Interstellar Molecules

From a presentation to the 2009
Ay 126 class by Scott Schnee

History

Interstellar molecular gas was discovered in the 1940s with the observation of absorption bands from electronic transitions in CH, CH^+, and CN superimposed on the spectra of bright stars. In the late 1960s, centimeter- and millimeter-wavelength radio observations detected emission from rotational transitions of OH (hydroxyl), CO (carbon monoxide), NH_3 (ammonia), and H_2CO (formaldehyde). The Copernicus satellite detected Far-UV absorption bands of H_2 (the Lyman & Werner electronic transition bands) and HD in the early 1970s, and Lyman FUSE (launched in 1999) has detected diffuse H_2 along nearly every line of sight it has looked (where it often gets in the way of lines from the extragalactic sources of interest to the observations!). Infrared observations beginning in the 1970s detected H_2 in emission from forbidden rotational-vibrational transitions in the Near-IR, with advances in IR array detectors in the late 1990s greatly expanding studies of these transitions.

Table 7.1

Interstellar molecules listed by number of atoms

Diatomic	Triatomic	Four atoms	Five atoms	Six atoms	Seven atoms	Eight atoms
H_2	C_3	*c*-C_3H	C_5	C_5H	C_6H	CH_3C_3N
AlF	C_2H	*l*-C_3H	C_4H	*l*-H_2C_4	CH_2CHCN	$HCOOCH_3$
AlCl	C_2O	C_3N	C_4Si	C_2H_4	CH_3C_2H	CH_3COOH(?)
C_2	C_2S	C_3O	*l*-C_3H_2	CH_3CN	HC_5N	C_7H
CH	CH_2	C_3S	*c*-C_3H_2	CH_3NC	$HCOCH_3$	H_2C_6
CH^+	HCN	C_2H_2	CH_2CN	CH_3OH	NH_2CH_3	CH_2OHCHO
CN	HCO	CH_2D^+(?)	CH_4	CH_3SH	*c*-C_2H_4O	CH_2CHCHO
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	CH_2CHOH	
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO		
CP	HOC^+	HNCO	HCOOH	NH_2CHO		
CSi	H_2O	HNCS	H_2CHN	C_5N		
HCl	H_2S	$HOCO^+$	H_2C_2O	HC_4N		
KCl	HNC	H_2CO	H_2NCN			
NH	HNO	H_2CN	HNC_3			
NO	MgCN	H_2CS	SiH_4			
NS	MgNC	H_3O^+	H_2COH^+			
NaCl	N_2H^+	NH_3				
OH	N_2O	SiC_3				
PN	NaCN	C_4				
SO	OCS					
SO^+	SO_2					
SiN	*c*-SiC_2					
SiO	CO_2					
SiS	NH_2					
CS	H_3^+					
HF	SiCN					
SH	AlNC					
FeO(?)	SiNC					

Nine atoms	Ten atoms	Eleven atoms	Twelve atoms	Thirteen atoms
CH_3C_4H	CH_3C_5N(?)	HC_9N	$CH_3OC_2H_5$	$HC_{11}N$
CH_3CH_2CN	$(CH_3)_2CO$			
$(CH_3)_2O$	NH_2CH_2COOH			
CH_3CH_2OH	CH_3CH_2CHO			
HC_7N				
C_8H				

Table from A. Wootten (www.cv.nrao.edu/~awootten/allmols.html).

While the dominant molecular species in the ISM is H2, because it is a homonuclear linear molecule with no permanent dipole moment all of the low-lying energy levels are quadrupole transitions with small transition probabilities (A-values) and relatively high excitation energies. The high excitation energies mean that these transitions are only excited at high temperatures or in strong UV radiation fields (i.e., fluorescence). Thus the most abundant molecule in the ISM, carrying most of the mass and playing a key role in excitation, thermal balance, and gas-phase chemistry, is virtually invisible to direct observation.

As a consequence, most of what we know about interstellar molecules comes from observations of so- called “tracer” species, primarily CO which is observed in its J=1–0 rotational transition at λ=2.6 mm. This and other molecular species are observed as emission lines from pure rotational transitions at centimeter to millimeter wavelengths. Like we saw in the case with the HI 21-cm line, we must account for stimulated emission as well as collisional and radiative effects when deriving the line properties. Since the formation of molecular species like CO occurs under conditions favorable for H2 formation, we will try to estimate the amount of H2 from the observed amount of CO with the assistance of a few simplifying assumptions.

Giant molecular clouds (GMCs)

Vast assemblages of molecular gas with masses of 10^4–10^6 times the mass of the sun are called **Giant molecular clouds** (GMC). The clouds can reach tens of parsecs in diameter and have an average density of 10^2–10^3 particles per cubic centimetre (the average density in the solar vicinity is one particle per cubic centimetre). Substructure within these clouds is a complex pattern of filaments, sheets, bubbles, and irregular clumps.[4]

The densest parts of the filaments and clumps are called "molecular cores", whilst the densest molecular cores are, unsurprisingly, called "dense molecular cores" and have densities in excess of 10^4–10^6 particles per cubic centimeter. Observationally molecular cores are traced with carbon monoxide and dense cores are traced with ammonia. The concentration of dust within molecular cores is normally sufficient to block light from background stars such that they appear in silhouette as dark nebulae.[6]

GMCs are so large that "local" ones can cover a significant fraction of a constellation such that they are often referred to by the name of that constellation, e.g. the Orion Molecular Cloud (OMC) or the Taurus Molecular Cloud (TMC). These local GMCs are arrayed in a ring in the neighborhood of the sun coinciding with the Gould Belt.[7] The most massive collection of molecular clouds in the galaxy, the Sagittarius B2 complex, forms a ring around the galactic centre at a radius of 120 parsec. The Sagittarius region is chemically rich and is often used as an exemplar by astronomers searching for new molecules in interstellar space.[8]

Rotational Transitions

See Kwok Chapter 7.4.

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

$$I = \mu r_0^2$$

where μ 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.

