

# Interstellar Molecular Excitation

## 1. Rotational Transitions

See Kwok Chapter 7.4.

Let us consider the rotational transitions of a diatomic molecule, such as CO. The moment of inertia for the molecule is given by,

$$I = \mu r_0^2$$

where  $\mu$  is the reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

and  $m_1$  and  $m_2$  are the mass of the two nuclei and  $r_0$  is the internuclear separation.

The energy levels of the rotational states are given by,

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

where  $J$  is the rotational quantum number.

For electric dipole transitions,  $\Delta J = \pm 1$ . Therefore, the frequencies for the transition from upper state  $i$  to lower state  $j = i - 1$  are given by,

$$\Delta E_{ij} = E_i - E_j = E_{J+1} - E_J$$

$$\Delta E_{ij} = \frac{h^2}{8\pi^2 I} [(J+1)(J+2) - J(J+1)]$$

$$\Delta E_{ij} = \frac{h^2}{8\pi^2 I} [J^2 + 3J + 2 - J^2 - J] = \frac{h^2}{8\pi^2 I} 2(J+1)$$

$$\nu_{ij} = 2B(J+1)$$

where

$$B = \frac{h}{8\pi^2 I}$$

Note that heavier molecules will have lower energy rotational transitions. For instance the CO (1-0) line is at 115 GHz, while CH<sup>+</sup> has its ground state 418 GHz. Also note that molecules such as H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> have no electric-dipole moment because their centers of mass are also their centers of charge, and therefore have no electric-dipole rotational transitions.

## 2. Temperature Measured by CO

See Kwok chapter 9 and Palla & Stahler chapter 6.

Here we will discuss how to use observations of CO lines to derive the temperature and column density of a molecular cloud.

First, let us define some useful quantities:

$$T_o \equiv \frac{h\nu}{k}$$

$$f(T) \equiv \frac{1}{e^{h\nu/kT} - 1} = \frac{1}{e^{T_o/T} - 1}$$

$$T_B \equiv \frac{c^2}{2\nu^2 k} [I_\nu(\tau) - I_\nu(0)]$$

$$\frac{n_i g_i}{n_j g_k} = \exp\left(\frac{-h\nu}{kT_{ex}}\right)$$

Here  $T_o$  is the equivalent temperature of a transition.  $T_B$  is called the *brightness temperature*, and it is a measure of the intensity of a line coming from the source. Recall that in the Rayleigh-Jeans limit  $B_\nu = \frac{2\nu^2 kT}{c^2}$ .  $T_{ex}$  is the *excitation temperature* and is a measure of the population distribution between energy states.

With these definitions in mind, we can write,

$$T_B = T_o [f(T_{ex}) - f(T_{BG})] [1 - e^{-\tau}]$$

Consider the case that  $\tau \gg 1$  ( $1 - e^{-\tau} \simeq 1$ ), which is almost always the case for the  $^{12}\text{C}^{16}\text{O}$  (1–0) transition. In this case,  $T_B = T_o [f(T_{ex}) - f(T_{bg})]$ .  $T_o$  is a known constant,  $T_{bg}$  is the temperature of the CMB (2.7 K), and  $T_B$  is the measured quantity from the telescope. With this measurement of the CO line, one gets  $T_{ex}$ . For an optically thick line, the level populations are in LTE, so  $T_{kin} = T_{ex}$ . Therefore, we have measured the kinetic temperature of a molecular cloud with this one observation.

### 3. Column Density Measured by CO

See Kwok Palla & Stahler chapter 6.1.3

Let us consider the case in which we have observed the (1–0) rotational lines of both  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$ . From the last section we know  $T_{ex}$  from the  $^{12}\text{C}^{16}\text{O}$  measurement. If we assume that  $T_{ex}$  is the same for the  $^{13}\text{C}^{16}\text{O}$  (1–0) transition as for  $^{12}\text{C}^{16}\text{O}$  (1–0), we can use the measured brightness of the  $^{13}\text{C}^{16}\text{O}$  (1–0) line to calculate  $\tau_{^{13}\text{CO}}$ , which is generally a lot less thick than  $^{12}\text{C}^{16}\text{O}$ . What we now want to do is derive the total column density of  $^{13}\text{C}^{16}\text{O}$ .

