HOW TO CALCULATE MOLECULAR COLUMN DENSITY

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ABSTRACT

The calculation of the molecular column density from molecular spectral (rotational or ro-vibrational) transition measurements is one of the most basic quantities derived from molecular spectroscopy. Starting from first principles where we describe the basic physics behind the radiative and collisional excitation of molecules and the radiative transfer of their emission, we derive a general expression for the molecular column density. As the calculation of the molecular column density involves a knowledge of the molecular energy level degeneracies, rotational partition functions, dipole moment matrix elements, and line strengths, we include generalized derivations of these molecule-specific quantities. Given that approximations to the column density equation are often useful, we explore the optically thin, optically thick, and low-frequency limits to our derived general molecular column density relation. We also evaluate the limitations of the common assumption that the molecular excitation temperature is constant, and address the distinction between beam- and source-averaged column densities. As non-LTE approaches to the calculation of molecular spectral line column density have become quite common, we summarize non-LTE models which calculate molecular cloud volume densities, kinetic temperatures, and molecular column densities. We conclude our discussion of the molecular column density with worked examples for C$^{18}$O, C$^{17}$O, N$_2$H$^+$, NH$_3$, and H$_2$CO. Ancillary information on some subtleties involving line profile functions, conversion between integrated flux and brightness temperature, the calculation of the uncertainty associated with an integrated intensity measurement, the calculation of spectral line optical depth using hyperfine or isotopologue measurements, the calculation of the kinetic temperature from a symmetric molecule excitation temperature measurement, and relative hyperfine intensity calculations for NH$_3$ are presented in appendices. The intent of this document is to provide a reference for researchers studying astrophysical molecular spectroscopic measurements.

Subject headings: ISM: molecules

1. INTRODUCTION

Molecular spectral line column densities are fundamental to the study of the physical and chemical conditions within dense molecular clouds. Chemical composition, molecular isomer and isotopomer ratios, molecular hydrogen column densities, and molecular volume densities are all based on a measure of the molecular column density. Past reviews and tutorials on this subject, including Genzel (1991), Evans et al (1991), Evans (1992), and Goldsmith & Langer (1999), along with spectroscopic textbooks such as Townes & Schawlow (1973), Gordy & Cook (1984), and Draine (2011) have provided an excellent basis upon which one can derive the molecular spectral line column density for a variety of dense molecular cloud environments. The intent of this tutorial is to provide students and scientists a general single reference point for the calculation of the molecular spectral line column density.

We have organized the document such that some basic background information is first provided to allow a contextual foundation to be lain for further calculations. This foundation includes a basic understanding of radiative transfer and statistical equilibrium (Sections 2 and 3), molecular degeneracy (Sections 5 and 6), partition functions (Section 7), line strength (Sections 8 and 9), and hyperfine structure (Section 10). The derivation of the most general form of the molecular spectral line column density is presented in Section 11. We also explore a number of commonly-used practical approximations to the calculation of the molecular spectral line column density in Section 12. As the calculation of the molecular spectral line column density normally assumes constant excitation temperature, we address the consequences of this assumption when non-LTE conditions are present in Section 12. We also summarize non-LTE approaches to the calculation of molecular cloud volume density, kinetic temperature, and molecular column density in Section 13.

Molecular cloud structure and its relationship to the spatial resolution of a measurement system affects the derivation of molecular spectral line column density. To quantify these effects we address the distinction between beam- and source-averaged column density in Section 14.

As worked examples are often illustrative for many astrophysical calculations, we provide step-by-step derivations of the molecular column density for several representative molecules; C$^{18}$O, C$^{17}$O, N$_2$H$^+$, NH$_3$, and...
H$_2$CO in Section 13. Appendices provide ancillary information on some subtleties often encountered when calculating molecular spectral line column density, including line profile functions (Appendix A), conversion between integrated flux and brightness temperature (Appendix B), the calculation of the uncertainty associated with an integrated intensity measurement (Appendix C), the calculation of spectral line optical depth using hyperfine or isotopologue measurements (Appendix D), the calculation of the kinetic temperature from a symmetric molecule excitation temperature measurement (Appendix E), and relative hyperfine intensity calculations for NH$_3$ (Appendix F).

2. RADIATIVE AND COLLISIONAL EXCITATION OF MOLECULES

When the energy levels of a molecule are in statistical equilibrium, the rate of transitions populating a given energy level is balanced by the rate of transitions which depopulate that energy level. For a molecule with multiple energy levels statistical equilibrium can be written as:

$$n_i \sum_j R_{ij} = \sum_j n_j R_{ji},$$

where $n_i$ and $n_j$ are the populations of the energy levels $i$ and $j$ and $R_{ij}$ and $R_{ji}$ are transition rates between levels $i$ and $j$. The transition rates contain contributions from:

- Spontaneous radiative excitation ($A_{ij}$)
- Stimulated radiative excitation and de-excitation ($R_{ij} \equiv n_i B_{ij} \int_0^\infty J_\nu \phi_{ij}(\nu) d\nu$)
- Collisional excitation and de-excitation ($n_{\text{collider}} C_{ij}$)

where $\phi_{ij}(\nu)$ is the line profile function and $J_\nu$ is defined as the integral of the specific intensity $I_\nu$ over the source of emission:

$$J_\nu \equiv \frac{1}{4\pi} \int I_\nu d\Omega.$$

Our statistical equilibrium equation then becomes:

$$n_i \left[ \sum_j \left( n_{\text{collider}} C_{ij} + B_{ij} \int_0^\infty J_\nu \phi_{ij}(\nu) d\nu \right) + \sum_j A_{ij} \right] = \sum_j n_j \left[ n_{\text{collider}} C_{ij} + B_{ji} \int_0^\infty J_\nu \phi_{ji}(\nu) d\nu \right] + \sum_{j > i} n_j A_{ji}.$$  \hspace{1cm} (3)

For a two-level system with $i$ defined as the lower energy level $l$ and $j$ defined as the upper energy level $u$, $\sum_{j < i} A_{ij} = 0$ and the statistical equilibrium equation (Equation 3) becomes:

$$n_l \left( n_{\text{collider}} C_{lu} + B_{lu} \int_0^\infty J_\nu \phi_{lu}(\nu) d\nu \right) = n_u \left( n_{\text{collider}} C_{ul} + B_{ul} \int_0^\infty J_\nu \phi_{ul}(\nu) d\nu + A_{ul} \right).$$  \hspace{1cm} (4)

As hydrogen ($H$) is the most abundant atom in the interstellar medium, and in dense molecular clouds most of the $H$ is in molecular form ($H_2$), $n_{\text{collider}}$ is usually assumed to be $n(H_2)$.

At this point we can derive the Einstein relations $A_{ul}$, $B_{ul}$, and $B_{lu}$ by considering only radiative excitation ($C_{lu} = C_{ul} = 0$) and complete redistribution over the line profile ($\phi_{lu}(\nu) = \phi_{ul}(\nu)$). Physically, this means that emitted and absorbed photons are completely independent. Equation 4 then becomes:

$$n_l B_{lu} \int_0^\infty J_\nu \phi_{lu}(\nu) d\nu = n_u B_{ul} \int_0^\infty J_\nu \phi_{ul}(\nu) d\nu + n_u A_{ul}$$  \hspace{1cm} (5)

For a system in thermal equilibrium, the relative level populations follow the Boltzmann distribution:

$$\frac{n_u}{n_l} = \frac{g_u}{g_l} \exp \left( -\frac{h\nu}{kT} \right),$$  \hspace{1cm} (6)

and the radiation field $J_\nu$ is described by the Planck Function $B_\nu(T)$:

$$B_\nu(T) \equiv \frac{2h\nu^3}{c^2} \left[ \exp \left( \frac{h\nu}{kT} \right) - 1 \right]^{-1}.$$  \hspace{1cm} (7)

Substituting Equations 4 and 5 into Equation 3 (which eliminates the line profile function $\phi_{lu}$) yields, after some rearrangement:

$$\left( \frac{c^2}{2h\nu^3} A_{ul} - \frac{g_l}{g_u} B_{lu} \right) \left[ \exp \left( \frac{h\nu}{kT} \right) - 1 \right] = \frac{g_l}{g_u} B_{lu} + B_{ul},$$  \hspace{1cm} (8)

which implies that:

$$g_l B_{lu} = g_u B_{ul}$$  \hspace{1cm} (9)

$$A_{ul} = \frac{2h\nu^3}{c^2} B_{ul}.$$  \hspace{1cm} (10)

For dipole emission, the spontaneous emission coefficient $A_{ul}$ can be written in terms of the dipole matrix element $|\mu_{ul}|^2$ as:

$$A_{ul} \equiv \frac{64\pi^4 \nu^3}{3hc^3} |\mu_{ul}|^2.$$  \hspace{1cm} (11)

3. RADIATIVE TRANSFER

The radiative transfer equation, ignoring scattering processes (such as those involving electrons or dust) is defined as follows (see Spitzer (1978) or Draine (2011) for details):

$$\frac{dI_\nu}{ds} = -\kappa_\nu I_\nu + j_\nu$$  \hspace{1cm} (12)
Where

\[ s \equiv \text{Path of propagation along the line of sight} \]
\[ I_\nu \equiv \text{Specific Intensity} \]
\[ \kappa_\nu \equiv \text{Absorption Coefficient} \]
\[ = \frac{h\nu}{4\pi} \left( n_1 B_{1\nu} - n_u B_{u\nu} \right) \phi_\nu \]
\[ = \frac{c^2}{8\pi\nu^2} g_\nu A_{ul} \left( 1 - \frac{g_\nu n_u}{g_u n_1} \right) \phi_\nu \]
\[ j_\nu \equiv \text{Emission Coefficient} \]
\[ = \frac{h\nu}{4\pi} A_{ul} n_u, \]

Since we generally do not know what the propagation path is for our measured radiation it is convenient to change independent variables from pathlength \( s \) to “optical depth” \( \tau_\nu \), which is defined as:

\[ d\tau_\nu \equiv \kappa_\nu ds, \]

where we use the convention adopted by Draine (2011) that the radiation propagates in the direction of increasing optical depth. Switching variables from \( s \) to \( \tau_\nu \) in our radiative transfer equation (Equation 12) results in the following radiative transfer equation:

\[ dI_\nu = S_\nu d\tau_\nu - I_\nu d\tau_\nu, \]

where we define the Source Function \( S_\nu \):

\[ S_\nu \equiv \frac{j_\nu}{\kappa_\nu}. \]

By multiplying both sides of Equation 17 by the “integrating factor” \( e^{\tau_\nu} \), we can integrate the radiative transfer equation from a starting point where \( \tau_\nu = 0 \) and \( I_\nu = I_\nu(0) \) to find that:

\[ e^{\tau_\nu} \left( dI_\nu + I_\nu d\tau_\nu \right) = e^{\tau_\nu} S_\nu d\tau_\nu \]
\[ e^{\tau_\nu} I_\nu - I_\nu(0) = \int_0^{\tau_\nu} S_\nu d\tau' \]
\[ I_\nu = I_\nu(0) e^{-\tau_\nu} + \int_0^{\tau_\nu} \exp \left[ - (\tau_\nu - \tau') \right] S_\nu d\tau'. \]

Equation 19 is a completely general solution to the equation of radiative transfer (again, assuming that scattering is neglected). It defines the intensity measured by the observer \( I_\nu \) as the sum of the background intensity \( (I_\nu(0)) \) attenuated by the interstellar medium \( \exp \left[ - (\tau_\nu) \right] \) plus the integrated emission \( (S_\nu d\tau') \) attenuated by the effective absorption due to the interstellar medium between the point of emission and the observer \( \exp \left[ - (\tau_\nu - \tau') \right] \).

For an infinitely large medium the radiation field would be defined as blackbody: \( I_\nu = B_\nu \). We further assume that the medium through which the radiation is traveling is uniform at an excitation temperature \( T_{ex} \), defined as:

\[ T_{ex} = \frac{h\nu/k}{\ln \left( \frac{n_1}{n_u g_\nu} \frac{g_u}{g_\nu} \right)}, \]

where \( n \) is the density \((\text{cm}^{-3})\) in the upper \((u)\) or lower \((l)\) energy level for a transition with frequency \( \nu \). The source function \( S_\nu \) is equivalent to the Planck Function at temperature \( T_{ex} \) (Equation 7): \( S_\nu = B_\nu(T_{ex}) \). This condition is sometimes referred to as “local thermodynamic equilibrium” (LTE). Equation 19 becomes:

\[ I_\nu = I_\nu(0) e^{-\tau_\nu} + \int_0^{\tau_\nu} \exp \left[ -(\tau_\nu - \tau') \right] B_\nu(T_{ex}) d\tau'. \]

If we further assume that \( T_{ex} \) is a constant, Equation 21 becomes:

\[ I_\nu = I_\nu(0) \exp(-\tau_\nu) + B_\nu(T_{ex}) \left[ 1 - \exp(-\tau_\nu) \right]. \]

Molecular spectral line measurements involve differentiating the measured intensity toward a reference position which contains only background intensity from that measured towards a molecular line source position:

\[ \Delta I_\nu \equiv I_\nu - I_\nu(0) \]
\[ = I_\nu(0) \exp(-\tau_\nu) + B_\nu(T_{ex}) \left[ 1 - \exp(-\tau_\nu) \right] - I_\nu(0) \]
\[ = B_\nu(T_{ex}) - B_\nu(T_{bg}) \left[ 1 - \exp(-\tau_\nu) \right]. \]

In many cases the specific intensity \( I_\nu \) is replaced by the Rayleigh-Jeans Equivalent Temperature, which is the equivalent temperature of a black body at temperature \( T \):

\[ J_\nu(T) \equiv \frac{h\nu}{\exp \left( \frac{h\nu}{kT} \right) - 1}. \]

If we further define the Radiation Temperature \( T_R \) as follows:

\[ T_R \equiv \frac{c^2}{2k\nu^2} \Delta I_\nu, \]

we can relate \( B_\nu(T) \) and \( J_\nu(T) \) as follows:

\[ \frac{c^2}{2k\nu^2} B_\nu(T) = J_\nu(T). \]

We can write our radiative transfer equation in a form which involves the observable Source Radiation Temperature \( T_R \) derived from a differencing measurement:

\[ T_R = f \left[ J_\nu(T_{ex}) - J_\nu(T_{bg}) \right] \left[ 1 - \exp(-\tau_\nu) \right], \]

where we have introduced an extra factor \( f \) which is the fraction of the spatial resolution of the measurement filled by the source (sometimes called the “filling factor”). See Ulich & Haus (1976) for a complete derivation of the source radiation temperature for the case of a single antenna position switched measurement.

