

THEORY OF MOLECULE

A **molecule** consists of two or more atoms with certain distances between them through interaction of outer electrons. Distances are determined by sum of all forces between the atoms. When the molecule takes up energy atoms are excited to vibrate around their equilibrium state. The vibration energy is quantized, which means it can only have certain values described by quantum numbers. Radiation is emitted during the transition of molecule vibration from the excited state to a lower or the ground state. The **frequency principle** must be fulfilled, which says that the frequency of the incident light must equal the energy difference between electron orbits (molecule vibrations). If the incident energy is too low, rotations are excited, i.e. far IR region (below 200 cm^{-1}) or microwaves for small molecules.

The stretching frequency of a bond can be approximated by Hooke's law.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

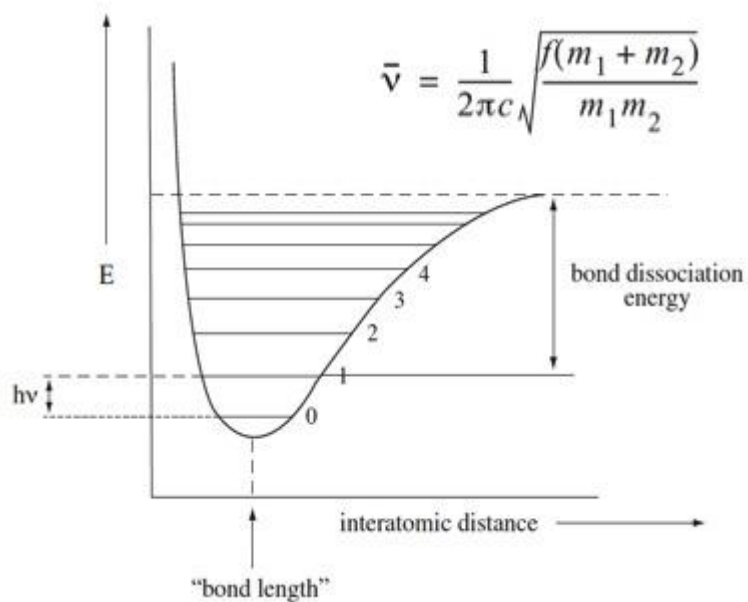
We can view a diatomic molecule as **one-dimensional harmonic oscillator** with the vibrating masses m_1 and m_2 on a weightless elastic spring (electrons are disregarded), which is characterized by the elastic force constant k . According to Hooke's law, the frequency of the vibration ν of the spring is related to the mass m and the force constant k of the spring.

If the equilibrium state r_0 is stretched by Δr , the sum of the spring displacement (x_1+x_2) a force F is active. The release of this force F induces vibration around the equilibrium state.

In the classical harmonic oscillator the energy is calculated as follows: $E = \frac{1}{2} k x^2$.

This means, that the energy or frequency depends on the magnitude of spring stretch or compression. However, vibrational motion is quantized as mentioned earlier and only vibrations which satisfy following formula are allowed: $E = (n+1/2) h\nu$, with $n =$ quantum number $(0, 1, 2, 3, \dots)$ and ν the frequency of the vibration. The lowest energy level is $\frac{1}{2} h\nu$ the next highest is $\frac{3}{2} h\nu$. This means that only transitions to the next energy level are allowed. The molecules will absorb an energy amount equal to $\frac{3}{2} h\nu - \frac{1}{2} h\nu$, or $h\nu$.

However, the molecule actually behaves as an **anharmonic oscillator**, which is due to the fact that a bond can not infinitely be compressed or stretched, it can break. As interatomic distances increase the energy reaches a maximum, the energy levels are not equidistant anymore like in the case of a harmonic oscillator. Allowed transitions become smaller in energy. Sometimes higher transitions can be observed, which are called overtones. Overtones have a lower intensity than the fundamental vibration.



The wavenumber in the case of the anharmonic oscillator can be calculated as shown in the image, where ν is the frequency in cm^{-1} , m_1 and m_2 are the masses of the atom in g and c is the speed of light in cm/s . This equation describes the relationship of bond strength and mass to the wavenumber. It incorporates the reduced mass $\mu = m_1 m_2 / m_1 + m_2$. As the force constant increases, the wavenumber increases. As the mass of the atoms increases, wavenumber decreases.

Vibrational modes

Vibrational modes can be divided into stretching (symmetric and asymmetric) and bending vibrations (in-plane and out-of plane).

The **selection rule** says, that vibrations are only IR active (or allowed), if the molecular dipole moment changes during the vibration.

A diatomic molecule with the same atoms cannot be excited to vibrate because no dipole moment is present. In contrast, molecules with various types of atoms can interact with incident radiation, and even if a dipole moment is not present in the beginning it can be induced due to antisymmetric displacement of the center of charge (e.g., CO₂).

A molecule of n atoms has $3N$ degrees of freedom. In a non-linear molecule 3 of these are rotational and 3 of these degrees are translational, and the remaining belong to fundamental vibrations (normal modes). In a linear molecule 2 degrees are rotational and 3 degrees are translational. The number of fundamental vibrations in a non-linear molecule is therefore $3N-6$ and in a linear molecule it is $3N-5$. The water molecule is an example for a non-linear molecule and has 3 fundamental vibrations ($3 \times 3 - 6$). The CO₂ molecule is an example for a linear molecule and has 4 fundamental vibrations ($3 \times 3 - 5$).

Degenerated vibrations: symmetrically equivalent vibrations having the same wavenumber, e.g., CO₂ bending vibrations

Coupled vibrations: bands with slightly different positions can occur due to the network of molecules in a structure.

Overtone bands: due to transitions of $2h\nu$, $3h\nu$, etc., lower intensity than the fundamental vibration band. Band position is at a slightly smaller frequency than the multiple of the fundamental vibrational frequency.

Combination vibrations: sum or difference of two vibrations, they can be helpful to determine the speciation of a molecule in sample

Source:

https://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/raman_ir.html