Recall the equation for the total absorption coefficient ( $\kappa_\nu$ ),

$$\kappa_\nu = \frac{h\nu}{4\pi}(n_j B_{ji} - n_i B_{ij})\phi_\nu$$

Recall also that

$$S_\nu = j_\nu/\kappa_\nu = \frac{2h\nu^3/c^2}{\exp(h\nu/kT_{ex}) - 1}$$

and

$$j_\nu = \frac{h\nu}{4\pi}n_u A_{ij}\phi_\nu$$

One can therefore write

$$\kappa_\nu = \frac{c^2 A_{ij} g_i}{8\pi\nu^2 g_j} \left[ 1 - \exp\left(\frac{h\nu}{kT_{ex}}\right) \right] n_j \phi_\nu$$

The optical depth is defined by

$$\tau_\nu \equiv \int \kappa_\nu ds$$

So, the optical depth of the  $^{13}\text{C}^{16}\text{O}$  (1–0) line is given by,

$$\tau = \frac{c^2 A_{ij} g_i}{8\pi\nu^2 g_j} \left[ 1 - \exp\left(\frac{h\nu}{kT_{ex}}\right) \right] \frac{n_j \Delta s}{\Delta\nu}$$

where  $\Delta s$  is the path length through the cloud and  $\Delta\nu$  is the FWHM of the Doppler-broadened line.

The total column density ( $n\Delta s$ ) in  $^{13}\text{C}^{16}\text{O}$  is given by,

$$N_{^{13}\text{CO}} = \frac{8\pi\nu^2\Delta\nu Q\tau g_0}{c^2 A_{10} g_1} \left[ 1 - \exp\left(-\frac{T_o}{T_{ex}}\right) \right]^{-1}$$

where  $\tau$  is the optical depth of the  $^{13}\text{C}^{16}\text{O}$  (1–0) line and  $Q$  is the partition function, used to correct for the fact that we only measure those molecules transitioning from the 1 - 0 state, but we want the total column density (over all the states). The partition function for these rotational levels is given by,

$$Q = \sum_{J=0}^{\infty} (2J + 1) \exp\left[-\frac{T_o J(J + 1)}{2T_{ex}}\right]$$

When attempting to measure column density, one should try to use an optically thin line.

#### 4. Vibrational Transitions of Diatomic Molecules

See Kwok chapter 7.5.

The energy associated with the stretching of the molecular bond (vibrations) is given by,

$$E_v = \left(v + \frac{1}{2}\right) h\nu_0$$

where  $v$  is the vibrational quantum number and

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

is the natural oscillator frequency and  $k$  is the spring constant.

For a molecule that is both rotating and vibrating, the energy levels will be given by,

$$E_{v,J} = \left(v + \frac{1}{2}\right) h\nu + J(J+1)hB - \frac{[BJ(J+1)]^2}{(1/2)kr_0^2 + 3BJ(J+1)}$$

where

$$v = \sqrt{\frac{kr_0^2 + 6BJ(J+1)}{\mu r_0^2}}$$

and the last term on the right comes from the correction due to a non-rigid rotation (variable moment of inertia).

The selection rule for vibrational transitions within the harmonic approximation is  $\Delta v = \pm 1$ . The ground-state vibrational transition ( $v = 1 \leftrightarrow 0$ ) is called the *fundamental transition*, and transitions from higher excited states directly to the ground state ( $v = n \leftrightarrow 0, n \geq 2$ ) are referred to as *overtones*. Transitions between excited states are called *hot bands*.

## 5. Molecular Hydrogen

See Kwok chapter 7.7.1.

The H<sub>2</sub> molecule has two identical nuclei and no permanent electric-dipole or magnetic-dipole moment. The only observable transitions are electric quadrupole transitions, which have  $\Delta J = -2, 0$  and  $2$  (called *O*, *Q* and *S* branches).

The *ortho* state of H<sub>2</sub> has odd  $J$  values, and the *para* state of H<sub>2</sub> has even values of  $J$ . In statistical equilibrium, the population ratio between ortho and para states is 3:1 ( $2I + 1$ ) where  $I$  is the sum of the nuclear spins of the nuclei ( $I = 0$  if the spins are antiparallel, and  $I = 1$  if they are parallel).

These lines are seen in the UV - NIR. One can discriminate between lines excited by collisions and radiation by the line strengths. For instance, radiative excitation will generally result in more flux in the  $\lambda < 2 \mu\text{m}$  lines.

