Lecture 18 The $\text{H}_2$ and CO Molecules

1. Review Items on Molecular Structure
2. The $\text{H}_2$ Molecule
3. The $^{12}\text{CO}$ Molecule
4. What's Missing

References
Herzberg, Molecular Spectra & Molecular Structure, Vol. 1 (1950)
Herzberg, The Spectra & Structure of Simple Free Radicals, (Cornell, 1971), esp. Parts I & II
Huber & Herzberg, Constants of Diatomic Molecules (1979)
Townes & Schawlow, "Microwave Spectroscopy" (Dover 1975)
1. Review Items on Molecular Structure

   a. Spectroscopic notation for electronic states
   Spherical symmetry familiar for atoms is replaced by other symmetries, e.g., rotational symmetry about an axis for symmetric rotors. This affects the conserved components of the electronic angular momentum, as illustrated in this short table for linear molecules:

<table>
<thead>
<tr>
<th>Angular Momentum</th>
<th>Symbol</th>
<th>Projection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electronic orbital</td>
<td>$L$</td>
<td>$\Lambda$</td>
</tr>
<tr>
<td>Electronic spin</td>
<td>$S$</td>
<td>$\Sigma$</td>
</tr>
<tr>
<td>Nuclear rotation</td>
<td>$R$</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>$J=L+R+S$</td>
<td>$\Lambda+\Sigma$</td>
</tr>
</tbody>
</table>

   For a more complete list of notations, see Townes & Schawlow, Table 7-1
b. Notation for Molecular States
Although $L$ is not conserved, $S$ is, and its magnitude is a good quantum number. Thus electronic states are denoted $^{2S+1}\Lambda$. A parity symbol may be added to indicate whether the wave function is even or odd under inversion in the plane perpendicular to the symmetry axis, as in $^{2S+1}\Lambda^{\pm}$. The behavior of the spatial wave function under nucleon exchange, as in the case of $H_2$, is indicated by the label $g$ or $u$, for the German gerade (even) or ungerade (odd), as in $^{2S+1}\Lambda^{\pm}_{g,u}$.

Finally, electronic states are ordered roughly in energy by letters, with the ground state being $X$ and excited states with letters at the beginning of the alphabet. For example, the ground state of $H_2$ is $X\,^{2S+1}\Sigma^{+}g$ (see figure below).
c. Term Values According to Herzberg

For reference the standard way of stating measured molecular frequencies for each electronic level is

\[ k = G(v) + B_v J(J + 1) - D_v [J(J + 1)]^2 + \cdots \]

\[ G(v) = \omega_e (v + \frac{1}{2}) - \omega_e \chi_e (v + \frac{1}{2})^2 + \cdots \]

\[ F_v (J) = B_v J(J + 1) - D_v [J(J + 1)]^2 + \cdots \]

\[ B_v = B_e - \alpha_e (v + \frac{1}{2}) + \cdots \]
d. Progression of Rotational Transitions

For the *pure rotational spectrum of a rigid rotor*, the photon energy in the transitions $J' = J \rightarrow J'' = J - 1$

$$\Delta E_J = E(J) - E(J - 1) = 2BJ$$

generates the sequence $2B, 4B, 6B \ldots$. For the *ro-vibrational spectrum*, the transitions involve the energy difference between the vibrational levels (and the electronic levels for an optical or UV transition) plus the difference in rotational energies:

$$\Delta E(v'J', v''J'') = \Delta E(v', v'')_{\text{vib}} + B' J' (J' + 1) - B'' J'' (J'' + 1)$$

For no change in the electronic state, $B' \& B''$ are similar. Substituting the appropriate changes for $R$ and $P$ transitions, $J' = J'' + 1$ & $J' = J'' - 1$ respectively, yields for the case $B' = B'' = B$:
\[ \Delta E(v', J', v'' J'')_R = \Delta E(v', v'')_{\text{vib}} + 2BJ' \]
\[ \Delta E(v', J', v'' J'')_P = \Delta E(v', v'')_{\text{vib}} - 2B(J'+1) \]

The \(R\)-transitions generate a sequence of rovib transition energies just like a simple rigid rotor, with energies laddered on top of the reference energy (the difference between the first level in each vibrational energy potential).

The \(P\)-transitions generate the opposite sequence of rovib transition energies with energies laddered below the reference energy

\[-6B \quad -4B \quad -2B \quad 0 \quad 2B \quad B \quad 6B\]

\(P\)-transitions \quad \(R\)-transitions

with a gap in the middle.
Rotational progression for Variable Rotational Constant

