

29.1: Rotational Spectroscopy

Rotational spectroscopy is concerned with the measurement of the energies of transitions between quantized rotational states of molecules in the gas phase. Rotational transitions of molecules are usually measured in the range $1 - 10 \text{ cm}^{-1}$ (microwave radiation) and rotational spectroscopy is therefore usually referred to as *microwave spectroscopy*.

Rotational spectroscopy is actively used by astrophysicists to explore the chemical composition of the interstellar medium using radio telescopes.

The rotational energies are derived theoretically by considering the molecules to be rigid rotors and applying the same treatment that we saw in [chapter 20](#). Correction terms might be applied to account for deviation from the ideal rigid rotor case. As we saw in [chapter 20](#), the quantized rotational energy levels of a rigid rotor depend on the angular moment of inertia, which in turn depends on the masses of the nuclei and the internuclear distance. Reversing the theoretical procedure of obtaining the energy levels from the distances, we can use the experimental energy levels to derive very precise values of molecular bond lengths (and in some complex case, also of angles). We will discuss below the simplest case of a diatomic molecule. For non-linear molecules, the moments of inertia are multiple, and only a few analytical method of solving the TISEq are available. For the most complicated cases, numerical methods can be used.

Rotation of diatomic molecules

Transitions between rotational states can be observed in molecules with a permanent electric dipole moment. The rigid rotor is a good starting point from which to construct a model of a rotating molecule. It is assumed that component atoms are point masses connected by rigid bonds. A linear molecule lies on a single axis and each atom moves on the surface of a sphere around the center of mass. The two degrees of rotational freedom correspond to the spherical coordinates, θ and φ , which describe the direction of the molecular axis. The quantum state is determined by two quantum numbers J and M . J defines the magnitude of the rotational angular momentum, and M its component about an axis fixed in space, such as an external electric or magnetic field. In the absence of external fields, the energy depends only on J . Under the rigid rotor model, the rotational energy levels, $F(J)$, of the molecule can be expressed as:

$$F(J) = BJ(J+1) \quad J = 0, 1, 2, \dots \quad (29.1.1)$$

where B is the rotational constant of the molecule and is related to its moment of inertia. In a diatomic molecule the moment of inertia about an axis perpendicular to the molecular axis is unique, so:

$$B = \frac{h}{8\pi^2 c I}, \quad (29.1.2)$$

with:

$$I = \frac{m_1 m_2}{m_1 + m_2} d^2, \quad (29.1.3)$$

where m_1 and m_2 are the masses of the atoms and d is the distance between them.

The selection rule for rotational spectroscopy dictate that during emission or absorption the rotational quantum number has to change by unity:

$$\Delta J = J' - J'' = \pm 1, \quad (29.1.4)$$

where J' denotes the lower level and J'' denotes the upper level involved in the transition. Thus, the locations of the lines in a rotational spectrum will be given by

$$\tilde{\nu}_{J'} \leftrightarrow J'' = F(J') - F(J'') = 2B(J'' + 1) \quad J'' = 0, 1, 2, \dots \quad (29.1.5)$$

The diagram illustrates rotational transitions that obey the $\Delta J = 1$ selection rule in figure 29.1.1¹. The dashed lines show how these transitions map onto features that can be observed experimentally. Adjacent $J'' \leftarrow J'$ transitions are separated by $2B$ in the observed spectrum. Frequency or wavenumber units can also be used for the x axis of this plot.

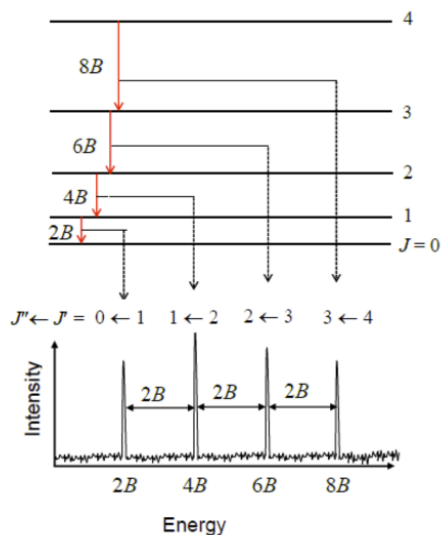


Figure 29.1.1: Rotational energy levels and line positions calculated in the rigid rotor approximation.

The probability of a transition taking place is the most important factor influencing the intensity of an observed rotational line. This probability is proportional to the population of the initial state involved in the transition. The population of a rotational state depends on two factors. The number of molecules in an excited state with quantum number J , relative to the number of molecules in the ground state, N_J/N_0 is given by the Boltzmann distribution:

$$\frac{N_J}{N_0} = e^{-\frac{E_J}{kT}} = \exp\left[-\frac{BhcJ(J+1)}{kT}\right], \quad (29.1.6)$$

where k is the Boltzmann constant and T is the absolute temperature. This factor decreases as J increases. The second factor is the degeneracy of the rotational state, which is equal to $2J+1$. This factor increases as J increases. Combining the two factors we obtain:

$$\text{population} \propto (2J+1) \exp\left[-\frac{E_J}{kT}\right], \quad (29.1.7)$$

in agreement with the experimental shape of rotational spectra of diatomic molecules.

1. This diagram is taken from [Wikipedia](#) by user Nnrw, and distributed under CC BY-SA 3.0 license.

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