4. COLUMN DENSITY

In order to derive physical conditions in the interstellar medium it is often useful to measure the number of molecules per unit area along the line of sight. This quantity, called the “column density”, is basically a first-step to deriving basic physical quantities such as spatial density, molecular abundance, and kinetic temperature. Using the two-energy level system defined above, we can express the column density as the number of molecules in energy level \( u \) integrated over the pathlength \( ds \):

\[ N_u \equiv \int n_u ds. \]
Since we want to use our molecular spectral line measurements to calculate the molecular column density, which will ultimately involve the radiative transfer properties of the molecular spectral line measured, we can use the definition of the optical depth (Equation 14), the definition of the absorption coefficient \( \kappa \) (Equation 14), and the Boltzmann equation for statistical equilibrium (Equation 1), the definition of the spontaneous emission coefficient \( A_{ul} \) (Equation 14), and our definition of the column density (Equation 28) to relate \( \tau_\nu \) to the number of molecules in the upper energy state \( N_u \):

\[
\tau_\nu = \frac{c^2}{8\pi\nu^3} g_u \phi_\nu \int ds' n_u(s') \left( 1 - \frac{g_l n_l(s')}{g_u n_u(s')} \right) = \frac{c^2}{8\pi\nu^3} g_u A_{ul} \phi_\nu \left( 1 - \frac{g_l N_u}{g_u N_l} \right) = \frac{c^2}{8\pi\nu^2} \left[ \int \exp \left( \frac{h\nu}{kT} \right) - 1 \right] A_{ul} \phi_\nu N_u = \frac{8\pi^3 |\mu_{ul}|^2}{3hc} \left[ \int \exp \left( \frac{h\nu}{kT} \right) - 1 \right] \phi_\nu N_u,
\]

where in the last step we have integrated over the line profile such that \( \int \phi_\nu = 1 \). Rearranging and converting our frequency axis to velocity (\( \frac{dv}{d\nu} = \frac{dc}{d\nu} \)) in Equation (29) we get an expression for the column density of molecules in the upper transition state (\( N_u \)):

\[
N_u = \frac{3h}{8\pi^3 |\mu_{ul}|^2} \left[ \int \exp \left( \frac{h\nu}{kT} \right) - 1 \right]^{-1} \int \tau_\nu dv. \tag{30}
\]

At this point we have our basic equation for the number of molecules in the upper energy state \( u \) of our two-level system. In order to relate this to the total molecular column density as measured by the intensity of a transition at frequency \( \nu \), we need to relate the number of molecules in the upper energy level \( u \) (\( N_u \)) to the total population of all energy levels in the molecule \( N_{tot} \). Assuming detailed balance at a constant temperature defined by the excitation temperature \( T_{ex} \), we can relate these two quantities as follows:

\[
\frac{N_{tot}}{N_u} = \frac{Q_{rot}}{g_u} \exp \left( \frac{E_u}{kT_{ex}} \right), \tag{31}
\]

where we have introduced the “rotational partition function” \( Q_{rot} \), a quantity that represents a statistical sum over all rotational energy levels in the molecule (see Section 4) and \( g_u \) the degeneracy of the energy level \( u \). Substituting for \( N_u \) in Equation (31) the total molecular column density becomes:

\[
N_{tot} = \frac{3h}{8\pi^3 |\mu_{ul}|^2} Q_{rot} g_u \exp \left( \frac{E_u}{kT_{ex}} \right) \times \left[ \exp \left( \frac{h\nu}{kT_{ex}} \right) - 1 \right]^{-1} \int \tau_\nu dv. \tag{32}
\]

In the following we show how to calculate the level degeneracy \( g_u \) (Section 3), the rotational partition function \( Q_{rot} \equiv \sum g_i \exp \left( -\frac{E_i}{kT} \right) \) (Section 7), the dipole matrix element \( |\mu_{ul}|^2 \) and associated line strength \( S \) and dipole moment \( \mu \) (such that \( |\mu_{ul}|^2 = S\mu^2 \); Section 5). For absorption lines where the integral of the optical depth over velocity may be derived from a spectrum, Equation (32) may be used directly to determine the total column density. For emission lines, the integral over optical depth is typically converted to an integrated intensity \( \int T dv \) (see Section 11). We derive several commonly-used approximations to Equation (32), including optically thin, optically thick, and the Rayleigh-Jeans approximation in Section 11. We also evaluate the limitations of the common assumption that the molecular excitation temperature is constant (Section 12), summarize non-LTE models of the molecular column density (Section 13), and the distinction between beam- and source-averaged column density (Section 14). We then close this discussion of molecular column density by working through several example calculations (Section 15). We also discuss some minor issues related to the assumed line profile function (Appendix A), the relationship between integrated fluxes and brightness temperatures (Appendix B), and the uncertainty associated with an integrated intensity measurement (Appendix C) in the appendices. In a calculation which utilizes the column density calculation formalism presented below, Appendix D describes the standard three-level model for low-temperature NH\(_3\) excitation often used to derive the kinetic temperature from measurements of the (1,1) and (2,2) inversion transitions of that molecule.

5. DEGENERACIES

For rotational molecular transitions the total degeneracy for an energy level of a transition is given by the product of rotational \((g_J)\) and spin \((g_I)\) degeneracies:

\[
g_u \equiv g_J g_K g_I. \tag{33}
\]

In the following we derive the expressions for these three contributions to the degeneracy of a molecular energy level.

5.1. Rotational Degeneracy \((g_J)\)

The rotational degeneracy due to the projection of the angular momentum on the spatial axis \( z \), \( g_J \), exists in all molecules and is given by:

\[
g_J = 2J_u + 1. \tag{34}
\]

5.2. \( K \) Degeneracy \((g_K)\)

The \( K \) degeneracy \((g_K)\) describes the degeneracy associated with the internal quantum number \( K \) in symmetric and asymmetric top molecules due to projections of the total angular momentum onto a molecular axis. Because of the opposite symmetry of the doubly-degenerate levels for which \( K \neq 0 \), \( g_K \) is defined as follows:

\[
g_K = 1 \text{ for } K=0 \text{ and all linear and asymmetric top molecules,} \tag{35}
\]

\[
= 2 \text{ for } K \neq 0 \text{ in symmetric top molecules.} \tag{36}
\]

K-level doubling is due to the asymmetry in the molecule about the molecular axes and removes the \( K \) degeneracy in asymmetric top molecules.
5.3. Nuclear Spin Degeneracy \( (g_I) \)

The nuclear spin degeneracy \( g_I \) takes account of the statistical weights associated with identical nuclei in a nonlinear molecule with symmetry (which most nonlinear molecules have). For a molecule with no symmetry or hyperfine splitting, each rotational level will have a nuclear spin degeneracy given by:

\[
g_n = \prod_i (2I_i + 1) = (2I + 1)^n \quad (37)
\]

\[
g_I = \frac{g_{\text{nuclear}}}{g_n}, \quad (38)
\]

where \( I_i \) represents the spin of the \( i \)th nucleus, \( \sigma \) is the number of identical nuclei, and \( g_{\text{nuclear}} \) is given in Table I for two of the largest classes of molecules found in the interstellar medium medium: those with two (\( C_{2v} \), symmetry\(^2\)) and three (\( C_{3v} \), symmetry\(^3\)) identical nuclei. Symmetry and hyperfine splitting changes \( g_I \) for all practical cases. Hyperfine splitting is covered elsewhere in this document, while symmetry considerations are well-covered by Gordy & Cook (1984) (Chapter III.4). See also Turner (1991) for a general discussion applicable to this document, while symmetry state (i.e. the para species) of a molecule, \( g_I = 1 \). In the following we list some examples of \( g_{\text{nuclear}} \) calculations for several molecules.

5.3.1. \( H_2CO \) and \( c-C_3H_3 \)

Formaldehyde (\( H_2CO \)) is a (slightly; \( \kappa = -0.96 \); see Equation \( 15 \)) prolate (see Section \( C \)) asymmetric top molecule, while Cyclopropenylidene (\( c-C_3H_3 \)) is a cyclic (slightly; \( \kappa = +0.69 \)) oblate (see Section \( B \)) asymmetric top molecule. Both have two opposing identical \( H \) (spin\(=\frac{1}{2} \)) nuclei. The coordinate wavefunction is symmetric/asymmetric for \( K_{-1} \) even/odd, respectively. Therefore, from the two identical spin \( \frac{1}{2} \) nuclei cases in Table I

\[
g_{\text{nuclear}} = (2I + 1)I = 1 \text{ for } K_{-1} \text{ even,} \quad (39)
\]

\[
= (2I + 1)(I + 1) = 3 \text{ for } K_{-1} \text{ odd.} \quad (40)
\]

5.3.2. \( NH_3 \) and \( CH_3CN \)

Ammonia (\( NH_3 \)) and Acetonitrile (\( CH_3CN \)) are symmetric top molecules with three opposing identical \( H \) (spin\(=\frac{1}{2} \)) nuclei. Therefore, from the three identical spin \( \frac{1}{2} \) nuclei cases in Table I

\[
g_{\text{nuclear}} = \frac{1}{3}(2I + 1)(4I^2 + 4I + 3) = 4 \text{ for } K=3n(41)
\]

\[
= \frac{1}{3}(2I + 1)(4I^2 + 4I) = 2 \text{ for } K\neq3n. \quad (42)
\]

5.3.3. \( c-C_3H \) and \( SO_2 \)

Cyclopropynyldyne (\( c-C_3H \)) is an oblate (\( \kappa = +0.17 \)) asymmetric top molecule with two opposing identical carbon (spin\(=0 \)) nuclei, while \( SO_2 \) is a prolate (\( \kappa = -0.94 \)) asymmetric top molecule with two opposing identical oxygen (spin\(=0 \)) nuclei. For both molecules the coordinate wavefunction is symmetric/asymmetric for \( K_{-1} \) even/odd, respectively. Therefore, from the two identical spin 0 nuclei cases in Table I

\[
g_{\text{nuclear}} = (2I + 1)I = 0 \text{ for } K_{-1} \text{ even,} \quad (43)
\]

\[
= (2I + 1)(I + 1) = 1 \text{ for } K_{-1} \text{ odd.} \quad (44)
\]

This indicates that half of the levels are missing (those for which \( K_{-1} \) is even).

6. SYMMETRY CONSIDERATIONS FOR ASYMMETRIC ROTOR MOLECULES

The symmetry of the total wavefunction \( \psi \) for a given rotational transition is determined by the product of the coordinate wavefunction \( \psi_c \psi_r \psi_t \) and the nuclear spin wavefunction \( \psi_n \). It is common to refer to a symmetric nuclear spin state as “ortho” and an anti-symmetric nuclear spin state as “para”. These wavefunctions are of two types: Fermions and Bosons. Table 2 lists the symmetries for the various wavefunctions in both cases for exchange of two identical nuclei.

Since an asymmetric top can be thought of as belonging to one of two limiting cases, prolate or oblate symmetric, we need to consider these two cases in the context of the coordinate wavefunction \( \psi_c \psi_r \psi_t \).

**Limiting Prolate:** We consider the symmetry of the coordinate wavefunctions with respect to rotation about the axis of least moment of inertia. Since the coordinate wavefunction \( \psi_c \psi_r \psi_t \) depends on the rotation angle \( \xi \) as \( \exp(\pm iK_{-1}\xi) \), it is symmetric when \( K_{-1} \) is even and antisymmetric when \( K_{-1} \) is odd. \( H_2CO \) is a limiting prolate asymmetric top molecule (though it is only slightly asymmetric).

**Limiting Oblate:** We consider the symmetry of the coordinate wavefunctions with respect to rotation about the axis of greatest moment of inertia. Since the coordinate wavefunction \( \psi_c \psi_r \psi_t \) depends on this rotation angle \( \xi \) as \( \exp(\pm iK_{+1}\xi) \), it is symmetric when \( K_{+1} \) is even and antisymmetric when \( K_{+1} \) is odd. \( NH_2D \) is a limiting oblate asymmetric top molecule.

The level of asymmetry in molecules is often described in terms of Ray’s asymmetry parameter \( \kappa \) (Ray, 1932):

\[
\kappa \equiv \frac{2B - A - C}{A - C}, \quad (45)
\]

where \( A, B, \) and \( C \) are constants which represent the three principle moments of inertia for an asymmetric rotor molecule (see Gordy & Cook (1984) for more information), usually expressed in megahertz (MHz). The limits to \( \kappa \) are:

- **B = A:** \( \kappa = +1 \) and the molecule is an oblate symmetric rotor.
- **B = C:** \( \kappa = -1 \) and the molecule is a prolate symmetric rotor.
Taking a more general example, the rotational angular momentum constants for H$_2$CO are $A = 281970.37$ MHz, $B = 38835.42558$ MHz, and $C = 34005.73031$ MHz. Equation (45) then yields $\kappa \simeq -0.961$, which means that H$_2$CO is nearly a prolate symmetric rotor.

7. ROTATIONAL PARTITION FUNCTIONS ($Q_{\text{ROT}}$)

For a parcel of gas that exchanges energy with the ambient medium, statistical mechanics states that the partition function $Q$ which describes the relative population of states in the gas is given by:

$$Q = \sum_i g_i \exp \left( -\frac{E_i}{kT} \right).$$

(46)

Following Gordy & Cook (1984) (chapter 3, section 3), the partition function for molecules in a gaseous state is a function of the electronic, vibrational, rotational, and nuclear spin states of the molecule. Assuming that there are no interactions between these states, the total partition function for the molecule can be expressed as the product of the partition functions of these four types of energy states:

$$Q = Q_e Q_v Q_r Q_n.$$

(47)

The ground electronic state of most molecules observed in the interstellar medium are stable, $^1\Sigma$ electronic states, although there are a few notable exceptions (i.e. OH $^2\Pi$, SO $^3\Sigma$, CN $^2\Sigma$, etc.). For these molecules $Q_e = 1$. For simplicity we will also assume that the molecules are in their ground vibrational state ($Q_v = 1$). This leaves us with rotational and nuclear partition functions comprising the total molecular partition function, which we can write as:

$$Q_{\text{rot}} = Q_r Q_n = \sum_{J,K,I} g_J g_K g_I \exp \left( -\frac{E_{JK}}{kT} \right),$$

(48)

where the degeneracies $g_J$, $g_K$, and $g_I$ are described in Section 5.1, Section 5.2, Section 5.3 respectively. See Turner (1991) for a nice general discussion listing expressions for $Q_{\text{rot}}$ in the high-temperature limit for a variety of molecules. In the following we derive the rotational partition function $Q_{\text{rot}}$ for linear, symmetric, and asymmetric rotor molecules.

7.1. Linear Molecule Rotational Partition Function

For linear molecules:

- $g_J = 2J + 1$ (Section 5.1)
- $g_K = 1$ (Section 5.2)
- $g_I = 1$ (since linear molecules with allowed electric dipole transitions are polar and have no center of symmetry)

which implies that Equation (48) becomes:

$$Q_{\text{rot}} = \sum_{J=0}^{\infty} (2J + 1) \exp \left( -\frac{E_J}{kT} \right).$$

(49)

The energy levels for a linear molecule can be described by a multi-term expansion as a function of $J(J+1)$ (Jennings et al. 1987):

$$E_J = h(B_0 J(J+1) - D_0 J^2(J+1)^2 + H_0 J^3(J+1)^3 - L_0 J^4(J+1)^4 + M_0 J^5(J+1)^5 + ...),$$

(50)
This level of accuracy is maintained even if one includes the lowest 51 levels of the molecule. Shown are $Q_{\text{rot}}$ (Equation 49) and the percentage differences between $Q_{\text{rot}}$ and the expansions of Equation 49 provided by Equation 52 (using terms to third-order in $\frac{hB}{kT}$) and Equation 53 (vertical scale on right).

An alternate approximation for linear polyatomic molecules is derived by McDowell (1988):  

$$Q_{\text{rot}} \approx \frac{kT}{hB_0} \exp \left( \frac{hB_0}{3kT} \right),$$  

which is reported to be good to 0.01% for $\frac{hB}{kT} \approx 0.2$ ($T > 13.7 \text{K}$ for CO) and is good to better than 1% for $T > 3.5 \text{K}$ (Figure 1). Note that Equation 53 reduces to Equation 52 when expanded using a Taylor Series.

### 7.2. Symmetric and Slightly-Asymmetric Rotor Molecule Rotational Partition Function

For symmetric and asymmetric rotor molecules:

- $g_J = 2J + 1$ (Section 5.1)
- $g_K = 1$ for $K = 0$ and 2 for $K \neq 0$ in symmetric rotors (Section 5.2)
- $g_K = 1$ for all $K$ in asymmetric rotors
- $g_I = \frac{\alpha_{\mu
u}\alpha_{\nu\mu}}{2(2I+1)}$ (See Table 11)

which implies that Equation 48 becomes:

$$Q_{\text{rot}} = \sum_{J=0}^{\infty} \sum_{K=-J}^{J} g_K g_I (2J + 1) \exp \left( -\frac{E_{JK}}{kT} \right).$$  

Like the energy levels for a linear molecule, the energy levels for a symmetric or slightly-asymmetric rotor molecule can be described by a multi-term expansion as a function of $J(J + 1)$:

$$E_{JK} = h(B_0 J(J + 1) + s_0 K^2 + D_J J^2 (J + 1)^2$$
$$+ D_{jk} J(J + 1)K^2 + D_K K^4 + H_{jkk} J(J + 1)K^4$$
$$+ H_{jjk} J^2(J + 1)^2 K^2 + H_{jkk} J^2(J + 1)^3$$
$$+ H_{kk} K^6 + ...),$$  

where $s_0 \equiv A_0 - B_0$ for a prolate symmetric rotor molecule and $s_0 \equiv C_0 - B_0$ for an oblate symmetric rotor, and the other constants represent various terms in the centrifugal distortion of the molecule. All constants are in megahertz (MHz). For rigid symmetric or slightly-asymmetric rotor molecules, using the rigid rotor approximation to the level energies:

$$E_{JK} = h \left( B_0 J(J + 1) + s_0 K^2 \right).$$  

From McDowell (1990) we can then approximate $Q_{\text{rot}}$ for a symmetric or slightly-asymmetric rotor molecule as follows:

$$Q_{\text{rot}} \approx \frac{\sqrt{4\pi \sigma}}{\sigma} \exp \left( \frac{hB_0(1 - m)}{12kT} \frac{kT}{hB_0} \right)$$
$$\times \left[ 1 + \frac{1}{90} \left( \frac{hB_0(1 - m)}{kT} \right)^2 + ... \right],$$  

where

$$m = \frac{B_0}{A_0}$$

for a prolate symmetric rotor molecule,

$$= \frac{B_0}{C_0}$$

for an oblate symmetric rotor molecule,

$$= \frac{B_0^2}{A_0 C_0}$$

for a slightly-asymmetric rotor molecule (see Herzberg (1945)).