The rotational constant varies with the state. Even for the same vibrational & electronic state, we expect $B$ to decrease with increasing $J$ for large $J$ due to centrifugal effects. We therefore redo the calculation of the R and P transition energies for unequal $B'$ & $B''$. Following Herzberg,

$$\Delta E(m) = \Delta E_0 + (B'+B'')m + (B'-B'')m^2$$

$m = J + 1$ for the R branch & $m = -J$ for the P branch

For small $m$, we get the previous linear behavior. For a diatomic molecule in its ground vibrational & electronic state, we expect $B' < B''$. So for $m > 0$ (R branch), we see that there is a value of $m$ where $\Delta E$ stops increasing with $m$

$$m = \frac{B''+B'}{B''-B'}$$

Approaching this value, the increments become small & and the lines pile up, forming a “bandhead”.
3. The $\text{H}_2$ Molecule

a. Symmetry Considerations – The electrons have total spin $S = 0 \& 1$, which are anti-symmetric and symmetric under exchange. The Exclusion Principle requires the corresponding spatial wave functions to have the opposite symmetry. Thus there are two basic types of potential curves, *singlet and triplet*, which have attractive and repulsive properties (illustrated in the figure by the curves X and b, respectively). The triplet state has higher kinetic energy and less Coulomb attraction because of its odd spatial wavefunction.

The protons have total spin $I = 0 \& 1$. To satisfy the Exclusion Principle, $I = 0$ “para” states are paired with even $J$ while $I = 1$ “ortho” states are paired with odd $J$, where $J$ is the rotational quantum number.
b. Potential Energy Curves for H₂

Lyman band absorption followed by dissociation into the X continuum

0.75 Å
c. **The Electronic Levels** - The ground state is $X\ ^1\Sigma^+_g$ because it has the quantum numbers: $S = 0, \ L = 0, \ \Lambda = 0, \ & \ J = 0$. It has a manifold of 30 vibrational levels, each with an infinite number of rotational states.

The next two singlet electronic levels are $B\ ^1\Sigma^+_g$ and $C\ ^1\Pi^+_u$. Their potential curves asymptote to separated H atoms in 1s and 2s,p states, well above the dissociation energy into two H(1s) atoms. Levels B & C are connected to ground by allowed electric-dipole transitions, the molecular analogs of the H I Ly-α transition. These are the $H_2\ Lyman\ and\ Werner\ bands$, starting at 1108 Å and 1040 Å, & spread more or less uniformly across the far UV band from the HI Lyman edge at 911.7 Å to the threshold near 1100 Å. Typical oscillator strengths are $\sim 10^{-2}$. They were detected by Carruthers in a rocket experiment & extensively observed in diffuse clouds by the UV satellites Copernicus and FUSE.
Ly α Pumped Fluorescence of H$_2$

Ly-α is often a very strong line covering several Å. It can overlap many Lyman band H$_2$ lines. The process is sensitive to T and the abundance of H$_2$. It can be used as a thermometer.

First observed in sunspot spectra by Jordan (1977), analyzed theoretically by Shull (1978), and most recently observed in the nearby T Tauri TW Hydrae (Heczeg et al. 2002). This process does require special conditions, i.e., Ly-α irradiation of H$_2$. 

Fig. 4.10. Fluorescence of H$_2$ with Lyα. In order for this process to occur, the molecular hydrogen has to be both vibrationally and rotationally excited, which requires a temperature above about 1000 K.
Herczeg et al.

Detection by FUSE of fluorescent H2 emission following absorption of the Ly-\(\alpha\) line etc. by the Lyman bands in the T Tauri star TW Hydrae
d. **Near Infrared Transitions** – The ground level vibrational constant is $\omega \sim 4400$ cm$^{-1}$ (6330 K), and gives rise to rovib transitions in the NIR near 2.2 $\mu$m. They are observed in warm regions, where they are collisionally excited, and in regions near far UV sources, where they would be emitted as part of the fluorescence following absorption of a Lyman or Werner band photon. Neutral gas near a star-forming region is a good example.

Because H$_2$ has no dipole moment, these are **weak quadrupole transitions**; a favorite is the 1-0 S(1) line at 2.12 $\mu$m. The notation stands for the transition: $v' = 1, J' = 3 \rightarrow v'' = 0, J'' = 1$, based on the expanded notation:

<table>
<thead>
<tr>
<th>J'</th>
<th>O</th>
<th>P</th>
<th>Q</th>
<th>R</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>J''-2</td>
<td>J''-1</td>
<td>J''</td>
<td>J''+1</td>
<td>J''+2</td>
<td></td>
</tr>
</tbody>
</table>
d. **Mid Infrared Transitions** – The ground level rotational constant is $B = 60.85 \text{ cm}^{-1} (87.6 \text{ K})$. Pure rotational transitions occur in the MIR shortwards of 28 µm. They are observable in lukewarm regions ($T > 300 \text{ K}$) where they can be collisionally excited, and possibly in regions near UV and X-ray sources. They are very weak quadrupolar transitions.

