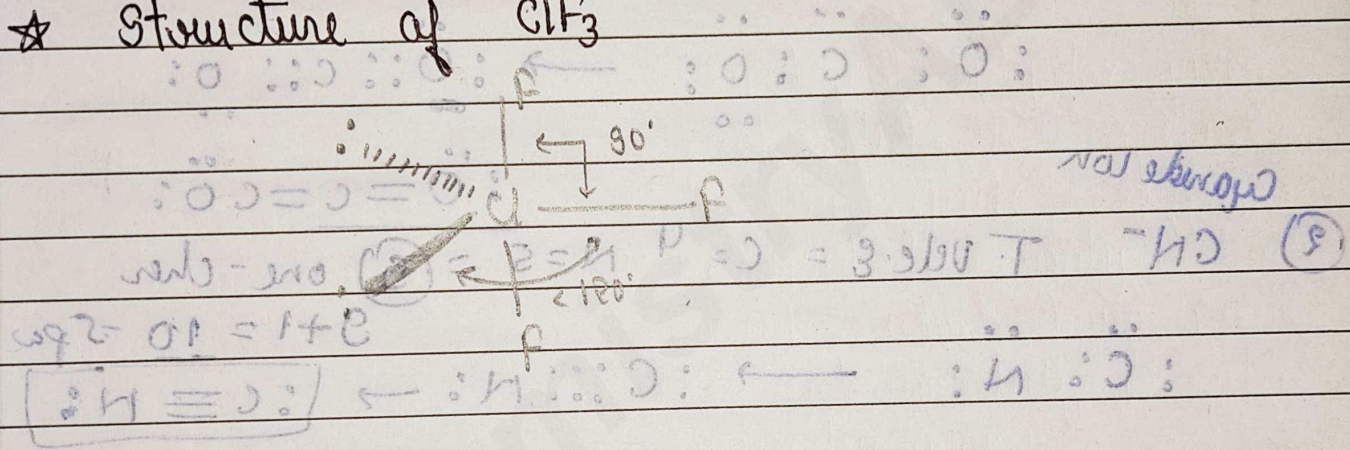
The formal charges of the SO_2 with the single bond and a double bond is larger than the SO_2 with two double bonds. So that the SO_2 with two double bond is correct structure.

★ Structure of N_2O :-

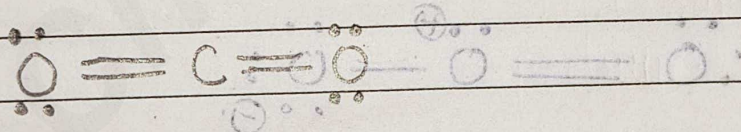


Electronegativity of oxygen is higher than nitrogen. This means a negative charge on oxygen atom is more stable than a negative charge on nitrogen atom.

★ Structure of ClF_3



★ Structure of CO_2



★ Structure of NO_3^-

