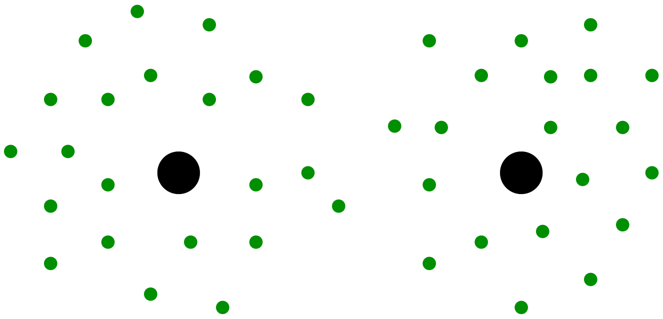
IX. Molecules

A. Motivations

- Molecules are the principal coolants (with dust) in denser, netural gas ($n > 10^2\,\mathrm{cm}^{-3}$)
- Ultimately, these particles enable star formation
- Molecules are useful diagnostics of the ISM, especially star-forming regions
- Molecules enable unique physical experiments (e.g. constraints on variations in the fundamental constants, e.g. Thompson 1979)

B. Born-Oppenheimer Approximation

- Diatomic molecules



- Molecular vs. atomic structure
  - ◇ Electrons have less symmetry in molecules
  - ◇ Molecule has more degrees of freedom
    - ▲ Electronic configurations
    - ▲ Rotations about the axes perpendicular to the line connecting the nuclei
    - ▲ Vibrations along the line centers
- Key: The molecular degrees of freedom generally decouple
  - ◇ Treat each independently (more or less)
  - ◇ Why? The energies have significantly different magnitude
  - ◇ $m_e \ll M$
    - ▲ Electrons have very small inertia compared to the nuclei
    - ▲ Electrons react quickly to changes in the nuclei
    - ▲ Electrostatic configurations decouple from the nuclear motions

C. Approximate Energies

- Electrostatic energy
  - ◇ Parameterized by the nuclear separation R

    - ▲ Expect R is on the order of the Bohr radius (i.e. $R_0 \sim a_0$)
    - ▲ Expect energies comparable to energy levels in an atom

$$E_{el} \sim \frac{e^2}{a_0} = \frac{\hbar^2}{m_e a_0^2} \tag{1}$$

  - ◇ Frequencies

$$\hbar\omega_{el} \sim E_{el} \tag{2}$$

    - ▲ $\lambda_{el} \sim 1000\text{Å}$
    - ▲ Ultraviolet or optical, e.g. Lyman-Werner transitions
- Vibrational Energies
  - ◇ Displace the nuclei by ΔR from the equilibrium separation R_0
  - ◇ Expect energies with form like the simple harmonic oscillator (SHO)

$$\frac{1}{2} M \omega_{vib}^2 \Delta R^2 \tag{3}$$

  - ◇ If the displacement is comparable to $R_0 \sim a_0$, then we expect energies comparable to the depth of the potential well

$$\frac{1}{2} M \omega_{vib}^2 a_0^2 \sim E_{el} \tag{4}$$

  - ◇ Vibrational energy

$$\hbar\omega_{vib} \sim \left(\frac{m_e}{M}\right)^{\frac{1}{2}} E_{el} \tag{5}$$

    - ▲ For $m_e/M \sim 10^{-3}$ or 10^{-4}, these photons will lie in the near or mid-infrared
    - ▲ For H_2, $\lambda_{vib} \approx 2\mu\text{m}$
- Rotational Energies
  - ◇ Rotate about axes perpendicular to the line connecting the nuclei
  - ◇ Moment of inertia

$$I \sim M a_0^2 \tag{6}$$

  - ◇ Angular momentum

$$L \sim I\omega_{rot} \sim M a_0^2 \omega_{rot} \tag{7}$$

  - ◇ Energies
    - ▲ Angular momentum is quantized in units of $\hbar/2$
    - ▲ Therefore

$$E_{rot} = \hbar\omega_{rot} \sim \frac{\hbar^2}{M a_0^2} \sim \frac{m_e}{M} E_{el} \tag{8}$$

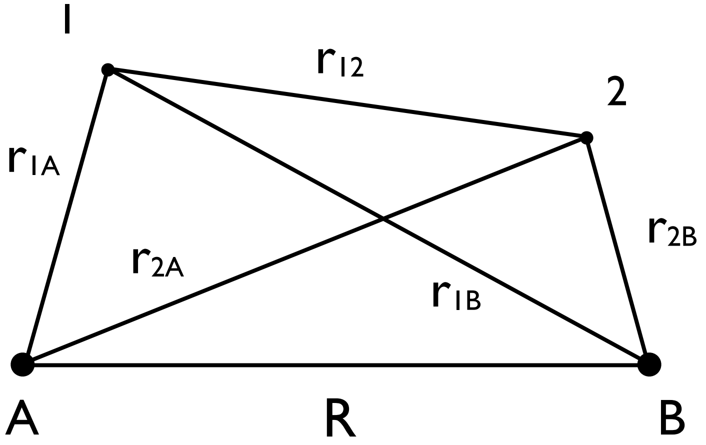
  - ◇ Frequencies
    - ▲ For $m_e/M \sim 10^{-3} \sim 10^{-4}$, photons will lie in the millimeter range
- Decoupling of Energies

$$E_{rot} : E_{vib} : E_{el} \ \sim \ \left(\frac{m_e}{M}\right) : \left(\frac{m_e}{M}\right)^{\frac{1}{2}} : 1 \tag{9}$$

- ◇ Hierarchy provides a clean basis for perturbation theory
- ◇ This is the physics behind the Born-Oppenheimer approx

D. Hamiltonian for a Diatomic Molecule

- Coordinates



- Ignoring spin-orbit coupling and relativistic corrections
- Separate kinetic energy of the nucleus from the electronic energies

$$H = H_{AB} + H_{el} \tag{10}$$

$$H_{AB} \equiv -\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 \tag{11}$$

$$H_{el} \equiv -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) + V \tag{12}$$

$$V \equiv -\frac{Z_A e^2}{r_{1A}} - \frac{Z_B e^2}{r_{1B}} - \frac{Z_A e^2}{r_{2A}} - \frac{Z_B e^2}{r_{2B}} + \frac{Z_A Z_B e^2}{R} + \frac{e^2}{r_{12}} \tag{13}$$

- ◇ Note the ∇ operators refer to differentiation with respect to vectors $\vec{r}_A, \vec{r}_B, \ldots$
- ◇ Meanwhile

$$r_{12} \equiv |\vec{r}_1 - \vec{r}_2| \tag{14}$$

$$R \equiv |\vec{r}_A - \vec{r}_B| \tag{15}$$

(16)

- Schroedinger equation

$$H\Psi_E = i\hbar\frac{\partial \Psi_E}{\partial t} \tag{17}$$

- ◇ H has no explicit time dependence
- ◇ Expect energy eigenstates of the form

$$\Psi_E = u(\vec{r}_A, \vec{r}_B, \vec{r}_1, \vec{r}_2)\mathrm{e}^{-iEt/\hbar} \tag{18}$$