**para H$_2$ $I = 0$**

- $J=0$ $\rightarrow$ $0 \text{ K}$
- $J=2$ $\rightarrow$ $512 \text{ K}$
- $J=4$ $\rightarrow$ $1707 \text{ K}$

**ortho H$_2$ $I = 1$**

- $J=0$ $\rightarrow$ $0 \text{ K}$
- $J=1$ $\rightarrow$ $171 \text{ K}$
- $J=3$ $\rightarrow$ $1024 \text{ K}$

17µm

28.2µm

12.3µm

28.2µm

17µm
2. The $^{12}$CO Molecule

CO has some big advantages over H2:

1. It has a small but finite permanent dipole moment (0.110 Debye) so that its pure rotational and rovib transitions are relatively strong (compared to H$_2$).
2. Its long wavelength transitions occur in reasonably good portions of the spectrum, i.e., in the NIR and mm bands.
3. Its strong binding means that it is widely distributed with a roughly constant abundance (at least where most hydrogen is molecular).
\[
(D(\text{CO}) = 11.09 \text{ eV compared to } D(\text{H}_2) = 4.48 \text{ eV})
\]
4. It has useful isotopic variants, $^{13}$CO, C$^{17}$O, & C$^{18}$O.
Energy Levels of CO

![Diagram of energy levels for CO]
Spectroscopic Constants in cm\(^{-1}\)

We follow Herzberg’s formula for the energy levels expressed in wave numbers \((k = E/ch)\):

\[
k = G(v) + B_v J(J + 1) - D_v [J(J + 1)]^2 + \cdots
\]

<table>
<thead>
<tr>
<th>(v)</th>
<th>0</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_v)</td>
<td>1.922529</td>
<td>1.905026</td>
<td>1.887524</td>
</tr>
<tr>
<td>(D_v \times 10^6)</td>
<td>6.1206</td>
<td>6.1203</td>
<td>6.120</td>
</tr>
<tr>
<td>(G(v) - G(0))</td>
<td>2143.272</td>
<td>4260.64</td>
<td></td>
</tr>
</tbody>
</table>

In temperature units:

\[B_0 = 2.766 \text{ K} \quad \& \quad \theta_0 = (ch/k_B) [G(1) - G(0)] = 3084 \text{ K}.\]
Summary of the Diagnostic Lines

a. UV – CO is something like a heavy H$_2$: The UV bands occur in the far UV near 1000 Å with oscillator strengths of the same order of magnitude (10$^{-2}$) as for H$_2$. They have have been detected in absorption towards diffuse clouds where the CO maximum abundance is 10$^{-5}$.

b. NIR - $\Delta v = 1$ transitions define the fundamental bands

$\Delta v = 2$ transitions define the 1st overtone bands, etc

\[
\begin{align*}
4 \rightarrow 1 & : 6859 \text{ cm}^{-1} \\
3 \rightarrow 1 & : 4260 \text{ cm}^{-1} \\
2 \rightarrow 1 & : 2143 \text{ cm}^{-1} \\
1 \rightarrow 1 & : 0 \text{ cm}^{-1}
\end{align*}
\]

\begin{align*}
4 & \rightarrow 1 \leftarrow 3 \rightarrow 2 \rightarrow 1 \rightarrow 0 \\
2.3 \mu m & \leftarrow 4.6 \mu m \\
A(1-0) & \sim 37 \text{ s}^{-1}
\end{align*}
CO 1\textsuperscript{st} Overtone Band Head

Fig. 2.—Spectrum of the $\nu = 2$–0 band head of CO. This spectrum has been divided by a spectrum of an early-type star and then smoothed by a 2 pixel boxcar. The intensity scale is arbitrary. The 1 $\sigma$ error bar is $\pm 2.1$. The smooth line is a synthetic spectrum for a single temperature slab using a sech line profile with FWHM = $37$ km s$^{-1}$, a temperature of $3500$ K, and an optical depth of $0.3$ in the R(51) line.

Carr & Tokunaga (1992)
C. mm band – pure rotational bands in the ground electronic & vibrational level. For small $J$

$$E_J = J(J+1)B \quad \Delta E_J = E_J - E_{J-1} = 2BJ$$

$$B = 1.922529 \text{ cm}^{-1} \quad 2B/k_B = 5.532 \text{ K}$$

With all the previously mentioned advantages, CO is the ideal diagnostic & coolant for cold clouds with $T \sim 10$-100 K.

CO has been detected from the ground throughout much of mm and sub-mm bands. Very dry conditions are needed at high frequencies, e.g., the Atacama desert plateau (for ALMA). The CO 9-8 1.087 THz line has been detected (Marrone et al. 2004) from 5525 m in N. Chile.

\[
A_{10} = 7.17 \times 10^{-8} \text{ s}^{-1} \quad A_{J,J-1} = \frac{3J^4}{(2J+1)} A_{10}
\]
4. What’s Missing

So far we have discussed some of the elementary spectroscopy needed to study the cooler parts of the ISM. With respect to H$_2$ and CO, perhaps the most important interstellar molecules, we still need to discuss several basic questions:

1. How are they formed and how are they destroyed?
2. How are they excited?
3. What roles do they play in determining the physical conditions in the ISM (which affect the answers to the first two questions).
4. How can we use the observations of H$_2$ & CO to understand the evolution of interstellar clouds and the formation of stars.