H<sub>2</sub> can be seen in absorption against continuum sources with the  $v = 1 \rightarrow 0S(0)$  and  $S(1)$  lines are  $2.22$  and  $2.12 \mu\text{m}$ . If the CO  $v = 2 \rightarrow 0$  ( $\sim 2.3 \mu\text{m}$ ) vibrational bands are also seen in the same sources then one can derive the H<sub>2</sub> to CO abundance ratio.

Ground state rotational quadrupole transitions of H<sub>2</sub>, such as the *para*  $S(0)J = 2-0$  and *ortho*  $S(1)J = 3-1$ , can be observed at  $28.2$  and  $17.0 \mu\text{m}$ . These lines are only observable from space, but they are the best means of direct determination of the “low” temperature molecular hydrogen mass in the ISM. However, the  $S(0)J = 2-0$  line requires the excitation of the  $J = 2$  rotational state, which is  $500$  K above the ground state. At low temperatures, H<sub>2</sub> will be confined entirely to the ground ( $J = 0,1$ ) state, and there is no emission mechanism that can be used to determine the abundance of molecular H<sub>2</sub>.

## 6. Hyperfine Lines in Molecules

See Kwok chapter 7.7.3.

Nuclear spin can introduce hyperfine splittings in molecular transitions, as we already discussed in the atomic case.  $^{14}\text{N}$  has a nuclear spin of 1, and the rotational states of HCN are split into three hyperfine components corresponding to  $F = J - 1, J, J + 1$ . The relative intensities of the  $F = 2 \rightarrow 1$ ,  $F = 1 \rightarrow 1$  and  $F = 0 \rightarrow 1$  hyperfine transitions correspond to the statistical weights of the upper states ( $2F + 1$ ) and therefore have values of 5:3:1, respectively. HCN is widely observed in molecular clouds, and the relative intensities of the hyperfine lines can be used to determine temperature and optical depth.

Similarly,  $\text{N}_2\text{H}^+$  has hyperfine lines from each of the N atoms, and has 7 components with separations on the order of  $\sim 0.2$  MHz. Such separations can not be observed in the laboratory due to pressure broadening, but can be observed in molecular clouds.

Although  $^{12}\text{C}^{16}\text{O}$  has no nuclear spin, some isotopes (e.g.  $^{13}\text{C}$  and  $^{17}\text{O}$ ) do have nuclear spin, and hyperfine lines of these isotopologues of CO can be observed. This makes it much easier to derive the optical depth of the most commonly observed molecule.

## 7. Symmetric Tops

See Kwok chapter 7.8.

A molecule with an axis of rotational symmetry with two equal moments of inertia is called a *symmetric top*. For a (prolate) linear molecule, its moment of inertia along its molecular axis ( $I_A$ ) is very small and the two other moments of inertia ( $I_B$  and  $I_C$ ) are equal.

For an oblate symmetric rotator  $I_A = I_B < I_C$ . In general, the rotational constants are given by,

$$A, B, C = \frac{h}{8\pi^2 I_{A,B,C}}$$

The rotational levels of a symmetric top are given by  $J$  and  $K$ , where  $J$  is the total angular momentum quantum number, and  $K$  is the projection of the angular momentum onto the axis of symmetry.  $K$  can take values from  $-J$  to  $J$ , but the rotational energy is the same for clockwise and counterclockwise rotation, so there are only  $J + 1$   $K$  states for each  $J$ . The rigid rotator energy levels are given by,

$$E_{JK} = BhJ(J + 1) + (A - B)hK^2$$

and

$$E_{JK} = BhJ(J + 1) + (C - B)hK^2$$

for a prolate and oblate top, respectively.

The selection rules for electric-dipole transitions are:

$$\Delta K = 0$$

$$\Delta J = 0, \pm 1$$

Because  $\Delta K = 0$ , we see that the transition frequency associated with  $E_{JK} - E_{(J-1),K}$  is independent of  $K$ . Successive rotational transitions ( $J = 1 \rightarrow 0, 2 \rightarrow 1$ , etc.) are separated by  $2B$  in frequency, as was the case for linear molecules. For non-rigid rotators, centrifugal distortion will create a  $K$  dependence on the energy levels  $E_{JK}$  (see Kwok chapter 7.8.2).