Rotational Transitions

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,

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

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

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

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

where

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

Rotational Transitions

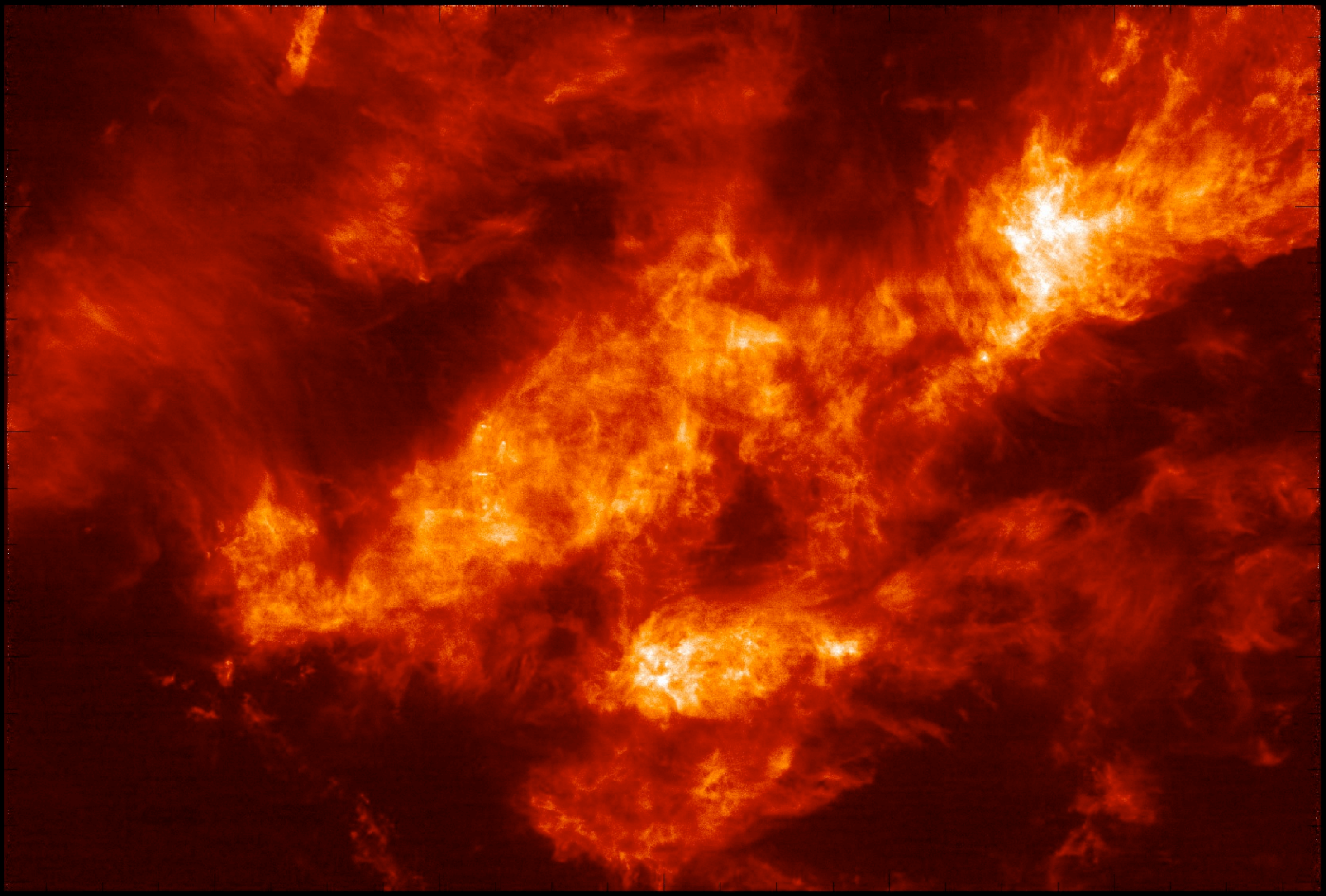
$$\nu_{ij} = 2B(J_j + 1)$$

where

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

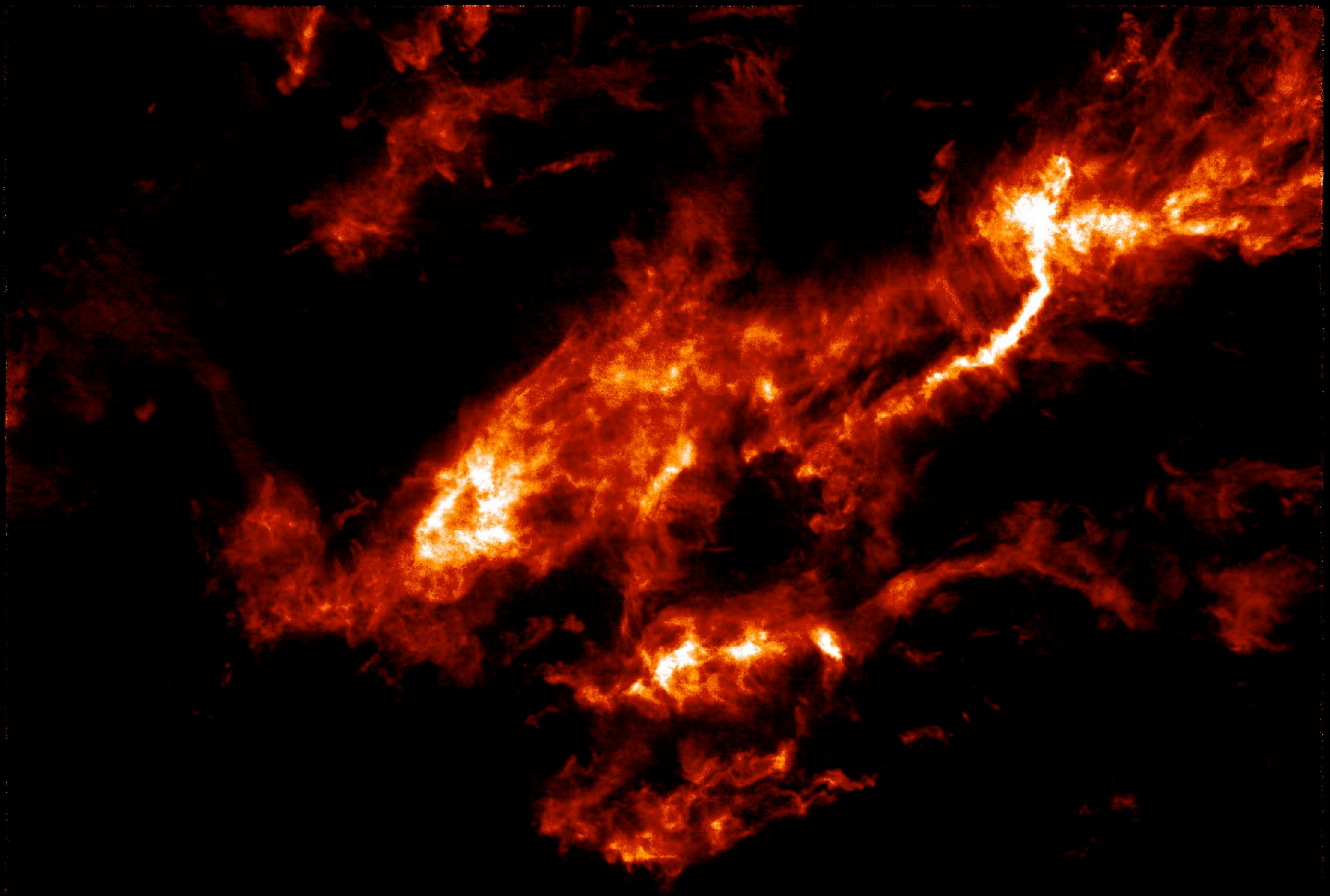
Note that heavier molecules will have lower energy rotational transitions. For instance the CO (1–0) line is at 115 GHz, while CH^+ has its ground state 418 GHz. Also note that molecules such as H_2, O_2 and N_2 have no electric-dipole moment because their centers of mass are also their centers of charge, and therefore have no electric-dipole rotational transitions.

Taurus Molecular Cloud in ^{12}CO



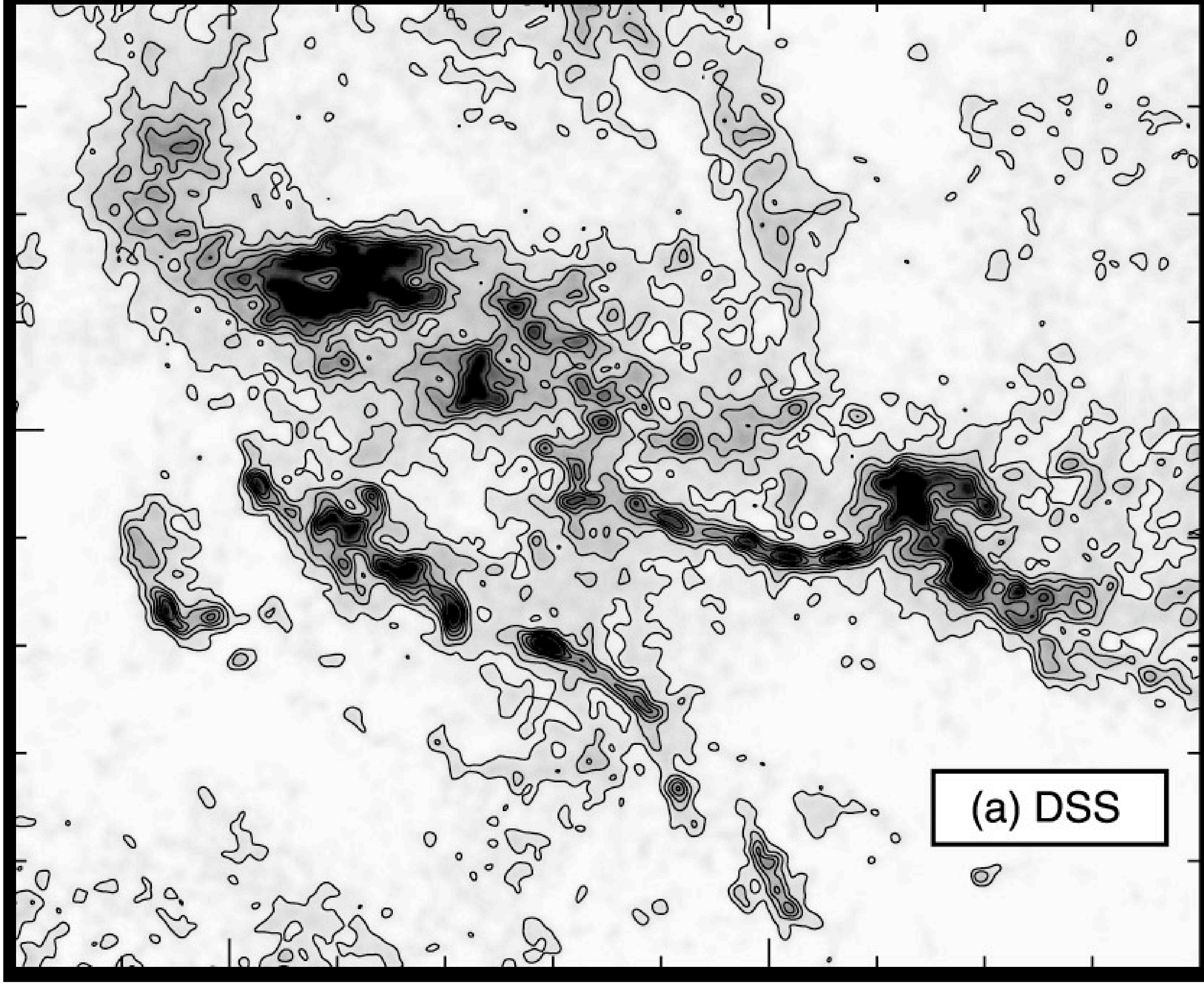
(Goldsmith et al.)

Taurus Molecular Cloud in ^{13}CO



(Goldsmith et al.)

Taurus Molecular Cloud in A_V



(Dobashi et al. 2005)

Temperature Measured by CO

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:

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

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

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

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

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.

Temperature Measured by CO

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 $^{12}C^{16}O$ (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.

Column Density Measured by CO

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

Column Density Measured by CO

Recall the equation for the total absorption coefficient (κ_ν),

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

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

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

Column Density Measured by CO

The optical depth is defined by

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

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

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

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

Column Density Measured by CO

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

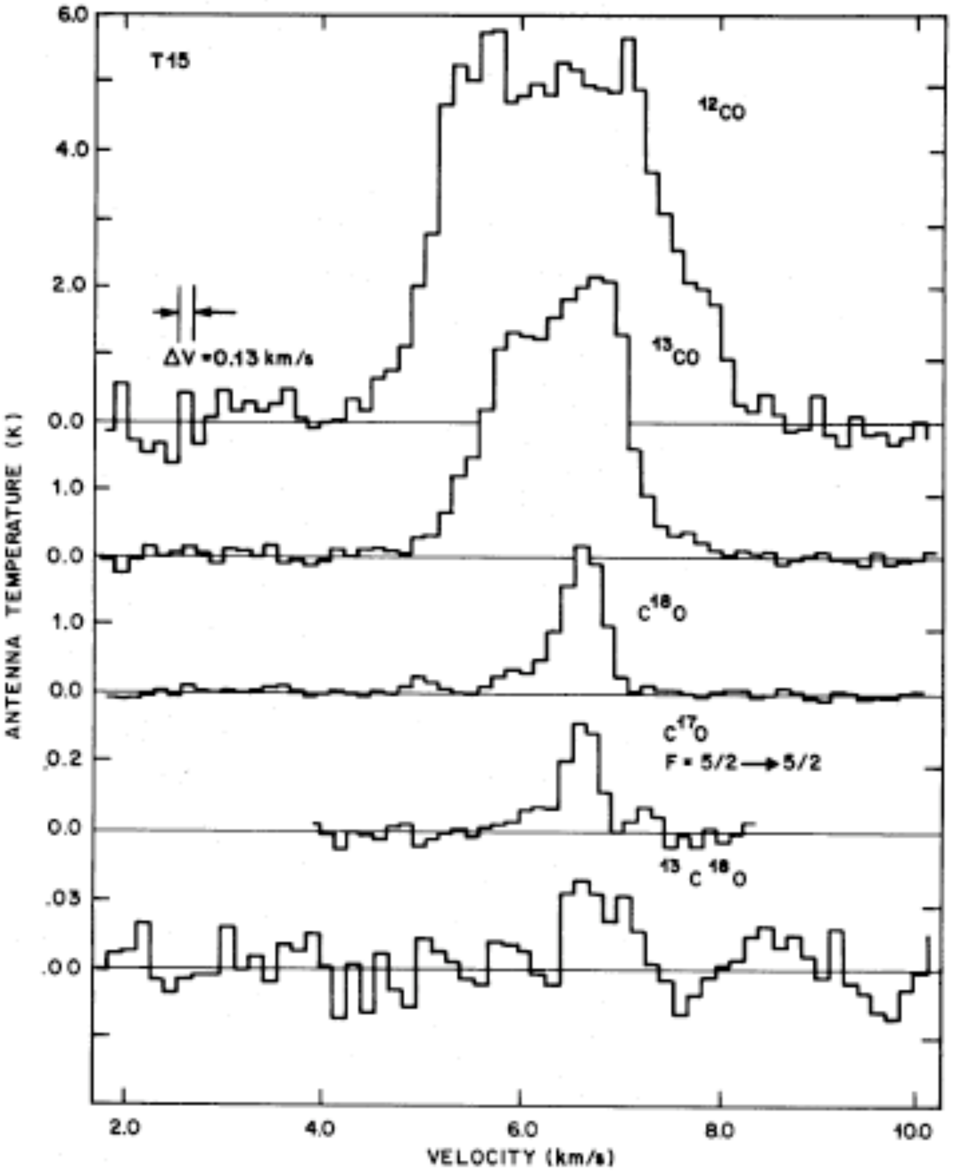
$$N_{13CO} = \frac{8\pi\nu^2\Delta\nu Q\tau}{c^2 A_{10}}\frac{g_0}{g_1}\left[1 - \exp\left(-\frac{T_o}{T_{ex}}\right)\right]^{-1}$$