---

* Slightly-asymmetric rotor molecules are defined such that $B_0 \approx C_0$. In Equation 53 replace $B$ with $\sqrt{B_0 C_0}$. 

---

**Figure 1.** Rotational partition function calculations for CO using the lowest 51 levels of the molecule. Shown are $Q_{\text{rot}}$ (Equation 49) and the percentage differences between $Q_{\text{rot}}$ and the expansions of Equation 49 provided by Equation 52 (using terms to third-order in $\frac{hB}{kT}$) and Equation 53 (vertical scale on right).
If we expand the exponential and take only up to first order terms in the expansion in Equation \(57\)

\[ Q_{\text{rot}} \approx \frac{\sqrt{m\pi}}{\sigma} \left( 1 + \frac{hB_0(4 - m)}{12kT} + \ldots \right) \left( \frac{kT}{hB_0} \right)^{3/2} \approx \frac{\sqrt{m\pi}}{\sigma} \left( \frac{kT}{hB_0} \right)^{3/2} \approx \frac{1}{\sigma} \left[ m\pi \left( \frac{kT}{hB_0} \right)^3 \right]^{1/2}, \tag{58} \]

which is the equation for symmetric rotor partition functions quoted by Gordy & Cook (1984) (Chapter 3, Equations 3.68 and 3.69). Figure 2 compares \(Q_{\text{rot}}\) calculated using Equation 57 and the approximate forms given by Equation 57 and Equation 58 for NH\(_3\). In this example Equation 57 is good to \(\lesssim 20\%\) for \(T_K > 10\) K and \(\lesssim 0.25\%\) for \(T_K > 50\) K, while Equation 58 is much less accurate, good to \(\lesssim 40\%\) for \(T_K > 10\) K and \(\lesssim 6\%\) for \(T_K > 50\) K.

8. DIPOLE MOMENT MATRIX ELEMENTS \((|\mu_{JK}|^2)\) AND LINE STRENGTHS \((S)\)

The following discussion is derived from the excellent discussion given in Gordy & Cook (1984), Chapter II.6. A detailed discussion of line strengths for diatomic molecules can be found in Tatum (1984). Spectral transitions are induced by interaction of the electric or magnetic components of the radiation field in space with the electric or magnetic dipole components fixed in the rotating molecule. The strength of this interaction is called the line strength \(S\). The matrix elements of the dipole moment with reference to the space-fixed axes \((X,Y,Z)\) for the rotational eigenfunctions \(\psi_r\) can be written as follows:

\[ \int \psi_r^* \mu_F \psi_{r'} \, d\tau = \sum_g \mu_g \int \psi_r^* \Phi_{Fg} \psi_{r'} \, d\tau, \tag{59} \]

where \(\Phi_{Fg}\) is the direction cosine between the space-fixed axes \(F=(X,Y,Z)\) and the molecule-fixed axes \(g=(x,y,z)\). The matrix elements required to calculate line strengths for linear and symmetric top molecules are known and can be evaluated in a straightforward manner, but these calculations are rather tedious because of the complex form of the eigenfunction. Using commutation rules between the angular momentum operators and the direction cosines \(\Phi_{Fg}\), Cross et al. (1944) derive the nonvanishing direction cosine matrix elements in the symmetric top representation \((J,K,M)\):

\[ \langle J, K, M | \Phi_{Fg} | J', K', M' \rangle = \langle J | \Phi_{Fg} | J' \rangle \times \langle J, K | \Phi_{Fg} | J', K' \rangle \langle J, M | \Phi_{Fg} | J', M' \rangle. \tag{60} \]

where \(M\) is the projection of the total angular momentum \(J\) on a fixed space axis. There are \(2J+1\) projections of \(M\) allowed. The dipole moment matrix element \(|\mu_{JK}|^2\) can then be written as:

\[ |\mu_{JK}|^2 = \sum_{F=X,Y,Z} \sum_{M'} |\langle J, K, M | \mu_F | J', K', M' \rangle|^2, \tag{61} \]

where the sum over \(g = x, y, z\) is contained in the expression for \(\mu_{JK}\) (Equation 59). Table 3 lists the direction cosine matrix element factors in Equation 60 for symmetric rotor and linear molecules. In the following we give examples of the use of the matrix elements in line strength calculations.

9. LINEAR AND SYMMETRIC ROTOR LINE STRENGTHS

For all linear and most symmetric top molecules, the permanent dipole moment of the molecule lies completely along the axis of symmetry of the molecule \((\mu = \mu_z)\). This general rule is only violated for the extremely-rare “accidentally symmetric top” molecule (where \(I_x = I_y\)). For all practical cases, then, Equation 61 becomes:

\[ |\mu_{JK}|^2 = \mu^2 \sum_{F=X,Y,Z} \sum_{M'} |\langle J, K, M | \Phi_{Fg} | J', K', M' \rangle|^2 = \mu^2 S, \tag{62} \]

where we have defined the line strength \(S\) as:

\[ S \equiv \sum_{F=X,Y,Z} \sum_{M'} |\langle J, K, M | \Phi_{Fg} | J', K', M' \rangle|^2. \tag{63} \]

9.1. \((J, K) \rightarrow (J - 1, K)\) Transitions

Using the matrix element terms listed in the fourth column of Table 3 with the definition of the direction cosine matrix elements (Equation 60), we can write the terms which make-up Equation 62 for the case \((J, K) \rightarrow (J - 1, K)\)
Applying these terms to the dipole moment matrix element (Equation 61) which simply entails squaring each of the three terms in Equation 64 and expanding the $\pm$ terms and using the definition of $|\mu_{\text{lin}}|^2$ (Equation 63):

$$
S = \left( \frac{(J^2 - K^2)}{J(4J^2 - 1)} \right) \left( J^2 - M^2 \right)
+ \frac{1}{2} \left[ (J - M)(J - M - 1) + (J + M)(J + M - 1) \right].
$$

Reducing Equation 65 results in the following for a symmetric top transition $(J, K) \rightarrow (J, K)$:

$$
S = \frac{K^2}{J(J+1)} 	ext{ for } (J, K) \rightarrow (J, K).
$$

9.3. $(J, K) \rightarrow (J + 1, K)$ Transitions

Using the matrix element terms listed in the second column of Table 3 with the definition of the direction cosine matrix elements (Equation 60), we can write the terms which make-up Equation 62 for the case $(J, K) \rightarrow (J + 1, K)$ as follows:

$$
|\mu_{\text{lin}}|^2 = \mu^2 \left( \frac{2K}{4J(J+1)} \right) \times \left\{ 2M \pm [J(J+1) - M(M+1)]^{1/2} \right\}.
$$

Applying these terms to the dipole moment matrix element (Equation 61) and using the definition of $|\mu_{\text{lin}}|^2$

\footnote{Also referred to as “P-branch transitions”.
\footnote{Also referred to as “Q-branch transitions”.
\footnote{Also referred to as “R-branch transitions”.

\begin{table}
\centering
\caption{Direction Cosine Matrix Element Factors* for Linear$^b$ and Symmetric Top Molecules}
\begin{tabular}{|c|c|c|c|}
\hline
Matrix Element Term & $J+1$ & $J$ & $J-1$ \\
\hline
$\langle J|\Phi_{F_3}\rangle|J'\rangle$ & $4(J+1)[(2J+1)(2J+3)]^{1/2}$ & $[4J(J+1)]^{1/2}$ & $[4J(4J^2+1)]^{1/2}$ \\
$\langle J, K|\Phi_{F_3}\rangle|J', K\rangle$ & $2[(J+1)^2 - K^2]^{1/2}$ & $2K$ & $-2(J^2 - K^2)^{1/2}$ \\
$\langle J, K|\Phi_{F_3}\rangle|J', K, \pm 1\rangle = \mp i\langle J, K|\Phi_{F_3}\rangle|J', K \pm 1\rangle$ & $2[(J \pm K + 1)(J \pm K + 2)]^{1/2}$ & $[J(J+1) - K(K+1)]^{1/2}$ & $\mp [J \mp K](J \mp K - 1)]^{1/2}$ \\
$\langle J, M|\Phi_{B_3}\rangle|J', M, \pm 1\rangle = \mp i\langle J, M|\Phi_{B_3}\rangle|J', M \pm 1\rangle$ & $2[(J+1)^2 - M^2]^{1/2}$ & $2M$ & $-2(J^2 - M^2)^{1/2}$ \\
\hline
\end{tabular}
\footnote{Derived from Gordy & Cook (1984), Table 2.1, which is itself derived from Cross et al. (1944).}
\footnote{For linear molecules, set $K=0$ in the terms listed.}
\end{table}
Reducing Equation (71) results in the following for a symmetric top transition \((J, K) \to (J + 1, K)\):

\[
S = \frac{(J + 1)^2 - K^2}{(J + 1)(2J + 1)} \quad \text{for} \quad (J, K) \to (J + 1, K).
\] (72)

To derive the equation for a linear molecule transition \(J \to J + 1\), simply set \(K = 0\) in Equation (72).

10. HYPERFINE STRUCTURE AND RELATIVE INTENSITIES

Hyperfine splitting in molecular spectra occurs when a nucleus in the molecule has non-zero nuclear spin. Hyperfine splitting is commonly observed in molecules that contain \(^1H\) (I = 1/2), \(^2D\) (I = 1), \(^13C\) (I = 1/2), \(^14N\) (I = 1), \(^15N\) (I = 1/2), \(^17O\) (I = 5/2), and \(^33S\) (I = 3/2) nuclei. For a molecule with a single coupling nucleus, the vector addition of angular momenta is used to define a new hyperfine quantum number, \(F\), such that \(F = \vec{I} + \vec{J}\) is the total molecular angular momentum, where \(\vec{I}\) and \(\vec{J}\) are the nuclear spin and rotational angular momentum of the molecule respectively (\(\vec{I}\) precess around \(\vec{F}\)). The allowed scalar values of \(F\) are given by

\[
F = J + I, J + I - 1, ..., |J - I|.
\] (73)

Selection rules stipulate that \(\Delta F = 0, \pm 1\) (but \(F = 0\) cannot go to 0). For example, the \(^14N\) nucleus in HCN is responsible for strong hyperfine coupling because the spin of \(^14N\) is I = 1. Equation (74) shows that the J = 0 level remains unsplit (F = 1), the J = 1 level splits into a triplet (F = 2, 1, 0), and the J = 2 level also splits into a triplet (F = 3, 2, 1). The selection rule allows 3 hyperfine transitions from \(J = 1\) – 0 and six hyperfine transitions from \(J = 2\) – 1. Since I = 1 and the Clebsch-Gordon series (Equation (73)) terminates with \(F = |J - I|\), all of the levels with J > 2 will also be split into triplets.

The relative strengths can be calculated by using irreducible tensor methods (see Gordy & Cook [1984] Chapter 15). We define the relative strength such that the sum of the relative strength, \(R_n\), of all transitions from \(F'\) \(\to\) \(F\) for a given \(J'\) \(\to\) \(J\) are equal to one:

\[
\sum_{F'F} R_n(J'F' \to JF) = 1.
\] (74)

The relative line strengths are calculated in terms of a 6 – \(j\) symbol,

\[
R_n(J'F' \to JF) = \frac{(2F + 1)(2F' + 1)}{(2I + 1)} \left\{ \begin{array}{c} I \ F' \\ 1 \ J \ F \end{array} \right\}^{J'}^2.
\] (75)

With the aid of 6 – \(j\) Tables [Edmonds, 1960] and the property that 6 – \(j\) symbols are invariant with permutation of the columns, we find the appropriate 6 – \(j\) symbol for each transition:

\[
\left\{ \begin{array}{ccc} a & b & c \\ 1 & c - 1 & b - 1 \end{array} \right\}^2 = \frac{s(s + 1)(s - 2a - 1)(s - 2a)}{(2b - 1)(2b + 1)(2c - 1)2c(2c + 1)}
\]

\[
\left\{ \begin{array}{ccc} a & b & c \\ 1 & c - 1 & b \end{array} \right\}^2 = \frac{2(s + 1)(s - 2a)(s - 2b)(s - 2c + 1)}{2b(2b + 1)(2c - 1)2c(2c + 1)}
\]

\[
\left\{ \begin{array}{ccc} a & b & c \\ 1 & c - 1 & b + 1 \end{array} \right\}^2 = \frac{(s - 2b - 1)(s - 2b)(s - 2c + 1)(s - 2c + 2)}{(2b + 1)(2b + 2)(2c - 1)2c(2c + 1)}
\]

\[
\left\{ \begin{array}{ccc} a & b & c \\ 1 & c & b \end{array} \right\}^2 = \frac{2(b + 1) + 2c(c + 1) - 2a(a + 1)^2}{2b(2b + 1)(2b + 2)c(2c + 1)(2c + 2)}
\] (76)

where \(s = a + b + c\). For example, in the case of the \(J = 1\) – 0 F = 2 – 1 transition of HC\(^14\)N, the first 6 – \(j\) symbol in Equation (76) should be used with \(a = I = 1\), \(b = F' = 2\), and \(c = J' = 1\).

The formalism above may be generalized when multiple coupling nuclei are present. By extension, an arbitrary number, \(n\), of coupling nuclei may be included in the nested vector addition of angular momenta (i.e. \(F_1 = \vec{I} + \vec{J}_1\), \(F_2 = \vec{F}_1 + \vec{I}_2\), \(\cdots\), \(F_n = \vec{F}_{n-1} + \vec{I}_n\)) and the relative intensities can be calculated by multiplying the relative strength equation \(n\) times with appropriate quantum numbers for each step in the nested vector addition. For example, in the case of two coupling nuclei with unequal strength, such as the outer \((I_1)\) and inner \((I_2)\) \(^{14}\)N of \(\text{N}_2\)H\(^+\), the nested coupling scheme \(F_1 = \vec{J} + \vec{I}_1\) and \(\vec{F} = \vec{F}_1 + \vec{I}_2\) is used. The relative strength of the hyperfine transitions are then given by

\[
R_i(J'F'_1F'_2 \to JF_1F_2) = \frac{(2F'_1 + 1)(2F_1 + 1)(2F'_2 + 1)(2F + 1)}{(2I_1 + 1)(2I_2 + 1)} \times \left\{ \begin{array}{c} F_1 \\ 1 \ J \ F_2 \end{array} \right\}^J_1 \left\{ \begin{array}{c} F'_1 \ F'_2 \\ 1 \ F_1 \ F \end{array} \right\}^J.
\] (77)

While we have specifically discussed hyperfine splitting from nuclei with unequal coupling in this section, the addition of vector angular momenta in quantum mechanics is a general problem and the formalism above may be extended to problems with equal coupling nuclei (i.e. H\(_2\)CO) or for fine structure splitting (i.e. in molecules with electronic states with total electronic spin \(S > 0\)) with an appropriate mapping of the quantum numbers.

We end this section by noting an important caveat with regards the interpretation of the relative intensities of hyperfine transitions. Anomalies between observed hyperfine transition intensities and those predicted by the quantum mechanics described in...
this section have been observed (see Kwan & Scoville [1973], Guilloteau & Baudry [1981], Walmsley et al. [1982], Stutzki et al. [1984], Stutzki & Winnewisser [1985], Bachiller et al. [1997], Daniel et al. [2000], and Hily-Blant et al. [2010] for examples). These anomalies are likely due to spectral line overlap between hyperfine transitions and can result in non-LTE hyperfine ratios.

11. APPROXIMATIONS TO THE COLUMN DENSITY EQUATION

In the following we derive several commonly-used approximations to the column density Equation (32). Optically thin ($\tau \ll 1$), optically thin when in the Rayleigh-Jeans limit ($h\nu \ll kT_{ex}$), and optically thin when in the Rayleigh-Jeans limit and negligible background emission ($T_{bg} \ll T_{ex}$).