## 8. Ammonia and Inversion Transitions

The ammonia ( $\text{NH}_3$ ) molecule is an example of a symmetric top molecule.  $\text{NH}_3$  can undergo an inversion transition where the N atom flips from one side of the plane defined by the three H atoms to the other side. This splits each of the rotational levels into two states. The lower state is labelled + or *s* (for symmetric) and the upper state is labelled - or *a* (for antisymmetric).

Because the energy separations for the low rotational levels is small, the inversion states can be easily excited. For instance, the  $\text{NH}_3$  ( $J, K$ ) (1,1) and (2,2) states are observed at 23.6945 and 23.7226 GHz. Each of the inversion lines is split into 18 hyperfine components due to interaction between the electric-quadrupole moment of the N nucleus and the electric field of the electrons and due to magnetic interactions associated with the H nuclei.

Because the frequencies of the  $\text{NH}_3$  (1,1) and (2,2) inversion transitions are so close, they can often be observed simultaneously. The relative population of the (1,1) and (2,2) states depends on the kinetic temperature of the gas, and the hyperfine transitions allows precise measurement of the optical depth and kinematics of the gas.

## 9. Asymmetric Rotators

If none of the principal moments of inertia are equal, then a molecule is called an *asymmetric rotator*. In this case,  $K$  (the angular momentum projected onto the symmetry axis) is no longer a good quantum number. Instead, the quantities  $K_{-1}$  and  $K_1$  (the limiting cases of prolate and oblate symmetric tops) are used, and the energy levels are designated as  $J_{K_{-1},K_1}$ .

### 9.1. Water

The rotational constants for H<sub>2</sub>O are all quite different ( $A \neq B \neq C$ ), so it is an example of an asymmetric top. Each of the rotational quantum numbers  $J$  is split into  $2J + 1$  levels, which are described by two additional labels  $K_{-1}$  and  $K_1$ .  $K_{-1}$  takes values  $0, \dots, J$  and takes values  $K_1 = J - K_{-1}$  or  $K_1 = J - K_{-1} + 1$  (except when  $K_{-1} = 0$ , in which case  $K_1 = J - K_{-1}$ ).

For example, if  $J = 0$ , then the only allowed state ( $J_{K_{-1},K_1}$ ) is  $0_{00}$ . For  $J = 1$ ,  $K_{-1}$  can take values 0 or 1 and the allowed states are  $1_{01}$ ,  $1_{10}$  and  $1_{11}$ . The total number of states is  $2J + 1$ .

The selection rules are:

$$\Delta J = 0, \pm 1 \text{ and}$$

$$(K_{-1}, K_1) = ++ \leftrightarrow -- \text{ and } -+ \leftrightarrow +-,$$

so there is no cross transition between *ortho* and *para* states.

These selection rules allow for transitions down each  $J$  ladder (e.g.  $4_{32} - 4_{23}$  where  $\Delta J = 0$ ) as well as transitions to the next ladder (e.g.  $5_{32} - 4_{41}$  where  $\Delta J = 1$ ). Although most of these transitions are in the far-infrared, sometimes two states in adjacent ladders can be very close in energy and the transition can occur in the radio region (e.g., the  $6_{16} - 5_{23}$  at 22 GHz).

For these radio transitions, when the upper state (e.g.  $6_{16}$ ) is at the bottom of the ladder, molecules often accumulate in those states, resulting in a *population inversion* ( $n_i g_j / n_j g_i > 1$ ).

Recall (Kwok eq 5.15) that the atomic absorption coefficient is given by,

$$a_\nu = \left( 1 - \frac{n_i g_j}{n_j g_i} \right) \frac{h\nu}{4\pi} B_{ij} \phi_\nu$$

In a population inversion, the absorption coefficient is negative, as is the optical depth. This results in an exponential increase of line intensity with path length, as each stimulated absorption will induce further stimulated emission. This is known as *masing*, and the

intensities of maser lines are very bright and easy to detect.

Besides  $\text{H}_2\text{O}$ , other examples of masers are  $\text{CH}_3\text{OH}$  (similar to a symmetric top) and  $\text{OH}$ . Maser lines are especially useful because they are compact and bright enough to be mapped by interferometers, and are often used as a signpost of star formation, as they are associated with UCH II regions, disks, jets and outflows.