where τ is the optical depth of the ^{13}C^{16}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.

Isotopologues of CO



(Frerking, Langer and Wilson, 1982)

Spectra taken in Taurus molecular cloud in a region with $A_V = 13.3$

Vibrational Transitions of Diatomic Molecules

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

$$E_v = (v + \frac{1}{2})hv_0$$

where v is the vibrational quantum number and

$$v_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

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

Vibrational Transitions of Diatomic Molecules

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

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

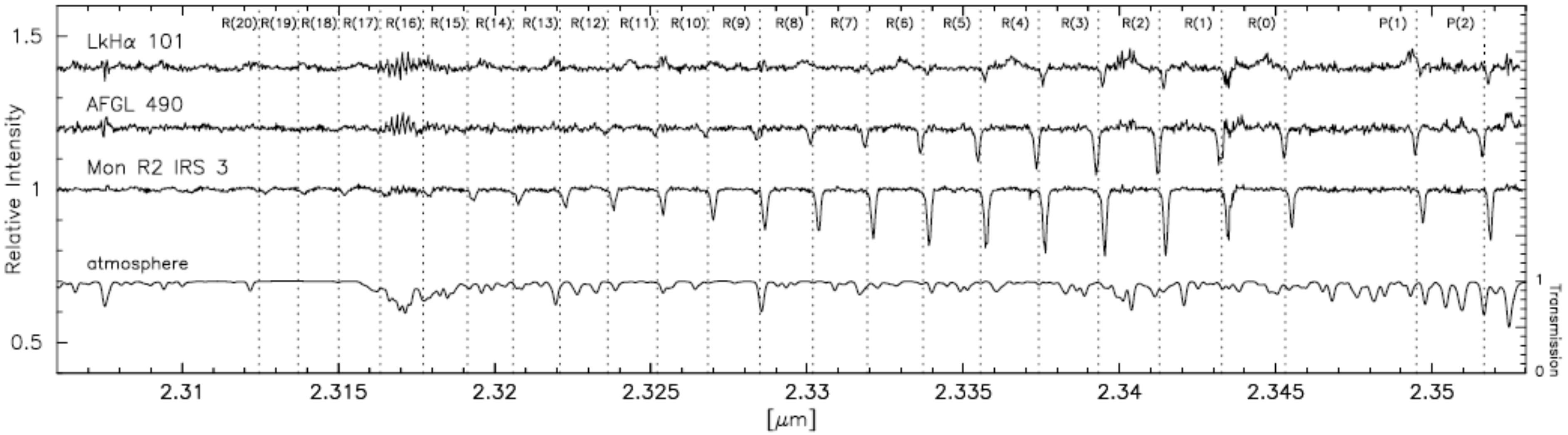
where

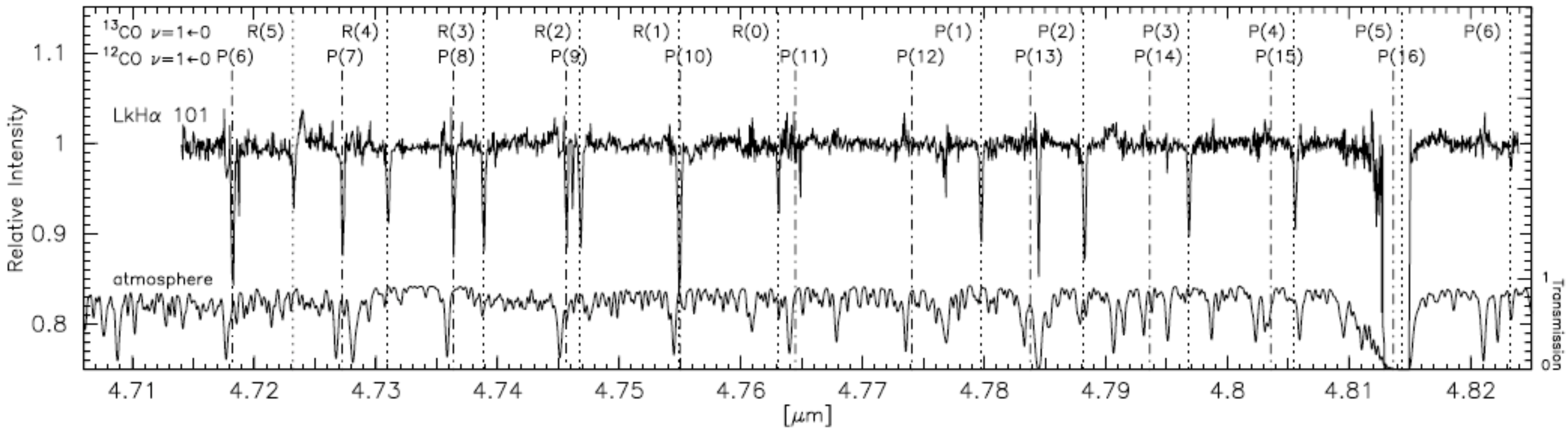
$$v = \sqrt{\frac{kr_0^2 + 6BJ(J+1)}{\mu r_0^2}}$$

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 $\Delta\nu = \pm 1$. The gound-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*.

Vibrational Bands of CO





(Goto et al. 2003)

H_2

The H_2 molecule has two identical nulei 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_2 has odd J values, and the *para* state of H_2 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 $\lambda < 2$ μm lines.