  - ◇ Time independent Schroedinger equation

$$H|u> \; = \; E|u> \tag{19}$$

- Born-Oppenheimer Approximation
  - ◇ Note the operator H_{AB} is a factor m_e/M smaller than the kinetic terms in H_{el}
  - ◇ Separate $|u>$ into terms with the electrons and terms with the nuclei

$$|u> = u_{el}(\vec{r}_1, \vec{r}_2, R)u_{AB}(\vec{r}_A, \vec{r}_B) \tag{20}$$

    - ▲ Not entirely separated
    - ▲ u_{el} has dependence on R, the nuclear separation
- Examining the time-independent Schroedinger Equation

$$u_{AB}H_{el}u_{el} + H_{AB}u_{el}u_{AB} = Eu_{el}u_{AB} \tag{21}$$

  - ◇ Expand the second term (Leibnitz's Rule)

$$H_{AB}u_{el}u_{AB} = u_{el}H_{AB}u_{AB} - \frac{\hbar^2}{M_A}\nabla_A u_{el} \cdot \nabla_A u_{AB} - \tag{22}$$

$$\frac{\hbar^2}{M_B}\nabla_B u_{el} \cdot \nabla_B u_{AB} \; + \; u_{AB}H_{AB}u_{el} \tag{23}$$

  - ◇ Note (because u_{el} depends only on R)

$$\nabla_A u_{el} = \frac{\vec{R}}{R}\frac{\partial u_{el}}{\partial R} = -\nabla_B u_{el} \tag{24}$$

  - ◇ The middle terms in Equation (23) can be rewritten as

$$\hbar^2 \frac{\partial u_{el}}{\partial R}\frac{\vec{R}}{R} \cdot \left(\frac{1}{M_B}\nabla_B - \frac{1}{M_A}\nabla_A\right) u_{AB} \tag{25}$$

  - ◇ The term in the parenthesis is proportional to $\vec{v}_A - \vec{v}_B$ which should average to zero for a bound molecule
  - ◇ The last term in Equation (23) can be ignored

$$u_{AB}H_{AB}u_{el} = \frac{m_e}{M}u_{AB}H_{el}u_{el} \tag{26}$$

  - ◇ Therefore, the second term has been reduced to

$$H_{AB}u_{el}u_{AB} \approx u_{el}H_{AB}u_{AB} \tag{27}$$

- Altogether, our time-independent Schroedinger equation becomes

$$u_{AB}H_{el}u_{el} + u_{el}H_{AB}u_{AB} = Eu_{el}u_{AB} \tag{28}$$

- ◇ Rewriting

$$\frac{1}{u_{el}} H_{el} u_{el} = -\frac{1}{u_{AB}} H_{AB} u_{AB} + E \tag{29}$$

- ◇ RHS depends only on $\vec{r}_A$ and $\vec{r}_B$
- ◇ LHS depends only on $\vec{r}_1$ and $\vec{r}_2$ + a parameter dependence on R

- Separation of variables
  - ◇ Both sides must equal a constant $E_{el}(R)$

$$H_{el}|u_{el}> = E_{el}(R)|u_{el}> \tag{30}$$

$$H_{AB}|u_{AB}> + E_{el}(R)|u_{AB}> = E|u_{AB}> \tag{31}$$

$$\tag{32}$$

  - ◇ We have separated the electronic degrees of freedom from the motions of the nuclei

E. Energy Levels

- Separating translational and internal degrees of freedom
  - ◇ Coordinate transformation
  - ◇ Center of mass

$$\vec{R}_{CM} \equiv \frac{M_A \vec{r}_A + M_B \vec{r}_B}{M_A + M_B} \tag{33}$$

  - ◇ Relative displacement

$$\vec{R} \equiv \vec{r}_A - \vec{r}_B \tag{34}$$

  - ◇ Hamiltonian

$$H_{AB} = -\frac{\hbar^2}{2M}\nabla^2_{CM} - \frac{\hbar^2}{2\mu}\nabla^2_R \tag{35}$$

$$\mu \equiv \frac{M_A M_B}{M_A + M_B} \tag{36}$$

$$M \equiv M_A + M_B \tag{37}$$

  - ◇ Express our state u_{AB} in terms of $\vec{R}$ and $\vec{R}_{CM}$

$$u_{AB} = u_{trans}(\vec{R}_{CM}) u_{int}(\vec{R}) \tag{38}$$

    - ▲ u_{trans} describes the translational motions of the nuclei
    - ▲ u_{int} describes the internal motions of the nuclei

- Nuclear equation

$$\frac{1}{u_{trans}}\left(-\frac{\hbar^2}{2M}\nabla^2_{CM} u_{trans}\right) = \frac{1}{u_{int}}\left(\frac{\hbar^2}{2\mu}\nabla^2_R u_{int}\right) - E_{el}(R) + E \tag{39}$$

  - ◇ Examining the equation

- ▲ LHS depends only on $\vec{R}_{CM}$
- ▲ RHS depends only on $\vec{R}$
- ▲ Separation of variables implies each side of Equation (39) must equal a constant E_{trans}

◇ Separation

$$-\frac{\hbar^2}{2M}\nabla^2_{CM}u_{trans} = E_{trans}u_{trans} \tag{40}$$

$$-\frac{\hbar^2}{2\mu}\nabla^2_{R}u_{int} + E_{el}(R)u_{int} = E_{int}u_{int} \tag{41}$$

$$\text{with } E_{int} = E - E_{trans} \tag{42}$$

◇ We have reduced the motions of the nuclei to translations and internal motions

- Vibrations + Rotations (Internal energies)

$$-\frac{\hbar^2}{2\mu}\nabla^2_{R}u_{int} + E_{el}(R)u_{el} = E_{int}u_{int} \tag{43}$$

◇ Motions of nuclei A relative to nuclei B are expressed in identical fashion to a single particle with reduced mass μ in a central force field

◇ Hamiltonian is spherically symmetric

- ▲ Introduce spherical coordinates

$$\nabla^2_R = \frac{1}{R^2}\left[\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) - \frac{L^2}{\hbar^2}\right] \tag{44}$$

- ▲ Usual separation of variables

$$u_{int}(\vec{R}) = \frac{1}{R}Z_{vib}(R)Y_{\ell m}(\theta,\phi) \tag{45}$$

◇ Psuedo-spherical harmonics

- ▲ Usual angular momentum rules

$$L^2 Y_{Jm} = J(J+1)\hbar^2 Y_{Jm} \tag{46}$$

$$L_z Y_{Jm} = m\hbar Y_{Jm} \tag{47}$$

- ▲ Two angular coordinates correspond (sort of) to the two degrees of freedom for the rotation axes

◇ ‘Radial’ equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2Z_{vib}}{dR^2} + E_{el}(R)Z_{vib} = \left[E_{int} - \frac{J(J+1)\hbar^2}{2\mu R^2}\right]Z_{vib} \tag{48}$$

- ▲ Expresses the motions along the line of centers of the nuclei

◇ Harmonic oscillator approximation

- ▲ Assume the potential $E_{el}(R)$ follows a simple potential well with minimum energy at separation R_0
  - ○ i.e. $R = R_0$ corresponds to a minimum in $E_{el}(R)$
  - ○ Taylor expand around R_0

$$E_{el}(R) = E_{el}(R_0) + \frac{1}{2}\mu\omega_0^2(R - R_0)^2 + \ldots \tag{49}$$

$$\text{where } \mu\omega_0^2 \equiv E''_{el}(R_0) \tag{50}$$

  - ○ Change of variables: $x \equiv R - R_0$
- ▲ Equation (48) to lowest order reduces to the SHO equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2 Z_{vib}}{dx^2} + \frac{1}{2}\mu\omega_0^2 x^2 Z_{vib} = E_{vib} Z_{vib} \tag{51}$$

$$\text{where } E_{vib} \equiv E_{int} - E_{el}(R_0) - \frac{J(J+1)\hbar^2}{2\mu R_0^2} \tag{52}$$