11.1. Optically Thin Approximation

If we assume that $\tau \ll 1$, the radiative transfer equation (Equation 27) becomes:

$$T_R = \int \left[ J(T_{ex}) - J(T_{bg}) \right] \tau, \quad (78)$$

and the column density equation (Equation 29) becomes:

$$\begin{align*}
N_{tot}^{thin} = & \left( \frac{3h}{8\pi^3\nu S\mu^2 R_i} \right) \left( \frac{Q_{rot}}{g_j g_k g_I} \right) \exp \left( \frac{E_u}{kT_{ex}} \right) \exp \left( \frac{h\nu}{kT_{ex}} \right) - 1 \\
& \times \int \left[ \frac{T_R d\nu}{f(T_{ex}) - f(T_{bg})} \right]. \quad (79)
\end{align*}$$

The $J_p(T_{ex}) - J_p(T_{bg})$ term may be removed from the integral because the Planck function does not vary substantially across the frequency extent of a typical spectral line. For example, if we take the CO $J = 1 - 0$ transition at 115 GHz, then for a spectral line with a full width at half maximum of 200 MHz (corresponding to an extent of 520 km s$^{-1}$), the fractional change in the Planck function across the spectral line is less than 0.3% for all excitation temperatures above the CMB. For most sources within the Milky Way Galaxy, the extent of a spectral line is an order of magnitude smaller and the corresponding change in the Planck function across the transition is also smaller. The fractional uncertainty in the Planck function increases as the frequency of the transition increases, however, even at 1 THz, the fractional uncertainty is still less than 3% for a 500 km/s wide transition. As a result, the $J_p(T_{ex}) - J_p(T_{bg})$ term is approximately constant in all realistic cases and the integral term in Equation (79) reduces to just the integrated intensity of the spectral line:

$$\begin{align*}
N_{tot}^{thin} = & \left( \frac{3h}{8\pi^3\nu S\mu^2 R_i} \right) \left( \frac{Q_{rot}}{g_j g_k g_I} \right) \exp \left( \frac{E_u}{kT_{ex}} \right) \exp \left( \frac{h\nu}{kT_{ex}} \right) - 1 \\
& \times \int \left[ \frac{T_R d\nu}{f(T_{ex}) - f(T_{bg})} \right]. \quad (79)
\end{align*}$$

11.2. Optically Thin with Rayleigh-Jeans Approximation

Assume that $\tau \ll 1$ and $h\nu \ll kT_{ex}$. This reduces the term in $[ ]$ in Equation (32) to $\frac{h\nu}{kT_{ex}}$, $J_p(T)$ to $T$, and reduces the radiative transfer equation to that derived in Equation (32). Equation (32) then reduces to

$$N_{tot}^{thin+RJ} = \left( \frac{3k}{8\pi^3\nu S\mu^2 R_i} \right) \left( \frac{Q_{rot}}{g_j g_k g_I} \right) \exp \left( \frac{E_u}{kT_{ex}} \right) \times \int \frac{T_R d\nu}{f(T_{ex}) - f(T_{bg})}. \quad (81)$$

We test the validity of these approximations by comparing the ratio of Equation (30) ($N_{tot}^{thin}$) to Equation (31) ($N_{tot}^{thin+RJ}$) in Figure 3. The column density calculated from Equation (30) is always less than the column density calculated from Equation (31) in the Rayleigh-Jeans limit. Darker shading corresponds to worse agreement between the equations. For example, the Rayleigh-Jeans approximation is a good approximation (less than 5% disagreement between equations) for the low frequency (4.8 GHz) H$_2$CO K-doublet transition for all excitation temperatures. The Rayleigh-Jeans approximation is still a good approximation for the NH$_3$ inversion transitions (e.g. (1,1), (2,2), etc.) at 24 GHz with less than 10% disagreement between the equations for $T_{ex} > 5K$. Rayleigh-Jeans failure is more apparent for transitions at millimeter and shorter wavelengths. For instance, the C$^{18}$O $J = 1 - 0$ line at 109.7 GHz has more than 15% disagreement between the optically-thin and optically-thin plus Rayleigh-Jeans approximations for $T_{ex} < 9 K$ that rapidly increases toward lower excitation temperatures. It is possible to use Equation (31) at submillimeter wavelengths $\nu > 300$ GHz if the excitation temperature is large (i.e. less than 10% disagreement at 300 GHz if $T_{ex} > 26 K$); however, for most cases in dense regions of molecular clouds where the tracer is sub thermally populated with low excitation temperatures, Equation (30) should be used.

11.3. Optically Thin with Rayleigh-Jeans Approximation and Negligible Background

Assuming that the temperature of the background source (i.e. the cosmic microwave background radiation) is small in comparison to the molecular excitation temperature ($T_{bg} \ll T_{ex}$), Equation (31) becomes

$$N_{tot}^{thin+RJ+noBG} = \left( \frac{3k}{8\pi^3\nu S\mu^2 R_i} \right) \left( \frac{Q_{rot}}{g_j g_k g_I} \right) \times \exp \left( \frac{E_u}{kT_{ex}} \right) \int \frac{T_R d\nu}{f}. \quad (82)$$

We test when it is appropriate to use this approximation by comparing the column density calculated with Equation (30) ($N_{tot}^{thin}$) versus Equation (32) ($N_{tot}^{thin+RJ+noBG}$). The ratio of these two equations is given by $N_{tot}^{thin}/N_{tot}^{thin+RJ+noBG} = J_p(T_{ex})/J_p(T_{ex}) - J_p(T_{bg})$. Figure 3 shows contours of this ratio as a function of $T_{ex}$ and the transition frequency. The general trend is such that the thin+RJ+noBG approximation is poor for low frequencies and for low $T_{ex}$. At first,
11.4. Not Optically Thin Approximation

If we assume that \( \tau_{\nu} \gtrsim 1 \), we use the radiative transfer equation (Equation 27) to solve for \( \tau_{\nu} \):

\[
\tau_{\nu} = -\ln \left[ 1 - \frac{T_R}{\int [J(T_{ex}) - J(T_{bg})]} \right],
\]

and insert this expression for \( \tau_{\nu} \) in the column density equation (Equation 32):

\[
N_{\text{tot}}^{\text{thick}} = \left( \frac{3h}{8\pi^{3}S_{\mu}^{2}R_{\nu}} \right) \left( \frac{Q_{\text{rot}}}{g_{i}g_{f}k_{B}T_{ex}} \exp \left( \frac{E_{u}}{kT_{ex}} \right) - 1 \right)
\times \int (1 - \exp(-\tau_{\nu})) \, dv.
\]

Note that Equation 84 is quite general, applicable to all values of \( \nu, \tau, T_{ex}, T_{bg} \), and \( T_R \). Furthermore, one can derive a simple relationship between the column density derived assuming \( \tau \ll 1 \) and those derived assuming \( \tau \not\ll 1 \) by noting that one can write \( N_{\text{tot}}^{\text{thin}} \) (Equation 80) using the radiative transfer equation (Equation 27) as follows:

\[
N_{\text{tot}}^{\text{thin}} = N_{\text{tot}}^{\text{thick}} \frac{\tau}{1 - \exp(-\tau_{\nu})}.
\]

The factor \( \tau/(1 - \exp(-\tau_{\nu})) \) is the “optical depth correction factor” derived by Goldsmith & Langer (1999).

Note that Equation 86 also applies to the approximation cases \( h\nu \ll kT_{ex} \) (Section 11.2) and \( T_{bg} \ll T_{ex} \) (11.3).

12. THE CONSEQUENCES OF ASSUMING A CONSTANT EXCITATION TEMPERATURE

The calculation of column density requires a determination of the gas excitation temperature (Equation 35). The excitation temperature is a very general concept that describes an energy density (in units of temperature), whether kinetic, radiative, rotational, vibrational, spin, etc.

Since molecules are fundamentally multi-level systems, an excitation temperature may be defined for each transition allowed via electric dipole (or magnetic dipole or electric quadrupole) selection rules. Most molecules (in particular, dense gasacers) in the ISM are in non-LTE with different gas excitation temperatures for different transitions. However, to simplify the problem of calculating the total molecular column density from a single

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8 The condition \( \tau \gtrsim 1 \) is often somewhat erroneously referred to as “optically thick”; while in fact the analysis presented in this section is appropriate for all conditions excluding \( \tau \ll 1 \).

9 You can also define an “excitation temperature” between levels which are not radiatively coupled - e.g. the (1,1) and (2,2) inversion states of NH$_3$. This is usually called a rotation temperature $T_{rot}$. 

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Figure 3. In the top panel we compare the molecular column density calculated assuming optically-thin \( (N_{\text{tot}}^{\text{thin}}; \text{Equation 80}) \) and optically-thin within the Rayleigh-Jeans approximation \( (N_{\text{tot}}^{\text{thin}+RJ}; \text{Equation 81}) \). In the bottom panel we show the comparison between molecular column density calculated assuming optically-thin and optically-thin within the Rayleigh-Jeans approximation and with the assumption of negligible background emission \( (N_{\text{tot}}^{\text{thin}+RJ+noBG}; \text{Equation 82}) \).
transition, the constant excitation temperature approximation (CTEX) is usually assumed where all transitions have the same excitation temperature

\[ T_{\text{ex}} = T_{\text{ex,CTEX}} \forall \nu \rightarrow l. \quad (87) \]

The optically thin column densities using Equation 80 are shown in Figure 4 for the three lowest energy transitions of the HCO\(^+\) molecule that are observable from the ground in atmospheric windows. Note that the column density equation diverges for \( T_{\text{ex,CTEX}} \rightarrow 2.735 \text{K} \) due to the \( J_u(T_{\text{ex}}) - J_v(T_{\text{by}}) \) term in the denominator. This divergence has the consequence that as the level populations approach equilibrium with the CMB, it becomes more difficult to accurately determine the column density. The plotted curves show \( N_{\text{thin}}/I \) or the column density in the optically thin limit for an integrated intensity of 1 K km/s. These curves should be multiplied by the observed integrated intensity and corrected for any optical depth effects by \( \tau/(1-\exp(-\tau)) \). The 1 \(-\) 0 transition is the least sensitive transition to changes in the excitation temperature above 3 K with a minimum at \( T_{\text{ex,CTEX}} = 7.46 \text{K} \). As a result, the difference between assuming an excitation temperature between 5 K and 10 K results in a less than 10% uncertainty in the calculated column density assuming CTEX. This statement is in general true for the 3 mm transitions of several famous dense gas tracers such as HCO\(^+\), HCN, \( \text{N}_2\text{H}^+ \), and CS. If a lower limit to the column density is desirable, then the column density can be calculated at the excitation temperature of the minimum excitation temperature curve (e.g. \( N_{\text{thin}}/I > 1.03 \times 10^{12} \text{cm}^{-2} / \text{K km/s} \) for the HCO\(^+\) \( J = 1 \rightarrow 0 \) transition at \( T_{\text{ex,CTEX}} = 7.46 \text{K} \).

Estimating the total column density from higher energy transitions is more uncertain for low excitation temperatures. Unfortunately, this situation does occur in observations of dense cores in the ISM where the dense gas tracer is typically both optically thick and very subthermally populated (see Shirley et al. 2013). For the HCO\(^+\) \( J = 4 \rightarrow 3 \) transition, the uncertainty in the total column density calculation between assuming an excitation temperature of 5 K versus 10 K is a factor of 40! The \( J = 4 \rightarrow 3 \) curve does not reach its minimum until \( T_{\text{ex,CTEX}} = 43.55 \text{K} \), close to the energy of the \( J = 4 \) level above ground (\( E_u/k = 42.80 \text{K} \)). It is therefore advisable to observe transitions with \( E_u/k \) that are comparable to the typical excitation temperature to minimize this uncertainty.

Proper estimation of the gas excitation temperature usually requires observations of multiple transitions coupled with modeling of the statistical equilibrium and radiative transfer. In general, the excitation temperature is a sigmoid function that varies between the background radiation temperature at low density and the gas kinetic temperature at high density. At low gas densities, collisions are not as important for setting the level populations as interaction with the background radiation field and the excitation temperature equilibrates with the radiation temperature. At high gas densities, collisions dominate in setting the level populations and the excitation temperature equilibrates to the gas kinetic temperature of the dominant collisional partner. A transition is said to be “thermalized” if \( T_{\text{ex}} \) is equal to \( T_K \). Subthermal excitation indicates that \( T_{\text{ex}} \) is less than \( T_K \).

In the general case of non-LTE in the ISM, it is possible that some transitions for a particular molecule may be thermalized (i.e. CO \( J = 1 \rightarrow 0 \)), while higher energy levels are subthermally populated (i.e. CO \( J = 6 \rightarrow 5 \)). Strong non-LTE effects are also observed in some cases (i.e. masers where naturally occurring population inversions can occur). Most molecular transitions of dense gas tracers observed in the ISM are subthermally populated. Multi-level effects can cause departures from the sigmoid shape. For example, a bottleneck due to longer rates of spontaneous decay, \( A_{ij} \sim \nu^3 \), for low \( J \) transitions can cause super-thermal excitation in the \( J = 1 \rightarrow 0 \) transition where, over a narrow range of densities, \( T_{\text{ex}} > T_K \). A full discussion of multi-level statistical equilibrium with radiative transfer is beyond the scope of this tutorial. There are situations where the excitation temperature can be directly estimated from the observations. If it is known that the line is very optically thick, then the \( (1-e^{-\tau}) \) term in the radiative transfer equation (Equation 27) approaches 1 and the excitation temperature may be solved analytically with an assumption of the gas filling factor:

\[ T_{\text{ex,obs}} = \frac{h\nu/k}{\ln \left(1 + \frac{h\nu/k}{T_{\text{ex}}/1+\nu/(c\text{mb})}\right)} \quad (if \tau >> 1). \quad (88) \]

Molecular line ratios of well resolved hyperfine transitions or ratios of isotopologues may be used to determine the optical depth in a line by taking ratios of Equation 27 (see Appendix D), although these methods usually assume that the excitation temperature in each hyperfine line or among different isotopologue transitions are the same which may not always be true.

Figure 5 shows the dependence of Equation 27 on the...
Based solutions normally rely on the measurements of equilibrium and radiative transfer equations. These model-to-the solution of the coupled multi-level statistical equilibrium and radiative transfer equations. At the heart of the LVG approximation is the assumption that photons which are emitted within the modelled molecular cloud escape quickly from the cloud due to the large velocity gradient (often assumed to be a result of cloud collapse). As discussed in Mangum & Shirley (2013), in the LVG approximation the escape probability is given by \( \beta = \frac{T_{ex}}{T_{ex}^0} \) within a uniform collapsing spherical geometry. The molecular cloud is assumed to have uniform volume density, kinetic temperature, and molecular column density. Inputs to an LVG model include a specification of the molecular spectrum and collisional excitation rates involving the primary collision partner in the molecular cloud (usually assumed to be \( H_2 \)) and the molecular species under study. Although the LVG approximation entails the use of a rather simplified uniform physical model, it often produces plausible physical conditions for environments where the transitions used to constrain the model are not too optically thick.

Other non-LTE approaches include the generalized escape probability code RADEx (van der Tak et al. 2007), microturbulent velocity models (Leung & Liszt 1976) and Monte Carlo approaches (Brinch & Hogerheijde 2010). In the microturbulent model solution the molecular cloud is assumed to have a power-law distribution in volume density and kinetic temperature with a line profile that is produced due to a combination of thermal and turbulent motions. The radiative transfer equation is iteratively solved using a quasi-diffusion method. Monte Carlo models are generalized solutions to the radiative transfer in molecular clouds which incorporate up to three dimensions of arbitrarily complex structure. This complex structure is organized into a grid of cells with uniform volume density, kinetic temperature, and molecular abundance. By ray tracing along random paths through this grid the radiative transfer equation is iteratively solved.

Even though non-LTE approaches result in a more accurate representation of the physical conditions in a molecular cloud, they must be constrained by multiple molecular spectral line measurements from a given molecular species. Non-LTE models also require knowledge of the collisional excitation rates for the molecular species under study. Collisional excitation rates for a wide variety of molecules have been calculated (see, for example, the Leiden Atomic and Molecular Database (LAMDA); Schöier et al. 2003). In general, though, limitations to their accuracy and kinetic temperature range can result in added uncertainty in non-LTE modelling of radiative transfer. Due to these limitations, LTE

Figure 5. The ratio of the excitation temperature at a given gas filling fraction compared to the excitation temperature calculated assuming a gas filling fraction \( f = 1 \). The four curves correspond to spectral lines with \( T_R = 0.1, 1, 10, 100 \) K. The curves are calculated for a transition at 3 mm. The curves are a weak function of the transition frequency. The horizontal dashed line correspond to an error in \( T_{ex} \) of 10% compared to the \( f = 1 \) assumption.

filling fraction by plotting the ratio of the excitation temperature at a filling fraction, \( f \), divided by the excitation temperature with a filling fraction of \( f = 1 \) (the usual assumption when filling fraction is unknown). For intense spectral lines \( T_R > 1 \) K, calculation of \( T_{ex} \) from Equation 27 is very sensitive to the gas filling fraction. For a line with \( T_R = 1 \) K, \( T_{ex} \) is 28% larger for \( f = 0.5 \). \( T_{ex}(f) \) quickly increases toward lower gas filling fractions. The dependence on gas filling fraction is steeper for brighter lines and flatter for weaker lines. The curves plotted in Figure 5 are not a strong function of the wavelength for transitions with \( \lambda > 1 \) cm.