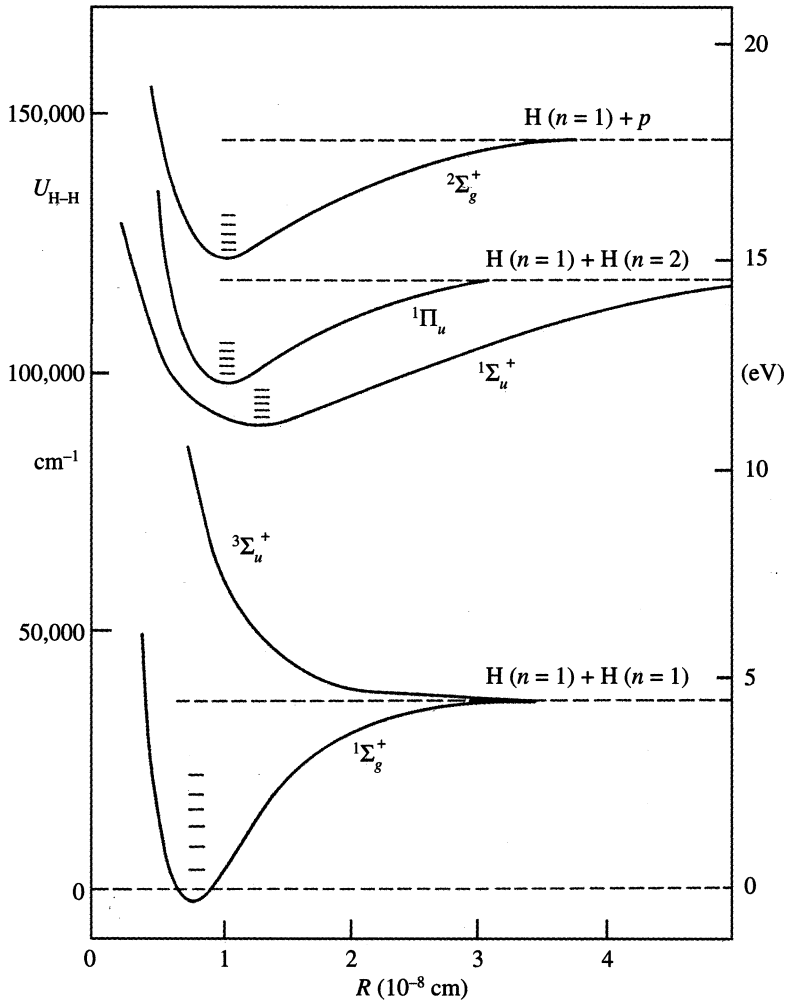


Figure 7.1

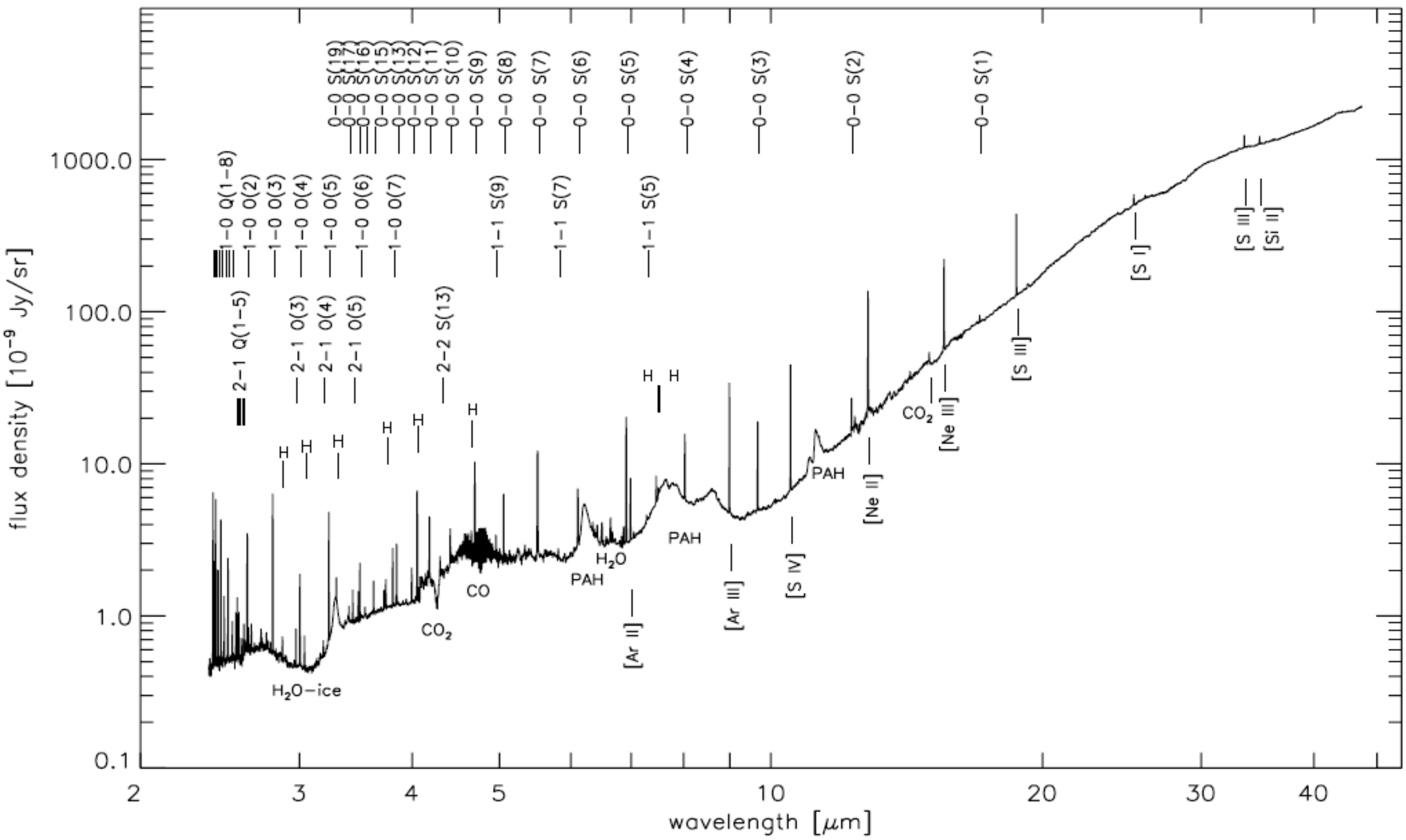
Energy diagram of the lower electronic states of H_2. The short horizontal lines in each of the bound states indicate the vibrational levels. The transitions from the ground state $^1\Sigma_g^+$ to the excited states $^1\Sigma_u^+$ and $^1\Pi_u$ are called Lyman and Werner bands, respectively. (Figure adapted from Watson, 1975, in *Atomic and Molecular Physics and the Interstellar Matter*, Les Houches, p. 177.)

H_2

H_2 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 μm. If the CO $v = 2 \rightarrow 0$ (~ 2.3 μm) vibrational bands are also seen in the same sources then one can derive the H_2 to CO abundance ratio.

Ground state rotational quadrupole transitions of H_2, 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 μm. These lines are only observable from space, but they are the best means of direct determination of the "low" temperature molecular hydrogen mass i nthe 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_2 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_2.

Vibrational Lines of H_2



(Rosenthal et al. 2000)

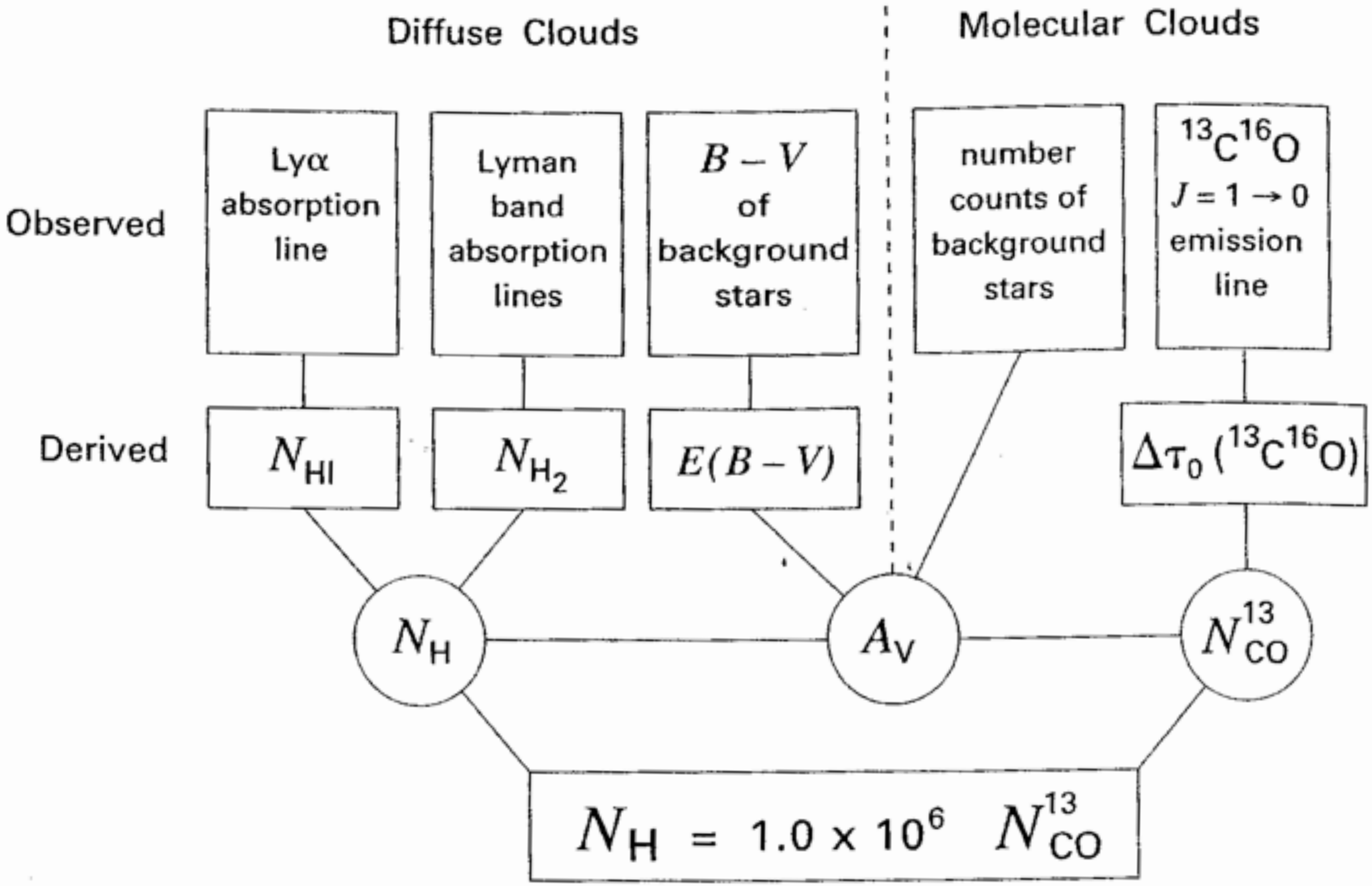


Figure 6.2 Steps in deriving the relationship between the $^{13}C^{16}O$ and the total hydrogen column densities.

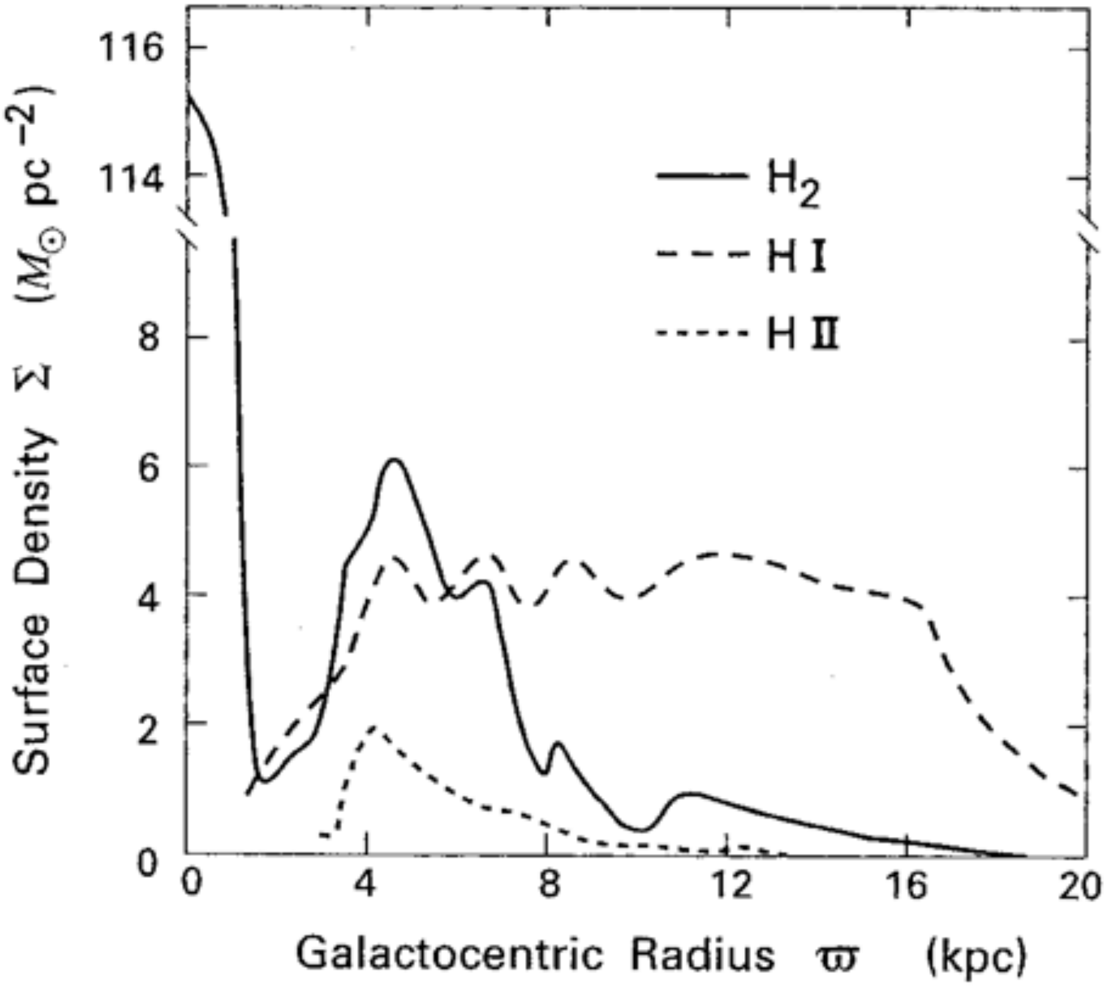


Figure 2.3 Galactic surface densities of H_2, HI, and HII gas. The densities are shown as a function of radial distance from the Galactic center. Note the high central peak of the molecular component. The ionized component shown is only that within HII regions.