◇ Energies

- ▲ Define rotation energy

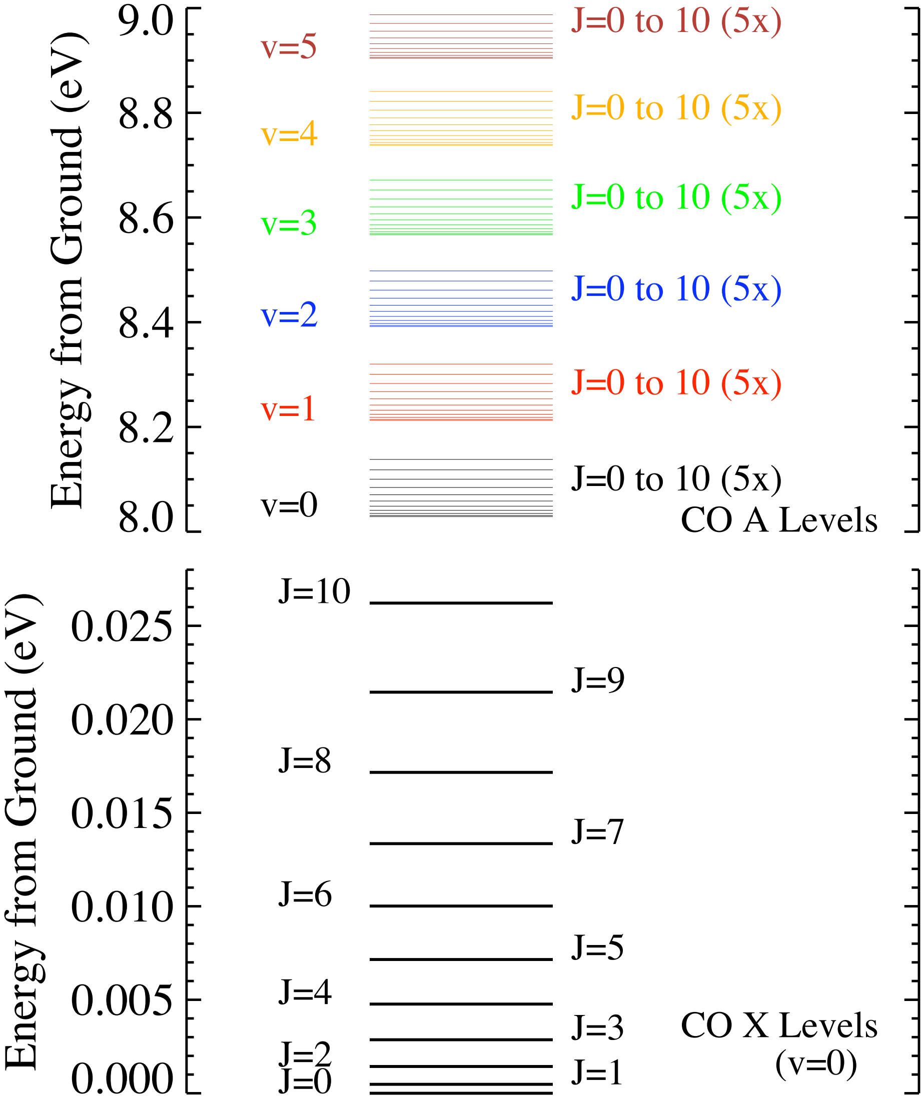
$$E_{rot} \equiv \frac{J(J+1)\hbar^2}{2\mu R_0^2} = J(J+1)B \tag{53}$$

  - ○ B is the rotational constant of the molecule
  - ○ Typically B is determined experimentally
- ▲ Vibrational energy

$$E_{vib} = \left(n + \frac{1}{2}\right)\hbar\omega_0 \qquad n = 0, 1, 2, \ldots \tag{54}$$

- ▲ Internal energy is then the sum over 3 terms

$$E_{int} = E_{el}(R_0) + E_{vib} + E_{rot} \tag{55}$$



- Example: Lowest two electronic levels of CO
  - ◇ The lower panel shows the rotational levels for CO in the ground state ($X^1\Sigma^+$)
    - ▲ These are shown for the lowest vibrational level ($n = 0$; here notated with v instead of n)
    - ▲ The energies have the form

$$E = J(J+1)B \quad \text{with } B = 2.77\,\text{K}\ (0.000239\text{eV}) \tag{56}$$

  - ◇ The upper panel shows the roto-vibrational levels for the first electronic level above ground ($A^1\Pi$)
    - ▲ One can see the electronic energy is ≈ 8eV
    - ▲ The vibrational levels (notated by v) have spacings following the SHO with $\hbar\omega_0/k = 3100$K
    - ▲ I have multiplied the rotation energies by 5 for presentation purposes

F. Energy States

- Spectroscopic Notation
  - ◇ Electronic levels (analogous to $n = 1, 2, 3, \dots$)
    - ▲ X $\equiv$ Ground state
    - ▲ Bound excited states (for H_2) = B,C,D,...
    - ▲ Unbound excited states = $a, b, c, \dots$
  - ◇ Orbital angular momentum (Λ)
    - ▲ Atoms: Electronic potential is spherically symmetric $\Rightarrow$ Total angular momentum is conserved
    - ▲ Diatomic molecules: Symmetry about the line of centers $\Rightarrow$ Only the component about the nuclear axis is a constant of the motion
      - ○ Refer to this component of the angular momentum as Λ
      - ○ Labels: $\Lambda = 0, 1, 2 \rightarrow \Sigma, \Pi, \Delta$
    - ▲ Other components of the angular momentum precess $\Rightarrow$ the total angular momentum precesses
  - ◇ Electron-spin angular momentum (Σ)
    - ▲ Similar to Λ, the only component which is a constant of the motion (unless $\Lambda = 0$) is the component along the internuclear axis
    - ▲ Refer to this component of S as Σ (to be confused with Σ the $\Lambda = 0$ state as S the $\ell = 0$ state is confused with spin)
    - ▲ Values: $\Sigma = -S, -S+1, \dots, S-1, S$
  - ◇ 'Total' Angular Momentum (Ω)
    - ▲ Sum of the internal components of the spin and orbital angular momentum (i.e. $\Omega = \Lambda + \Sigma$)
    - ▲ <u>Not</u> a vectoral sum
  - ◇ Planar Symmetry
    - ▲ If the electronic wave function changes sign under a reflection through any plane connecting the two nuclei $\Rightarrow$ '- state'
    - ▲ Otherwise, '+ state'
  - ◇ Center symmetry
    - ▲ If the wave function changes sign when reflected through the center of nuclear charge $\Rightarrow$ 'u state'
    - ▲ Otherwise, 'g state'
  - ◇ Nuclear spin
    - ▲ H_2 has two nuclear states: ortho (spin aligned) and para (spin anti-aligned)
    - ▲ ortho has 3× degeneracy over para
  - ◇ Fig (Shull & Beckwith, 1982, ARAA)

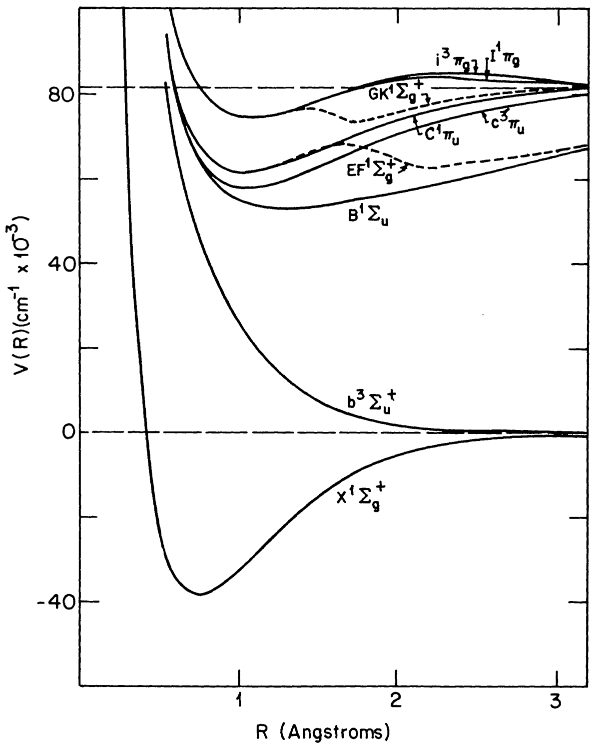


Figure 1 Total energy as a function of internuclear separation for low-lying states of H_2. Horizontal dashed lines denote total energy of two H atoms at infinite separation (both atoms in ground state; one atom in ground state and the other in the first excited states).