If the line is optically thin, then it is not possible to determine the excitation temperature from a single transition as the observed line temperature, \( T_R \), is degenerate with excitation temperature, optical depth, and filling fraction. However, in this case, the excitation temperature can still be estimated from multiple transitions using a rotation diagram. A detailed discussion of the limits of the CTEX approximation for HCO\(^+\) observations may be found in Shirley et al. (2013).

13. NON-LTE APPROACHES TO THE DERIVATION OF MOLECULAR COLUMN DENSITY

Although beyond the scope of this tutorial, we should mention that there are a number of non-LTE approaches to the solution of the coupled multi-level statistical equilibrium and radiative transfer equations. These model-based solutions normally rely on the measurements of a number of molecular spectral lines from a given species to constrain the physical conditions within the dense gas environment under study. If one is interested in the global physical conditions within a molecular cloud, the radiative transfer solution for these models is simplified greatly by the introduction of a geometrically-averaged escape probability (usually denoted by \( \beta \)). A number of escape probability expressions which depend upon the assumed molecular cloud geometry and global velocity field can be used in these global cloud models (see van der Tak et al. (2004) for an excellent discussion). One of the most popular of these non-LTE escape probability models incorporates the Large Velocity Gradient (LVG) approximation (Sobolev 1960) to the solution of the radiative transfer and statistical equilibrium equations. At the heart of the LVG approximation is the assumption that photons which are emitted within the modelled molecular cloud escape quickly from the cloud due to the large velocity gradient (often assumed to be a result of cloud collapse). As discussed in Mangum & Wootten (1993) and van der Tak et al. (2007), in the LVG approximation the escape probability is given by \( \beta = \frac{T_{ex}}{T_{ex}^0} \) within a uniform collapsing spherical geometry. The molecular cloud is assumed to have uniform volume density, kinetic temperature, and molecular column density. Inputs to an LVG model include a specification of the molecular spectrum and collisional excitation rates involving the primary collision partner in the molecular cloud (usually assumed to be \( H_2 \)) and the molecular species under study. Although the LVG approximation entails the use of a rather simplified uniform physical model, it often produces plausible physical conditions for environments where the transitions used to constrain the model are not too optically thick.

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calculations of the molecular column density are often satisfactory with limited measurements.

14. BEAM-AVERAGED VERSUS SOURCE-AVERAGED COLUMN DENSITY

An aspect of the calculation of molecular column density from a spectral line measurement that is often overlooked is the difference between beam- and source-averaged measurements. Beam-averaged molecular column densities are derived from spectral line measurements with a defined spatial resolution element (a radio telescope “beam” $\theta_{\text{beam}}$). Without an understanding of the actual spatial extent of the measured emission (i.e. $\theta_{\text{beam}} > \theta_{\text{source}}$), one normally assumes that it is simply averaged over the beam of the measurement, or “beam-averaged”. For measurements which resolve the spatial extent of emission (i.e. $\theta_{\text{beam}} < \theta_{\text{source}}$), spectral line measurements measured over a source, usually considered “extended”, result in “source-averaged” molecular column densities.

15. MOLECULAR COLUMN DENSITY CALCULATION EXAMPLES

In the following we describe in detail some illustrative calculations of the molecular column density. These example molecules were chosen for their commonality ($^{18}$O is an abundant, though often optically-thin, isotopomer of CO), relatively simple hyperfine structure ($^{17}$O), somewhat more complex hyperfine structure ($^{2}$H$^{2}$O), or general usage as kinetic temperature (NH$_{3}$) or volume density (H$_{2}$CO) probes. In these examples we adopt the more conventional notation for a generic (emission or absorption) transition, i.e. $J = 1 - 0$, instead of the more explicit (and somewhat less convenient) “$J = 1 \rightarrow 0$” notation. We also address a common point of confusion for students learning this material and its reliance on CGS (Centimeter-Gram-Second) units. For the calculations presented below dipole moments are quoted in the CGS unit “Debye”, which is equal to $10^{-18}$ esu (electrostatic units). A good source for molecular dipole moments ($\mu$) and rotational constants (i.e. $A_{0}$, $B_{0}$, $C_{0}$) is the Jet Propulsion Laboratory (JPL) Molecular Spectroscopy database and spectral line catalog (Pickett et al. 1998)[10].

15.1. $^{18}$O

To derive the column density for $^{18}$O from a measurement of its $J = 1 - 0$ transition we use the general equation for molecular column density (Equation 82) with the following properties of the $C^{18}$O $J = 1 - 0$ transition:

$$S = \frac{J_{u}}{2J_{u} + 1}$$

$$\mu = 0.1098 \text{ Debye} = 1.098 \times 10^{-19} \text{ esu}$$

$$B_{0} = 57635.96 \text{ MHz}$$

$$g_{J} = 2J_{u} + 1$$

$$g_{K} = 1 \text{ (for linear molecules)}$$

$$g_{I} = 1 \text{ (for linear molecules)}$$

$$Q_{\text{rot}} \approx \frac{kT}{hB} + \frac{1}{3} \text{ (Equation 52)}$$

$$\approx 0.38 (T + 0.88)$$

$$E_{u} = 5.27 \text{ K}$$

$$\nu = 109.782182 \text{ GHz}$$

which leads to:

$$N_{\text{tot}}(C^{18}O) = \frac{3h}{8\pi^{2}\mu^{2}J_{u}R_{i}} \left( \frac{kT_{ex}}{hB} + \frac{1}{3} \right) \exp \left( \frac{E_{u}}{kT_{ex}} \right)$$

$$\times \left[ \exp \left( \frac{h\nu}{kT_{ex}} \right) - 1 \right]^{-1} \int \tau_{\nu} dv. \quad (89)$$

Assuming that the emission is optically thin ($\tau_{\nu} \ll 1$; Equation 80), Equation 89 becomes:

$$N_{\text{tot}}(C^{18}O) = \frac{4.79 \times 10^{13} (T_{ex} + 0.88) \exp \left( \frac{5.27}{T_{ex}} \right)}{\exp \left( \frac{5.27}{T_{ex}} \right) - 1} \left[ \frac{T_{B} \Delta v (km/s)}{\int (J_{\nu}(T_{ex}) - J_{\nu}(T_{bg}))} \right] \text{ cm}^{-2}. \quad (90)$$

If we are using integrated fluxes ($S_{\nu} \Delta v$) instead of integrated brightness temperatures, we use Equation 82 (see Appendix B), with the assumption that $\tau \ll 1$:

$$N_{\text{tot}}(C^{18}O) = \frac{3c^{2}}{16\pi^{3}\Omega_{s} \mu^{2}e^{3}} \left( \frac{Q_{\text{rot}}}{\beta_{J_{u}K_{g}I}} \right) \exp \left( \frac{E_{u}}{kT} \right) \int S_{\nu} \Delta v$$

$$\times \left[ \frac{S_{\nu}(J_{\nu}) \Delta v (km/s)}{\int (J_{\nu}(T_{ex}) - J_{\nu}(T_{bg}))} \right] \text{ cm}^{-2}. \quad (91)$$

where we have assumed a Gaussian source ($\Omega_{s} = 1.133 \theta_{\text{maj}} \theta_{\text{min}}$) with $\theta_{\text{maj}}$ and $\theta_{\text{min}}$ the major and minor source diameters (in arcseconds).

15.2. $^{17}$O

$^{17}$O is a linear molecule with hyperfine structure due to interaction with the electric quadrupole moment of the $^{17}$O ($I = \frac{5}{2}$) nucleus. Using the selection rule:

$$F = J + I, J + I - 1, J + I - 2, \ldots, |J - I|,$$

we find that each J-level is split into the hyperfine levels indicated in Table 4 (for the first five J-levels). Since

---

[10] Available online at http://spec.jpl.nasa.gov (use the “catalog directory with links” to access dipole moment and molecular constants information).
Table 4

| J | Number of Energy Levels | Allowed F |
|---|------------------------|-----------|
| 0 | 1                      | 3/2, 1/2  |
| 1 | 3                      | 5/2, 3/2, 1/2 |
| 2 | 5                      | 7/2, 5/2, 3/2, 1/2 |
| 3 | 7                      | 9/2, 7/2, 5/2, 3/2, 1/2 |
| 4 | 9                      | 11/2, 9/2, 7/2, 5/2, 3/2, 1/2 |

Figure 6. Electric quadrupole hyperfine energy level structure for the $J=0, 1,$ and 2 levels of C$^{17}$O. Note that the $3 (J = 1 − 0)$ and $9 (J = 2 − 1)$ allowed transitions are marked with arrows ordered by increasing frequency from left to right.

The selection rules for the single-spin coupling case is, $\Delta F = 0, \pm 1,$ and $\Delta J = \pm 1,$ there are 3, 9, and 14 allowed hyperfine transitions for the $J = 1 − 0, J = 2 − 1,$ and $J = 3 − 2$ transitions, respectively. Figure 6 shows the energy level structure for the $J = 1 − 0$ and $J = 2 − 1$ transitions.

We can calculate the relative hyperfine intensities ($R_i$) for the $J = 1 − 0$ and $J = 2 − 1$ transitions using the formalism derived in Section 10. Using the formalism described in Section 10 we can derive the relevant $R_i$ for the electric quadrupole hyperfine coupling cases ($R_i(F,J), I = \frac{5}{2}$, Table 5). Figure 7 shows the synthetic spectra for the C$^{17}$O $J = 1 − 0$ and $J = 2 − 1$ transitions.

To derive the column density for C$^{17}$O from a measurement of its $J = 1 − 0$ transition we use the general equation for molecular column density (Equation 32), with the following properties of the C$^{17}$O $J = 1 − 0$ transition:

\[ S = \frac{J_u}{2J_u + 1} \]
\[ \mu = 0.11032 \text{ Debye} = 1.1032 \times 10^{-19} \text{ esu} \]
\[ B_0 = 56179.9911 \text{ MHz} \]
\[ g_J = 2J_u + 1 \]
\[ g_K = 1 \text{ (for linear molecules)} \]
\[ g_I = 1 \text{ (for linear molecules)} \]
\[ Q_{\text{rot}} \approx \frac{kT}{\hbar B} + \frac{1}{3} \text{ (Equation 52)} \]
\[ \approx 0.37 (T + 0.90) \]
\[ E_u = 5.39 \text{ K} \]
\[ R_i = \frac{3}{9} \]
outer N nucleus has a much larger coupling strength than see Shirley et al. (2005); Pagani et al. (2009). Since the interaction between its spin and the quadrupole moments

\[ \text{Equation 80}, \text{Equation 92 becomes:} \]

\[ \text{Assuming that the emission is optically thin (} \tau_{\nu} \ll 1; \text{ Equation 80), Equation 92 becomes:} \]

\[ \text{where } \nu \text{ is the frequency of the hyperfine transition used. For example, if the } F=2 \rightarrow 1, 0 \text{ hyperfine was chosen for this calculation, } R_i = \frac{3}{2}. \text{ (See Table 5) and } \nu = 112359.285 + 0.724 \text{ MHz = 112.360099 GHz. Equation 93 then becomes:} \]

\[ \text{the inner N nucleus, the hyperfine structure can be determined by a sequential application of the spin coupling:} \]

\[ \hat{F} = \hat{J} + I_N, \]

\[ \hat{F} = \hat{F}_1 + I_N. \]

When the coupling from both N nuclei is considered:

- The } J = 0 \text{ level is split into 3 energy levels,
- The } J = 1 \text{ level is split into 7 energy levels,
- The } J = 2 \text{ and higher levels are split into nine energy levels.

Since the selection rules for the single-spin coupling case apply, } \Delta F_1 = 0, \pm 1, \Delta F = 0, \pm 1, 0 \rightarrow 0, \text{ and } \Delta J = \pm 1, \text{ there are 15, 34, and 38 hyperfine transitions for the } J = 1 \rightarrow 0, J = 2 \rightarrow 1, \text{ and } J = 3 \rightarrow 2 \text{ transitions, respectively. Figure 8 shows the energy level structure for the } J = 1 \rightarrow 0 \text{ transition.

To illustrate the hyperfine intensity calculation for } \text{nH}^+, \text{ we derive the relative intensities for the } J = 1 \rightarrow 0 \text{ transition. Relative intensities, derived using the formalism presented in Section 10 and Equation 57, are listed in Tables 6 and 7. Figure 9 shows the synthetic spectrum for the } nH^+ J = 1 \rightarrow 0 \text{ transition.

To derive the column density for } nH^+ \text{ we start with the general equation for the total molecular column den-
Table 7
Inner Nitrogen (F) Hyperfine Intensities for N$_2$$^+$ J = 1 − 0

| $F' \rightarrow F^a$ | $F'_1 \rightarrow F_1^a$ | a | b | c | $\frac{(2F'+1)(2F+1)}{(2J_N+1)}$ | 6j | $R_i(F,F_1)$ |
|---------------------|------------------------|---|---|---|-------------------------------|---|----------------|
| (1,0)               | (0,1)                  | 1 | 0 | 1 | 1                            |   | 1/2                        |
| (1,1)               | (0,1)                  | 1 | 1 | 1 | 3                            |   | 1/2                        |
| (1,2)               | (0,1)                  | 1 | 1 | 2 | 5                            |   | 1/2                        |
| (0,1)               | (1,1)                  | 1 | 1 | 1 | 1                            |   | 1/2                        |
| (1,0)               | (1,1)                  | 1 | 1 | 1 | 3                            |   | 1/2                        |
| (1,1)               | (1,1)                  | 1 | 1 | 2 | 5                            |   | 1/2                        |
| (1,2)               | (1,1)                  | 1 | 1 | 2 | 5                            |   | 1/2                        |
| (2,1)               | (1,1)                  | 1 | 1 | 2 | 5                            |   | 1/2                        |
| (2,2)               | (1,1)                  | 1 | 2 | 1 | 2                            |   | 1/2                        |
| (1,0)               | (2,1)                  | 1 | 2 | 1 | 1                            |   | 1/2                        |
| (1,1)               | (2,1)                  | 1 | 1 | 2 | 3                            |   | 1/2                        |
| (1,2)               | (2,1)                  | 1 | 1 | 2 | 5                            |   | 1/2                        |
| (2,1)               | (2,1)                  | 1 | 2 | 2 | 5                            |   | 1/2                        |
| (2,2)               | (2,1)                  | 1 | 2 | 2 | 5                            |   | 1/2                        |
| (3,2)               | (2,1)                  | 1 | 2 | 3 | 7                            |   | 1/2                        |

$^a$ $I_N = 1.$

Table 8
Hyperfine Intensities$^a$ for N$_2$$^+$ J=1 − 0

| $F' \rightarrow F^b$ | $F'_1 \rightarrow F_1^b$ | $J' \rightarrow J$ | $R_i(F_1,J) R_i(F,F_1)$ | $\Delta \nu^b$ (kHz) | $R_i(\text{obs})^c$ |
|---------------------|------------------------|-------------------|--------------------------|----------------------|-------------------|
| (0,1)               | (1,1)                  | (1,0)             |                          | −2155.7              | 3/7               |
| (2,2)               | (1,1)                  | (1,0)             |                          | −1859.9              | 3/7               |
| (2,1)               | (1,1)                  | (1,0)             |                          | −1723.4              | 3/7               |
| (1,1)               | (1,1)                  | (1,0)             |                          | −297.1               | 3/7               |
| (1,0)               | (1,1)                  | (1,0)             |                          | +0.0                 | 3/7               |
| (1,2)               | (2,1)                  | (1,0)             |                          | +189.9               | 3/7               |
| (1,0)               | (2,1)                  | (1,0)             |                          | +2488.3              | 3/7               |
| (1,1)               | (0,1)                  | (1,0)             |                          | +2448.3              | 3/7               |
| (1,0)               | (1,1)                  | (1,0)             |                          | +2448.3              | 3/7               |
| (1,0)               | (0,1)                  | (1,0)             |                          | +2448.3              | 3/7               |
| (1,0)               | (0,1)                  | (1,0)             |                          | +2448.3              | 3/7               |

$^a$ The sum of the relative intensities $\sum_i R_i = 1.0.$
$^b$ Frequency offset in kHz relative to 93173.7767 MHz (Caselli et al. 1995).
$^c$ Since the J=0 level has no hyperfine splitting, only the sum of all transitions into the J=0 is observed.

sity (Equation 32) with:

\[
S = \frac{J_u}{2J_u + 1} \quad \text{(see Section 9.1)}
\]

\[
\mu = 3.37 \text{ Debye} = 3.37 \times 10^{-18} \text{ esu}
\]

\[
B_0 = 46586.88 \text{ MHz}
\]

\[
R_i = \text{(see Section 10 or, for J=1-0, see Table 8)}
\]

\[
g_J = 2J_u + 1
\]

\[
g_K = 1 \quad \text{(for linear molecules)}
\]

\[
g_I = 1 \quad \text{(for linear molecules)}
\]

\[
Q_{rot} \simeq \frac{kT}{hB} + \frac{1}{3} \quad \text{(Equation 132)}
\]

\[
\simeq 0.45 (T + 0.74)
\]

\[
E_u = 4.4716 \text{ K}
\]

which leads to:

\[
N_{tot}(N_2H^+) = \frac{3h}{8\pi^3 \mu^2 J_u R_i} \exp \left( \frac{E_u}{kT_{ex}} \right)
\]

\[
\times \left[ \exp \left( \frac{h\nu}{kT_{ex}} \right) - 1 \right]^{-1} \int \tau_0 \, dv. \quad (95)
\]
transition intensities as described in Appendix D.