Hyperfine Lines in Molecules

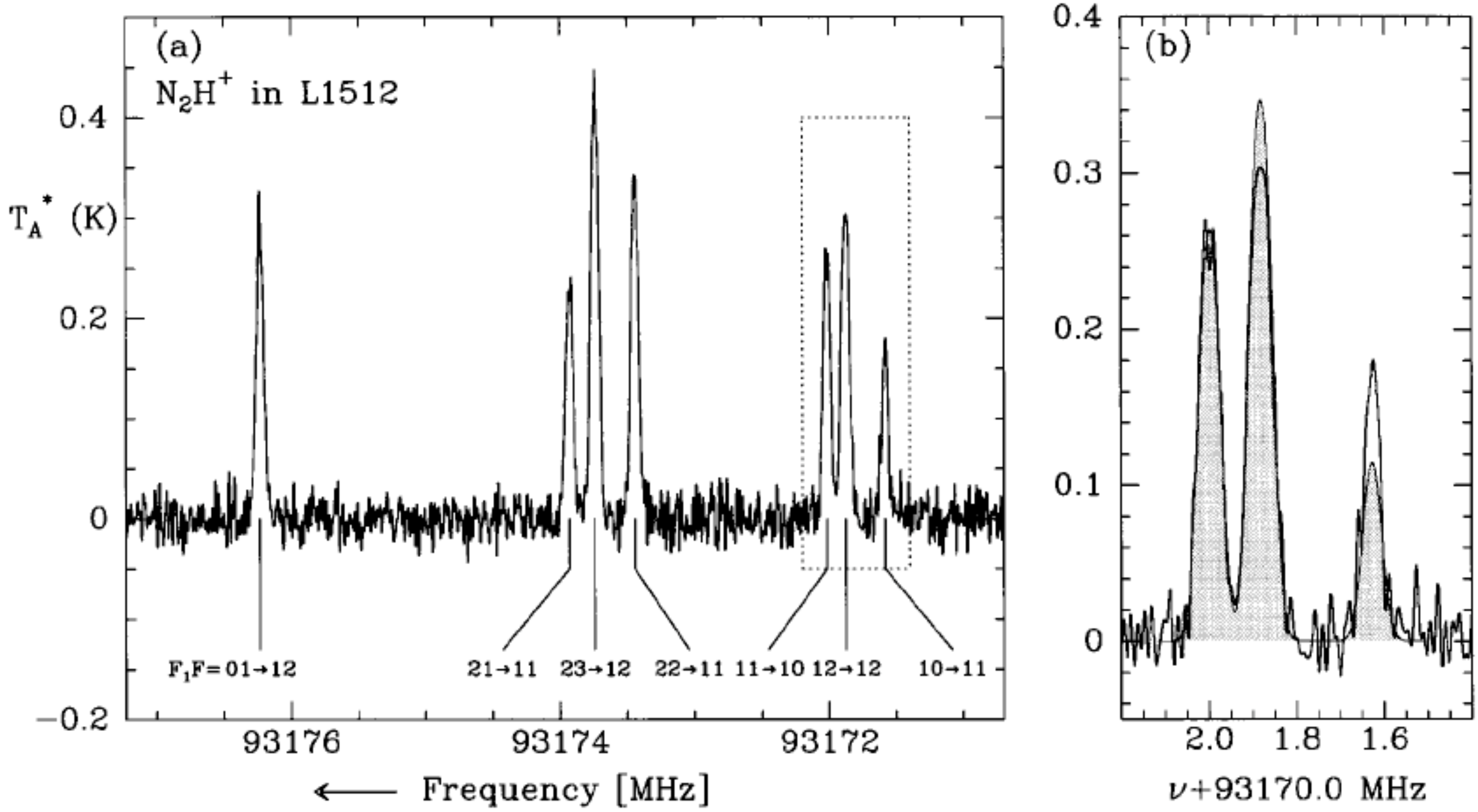
Nuclear spin can introduce hyperfine splittings in molecular transitions, as we already discussed in the atomic case. ^{14}N has a nuclear spin of 1, and the rotatinoal states of HCN are split into three hyperfine components corresponding to $F = J - 1, J, J + 1$. The relative intensities of the $F = 2 \rightarrow 1$, $F = 1 \rightarrow 1$ 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, N_2H^+ has hyperfine lines from each of the N atoms, and has 7 components with separations on the order of ~ 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}C^{16}O has no nuclear spin, some isotopes (e.g. ^{13}C and ^{17}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.

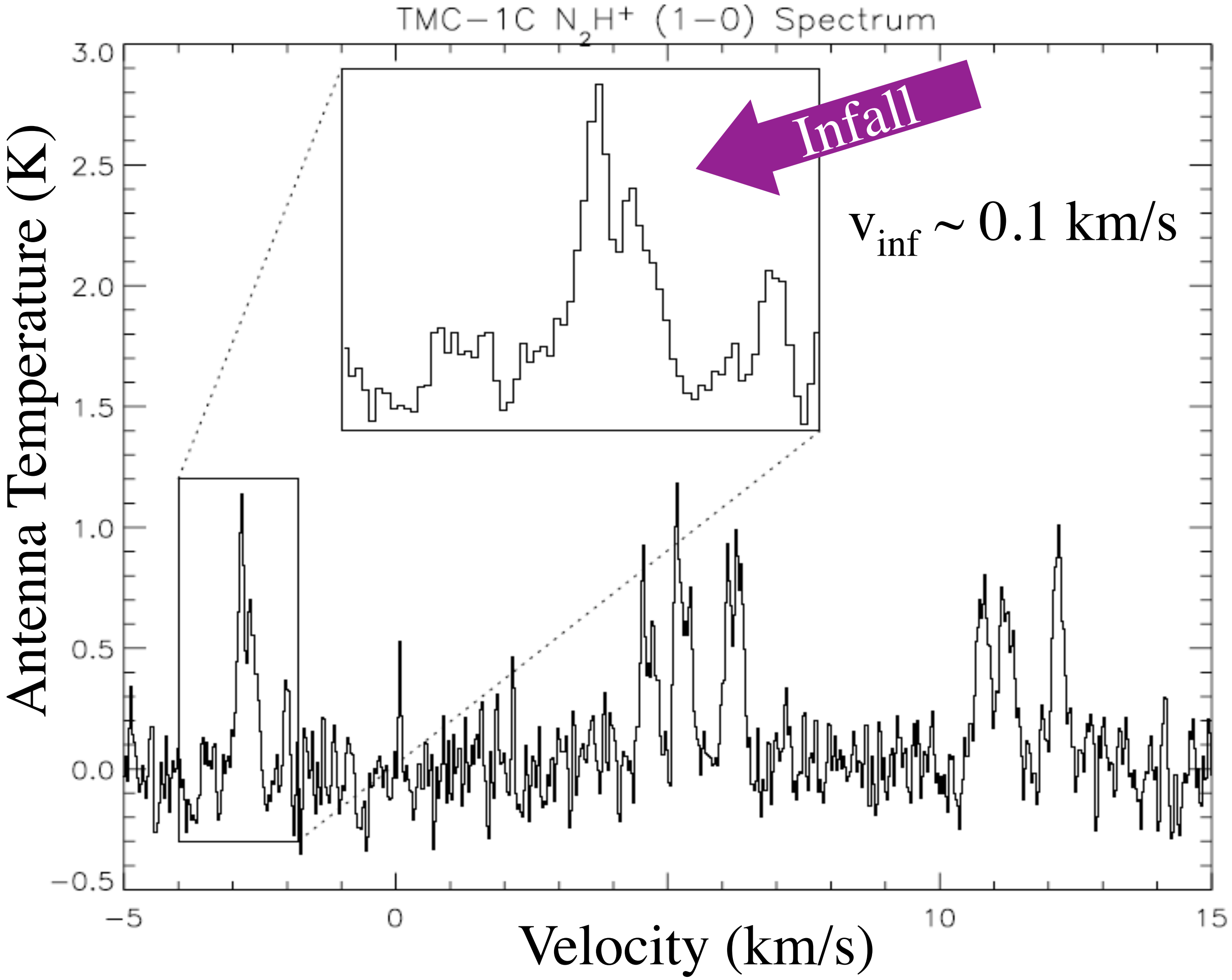
N_2H^+ Spectrum

(Caselli, Myers & Thaddeus, 1995)