- Selection Rules for Electric Dipole Transitions
  - ◇ Orbital angular momentum

$$\Delta\Lambda = 0, \pm 1 \tag{57}$$

  - ◇ Spin

$$\Delta S = 0 \tag{58}$$

  - ◇ Plane symmetry

$$+ \rightarrow + \quad \text{or} \quad - \rightarrow - \tag{59}$$

  - ◇ Center symmetry

$$g \rightarrow u \quad \text{or} \quad u \rightarrow g \tag{60}$$

  - ◇ Nuclear

$$\text{ortho} \rightarrow \text{para is forbidden}$$

  - ◇ Dipole moment must change!

$$<\phi_f|\vec{d}|\phi_i> \neq 0 \tag{61}$$

- Astrophysical consequences

(a) $\Delta S = 0$ stabilizes H_2 against photo-dissociation

$$X^1\Sigma_g^+ + \gamma \rightarrow b^3\Sigma_u^+ \quad \text{is forbidden} \tag{62}$$

(b) Photo-dissociation is generally a two-step process

$$\gamma + X^1\Sigma_g^+ \ \rightarrow B^1\Sigma_u^+ \rightarrow \text{(unstable vibrational continuum state)} + \gamma \qquad (63)$$

(c) Change in dipole reduces the likelihood of H_2 formation

$$\mathrm{H}(1s) + \mathrm{H}(1s) \rightarrow X^1\Sigma_g^+ \ + \ \gamma \quad \text{is forbidden} \qquad (64)$$

- ◇ This significantly reduces the likelihood of H_2 formation
- ◇ H_2 forms via 3-body collisions or with dust grains as the catalyst

G. Molecular Spectroscopy

- Limit the discussion to electric dipole transitions
- Perturbation theory

$$\begin{aligned} H^{(1)} &= \frac{e}{mc}\vec{A}\cdot\vec{p} \\ &= -\vec{E}\cdot\vec{d} \end{aligned}$$

- Dipole moment
  - ◇ $\vec{d}$ is the electronic dipole moment
  - ◇ Express it in terms of a nuclear and electric part

$$\vec{d} = \vec{d}_{el} + \vec{d}_{nuc} \qquad (65)$$

  - ◇ Define positions relative to the center-of-mass

$$\vec{X} = \vec{r} - \vec{R}_{CM} \qquad (66)$$

  - ◇ Electronic dipole moment becomes

$$\vec{d}_{el} = \sum_{j=1}^{N} \vec{d}_j$$

with $\vec{d}_j \equiv -e\vec{X}_j$, the dipole moment of the j-th electron

  - ◇ Nuclear dipole moment

$$\vec{d}_{nuc} = Z_A e\vec{X}_A + Z_B e\vec{X}_B \qquad (67)$$

    - ▲ Note: $\vec{X}_A = (M_B/M)\vec{R}$, $\vec{X}_B = -(M_A/M)\vec{R}$
    - ▲ Therefore, $\vec{d}_{nuc}$ vanishes for a homonuclear molecule

- As always, probabilities and transition rate will depend on this matrix element

$$<f|H^{(1)}|i> = -<f|\vec{E}_\omega\cdot(\vec{d}_{el} + \vec{d}_{nuc})|i> \qquad (68)$$

- ◇ $\vec{E}_\omega$ is the Fourier transform of $\vec{E}$: $[\vec{E}_\omega = -i\omega/c\vec{A}(\omega)]$
- ◇ For molecules, our time-independent energy eigenfunctions have this form

$$|u\!> = \frac{1}{R} Z_{vib}(R) Y_{Jm}(\theta,\phi) u_{trans} u_{el} \Sigma \tag{69}$$

  - ▲ Σ is the electron-spin wave function
- ◇ $H^{(1)}$ is independent of the translational state of the molecular u_{trans}
  - ▲ Therefore, $u^i_{trans} = u^f_{trans}$ or the matrix element vanishes
  - ▲ For the following, assume $u^i_{trans} = u^f_{trans} = 1$

(a) Pure rotational spectra

- Assume the initial and final electronic and vibrational states remain the same
- The matrix element reduces to

$$<\!f|H^{(1)}|i\!> = \int d\Omega Y_{J'm'} <\!Z_{vib}|H_D|Z_{vib}\!> Y_{Jm} \tag{70}$$

- Permanent Dipole Moment
  - ◇ Examining the radial part

$$<\!Z_{vib}|H_D|Z_{vib}\!> \equiv -\int_0^\infty \vec{E}_\omega \cdot \vec{D}(R,\theta,\phi)|Z_{vib}(R)|^2 dR \tag{71}$$

    - ▲ Integral over the separation only!
    - ▲ Introduce $\vec{D}$ as follows
  - ◇ $\vec{D}(R,\theta,\phi)$ is the dipole moment $\vec{d}$ after integrating over all electronic coordinates (including spin)

$$\vec{D}(R,\theta,\phi) = \int \vec{d} u_{el}(\vec{X}_1, \vec{X}_2, \ldots, \vec{X}_N; R)\, d^3X_1 d^3X_2 \ldots d^3X_N \tag{72}$$

    - ▲ $\vec{D}$ is referred to as the permanent dipole moment
    - ▲ For the matrix element to not vanish, obviously $\vec{D} \neq 0$
    - ▲ Contrast with atoms where we simply require $\vec{d}$ changes in the transition

$$<\!f|\vec{d}|i\!> \neq 0$$

  - ◇ H_2
    - ▲ No permanent dipole moment
    - ▲ Rotational transitions are not allowed!
  - ◇ Consider the angular dependence of $\vec{D}$
    - ▲ Obviously, $\vec{D}_{nuc} = \vec{d}_{nuc}$ lies along the line-of-centers of the two nuclei
    - ▲ Therefore, $\vec{D}_{nuc}$ only depends on the magnitude of $\vec{R}$

- ▲ In addition, the reflection symmetry of the electronic distribution implies $\vec{D}_{el}$ (but not $\vec{d}_{el}$) has no component ⊥ to $\vec{R}$
- ▲ Therefore $\vec{D}$ has no functional dependence on θ, ϕ

$$\vec{D} \; = \; D(R)\, \frac{\vec{R}}{R} \tag{73}$$

- • Electric-dipole transition (for a molecule like CO)
  - ◇ 'Rigid rotator' model → Evaluate $D(R)$ at R_0

$$D(R) \approx D(R_0) \equiv D_0 \tag{74}$$

  - ▲ D_0 is referred to as the reduced dipole moment
  - ▲ Warning: In the literature, D_0 is often written as μ
  - ▲ First (trivial) selection rule: $D_0 \neq 0$
  - ◇ Consider the usual orientations of $\hat{\varepsilon}$
  - ▲ $\hat{\varepsilon} \parallel \hat{z}$

$$\vec{E}_\omega \cdot \vec{D} \propto |E_\omega| D_0 T_k^{(1)} \tag{75}$$

    i. Standard selection rules for the angular terms

    ii. $\Delta J = \pm 1, \Delta m = 0$ (Parity prohibits $\Delta J = 0$)