Of the 15 hyperfine split levels only 7 are observed due to the fact that there is no hyperfine splitting of the J=0 level, but it is degenerate in energy. Grouping of the indicated transitions show the 7 observed transitions. Transitions are ordered by increasing frequency from left to right.

Synthetic spectra for the \( N_2 \) and \( H^+ \) are shown. Horizontal axes are offset velocity (top) and frequency (bottom) relative to 93173.7767 MHz. Overlain as a dashed line is a synthetic spectrum. Assuming optically thin emission (Equation 80), we find that Equation 95 becomes:

\[
N_{\text{tot}}(N_2 H^+ (3, 2; 2, 1)) = \frac{2.59 \times 10^{14} \exp \left( \frac{47}{T_{\nu}} \right)}{\nu(GHz) R_i \exp \left( \frac{h \nu}{kT_{\text{ex}}} \right)} \times \left[ \frac{T_B \Delta v(km/s)}{f (J_{\nu}(T_{\text{ex}}) - J_{\nu}(T_{bg}))} \right] \text{cm}^{-2}, \quad (96)
\]

where \( \nu \) is the frequency of the hyperfine transition used. For example, if the \( F=(2,1) \), \( J=(1,0) \) hyperfine was chosen for this calculation, \( R_i = \frac{1}{T_{\nu}} \) (See Table 8) and \( \nu = 93.1737767 \) GHz. Equation 95 then becomes:

\[
N_{\text{tot}}(N_2 H^+ (3, 2; 2, 1)) = \frac{2.59 \times 10^{14} \exp \left( 47 \right)}{\nu(GHz) \exp \left( \frac{h \nu}{kT_{\text{ex}}} \right)} \times \left[ \frac{T_B \Delta v(km/s)}{f (J_{\nu}(T_{\text{ex}}) - J_{\nu}(T_{bg}))} \right] \text{cm}^{-2}. \quad (97)
\]

where the transition designation is in the \((F',F'_i;F,F_i)\) format. Note that this transition is blended with the nearby \( F'=1 \) and \( 2 (F'_i,H'_1) = (2,1) \) hyperfine transitions under many molecular cloud physical conditions.

15.4. \( NH_3 \)

Ammonia (\( NH_3 \)) is a symmetric top molecule with three opposing identical H (spin=\( \frac{1}{2} \)) nuclei. Quantum mechanical tunneling of the N nucleus through the potential energy plane formed by the H nuclei leads to inversion splitting of each \( NH_3 \) energy level. On top of this inversion splitting the energy levels are split due to two hyperfine interactions:

**J–I \(_N\):** Coupling between the quadrupole moment of the N nucleus (\( I_N = 1 \)) and the electric field of the H atoms, which splits each energy level into three hyperfine states. For this interaction the angular momentum vectors are defined as follows: \( \vec{F}_1 = \vec{J} + \vec{I}_N \).

**F \(_1\)–I \(_H\):** Coupling between the magnetic dipole of the three H nuclei (\( I_H = \frac{1}{2} \) for \( K \neq 0 \) or 3n \( \text{para} \), \( I_H = \frac{3}{2} \) for \( K=3n \) \( \text{ortho} \)) with the weak current generated by the rotation of the molecule. For this interaction the angular momentum vectors are defined as follows: \( \vec{F} = \vec{F}_1 + \vec{I}_H \).

Weaker N-H spin-spin and H-H spin-spin interactions also exist, but only represent small perturbations of the existing hyperfine energy levels.

Figure 11 shows all \( NH_3 \) energy levels below 1600 K, while Table 9 lists the level energies for \( J \leq 6 \). Figure 11 shows the rotational energy level diagram for the first four J-levels of \( NH_3 \), while Figure 12 shows the inversion and hyperfine level structure for the \( (1,1) \) and \( (2,2) \) transitions.

We can calculate the relative hyperfine intensities (\( R_i \)) for the \((1,1), (2,2), (3,3), \) and \((4,4)\) transitions using the formalism derived in Section 10. Using the formalism presented in Section 10, we can derive the relevant \( R_i \) for the quadrupole hyperfine (\( R_i(F_1, J), I_N = 1 \)) and magnetic hyperfine (\( R_i(F, F_i), I_H = \frac{1}{2} \) \( \text{para} \), \( K \neq 0 \) or 3n) and \( \frac{3}{2} \) \( \text{ortho} \), \( K = 3n \)) cases. The resultant total hyperfine intensities are derived by multiplying the magnetic hyperfine intensities (\( R_i(F, F_i) \)) by the associated quadrupole hyperfine intensities (\( R_i(F_1, J) \)). Tables 10 and 20 show the results of this calculation for the \( NH_3 \) \((1,1)\) and \( (2,2)\) transitions, respectively. Figure 13 shows the synthetic spectra for the \( NH_3 \) \((1,1)\) and \( (2,2)\) transitions.

---

11 Alternatively, one can derive \( \tau \) using the ratio of two hyperfine transition intensities as described in Appendix \( D \).
For illustration we can derive the column density equation for a para-NH$_3$ ($K \neq 0$ or $3n$) inversion ($\Delta K = 0$)
Figure 12. Inversion and hyperfine energy level structure for the (1,1) (top) and (2,2) (bottom) transitions of NH$_3$. Note that the 18 (1,1) and 24 (2,2) allowed transitions are marked with arrows ordered by increasing frequency from left to right. Adapted from Ho & Townes (1983).
transition. For para-NH$_3$ inversion transitions:

\[
S = \frac{K^2}{J_u(J_u+1)}
\]

\[
\mu = 1.468 \text{ Debye} = 1.468 \times 10^{-18} \text{ esu}
\]

\[
R_i = \text{(see Section 11 or, for (1,1) and (2,2), see Tables 19 and 20)}
\]

\[
g_J = 2J_u + 1
\]

\[
g_K = 2 \text{ for } K \neq 0
\]

\[
g_I = \frac{2}{3} \text{ for } K \neq 3n
\]

Doing the calculation in two stages, we can first derive the following equation for the molecular column density in NH$_3$ as derived from a measurement of a (J,K) inversion ($\Delta J = 0, \Delta K = 0$) transition assuming optically thin emission (see Rosolowsky et al. (2008) for the methodology to fit hyperfine transitions in the optically thick limit) using Equation 80:

\[
N_{tot}(NH_3) = \frac{3\hbar}{8\pi^3 \mu^2 R_i} \frac{J_u(J_u+1)}{K^2} \frac{Q_{rot}}{g_J g_K g_I} \\
\times \exp \left( \frac{E_u}{kT} \right) \frac{\hbar}{\nu_{\text{ex}}} \left[ \frac{\int T_{\text{HD}}dv}{\nu(T_{\text{ex}})} \right].
\]

(98)

Further assuming that we are measuring para-NH$_3$ (K≠0 or 3n), Equation 88 becomes:

\[
N_{tot}(NH_3) \simeq \frac{7.44 \times 10^{12} J_u(J_u+1)Q_{rot}}{R_i K^2(2J_u+1)} \\
\times \exp \left( \frac{E_u}{kT} \right) \frac{\hbar}{\nu_{\text{ex}}} \left[ \frac{\int T_{\text{HD}}dv(km/s)}{\nu(T_{\text{ex}})} \right] \text{ cm}^{-2}.
\]

(99)

15.5. H$_2$CO

Formaldehyde (H$_2$CO) is a slightly asymmetric rotor molecule with $\kappa \simeq -0.961$ (Equation 45), which means that H$_2$CO is nearly a prolate symmetric rotor. The slight asymmetry in H$_2$CO results in limiting prolate (quantum number K$_{-1}$) and oblate (quantum number K$_{+1}$) symmetric rotor energy levels that are closely spaced in energy, a feature commonly referred to as “K-doublet splitting”. Figure 14 shows the energy level diagram for H$_2$CO including all energy levels $E \leq 300$ K. In addition to the asymmetric rotor energy level structure H$_2$CO possesses spin-rotation and spin-spin hyperfine energy level structure. Magnetic dipole interaction between the H nuclei ($I_H = 0/1$ for para-/ortho-H$_2$CO) and rotational motion of the molecule result in spin-rotation hyperfine energy level splitting. Since the two H nuclei have equal coupling, the two H nuclei spins couple with each other first and the hyperfine coupling scheme is $I_H = I_i + I_2$ and $F = J = I_H$. Since the interchange of the two $^1$H atoms ($I_1 = I_2 = 1/2$) obey Fermi-Dirac statistics (total wave function is anti-symmetric to this interchange) and alternating K$_a$ ladders in H$_2$CO have a different rotational wavefunction symmetry, only ortho-H$_2$CO levels ($I_H = 1$) with K$_a$ = odd integers have hyperfine splitting. For the ortho-H$_2$CO 110–111 transition, the frequency offsets of these hyperfine transitions are $\Delta \nu \lesssim 18.5$ kHz. The weaker spin-spin interactions between the nuclei are generally not considered.

Table 10 lists the frequencies and relative intensities for the spin-rotation hyperfine transitions of the H$_2$CO 110−111, 211−212, and 312−313 transitions. Figure 15 shows the synthetic spectra for the H$_2$CO 110–111, 211−212, and 312−313 transitions. Note that the hyperfine intensities are exactly equal to those calculated for the spin-rotation hyperfine components of NH$_3$ (see Section 4).

For illustration we can derive the column density equation for a ortho-H$_2$CO (K$_{-1}$ odd) K-doublet ($\Delta K_{-1} = 0$)
Figure 14. Rotational energy level diagram for H$_2$CO including all energy levels with $E \leq 300$ K.

Table 10

| $F' \rightarrow F''$ | $J' \rightarrow J''$ | $\Delta_{HHH}F$ | a | b | c | $(2F'_{a}+1)(2F''_{b}+1)$ | 6J | $R_i(F_{1,J})$ |
|---------------------|---------------------|-----------------|---|---|---|---------------------|---|------------------|
| (1.0)               | (1.1)               | $-18.53$        | 1 | 1 | 1 | 1                   | $-\frac{1}{2}$ | $\frac{3}{2}$   |
| (0.1)               | (1.1)               | $-1.34$         | 1 | 1 | 1 | 1                   | $-\frac{1}{2}$ | $\frac{3}{2}$   |
| (2.2)               | (1.1)               | $-0.35$         | 1 | 2 | 1 | $\frac{3}{2}$      | $-\frac{3}{2}$ | $\frac{3}{2}$   |
| (2.1)               | (1.1)               | $+4.05$         | 1 | 1 | 2 | 5                   | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (1.2)               | (1.1)               | $+6.48$         | 1 | 1 | 2 | 5                   | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (1.1)               | (1.1)               | $+11.08$        | 1 | 1 | 1 | 3                   | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (1.1)               | (2.2)               | $-20.73$        | 1 | 2 | 2 | 5                   | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (1.2)               | (2.2)               | $-0.71$         | 1 | 2 | 2 | 5                   | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (2.1)               | (2.2)               | $-8.5$          | 1 | 2 | 2 | 5                   | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (3.3)               | (2.2)               | $+0.71$         | 1 | 3 | 2 | $\frac{3}{2}$      | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (3.2)               | (2.2)               | $+1.42$         | 1 | 2 | 3 | $\frac{3}{2}$      | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (2.3)               | (2.2)               | $+0.97$         | 1 | 2 | 3 | $\frac{3}{2}$      | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (2.2)               | (2.2)               | $+10.12$        | 1 | 2 | 2 | $\frac{3}{2}$      | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (2.3)               | (3.3)               | ...             | 1 | 3 | 3 | $\frac{3}{2}$      | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (4.3)               | (3.3)               | ...             | 1 | 3 | 4 | $\frac{3}{2}$      | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (4.4)               | (3.3)               | $+0.00$         | 1 | 4 | 3 | 27                  | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (3.3)               | (3.3)               | $-10.4$         | 1 | 3 | 3 | $\frac{3}{2}$      | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (2.2)               | (3.3)               | $+23.0$         | 1 | 2 | 3 | $\frac{3}{2}$      | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (3.4)               | (3.3)               | ...             | 1 | 3 | 4 | 21                  | $\frac{3}{2}$ | $\frac{3}{2}$   |
| (3.2)               | (3.3)               | ...             | 1 | 3 | 3 | $\frac{3}{2}$      | $\frac{3}{2}$ | $\frac{3}{2}$   |

$^a I_H = 1$ (ortho-H$_2$CO).

$^b$ Frequency offset in kHz relative to 4829.6596 MHz for $1_{10} - 1_{11}$, 14498.65 MHz for $2_{11} - 2_{12}$, and 28974.85 MHz for $3_{12} - 3_{13}$. 

$I_H = 1$ (ortho-H$_2$CO).
transitions. For ortho-H$_2$CO transitions:

\[
S = \frac{K^2}{J_u(J_u + 1)}
\]

\[
\mu = 2.331 \text{ Debye} = 2.331 \times 10^{-18} \text{ esu}
\]

\[
R_i = (\text{see Section 10 or, for } 1_{10} - 1_{11}, 2_{11} - 2_{12}, \text{ or } 3_{12} - 3_{13} \text{ see Table 10})
\]

\[
g_J = 2J_u + 1
\]

\[
g_K = 2 \text{ for } K \neq 0 \text{ (using the slightly-asymmetric rotor approximation),}
\]

\[
g_l = \frac{3}{4} \text{ for } K_1 \text{ odd}
\]

We can derive the following equation for the molecular column density in H$_2$CO as derived from a measurement of an ortho-H$_2$CO ($K_1$ odd) K-doublet transition assuming optically thin emission using Equation 30:

\[
N_{tot}(H_2CO) = \frac{3h}{8\pi^3 \mu^2 R_i} \frac{J_u(J_u + 1)}{K^2} \frac{Q_{rot}}{g_Jg_KeKg_l} \frac{1}{\exp \left( \frac{E_u}{kT_{ex}} \right) - 1} \left[ \int T_d dv \right. \\
\times \left. \exp \left( \frac{hv}{kT_{bg}} \right) - 1 \right] \int \left[ T_d dv(km/s) \right] \\
\simeq 9.83 \times 10^{11} J_u(J_u + 1)Q_{rot} R_iK^2(2J_u + 1) \\
\times \frac{1}{\exp \left( \frac{E_u}{kT_{ex}} \right) - 1} \left[ \int T_d dv(km/s) \right] \\
\left. \frac{1}{\exp \left( \frac{hv}{kT_{bg}} \right) - 1} \right] \int \tau_d dv. \quad (100)
\]

Note that the K-doublet transitions of H$_2$CO are rather unusual in that, due to an unusual collisional excitation effect, these transitions are often measured in absorption against the cosmic microwave background radiation. For $n(H_2) \lesssim 10^{6.5} \text{ cm}^{-3}$, a collisional selection effect overpopulates the lower energy states of the $1_{10} - 1_{11}$ through $5_{11} - 5_{15}$ transitions (Evans et al. 1973, Garrison et al. 1973). This overpopulation of the lower energy states results in a "cooling" of the $J \lesssim 5$ K-doublets to an excitation temperature that is lower than that of the cosmic microwave background. This causes the $J \lesssim 5$ K-doublet transitions to appear in absorption. For volume densities $n(H_2) \gtrsim 10^{6.5} \text{ cm}^{-3}$ and $T_K \approx 40 \text{ K}$ this collision pump is quenched. For these higher volume densities the $J \lesssim 5$ K-doublets are driven into emission over a wide range of kinetic temperatures and abundances (see Figure 1 in Mangum et al. 2008).