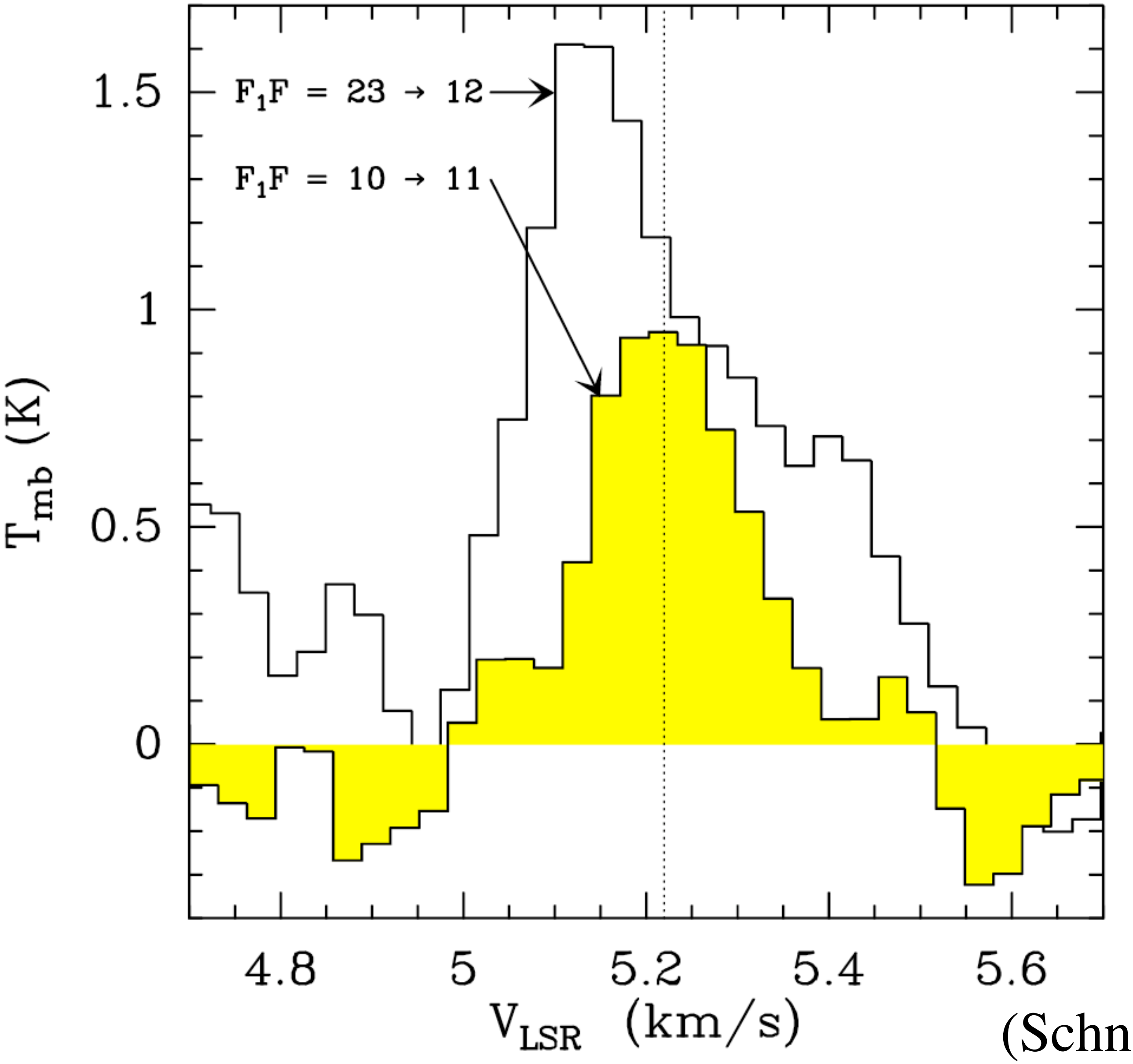
N_2H^+ Spectrum

(Schnee & Goodman, 2005)



$v_{inf} \sim 0.1$ km/s

N_2H^+ Infall



(Schnee et al. 2007b)

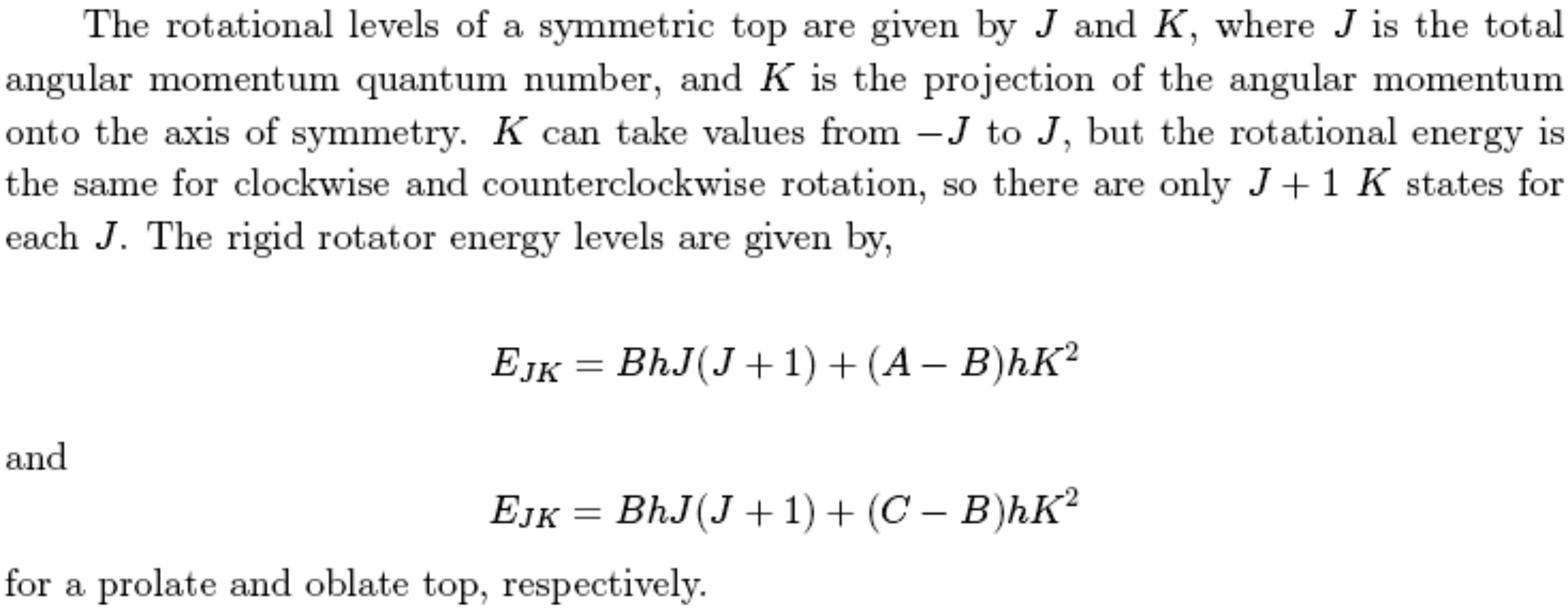
Symmetric Tops

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,

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

Symmetric Tops



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.

(N.B., these equations in Kwok (7.19) are in error)

Symmetric Tops

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 $2B$ is 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).

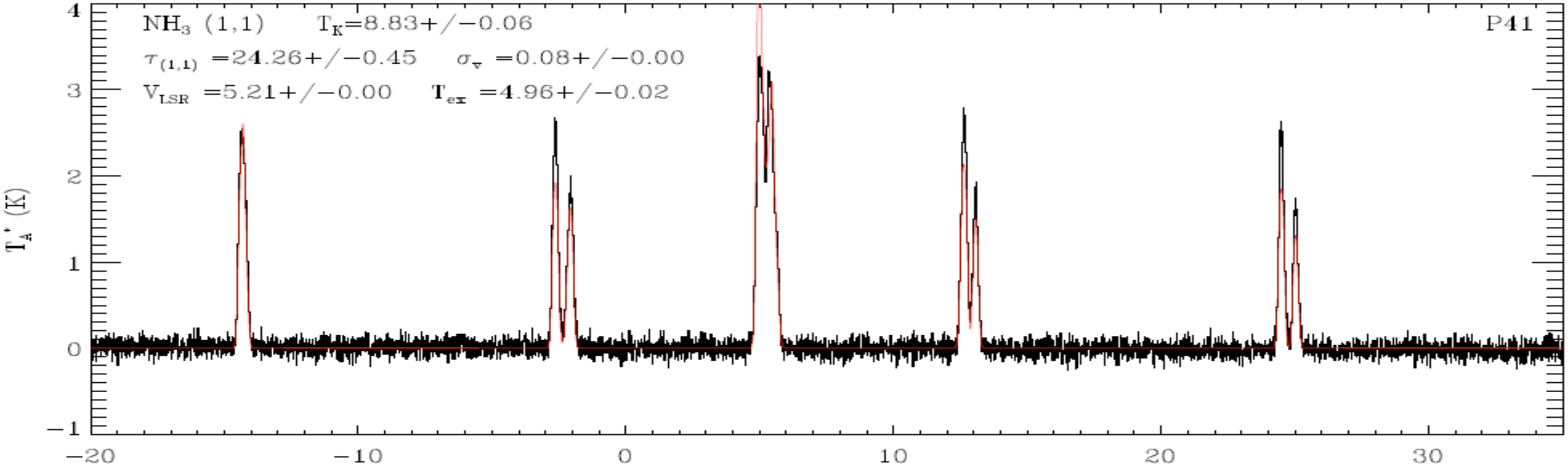
Symmetric Tops - NH_3

The ammonia (NH_3) molecule is an example of a symmetric top molecule. 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).

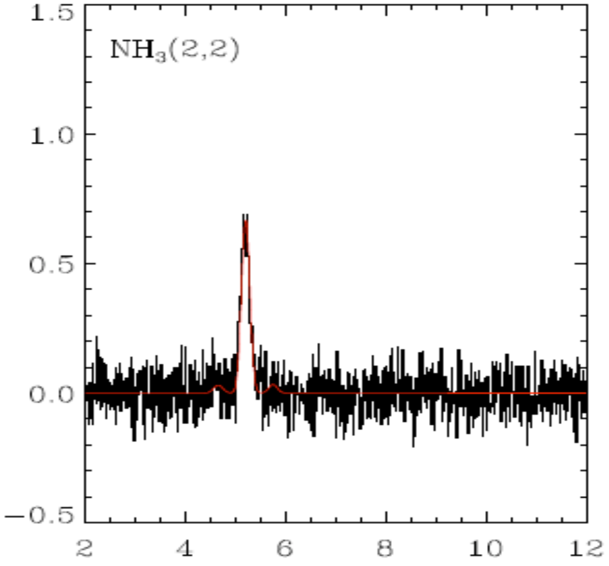
Because the energy separations for the low rotational levels is small, the inversion states can be easily excited. For instance, the NH_3 (J, K) (1,1) and (2,2) states are observed at 23.6945 and 23.7226 GHz. Each of the inversion lines is split into 18 hyperfine components due to interaction between 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 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.