  - ▲ $\hat{\varepsilon} \perp \hat{z}$: Same story except $\Delta m = \pm 1$
  - ◇ Transition dipole moment
  - ▲ De-excitation probability from $J' = J+1 \rightarrow J$
  - ▲ Evaluate by summing over all final m states

$$|D_{J+1,J}|^2 \equiv \sum_m D_0^2 |{<}Y_{Jm}|T_q^{(1)}|Y_{J+1,m'}{>}|^2 = \frac{J+1}{2J+3} D_0^2 \tag{76}$$

  - ◇ Rate of spontaneous emission

$$A_{J+1,J} = \frac{4\omega^3}{3\hbar c^3} |\vec{D}_{if}|^2 = \frac{4(J+1)\,\omega^3}{3(2J+3)\hbar c^3} D_0^2 \tag{77}$$

  - ◇ Energy
  - ▲ Simple rotation
  - ▲ For de-excitation, $J' = J+1 \rightarrow J$

$$E_{rot}^J = J(J+1)B \tag{78}$$

$$\hbar\omega = \Delta E = 2(J+1)B \tag{79}$$

  - ◇ Example: CO ($J = 1$ to 0)
  - ▲ $B = 2.77$K

- ▲ Energy

$$\Delta E = 5.54\,\mathrm{K} \tag{80}$$

$$\lambda = 2.6\,\mathrm{mm} \tag{81}$$

$$\nu = 115\,\mathrm{GHz} \tag{82}$$

- ▲ Probability

$$A_{10} = 6 \times 10^{-8}\,\mathrm{s}^{-1} \tag{83}$$

(b) Vibrational-rotational spectra

- Only the electronic state remains unchanged
- In the SHO approximation, the matrix element is

$$<f|H_d|i> = -|E_\omega| \int d\Omega Y^*_{Jm} <n|D|n'> T^k_q Y_{Jm} \tag{84}$$

  - ◇ T^k_q is the tensor mediating the interaction
  - ◇ Here, it is simply $\cos\theta$
- Expand $D(R)$ about R_0

$$D(R) = D_0 + x \left(\frac{dD}{dR} \right)_{R=R_0} + \mathcal{O}(x^2) \tag{85}$$

  - ◇ $x \equiv R - R_0$
  - ◇ First term corresponds to the pure rotational case (i.e. $n = n'$)
  - ◇ Higher order terms account for the vibrational modes
- Identify x as the sum of raising and lowering operators
  - ◇ Selection rules: $\Delta n = \pm 1$
  - ◇ Additionally:

$$\frac{dD}{dR}|_{R=R_0} \neq 0 \tag{86}$$

- Higher order terms of the $D(R)$ expansion
  - ◇ These allow for $\Delta n = \pm 2, \ldots$
  - ◇ Each term is down by a factor of

$$\frac{\hbar}{\mu\omega_0 R_0^2} \sim \left(\frac{m_e}{M} \right)^{\frac{1}{2}} \tag{87}$$

- Energies: Expect vibrational transitions to have $\Delta E = \hbar\omega_0$
  - ◇ Observationally, larger n levels have smaller spacings because the binding potential is not a pure quadratic well
  - ◇ Also, rotational states often change the moment of inertia
- Additional selection rules
  - ◇ Expect the same rules on J as for pure rotational transitions (i.e. $\Delta J = \pm 1$)

  - ◇ Only true for $\Lambda = 0$ (zero electronic angular moment along $\hat{R}$)
  - ◇ If $\Lambda \neq 0$, the parity of the electronic state can change (by flipping the sign of Λ) and $\Delta J = 0$ is allowed
- P and R branches
  - ◇ Energies for vibrational and rotational spectra,

$$E_{nJ} = (n + \frac{1}{2})\hbar\omega_0 + J(J+1)B \tag{88}$$

  - ◇ Frequencies
    - ▲ Transition $n' = n \pm 1$ and $J' = J + 1$ with $J = 0, 1, 2, \ldots$

$$\omega = \omega_0 + 2(J+1)B/\hbar \quad \textbf{R branch} \tag{89}$$

    - ▲ Transition $n' = n \pm 1$ and $J' = J - 1$ with $J = 1, 2, 3, \ldots$

$$\omega = \omega_0 - 2JB/\hbar \quad \textbf{P branch} \tag{90}$$

    - ▲ If $\Lambda = 0 \Rightarrow \Delta J \neq 0$ and there is no line at $\omega = \omega_0$
- Corrections to the Energy
  - ◇ True molecular spectra show departures from Equation (89)
  - ◇ Several of our approximations don't hold for real molecules
    - ▲ Centrifugal forces (especially for large J) distort the molecule $\Rightarrow$ Failure of the 'rigid rotator' approx
    - ▲ Expansion of $E_{el}(R)$ beyond the quadratic term implies additional 'overtones' at near-integral multiples of ω_0
  - ◇ Modified vibrational-rotational energy levels

$$E_{nJ} = \left[1 - A(n + \frac{1}{2})\right](n + \frac{1}{2})\hbar\omega_0 \ + \ [\,1 - CJ(J+1)\,]\,J(J+1)B \tag{91}$$

    - ▲ Fractional anharmonicity constant ($A = 0.027$ for H_2)
    - ▲ Fractional centrifugal constant ($C = 7.6 \times 10^{-4}$ for H_2)

(c) Electronic-Vibrational-Rotational Spectra

- "Vibronic" transitions
- Selection rules
  - ◇ Usual rules

$$\begin{aligned}
&\Delta J = 0, \pm 1 \\
&\Delta m = 0, \pm 1 \\
&\Delta J \neq 0 \text{ if } \Lambda = 0 \\
&J = 0 \rightarrow 0 \ \text{ is forbidden always} \\
&\Delta\Lambda = 0, \pm 1
\end{aligned}$$

  - ◇ Note, the electronic transitions do not require $D_0 \neq 0$
    - ▲ Therefore H_2 shows UV electronic transitions
    - ▲ And, the vibrational and rotational state can change ‘along the way’
- Matrix element

$$\vec{D}_{if} \propto \int dR\, Z^*_{vib,f}(R) Z_{vib,i}(R) \tag{92}$$

  - ◇ This integral has a non-zero value for any Δn value
  - ◇ ⇒ Vibronic transitions are not limited to $\Delta n = \pm 1$
  - ◇ Qualitatively assess $\vec{D}_{if}$ by considering the wave function of a particle in a potential well
    - ▲ For level n, the wave function has $n+1$ maxima between the turning points
    - ▲ The Δn transitions with the highest probability correspond to those when the wave functions show coincident maxima
    - ▲ The overlap factors are called Frank-Condon factors
- Band and branch structure
  - ◇ For emission spectra, the branches correspond to:
    - ▲ P branch: $\Delta J = +1$
    - ▲ Q branch: $\Delta J = 0$
    - ▲ R branch: $\Delta J = -1$
  - ◇ R(P) branch starts at highest (lowest) frequencies
  - ◇ Differences in the moments of inertia of the final and initial states lead to lines without equal spacing