16. SUMMARY

The most general form of the molecular spectral line column density is given by Equation 32:

\[
N_{tot} = \frac{3h}{8\pi^3 |\mu| \mu_a} \frac{Q_{rot}}{g_u} \exp \left( \frac{E_u}{kT_{ex}} \right) \\
\times \left[ \exp \left( \frac{hv}{kT_{bg}} \right) - 1 \right]^{-1} \int \tau_d dv. \quad (101)
\]

For absorption line measurements one should use the velocity integrated opacity directly in Equation 32. For
emission lines, the velocity integrated opacity is usually converted to an integrated intensity. In the optically thin limit, the column density becomes (Equation 86):

\[
N_{\text{tot}}^{\text{thin}} = \left( \frac{3h}{8\pi^2S\mu^2R_i} \right) \left( \frac{Q_{\text{rot}}}{g_J g_K g_I} \right) \exp \left( \frac{E_j}{kT} \right) \exp \left( \frac{h\nu}{kT} \right) - 1 \times \frac{1}{(J_J(T_{ex}) - J_J(T_{bg}))} \int \frac{T_R dv}{f}. \tag{102}
\]

The optically thick column density is related to the optically thin column density by Equation 88:

\[
N_{\text{tot}} = N_{\text{tot}}^{\text{thin}} \frac{\tau}{1 - \exp(-\tau)}. \tag{103}
\]

In this tutorial, we have carefully derived the terms in Equations 22, 23 and 24. Note, though, that these equations assume all energy levels are characterized by the same excitation temperature (the “CTEX LTE approximation”; See Section 12). We have also explored the limits of the CTEX approximation (Section 12). Non-LTE determinations of the column density require a coupled radiative transfer and statistical equilibrium calculation and can be performed with publically available tools.

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APPENDIX

LINE PROFILE FUNCTIONS

For a Gaussian profile the function \( \phi(\nu) \) is given by

\[
\phi(\nu) = \frac{1}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{(\nu - \nu_0)^2}{2\sigma^2} \right], \tag{A1}
\]

where \( \nu_0 \) and \( \nu \) are the central and offset frequencies of the line profile for a particle with mass \( M \) and velocity \( v \),

\[
2\sigma^2 = \frac{\nu_0^2}{c^2} \left( \frac{2kT_k}{M} + v^2 \right), \tag{A2}
\]
and
\[ \int \phi(\nu) d\nu = 1. \quad (A3) \]

The Gaussian profile has a FWHM given by (in both frequency and velocity):
\[ \Delta \nu_D = \frac{2 \nu_0}{c} \left[ \ln 2 \left( \frac{2kT_k}{M} + v^2 \right) \right]^2 \]
\[ \Delta v_D = 2 \left[ \ln 2 \left( \frac{2kT_k}{M} + v^2 \right) \right]^2, \quad (A4) \]

and a peak value given by:
\[ \phi(\nu)_{\text{peak}} = \frac{2 \sqrt{\ln 2}}{\sqrt{\pi} \Delta \nu_D v_0} = \frac{2 \sqrt{\ln 2}}{\sqrt{\pi} v_0 \Delta v_D}. \quad (A6) \]

If one uses peak values instead of integrating over a Gaussian profile to derive column densities, one must make the following correction:
\[ (N_{\text{tot}})_{\text{Gauss}} = 2 \frac{\ln 2}{\pi} (N_{\text{tot}})_{\text{peak}}. \quad (A7) \]

INTEGRATED FLUXES VERSUS BRIGHTNESS TEMPERATURES

All calculations in this document assume the use of integrated brightness temperatures (\( \int T_B \Delta \nu \)). If one uses integrated fluxes (\( \int S_{\nu} \Delta \nu \)), the total molecular column density assuming optically-thin emission (Equation 82) is modified by using the relationship between flux density and brightness temperature:
\[ S_{\nu} = \frac{2kT_B \nu^2}{c^2} \Omega_s, \quad (B1) \]
and becomes
\[ N_{\text{tot}} = \left( \frac{D}{2R_s} \right)^2 \frac{3c^2}{16\pi^3 S_{\mu^2} v^3} \left( \frac{Q_{\text{rot}}}{gJgK_{\text{nuclear}}} \right) \exp \left( \frac{E_u}{kT} \right) \int S_{\nu} \Delta \nu \]
\[ = \frac{3c^2}{16\pi^3 \Omega_s S_{\mu^2} \nu^3} \left( \frac{Q_{\text{rot}}}{gJgK_{\text{nuclear}}} \right) \exp \left( \frac{E_u}{kT} \right) \int S_{\nu} \Delta \nu. \quad (B2) \]

INTEGRATED INTENSITY UNCERTAINTY

For cases where you do not have a calculation from a fit to the integrated intensity of a spectral line, one can use the following estimate given a measurement of the baseline RMS and line profile properties.
\[ \int T_d \Delta \nu = \Delta \nu_c \sum_{n=1}^{N} T_n, \quad (C1) \]
\[ \equiv I, \]
where \( \Delta \nu_c \) is the spectral velocity channel width, \( T_n \) is a spectral channel value, and the line spans \( N \) channels. The statistical uncertainty of the integrated line intensity is given by:
\[ \sigma_I^2 = \sum_{n=1}^{N} \sigma_{T_n}^2 \left[ \frac{\partial I}{\partial T} \right]^2 + \sigma_{\Delta \nu_c}^2 \left[ \frac{\partial I}{\partial (\Delta \nu_c)} \right]^2 \]
\[ = \sum_{n=1}^{N} \sigma_{T_n}^2 (\Delta \nu_c)^2 \]
\[ = N \sigma_T^2 (\Delta \nu_c)^2, \quad (C2) \]
where we have used the fact that we know the velocity channel width (\( \sigma_{\Delta \nu_c} = 0 \)) and assuming that all of the channel noise values are equal. We can then write Equation (C2) as follows:
\[ \sigma_I = \sqrt{N \sigma_T \Delta \nu_c} \]
\[ = \sigma_T \sqrt{\Delta \nu_{\text{line}}} \Delta \nu_c, \quad (C3) \]
where we have used the fact that the spectral line width $\Delta v_{\text{line}} = N\Delta v_c$ to get the last expression for $\sigma_f$.

**HYPERFINE RATIOS AND OPTICAL DEPTH**

For molecules with measurable hyperfine splitting one can derive an estimate of the optical depth in a given transition. Starting with the form of the radiative transfer equation which involves the observable Source Radiation Temperature $T_R$ (Equation 27), we can write the ratio of two hyperfine transitions as follows:

$$\frac{T_R(m)}{T_R(s)} = \frac{f_m[J_v(T_{ex,m}) - J_v(T_{bg})] [1 - \exp(-\tau_{v,m})]}{f_s[J_v(T_{ex,s}) - J_v(T_{bg})] [1 - \exp(-\tau_{v,s})]}, \quad (D1)$$

where “m” and “s” refer to the main and satellite hyperfine components of a given rotational transition. If we further assume that the hyperfine levels are in LTE ($J_v(T_{ex,m}) = J_v(T_{ex,s})$)\(^{12}\) and that the two hyperfine components emit over the same volume of gas ($f_m = f_s$), Equation (D1) becomes:

$$\frac{T_R(m)}{T_R(s)} = \frac{1 - \exp(-\tau_{v,m})}{1 - \exp(-\tau_{v,s})}. \quad (D2)$$

In equilibrium the optical depths of the hyperfine transitions within a given rotational transition should be proportional to their relative intensities:

$$\frac{\tau_{v,s}}{\tau_{v,m}} = \frac{R_{i,s}}{R_{i,m}}. \quad (D3)$$

Inserting Equation (D3) into Equation (D2) results in a simple equation which allows for the calculation of the optical depth of a hyperfine transition (and, therefore, the rotational transition under study) using just the measured intensities of two of its component hyperfine transitions:

$$\frac{T_R(m)}{T_R(s)} (NH_3(1,1)) = \frac{1 - \exp(-\tau_{v,m})}{1 - \exp(-\frac{R_{i,s}}{R_{i,m}}\tau_{v,m})}. \quad (D4)$$

Taking the strongest and second-strongest transitions of the NH$_3$ (1,1) transition, from Table 11 we find that:

$$\frac{T_R(m)}{T_R(s)} (NH_3(1,1)) = \frac{1 - \exp(-\tau_{v,m})}{1 - \exp(-\frac{1}{2} \tau_{v,m})}. \quad (D5)$$

**EXCITATION AND KINETIC TEMPERATURE**

This section is drawn from Appendix A of Mangum et al. (1992). If the metastable ($J = K$; $A_{ij} < 10^{-7} \text{s}^{-1}$) states in NH$_3$ are coupled only through collisions and the populations in the upper non-metastable ($J \neq K$; $A_{ij} \sim 0.01 \text{s}^{-1}$) states in each K–ladder can be neglected, the populations in the metastable states are related through the Boltzmann equation. In molecular clouds, though, $\Delta K = 1$ collisions across K-ladders will deplete metastable states in favor of their next lower J metastable states. Therefore, for example, collisional de-excitation of the (2,2) transition will result in an increase in the population of the (2,1) state, followed by quick radiative relaxation of the (2,1) state into the metastable states. Therefore, for example, collisional de-excitation of the (2,2) transition will result in an increase in the population of the (2,1) state, followed by quick radiative relaxation of the (2,1) state into the metastable states. This implies that an excitation temperature, $T_{ex}(J',K'; J, K)$ relating the populations in the $(J',K')$ and $(J,K)$ states, $n(J',K')$ and $n(J,K)$, may be derived. From the Boltzmann equation

$$\frac{n(J',K')}{n(J,K)} = \frac{g(J',K')}{g(J,K)} \exp \left[ \frac{-\Delta E(J',K'; J, K)}{T_{ex}(J',K'; J, K)} \right], \quad (E1)$$

and the ratio of level $(J',K')$ and $(J,K)$ column densities (assuming $h\nu \ll kT_{ex}(J',K'; J, K)$) for the $(J,K)$ and $(J',K')$ transitions

$$\frac{N(J',K')}{N(J,K)} = \frac{J'(J'+1)K^2\tau(J',K')\Delta v(J',K')}{J(J+1)(K')^2\tau(J,K)\Delta v(J,K)}, \quad (E2)$$

and the fact that in a homogeneous molecular cloud

$$\frac{n(J',K')}{n(J,K)} = \frac{N(J',K')}{N(J,K)}, \quad (E3)$$

we find that

$$\frac{g(J',K')}{g(J,K)} \exp \left[ \frac{-\Delta E(J',K'; J, K)}{T_{ex}(J',K'; J, K)} \right] = \frac{J'(J'+1)K^2\tau(J',K')\Delta v(J',K')}{J(J+1)(K')^2\tau(J,K)\Delta v(J,K)}. \quad (E4)$$

\(^{12}\) Equivalently, one can use molecular isotopologues with the additional assumptions that one knows the isotopic ratio and there is no fractionation between that atomic ratio and the molecular ratio.

\(^{13}\) But note that anomalous hyperfine excitation has been observed in some molecules (see Section 10), notably the HCN J=1–0 transition (Loughnane et al. 2012). This would invalidate the equal-excitation temperature assumption.
Using

\[ \tau(J, K) = \left[ \sum R_{F,F'} / \sum R_m \right] \tau(J, K, m), \]  
(E5)

where \( R \) is the relative intensity for a quadrupole \((F,F')\) or main \((m)\) hyperfine component and

\[ I_{JK} \equiv \left[ \sum R_{F,F'} / \sum R_m \right], \]

for the \((1,1)\) and \((2,2)\) transitions, we can relate the total optical depth \( \tau(J, K, m) \) to the optical depth in the main hyperfine component \( \tau(J,K,m) \), noting that for \( \text{NH}_3 \) \( g(J,K) = 2J_u + 1 \), and solving Equation E4 for \( T_{ex}(J', K'; J, K) \) we find that

\[ T_{ex}(J', K'; J, K) = -\Delta E(J', K'; J, K) \]
\[ \times \left\{ \ln \left[ \frac{(2J + 1)J'(J' + 1)K^2J_{JK} \tau(J', K', m) \Delta v(J', K')}{(2J' + 1)J(J + 1)(K')^2J_{JK} \tau(J, K, m) \Delta v(J, K)} \right] \right\}^{-1}. \]  
(E6)

Using

\[ \frac{T_B(J, K, m)}{T_B(J', K', m)} = \frac{1 - \exp[-\tau(J, K, m)]}{1 - \exp[-\tau(J', K', m)]}, \]  
(E7)

which assumes equal excitation temperatures and beam filling factors in the \((J,K)\) and \((J',K')\) transitions. Solving Equation E7 for \( \tau(J', K', m) \) yields

\[ \tau(J', K', m) = -\ln \left[ 1 - \frac{T_B(J', K', m)}{T_B(J, K, m)} \frac{1 - \exp[-\tau(J, K, m)]}{1 - \exp[-\tau(J, K, m)]} \right]. \]  
(E8)

Substituting Equation E8 into Equation E6

\[ T_{ex}(J', K'; J, K) = -\Delta E(J', K'; J, K) \]
\[ \times \left\{ \ln \left[ \frac{(2J + 1)J'(J' + 1)K^2J_{JK} \Delta v(J', K')}{(2J' + 1)J(J + 1)(K')^2J_{JK} \Delta v(J, K)} \ln \left( 1 - \frac{T_B(J', K', m)}{T_B(J, K, m)} \frac{1 - \exp[-\tau(J, K, m)]}{1 - \exp[-\tau(J, K, m)]} \right) \right] \right\}^{-1}. \]  
(E9)

For \((J',K') = (2,2)\) and \((J,K) = (1,1)\), Equation E9 becomes:

\[ T_{ex}(2, 2; 1, 1) = -41.5 \left\{ \ln \left[ \frac{-0.283 \Delta v(2, 2)}{\tau(1, 1, m) \Delta v(1, 1)} \ln \left( 1 - \frac{T_B(2, 2, m)}{T_B(1, 1, m)} \frac{1 - \exp[-\tau(1, 1, m)]}{1 - \exp[-\tau(1, 1, m)]} \right) \right] \right\}^{-1}. \]  
(E10)
To derive the gas kinetic temperature from $T_{ex}(2,2;1,1)$, one uses statistical equilibrium (noting that only collisional processes are allowed between the different K–ladders), detailed balance, and the Boltzmann equation to calculate $T_K$ from $T_{ex}(J',K';J,K)$. Assuming that the populations in the (1,1) and (2,2) transitions are much greater than that in the higher lying levels of para–NH$_3$ and that the population of the non–metastable (2,1) level is negligible in comparison to that in the (1,1) level, we can use this “three–level model” of NH$_3$ to analytically derive an expression relating $T_{ex}(2,2;1,1)$ and $T_K$

$$1 + \frac{C(2,2;2,1)}{C(2,2;1,1)} = \left\{ \frac{g(1,1)}{g(2,2)} \exp \left[ \frac{\Delta E(2,2;2,1,1)}{T_{ex}(2,2;2,1,1)} \right] \right\} \left\{ \frac{g(2,2)}{g(1,1)} \exp \left[ -\frac{\Delta E(2,2;2,1,1)}{T_K} \right] \right\},$$  

(E11)

where $C(J',K';J,K)$ is the collisional excitation rate at temperature $T_K$ between levels $(J',K')$ and (J,K). Equation E11 can be re–written as

$$T_{ex}(2,2;1,1) \left\{ 1 + \left( \frac{T_K}{41.5} \right) \ln \left[ 1 + \frac{C(2,2;2,1)}{C(2,2;1,1)} \right] \right\} - T_K = 0.$$  

(E12)

Solutions of Equation E12 give $T_K$ for a measured $T_{ex}(2,2;1,1)$.