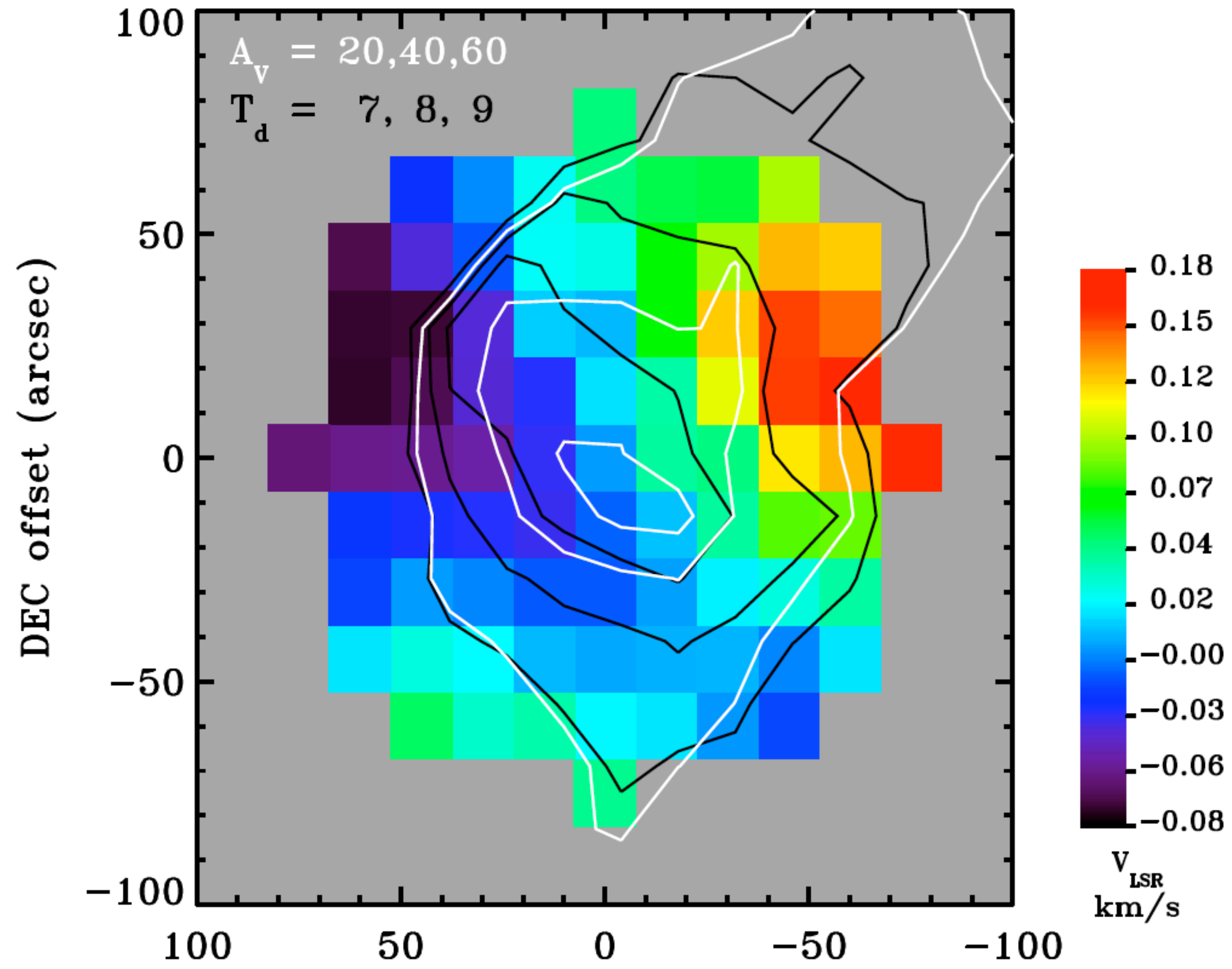
TMC-1C NH_3 Spectrum - GBT



(Schnee et al. in prep.)

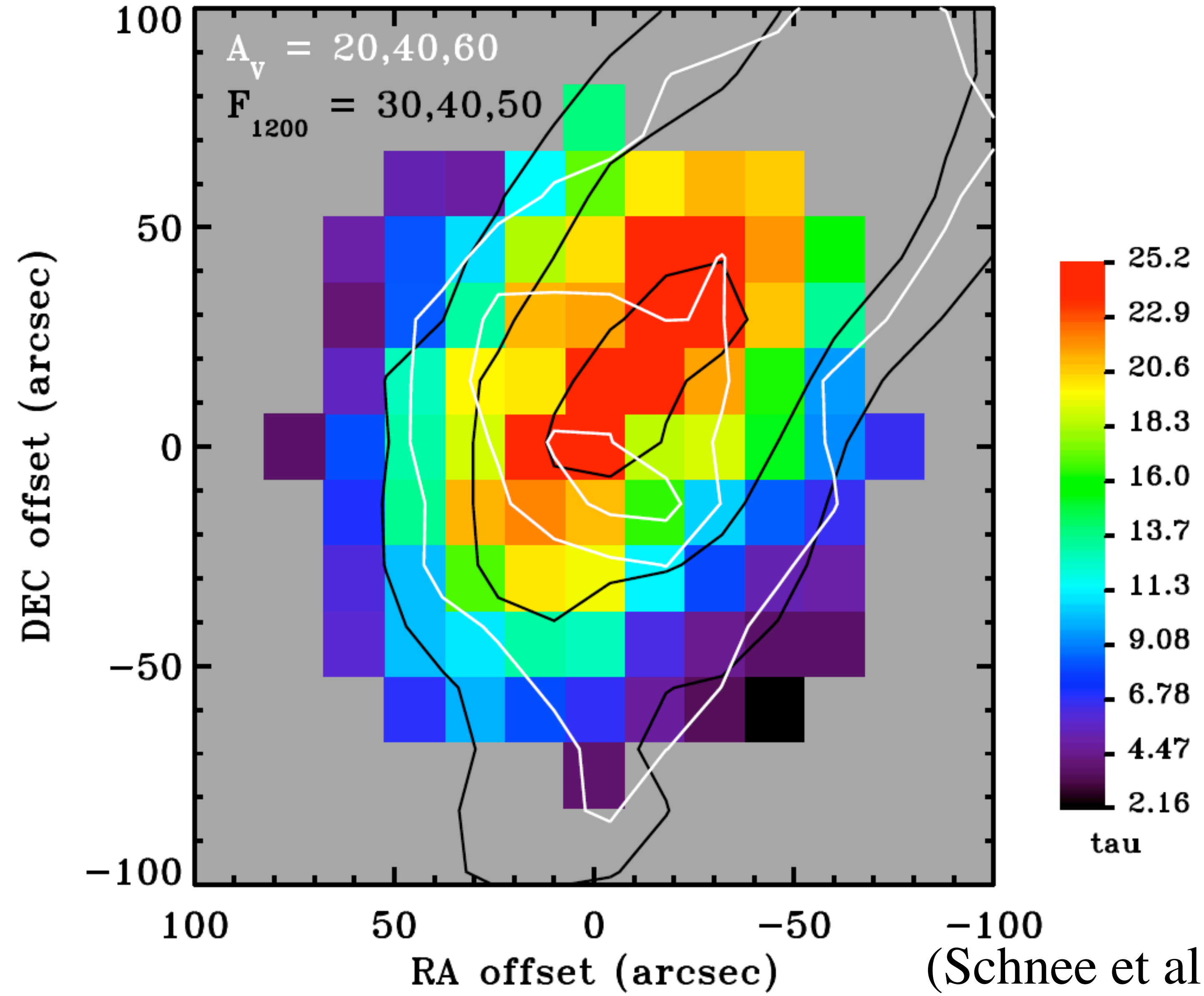


NH_3 Velocity Map - GBT



(Schnee et al. in prep.)

NH_3 Optical Depth Map - GBT



(Schnee et al. in prep.)

Asymmetric Tops

If none of the principal moments of intertia 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 quatities 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}.

Asymmetric Tops - H_2O

The rotational constants for H_2O 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, ..., 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 $2J + 1$.

Asymmetric Tops - H_2O

The selection rules are:
$\Delta J = 0, \pm 1$ and
$(K_{-1}, K_1) = {++} \leftrightarrow {--}$ 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* $(n_i g_j / n_j g_i > 1)$.

Asymmetric Tops - H_2O

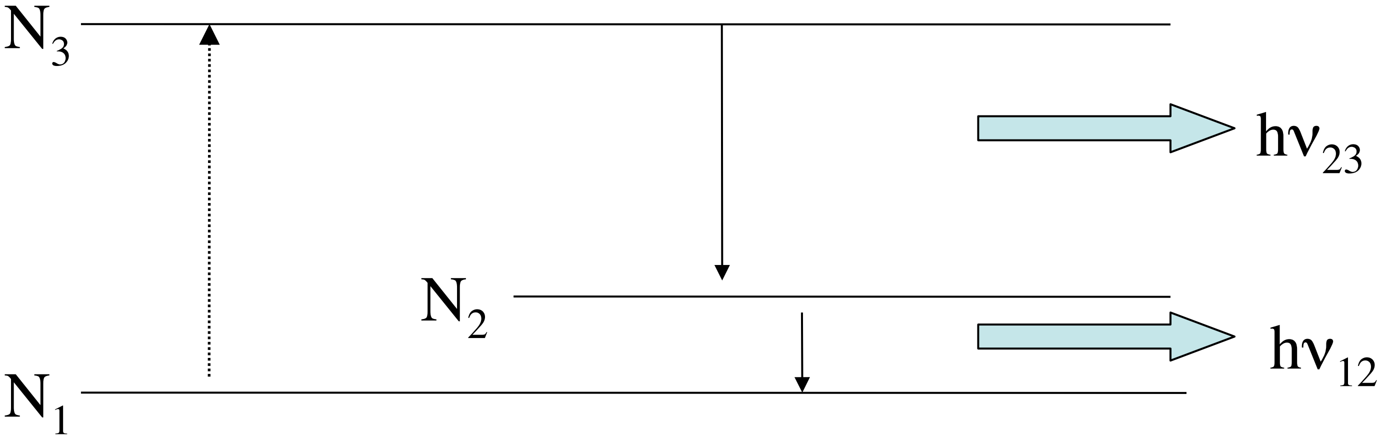
Recall (Kwok eq 5.15) that the atomic absorption coefficient is given by,

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

In a population inversion, the absorption coefficeint is negative, as is the optical depth. This results in an exponential increase of line intensity with path length, as each stimulated absoprtion will induce further stimulated emission. This is known as *masing*, and the intensities of maser lines are very bright and easy to detect.