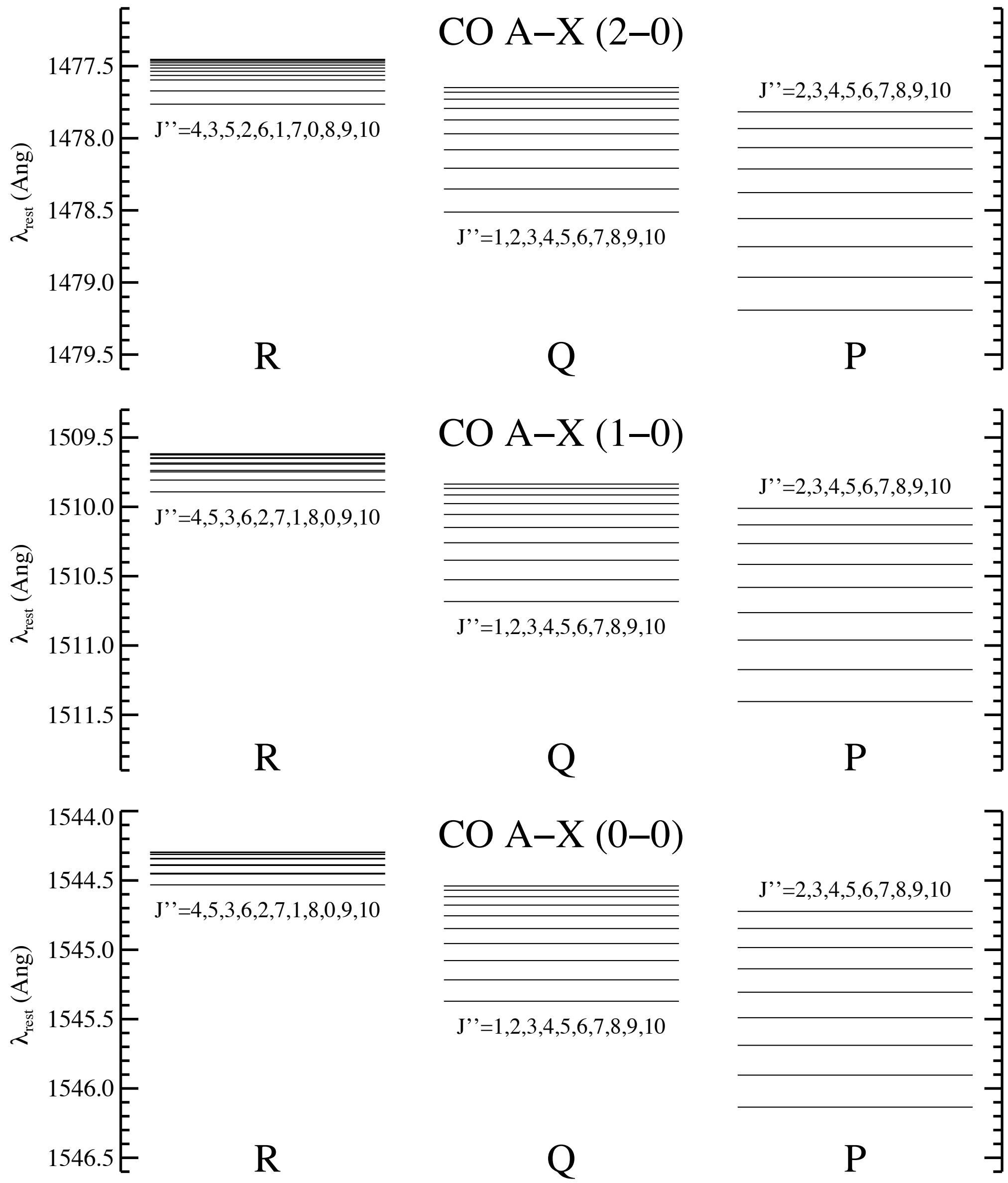
$$\nu_R = \nu_{el,vib} + h^{-1}\left[\, 2B + (3B - B')J - (B' - B)J^2 \,\right] \tag{93}$$

    - ▲ The J and J^2 terms have opposite sign
    - ▲ For small J and $B' > B$, ν_R increases with J until $J = J_{head}$
    - ▲ Then ν_R decreases!
  - ◇ P and Q branches behave differently

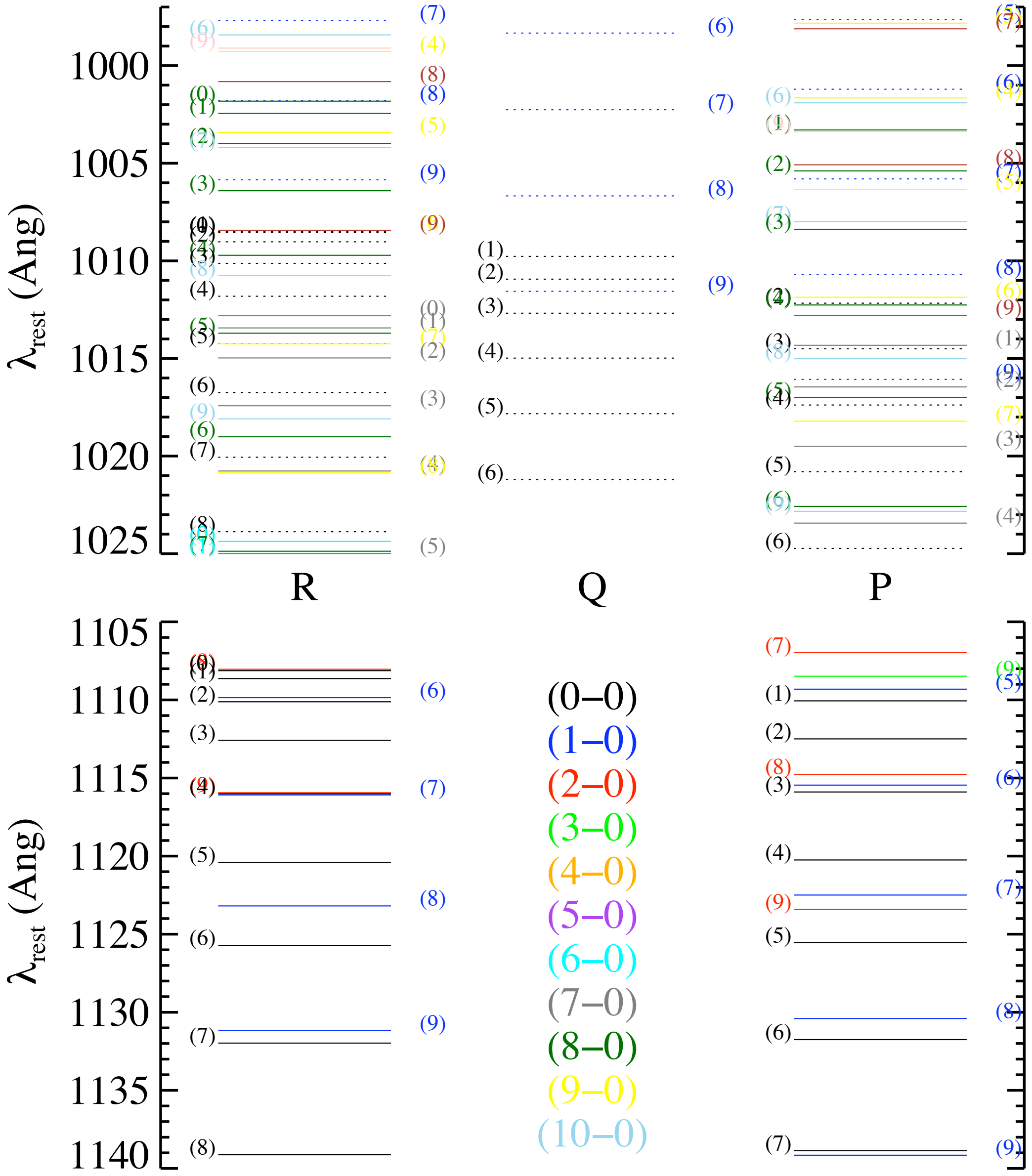
$$\nu_Q = \nu_{el,vib} - h^{-1}(B' - B)J(J+1) \tag{94}$$

$$\nu_P = \nu_{el,vib} - h^{-1}\left[\,(B' + B)J + (B' - B)J^2\,\right] \tag{95}$$

- In practice, this simple formalism breaks down, especially for larger R, P, Q levels
  - ◇ Use empirical data to determine the energy levels
  - ◇ The data are then fitted by a semi-analytic model (e.g. Dunham parameters)



