

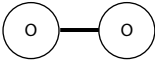
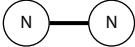
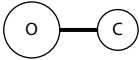
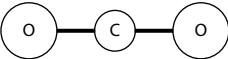
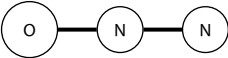
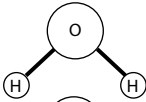
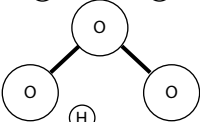
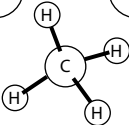
Molecule	Structure	Permanent Electric Dipole Moment?
Oxygen		linear No (magnetic dipole)
Nitrogen		linear No
Carbon Monoxide		linear Yes
Carbon Dioxide		linear No
Nitrous Oxide		linear Yes
Water		asymmetric top Yes
Ozone		asymmetric top Yes
Methane		spherical top Yes

Fig. 9.2: Molecular structure of several key atmospheric constituents. Also indicated is whether the molecule has a permanent electric dipole moment (note that oxygen has a permanent magnetic dipole moment).

rotation can be taken to pass through the two nuclei. For this axis, the moment of inertia $I_1 = 0$. The remaining two axes are perpendicular to each other and to the first; for them the moments of inertia are nonzero and $I_2 = I_3$. These properties also apply more generally to a *linear* polyatomic molecule — i.e., any molecule with all of its constituent atoms lying in a straight line.

Finally, we come to nonlinear polyatomic molecules, which have three nonzero moments of inertia. Depending on the symmetry of

the molecule, there are three possible cases: 1) all moments of inertia equal, corresponding to a *spherical symmetric top* molecule, 2) two equal and one different in the case of a *symmetric top* molecule, and 3) all three different — the so-called *asymmetric top*.

The significance of the above distinctions lies in the number of mechanically dissimilar modes of rotation available to a given molecule. There can be no rotational energy, and therefore no absorption or emission of radiation, in connection with a principal axis for which $I = 0$. Furthermore, axes of rotation for which the moments of inertia are equal are energetically indistinguishable and therefore give rise to identical absorption spectra. Thus, linear and spherical symmetric top molecules have the fewest distinct modes of rotation, and therefore the simplest absorption spectra due to rotational transitions, while asymmetric top molecules have the richest set of possible transitions, and therefore the most complex rotation spectra.

The following table summarizes the different types of rotational symmetry, in order of increasing complexity, and lists the most important atmospheric molecules in each category (see also Fig. 9.2).

Description	Moments of Inertia	Examples
Monoatomic	$I_1 = I_2 = I_3 = 0$	Ar
Linear	$I_1 = 0; I_2 = I_3 > 0$	N_2, O_2, CO_2, N_2O
Spherical symmetric top	$I_1 = I_2 = I_3 > 0$	CH_4
Symmetric top	$I_1 \neq 0; I_2 = I_3 > 0$	NH_3, CH_3Cl, CF_3Cl
Asymmetric top	$I_1 \neq I_2 \neq I_3$	H_2O, O_3

Quantization of Angular Momentum

A diatomic molecule may be regarded as a two-body rigid rotator consisting of two masses m_1 and m_2 separated by distance $r = r_1 + r_2$, where r_i is the distance of each mass m_i from the axis of rotation. For any freely rotating body, the axis of rotation coincides with the *center of mass* which, in this example, satisfies $m_1 r_1 = m_2 r_2$. It can be shown from (9.7) that the moment of inertia $I_2 = I_3 = I$ (recall that $I_1 = 0$ for a linear molecule) is given by

$$I = m' r^2, \quad (9.8)$$

where we introduce the so-called *reduced mass*

$$m' \equiv \frac{m_1 m_2}{m_1 + m_2} . \quad (9.9)$$

If the molecule is rotating with angular velocity ω , then its kinetic energy of rotation is

$$E = \frac{1}{2} I \omega^2 = \frac{L^2}{2I} , \quad (9.10)$$

where

$$L = I\omega \quad (9.11)$$

is the angular momentum. Quantum mechanics tells us (via Schrödinger's equation), that the angular momentum of our rigid molecule is restricted to discrete values given by

$$L = \frac{h}{2\pi} \sqrt{J(J+1)} , \quad (9.12)$$

where $J = 0, 1, 2, \dots$ is the *rotational quantum number*. Combining the above with (9.10) yields a set of discrete energy levels

$$E_J = \frac{1}{2} I \omega^2 = \frac{J(J+1)h^2}{8\pi^2 I} . \quad (9.13)$$

Problem 9.2: Equations (9.11) and (9.12) imply that the angular velocity ω of an object can only take on discrete (quantized) values. Explain why this quantization is not observable for macroscopic objects like frisbees and hula hoops.

Rotational Absorption Spectrum

If we now consider transitions between adjacent rotational states J and $J+1$ (it turns out that none other are allowed by quantum mechanics), we find that the associated energy change is

$$\Delta E = E_{J+1} - E_J = \frac{h^2}{8\pi^2 I} [(J+1)(J+2) - J(J+1)] , \quad (9.14)$$