NH$_3$ FREQUENCY AND RELATIVE INTENSITY CALCULATION TABLES
Frequency offset in kHz relative to 23694.495487 kHz (Kukolich ch 1976, Table I (calculated)).

\[
F = I_N + F_1 = J + I_N, \text{ where } I_N = 1 \text{ and } I_H = \frac{1}{2}.
\]

Frequency offset in kHz relative to 23694.495487 kHz [Kukolich 1976, Table I (calculated)].
How to Calculate Molecular Column Density

Table 16
F\(_1\)-I\(_H\) Hyperfine Frequencies and Intensities for NH\(_3\)(2,2)

| \(F'' \rightarrow F^a\) | \(F''_1 \rightarrow F_1^a\) | \(\Delta \nu_{HF}\)^{b} (kHz) | a | b | c | \(\frac{(2F'+1)(2F'+1)}{2(F'+1)}\) | 6j | R\(_i\)(F, \(F_1\)) |
|------------------------|--------------------------|-------------------------|---|---|---|--------------------------|---|------------------|
| (\(\frac{1}{2}, \frac{1}{2}\)) | (1,2) | -2099.027 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | 1 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{3}{2}, \frac{3}{2}\)) | (1,2) | -2058.265 | \(\frac{3}{2}\) | \(\frac{3}{2}\) | 2 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{7}{2}, \frac{7}{2}\)) | (1,2) | -2052.509 | \(\frac{7}{2}\) | \(\frac{7}{2}\) | 4 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{7}{2}, \frac{7}{2}\)) | (3,2) | -1297.079 | \(\frac{7}{2}\) | \(\frac{7}{2}\) | 24 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{5}{2}, \frac{5}{2}\)) | (3,2) | -1296.096 | \(\frac{5}{2}\) | \(\frac{5}{2}\) | 12 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{5}{2}, \frac{5}{2}\)) | (3,2) | -1255.335 | \(\frac{5}{2}\) | \(\frac{5}{2}\) | 3 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{4}{2}, \frac{4}{2}\)) | (1,1) | -44.511 | \(\frac{4}{2}\) | \(\frac{4}{2}\) | 4 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{4}{2}, \frac{4}{2}\)) | (2,2) | -41.813 | \(\frac{4}{2}\) | \(\frac{4}{2}\) | 12 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{7}{2}, \frac{7}{2}\)) | (3,3) | -41.444 | \(\frac{7}{2}\) | \(\frac{7}{2}\) | 24 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{3}{2}, \frac{3}{2}\)) | (2,2) | -1.051 | \(\frac{3}{2}\) | \(\frac{3}{2}\) | 2 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{1}{2}, \frac{1}{2}\)) | (2,2) | -1.051 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | 2 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{4}{2}, \frac{4}{2}\)) | (3,3) | +0.309 | \(\frac{4}{2}\) | \(\frac{4}{2}\) | 32 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{5}{2}, \frac{5}{2}\)) | (3,3) | +0.309 | \(\frac{5}{2}\) | \(\frac{5}{2}\) | 32 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{4}{2}, \frac{4}{2}\)) | (1,1) | +1.054 | \(\frac{4}{2}\) | \(\frac{4}{2}\) | 8 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{1}{2}, \frac{1}{2}\)) | (1,1) | +1.054 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | 2 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{4}{2}, \frac{4}{2}\)) | (2,2) | +39.710 | \(\frac{4}{2}\) | \(\frac{4}{2}\) | 12 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{5}{2}, \frac{5}{2}\)) | (3,3) | +42.045 | \(\frac{5}{2}\) | \(\frac{5}{2}\) | 24 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{3}{2}, \frac{3}{2}\)) | (1,1) | +46.614 | \(\frac{3}{2}\) | \(\frac{3}{2}\) | 4 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{3}{2}, \frac{3}{2}\)) | (2,3) | +125.584 | \(\frac{3}{2}\) | \(\frac{3}{2}\) | 18 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{3}{2}, \frac{3}{2}\)) | (2,3) | +1295.345 | \(\frac{3}{2}\) | \(\frac{3}{2}\) | 12 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{3}{2}, \frac{3}{2}\)) | (2,3) | +1296.328 | \(\frac{3}{2}\) | \(\frac{3}{2}\) | 24 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{3}{2}, \frac{3}{2}\)) | (2,1) | +2058.265 | \(\frac{3}{2}\) | \(\frac{3}{2}\) | 12 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |
| (\(\frac{3}{2}, \frac{3}{2}\)) | (2,1) | +2099.027 | \(\frac{3}{2}\) | \(\frac{3}{2}\) | 8 | \(\frac{1}{2}\) | \(\frac{1}{2}\) | \(\frac{1}{2}\) |

\(^{a}\) \(F = J + I_N\) and \(F_1 = J + I_N\), where \(I_N = 1\) and \(I_H = \frac{1}{2}\).

\(^{b}\) Frequency offset in kHz relative to 23722633.335 kHz (Kukolich 1963, Table II (calculated))
Table 17
F₁ - I₁ Hyperfine Frequencies and Intensities for NH₃(3,3)

| \( F' \rightarrow F'^{a} \) | \( F'_{1} \rightarrow F_{1}^{a} \) | \( \Delta \nu_{HF}^{b} \) (kHz) | a | b | c | \( \frac{\left(2F'_{1}+1\right)\left(2F_{1}+1\right)}{2(2F+1)} \) | 6j | \( R_{i}(F, F'_{1}) \) |
|---|---|---|---|---|---|---|---|---|
| (1, 1) | (1, 1) | -2324.577 | 3 | 3 | 20 | 12 | 2.14 | 63.9 |
| (2, 2) | (2, 2) | -2312.558 | 3 | 2 | 12 | 2.14 | 42.0 | 63.9 |
| (3, 3) | (3, 3) | -2304.415 | 3 | 2 | 6 | 2.14 | 42.0 | 63.9 |
| (4, 4) | (4, 4) | -2301.989 | 3 | 2 | 6 | 2.14 | 42.0 | 63.9 |
| (1, 1) | (1, 1) | … | 3 | 3 | 16 | 13 | 17 | 17 |
| (2, 2) | (2, 2) | … | 3 | 3 | 9 | 13 | 17 | 17 |
| (3, 3) | (3, 3) | … | 3 | 3 | 12 | 13 | 17 | 17 |
| (4, 4) | (4, 4) | … | 3 | 3 | 12 | 13 | 17 | 17 |
| (1, 1) | (1, 1) | (1, 1) | 4 | 4 | 30 | 12 | 16 | 16 |
| (2, 2) | (2, 2) | (2, 2) | 2 | 2 | 25 | 12 | 16 | 16 |
| (3, 3) | (3, 3) | (3, 3) | 2 | 2 | 16 | 12 | 16 | 16 |
| (4, 4) | (4, 4) | (4, 4) | 2 | 2 | 16 | 12 | 16 | 16 |
| (1, 1) | (1, 1) | (1, 1) | 3 | 3 | 12 | 15 | 17 | 17 |
| (2, 2) | (2, 2) | (2, 2) | 3 | 3 | 12 | 15 | 17 | 17 |
| (3, 3) | (3, 3) | (3, 3) | 3 | 3 | 20 | 15 | 17 | 17 |
| (4, 4) | (4, 4) | (4, 4) | 3 | 3 | 20 | 15 | 17 | 17 |
| (1, 1) | (1, 1) | (1, 1) | 2 | 2 | 12 | 15 | 17 | 17 |
| (2, 2) | (2, 2) | (2, 2) | 2 | 2 | 12 | 15 | 17 | 17 |
| (3, 3) | (3, 3) | (3, 3) | 2 | 2 | 12 | 15 | 17 | 17 |
| (4, 4) | (4, 4) | (4, 4) | 2 | 2 | 12 | 15 | 17 | 17 |

Continued on next page
Table 17

F1–I_H Hyperfine Frequencies and Intensities for NH3(3,3) (continued)

| F' → F^a | F'_1 → F_1^a | Δν_H^b (kHz) | a | b | c | \frac{(2F'+1)(2F+1)}{(2I_H+1)} | 6J | R_e(F,F_1) |
|-----------|---------------|---------------|----|----|----|-----------------|----|----------------|
| (\frac{7}{2}, \frac{1}{2}) | (3,4) | +1682.036 | \frac{7}{2} | 4 | \frac{7}{2} | 6 | \frac{\sqrt{22}}{12} | \frac{55}{216} |
| (\frac{5}{2}, \frac{1}{2}) | (3,4) | +1688.264 | \frac{5}{2} | 4 | \frac{5}{2} | 20 | \frac{\sqrt{38}}{12} | 75 |
| (\frac{5}{2}, \frac{7}{2}) | (3,4) | +1689.873 | \frac{5}{2} | 4 | \frac{7}{2} | 12 | \frac{28\sqrt{2}}{12} | 397 |
| (\frac{7}{2}, \frac{2}{2}) | (3,4) | ... | \frac{7}{2} | 4 | \frac{2}{2} | ... | \frac{3\sqrt{18}}{12} | \frac{3}{7} |
| (\frac{7}{2}, \frac{7}{2}) | (3,4) | ... | \frac{7}{2} | 4 | \frac{7}{2} | 12 | \frac{84\sqrt{2}}{12} | 1176 |
| (\frac{5}{2}, \frac{2}{2}) | (3,4) | ... | \frac{5}{2} | 4 | \frac{2}{2} | ... | \frac{6\sqrt{12}}{12} | \frac{77}{18} |
| (\frac{7}{2}, \frac{2}{2}) | (3,4) | ... | \frac{7}{2} | 4 | \frac{2}{2} | ... | \frac{21\sqrt{2}}{12} | 132 |
| (\frac{9}{2}, \frac{2}{2}) | (3,4) | ... | \frac{9}{2} | 4 | \frac{2}{2} | ... | \frac{21\sqrt{2}}{12} | 132 |
| (\frac{5}{2}, \frac{2}{2}) | (3,4) | ... | \frac{5}{2} | 4 | \frac{2}{2} | ... | \frac{14\sqrt{2}}{12} | 210 |
| (\frac{9}{2}, \frac{2}{2}) | (3,4) | ... | \frac{9}{2} | 4 | \frac{2}{2} | ... | \frac{14\sqrt{2}}{12} | 210 |
| (\frac{5}{2}, \frac{2}{2}) | (3,4) | ... | \frac{5}{2} | 4 | \frac{2}{2} | ... | \frac{14\sqrt{2}}{12} | 210 |
| (\frac{9}{2}, \frac{2}{2}) | (3,4) | ... | \frac{9}{2} | 4 | \frac{2}{2} | ... | \frac{14\sqrt{2}}{12} | 210 |

^a F = I_H + F_1 and F_1 = J + I_N, where I_N = 1 and I_H = \frac{3}{7}.

^b Frequency offset in kHz relative to 23870129.183 kHz [Kukolich 1967, Table III (calculated)].
### Table 18

| $F' \rightarrow F''$ | $F'_1 \rightarrow F'_1$ | $\Delta \nu_{HF}^b$ (kHz) | a      | b      | c      | $\frac{(2F'+1)(2F''+1)}{2F(2F+1)}$ | 6j      | $R_s(F,F'_1)$ |
|----------------------|-------------------------|--------------------------|--------|--------|--------|----------------------------------|--------|--------------|
| (3/2, 2)            | (3, 4)                  | -2485.883                | $\frac{1}{2}$ | $\frac{3}{2}$ | 40     | $\frac{1}{6}\sqrt{2}$             | $\frac{5}{7}$ |              |
| (3/2, 2)            | (3, 4)                  | -2481.291                | $\frac{1}{2}$ | $\frac{3}{2}$ | 24     | $\frac{2}{3}\sqrt{11}$            | $\frac{7}{5}$ |              |
| (3/2, 2)            | (3, 4)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 32     | $\frac{12}{5}\sqrt{14}$           | $\frac{3}{7}$ |              |
| (3/2, 2)            | (5, 4)                  | -1924.144                | $\frac{1}{2}$ | $\frac{3}{2}$ | 40     | $\frac{3}{2}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (5, 4)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 60     | $\frac{3}{2}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (5, 4)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 50     | $\frac{15}{7}\sqrt{22}$           | $\frac{5}{35}$ |              |
| (3/2, 2)            | (4, 4)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 40     | $\frac{3}{2}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (4, 4)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 32     | $\frac{3}{2}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (4, 4)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 40     | $\frac{3}{2}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (4, 4)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 40     | $\frac{18}{7}\sqrt{10}$           | $\frac{1}{35}$ |              |
| (3/2, 2)            | (5, 5)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 50     | $\frac{3}{2}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (5, 5)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 60     | $\frac{3}{2}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (6, 6)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 60     | $\frac{3}{2}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (6, 6)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 60     | $\frac{3}{2}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (3, 3)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 32     | $\frac{28}{5}\sqrt{2}$            | $\frac{1}{35}$ |              |
| (3/2, 2)            | (3, 3)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 18     | $\frac{4}{5}\sqrt{11}$            | $\frac{3}{7}$ |              |
| (3/2, 2)            | (3, 3)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 24     | $\frac{12}{5}\sqrt{11}$           | $\frac{3}{7}$ |              |
| (3/2, 2)            | (3, 3)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 24     | $\frac{12}{5}\sqrt{11}$           | $\frac{3}{7}$ |              |
| (3/2, 2)            | (4, 5)                  | +1931.301                | $\frac{1}{2}$ | $\frac{3}{2}$ | 50     | $\frac{5}{2}\sqrt{11}$            | $\frac{5}{35}$ |              |
| (3/2, 2)            | (4, 5)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 72     | $\frac{60}{7}\sqrt{2}$            | $\frac{5}{35}$ |              |
| (3/2, 2)            | (4, 5)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 72     | $\frac{60}{7}\sqrt{2}$            | $\frac{5}{35}$ |              |
| (3/2, 2)            | (4, 5)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 72     | $\frac{60}{7}\sqrt{2}$            | $\frac{5}{35}$ |              |
| (3/2, 2)            | (4, 5)                  | ...                      | $\frac{1}{2}$ | $\frac{3}{2}$ | 72     | $\frac{60}{7}\sqrt{2}$            | $\frac{5}{35}$ |              |

*a $F = I_H + F_1$ and $F_1 = J + I_N$, where $I_N = 1$ and $I_H = \frac{1}{2}$.

*b Frequency offset in kHz relative to 24139416.34 kHz [Kukolich & Wolsky 1978, Table II (calculated)]
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### Table 19

| $F' \rightarrow F$ | $F'_1 \rightarrow F_1$ | $J' \rightarrow J$ | $R_1(F_1, J)R_i(F, F_1)$ | $R_i(F, F_1)$ |
|---------------------|------------------------|-------------------|-------------------------|--------------|
| (1, 1)              | (0, 1)                 | (1, 1)            |                         |              |
| (2, 1)              | (0, 1)                 | (1, 1)            |                         |              |
| (1, 1)              | (2, 1)                 | (1, 1)            |                         |              |
| (1, 1)              | (2, 1)                 | (1, 1)            |                         |              |
| (1, 1)              | (1, 1)                 | (1, 1)            |                         |              |
| (1, 1)              | (1, 1)                 | (1, 1)            |                         |              |
| (1, 1)              | (2, 2)                 | (1, 1)            |                         |              |
| (1, 1)              | (2, 2)                 | (1, 1)            |                         |              |
| (1, 1)              | (1, 1)                 | (1, 1)            |                         |              |
| (1, 1)              | (1, 1)                 | (1, 1)            |                         |              |
| (1, 1)              | (1, 1)                 | (1, 1)            |                         |              |
| (1, 1)              | (1, 1)                 | (1, 1)            |                         |              |

* Compare with [Kukolich (1967)] Table IX after scaling $R_i$ by $(2I_H + 1)(2I_N + 1) = 6$ [Kukolich (1967)] lists unnormalized line strengths in their Table IX.

b Note that the sum of the relative intensities $\sum_i R_i = 1.0$.

### Table 20

| $F' \rightarrow F$ | $F'_1 \rightarrow F_1$ | $J' \rightarrow J$ | $R_1(F_1, J)R_i(F, F_1)$ | $R_i(F, F_1)$ |
|---------------------|------------------------|-------------------|-------------------------|--------------|
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |
| (1, 1)              | (1, 2)                 | (2, 2)            |                         |              |

* Compare with [Kukolich (1967)] Table IX after scaling $R_i$ by $(2I_H + 1)(2I_N + 1) = 6$ [Kukolich (1967)] lists unnormalized line strengths in their Table IX.

b Note that the sum of the relative intensities $\sum_i R_i = 1.0$. 