- This figure shows three vibrational bands ($n' = 0, 1, 2$) for the CO $A - X$ transition
    - ◇ These are well separated from one another
    - ◇ i.e. no overlap among the bands
- Note the y-axis is reversed (higher λ is down)
- R-branch
    - ◇ The J levels increase in energy for a few levels
    - ◇ But then reverse at $J = 5$
    - ◇ This leads to a high density of absorption lines and the observed 'band head'
- The Q, P-branches behave more normally



- This figure shows two slices of spectra in the Lyman-Werner bands of H_2
- Notation
  - ◇ Solid lines indicate Lyman $(B - X)$ transitions
  - ◇ Dotted are Werner $(C - X)$ transitions
  - ◇ Colors indicate the upper vibrational level $(n' = 0, 1, 2, 3..10)$
  - ◇ Numbers indicate the lower rotational level $(J'' = 0, 1, 2, 3, ..9)$
- Unlike CO, the vibrational and electornic bands overlap
  - ◇ This is a real mess!
  - ◇ And the opacity for $\lambda < 1100$Å from H_2 can be enormous!
- The following figures show data (Tumlinson et al. 2002, Prochaska et al. 2009)

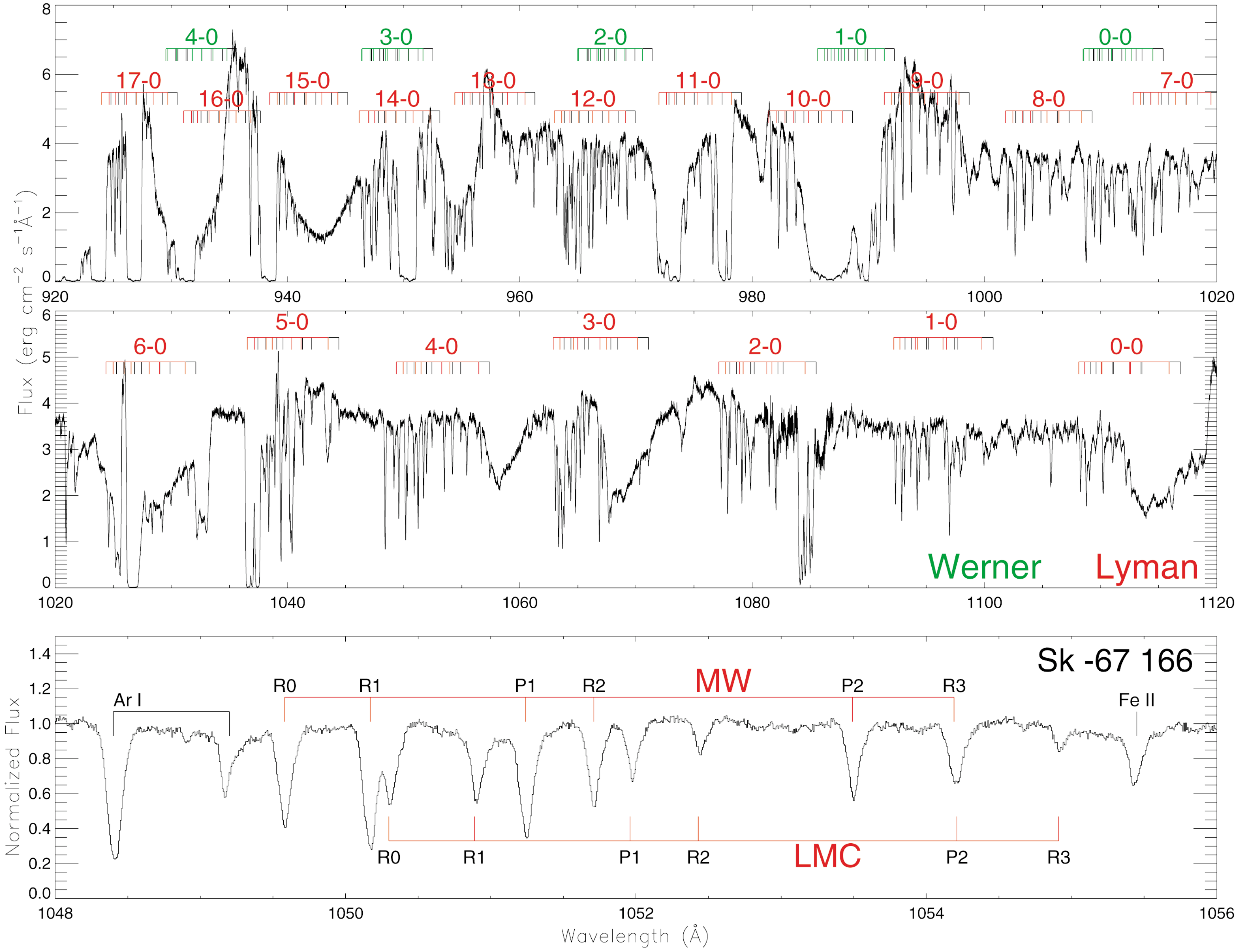
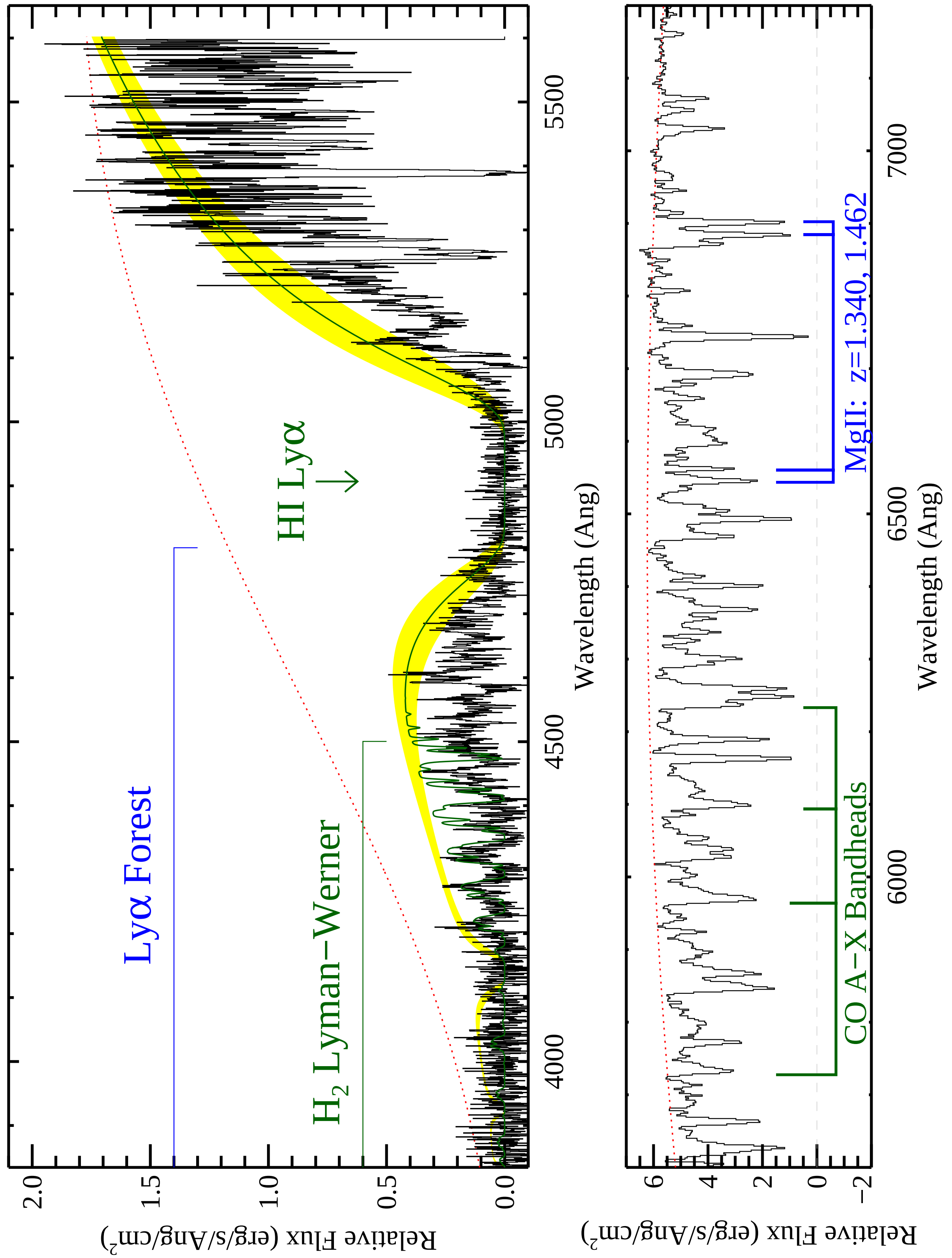


