

inertia I and therefore no rotational transitions.

- Molecular nitrogen (N_2), the most abundant atmospheric constituent, has neither electric nor magnetic dipole moment and therefore has no rotational absorption spectrum.
- Oxygen (O_2) also has no electric dipole moment but, unlike most other diatomic gases, it does have a permanent magnetic dipole moment. This property is what permits it to have rotational absorption bands at 60 and 118 GHz.
- Carbon dioxide (CO_2) has no permanent electric or magnetic dipole moment and is therefore radiatively inactive with respect to pure rotational transitions. However, bending vibrational motions can break the linear symmetry of the molecule and introduce an oscillating dipole moment whose presence permits combined vibration-rotation transitions at shorter wavelengths (see Section 9.2.2).
- All other major molecules found in the atmosphere exhibit permanent electric dipole moments and therefore also major rotational absorption bands.

9.2.2 Vibrational Transitions

The covalent bonds between two atoms in a molecule arise from a balance of attractive and repulsive electrostatic forces. The former dominates when the two atoms are relatively widely separated; the latter, due to mutual repulsion of the positively charged nuclei, takes over when the atoms get pushed too close together. The arrangement of atoms in a molecule at rest corresponds to the positions for which all attractive and repulsive forces exactly cancel.

Diatomic Molecules

The molecular bond is thus not rigid but behaves like a spring. In particular, for sufficiently small displacements, the force between two atoms in a diatomic molecule is given by

$$F = -k(r' - r) , \quad (9.19)$$

where k is analogous to a spring constant, and F is thus the restoring force when the separation r is smaller or greater than the equilibrium separation r' . Because the atoms have mass, the molecule would, in the classical limit, behave like a simple harmonic oscillator with resonant frequency

$$\nu' = \frac{1}{2\pi} \sqrt{\frac{k}{m'}}, \quad (9.20)$$

where m' is the reduced mass defined by (9.9).

In the quantum mechanical limit, however, the actual vibrational frequency ν of the the oscillator is quantized according to

$$\nu = \left(\nu + \frac{1}{2} \right) \nu', \quad (9.21)$$

where ν (letter 'V', not Greek 'nu') is the *vibrational quantum number* and, like the rotational quantum number J , can only take on non-negative integer values.

The energy associated with each frequency ν is the same as it is for a photon with the same frequency:

$$E_\nu = h\nu = \left(\nu + \frac{1}{2} \right) h\nu'. \quad (9.22)$$

A vibrational transition $\Delta\nu = \pm N$ therefore entails a change of energy

$$|\Delta E_\nu| = N h\nu', \quad (9.23)$$

and we see, somewhat to our amazement, that the photon frequency associated with the transition is just an integer multiple of the classical resonant frequency of the harmonic oscillator.

Vibration/Rotation Spectra

There are two important points to note:

- Vibrational transitions tend to be associated with considerably larger energies than rotational transitions. Therefore vibrational transitions give rise to absorption/emission lines at much shorter wavelengths — e.g., in the thermal and near IR bands — than those due to pure rotational transitions, which are generally associated with the far IR and microwave bands.

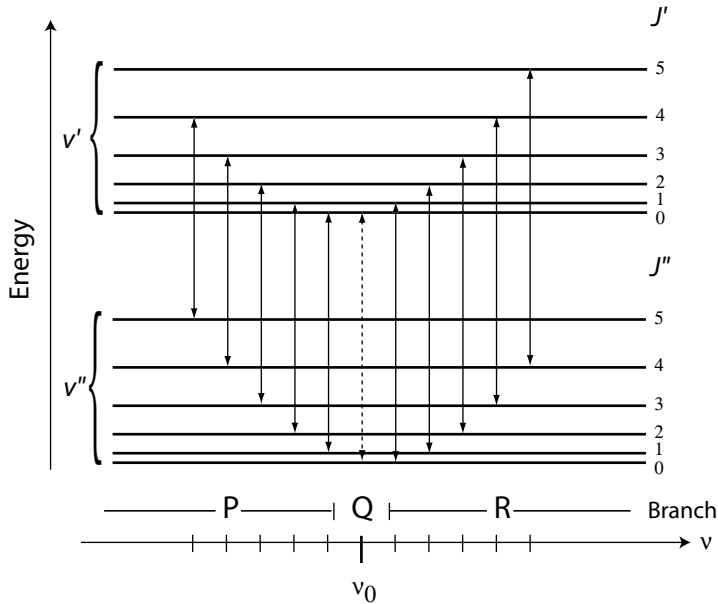


Fig. 9.3: Vibrational-rotational transitions for $\Delta v = \pm 1$, $\Delta J = [-1, 0, +1]$, showing the relative positions of the transitions in the spectrum. The P-branch corresponds to transitions involving $\Delta J = -1$, while the R-branch corresponds to $\Delta J = +1$. The Q-branch, when present, represents a superposition of all possible transitions involving $\Delta J = 0$ and occurs close to frequency $\nu_0 = \Delta E/h$, where ΔE is the energy associated with pure vibrational transitions.

- Vibrational and rotational transitions may, and usually do, occur simultaneously. It follows from the previous point that the energy (and photon wavelength) of combined vibration/rotation transition is slightly greater or less than that of a pure vibrational transition, depending on whether the rotational quantum number J increased or decreased during the transition. The effect of rotational transitions is therefore to split up vibrational absorption lines into a series of rather closely spaced separate lines.

The second of the above points is illustrated by Fig. 9.3, which depicts the positions of lines associated with various combinations of $\Delta v = \pm 1$ and $\Delta J = [-1, 0, 1]$. The nominal frequency of a pure vibrational transition ($\Delta J = 0$) is indicated in this figure as ν_0 and is approximately the same regardless of the value of J in force when