Besides H_2O, other examples of masers are CH_3OH (similar to a symmetric top) and 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.

Schematic of a Maser



Energy Levels for *Ortho* H_2O

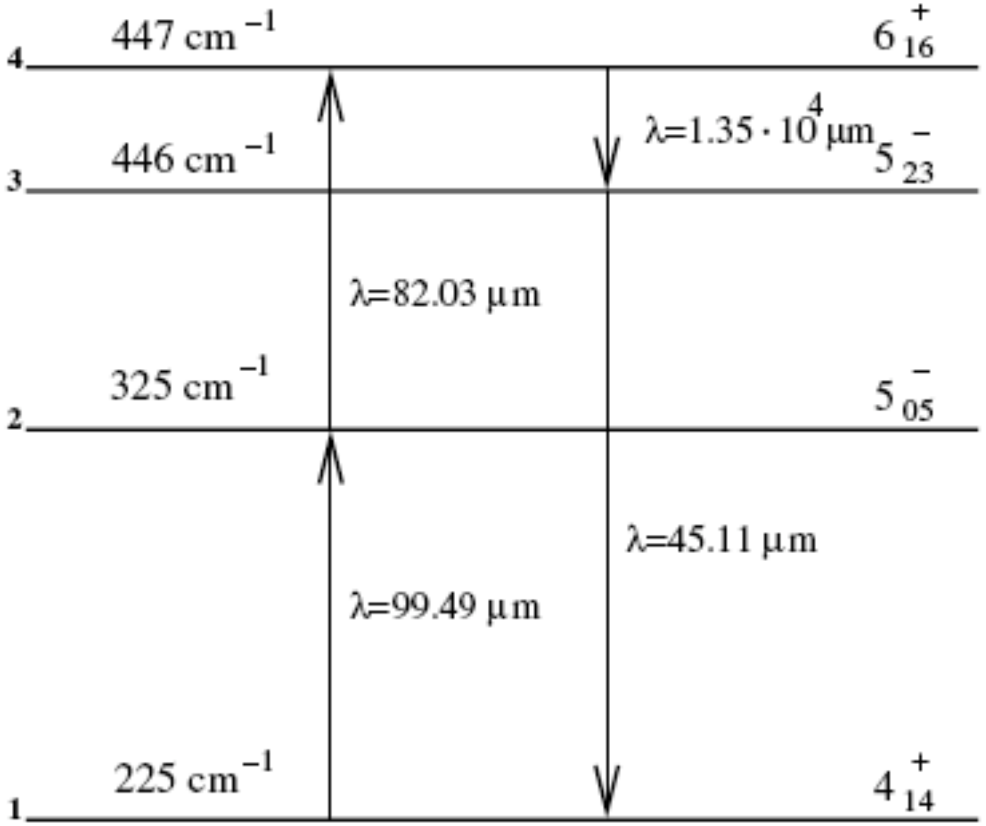
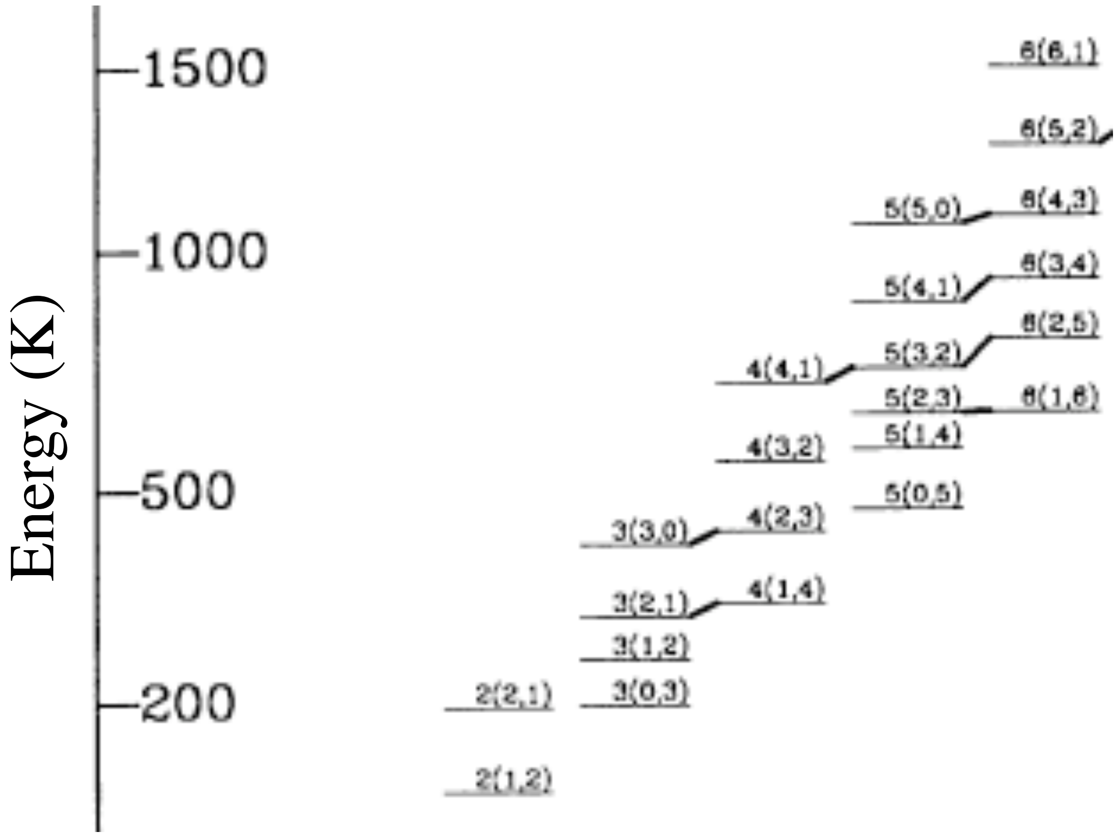


Fig. 1. A portion of the diagram of ortho-H_2O showing the rotational levels involved in the pumping of the $6_{16} \rightarrow 5_{23}$ maser.

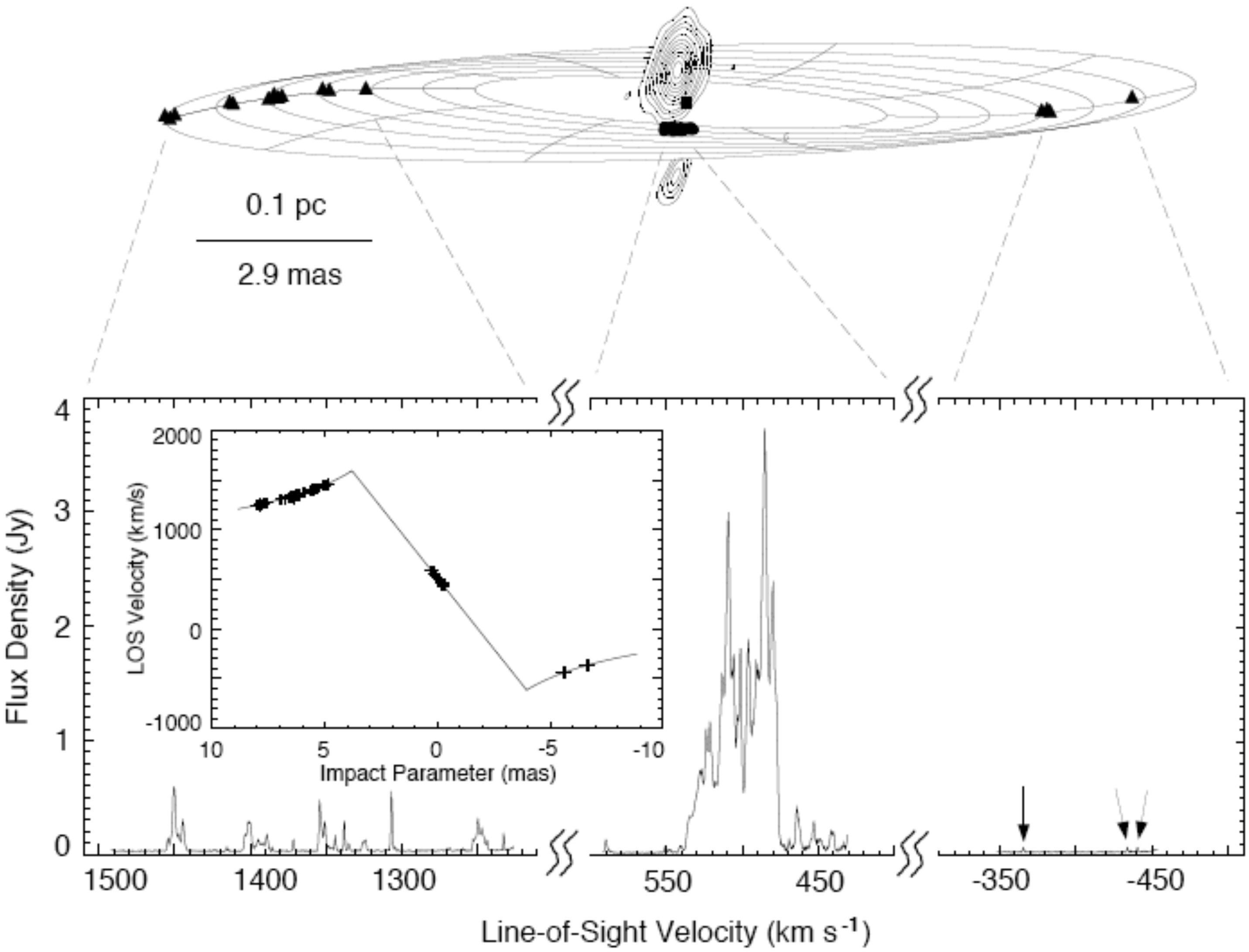
(Babkovskaia & Poutanen 2004)

Energy Levels for *Ortho* H_2O



(Neufeld & Melnick 2001)

NGC 4258



(Herrnstein et al. 1999)