FIG. 4.—*Upper two panels: FUSE* spectrum of the LMC star Sk −67°166. This sight line has $N(H_2) = 5.5 \times 10^{15}$ cm^{-2} in $J = 0$–3. The MW (*black*) and LMC (*green and red*) components are labeled within each band. *Lower panel:* Lyman 4–0 band of H_2. LMC and MW lines are labeled. See the text for more discussion of this figure.


Lyα Forest
H$_2$ Lyman−Werner
HI Lyα
Wavelength (Ang)
Relative Flux (erg/s/Ang/cm^2)
4000
4500
5000
5500
2.0
1.5
1.0
0.5
0.0
CO A−X Bandheads
MgII: z=1.340, 1.462
6000
6500
7000
6
4
2
0
−2

H. H_2 Formation

- Why focus on H_2 first?
  - ◇ H is the most abundant element
  - ◇ H_2 acts as a catalyst/seed for more complex molecules
  - ◇ H_2 is the principal source of opacity in the FUV. Its self-shielding inhibits photodissaociation of other molecules
- Primordial universe
  - ◇ Conditions
    - ▲ No metals, no dust
    - ▲ No photons except the CMB
  - ◇ Channel 1:

$$\mathrm{H} + \mathrm{H} \rightarrow \mathrm{H}_2 + \gamma \tag{96}$$

    - ▲ This channel is <u>very</u> slow because the radiative process is strictly forbidden
    - ▲ Estimated rate

$$R_{\mathrm{HH}} = 10^{-23} n_{\mathrm{H}}^2 \;\; \mathrm{cm}^{-3}\,\mathrm{s}^{-1} \tag{97}$$

  - ◇ Channel 2:

$$\mathrm{H}^+ + \mathrm{H} \rightarrow \mathrm{H}_2^+ + \gamma \tag{98}$$

$$\mathrm{H}_2^+ + \mathrm{H} \rightarrow \mathrm{H}_2 + \mathrm{H}^+ \tag{99}$$

    - ▲ Estimated rate of the 2nd reaction

$$R_{\mathrm{H}_2^+} \approx 10^{-9}\, n_{\mathrm{H}_2^+} n_{\mathrm{H}} \;\; \mathrm{cm}^{-3}\,\mathrm{s}^{-1} \tag{100}$$

    - ▲ Much faster than H + H
    - ▲ But, the formation of H_2^+ is very slow
    - ▲ Therefore, this channel is negligible in all astrophysical situations except for the very early universe ($z \gg 100$)
  - ◇ Channel 3:

$$\mathrm{H} + \mathrm{e}^- \rightarrow \mathrm{H}^- + \gamma \tag{101}$$

$$\mathrm{H} + \mathrm{H}^- \rightarrow \mathrm{H}_2 + \mathrm{e}^- \tag{102}$$

    - ▲ Estimated rate

$$R_{\mathrm{H}^-} = 1.3 \times 10^{-9}\, n_{\mathrm{H}^-} n_{\mathrm{H}} \;\; \mathrm{cm}^{-3}\,\mathrm{s}^{-1} \tag{103}$$

    - ▲ As fast as H_2^+ + H
    - ▲ And the production of H^- is <u>much</u> faster than H_2^+
    - ▲ For a mainly neutral region, we have

$$R_{\mathrm{H}^-} = 7.5 \times 10^{-23} \left[\frac{T}{100\,\mathrm{K}} \right] \left[\frac{x}{1.4 \times 10^{-4}} \right] n n_{\mathrm{H}} \;;\; \mathrm{cm}^{-3}\,\mathrm{s}^{-1} \tag{104}$$

  - ◇ The first star
    - ▲ The 3rd channel dominates the formation of H_2
    - ▲ This H_2 allows a primordial star to cool and collapse within a Hubble time
    - ▲ See Tegmark et al. 1997, Abel et al. 1998

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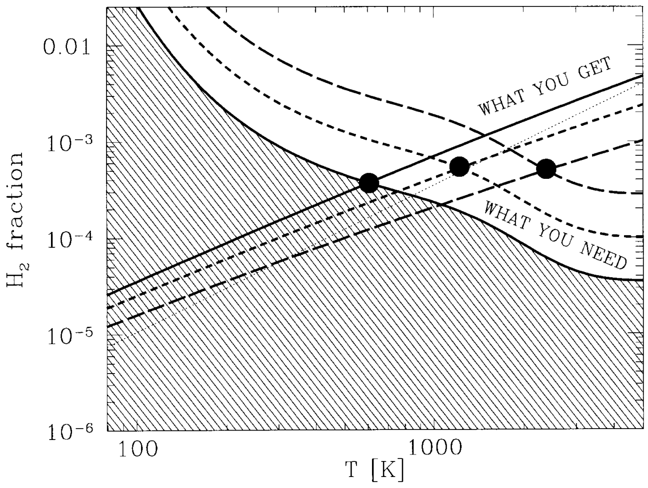

FIG. 1.—Molecular fraction needed and molecular fraction produced. The solid, short-dashed, and long-dashed lines correspond to lumps virializing at $z_{\mathrm{vir}} = 100$, 50, and 25, respectively. Only clouds above the downward sloping lines (outside the shaded region for $z_{\mathrm{vir}} = 100$) can cool in a Hubble time. The upward-sloping lines show the molecular fraction produced in a local Hubble time, so the minimum temperature needed for collapse is that where the pair of curves cross (*solid dots*; — lower z_{vir} require higher virial temperature). Electron depletion is the limiting factor above the thin dotted line, so we see that for $z \gtrsim 50$ the results are rather independent of the initial ionization fraction.

- Present-day universe
  - ◇ Metals, dusts and photons: Oh my!
  - ◇ The dominant formation channel is for H atoms to stick to a dust grain and form H_2 on the surface
  - ◇ Rate expression

$$R_d = \frac{1}{2} S(T, T_d) \eta n_d \sigma_d n_{\mathrm{H}} v_{\mathrm{H}} \tag{105}$$

    - ▲ $S(T, T_d)$ is the sticking probability of an H atom with temperature T onto a dust grain at T_d
    - ▲ η is the probability an adsorbed H atom will form H_2 on the surface before evaporating
    - ▲ v_{H} is the thermal speed of the H atoms

$$v_{\mathrm{H}} = 1.5 \times 10^4 T^{\frac{1}{2}} \tag{106}$$

  - ◇ Taking $n_d \sigma_d = 10^{-21} n$ with $n = 2n_{\mathrm{H}_2} + n_{\mathrm{H}}$

$$R_d = 5 \times 10^{-17} \left(\frac{T}{100\,\mathrm{K}} \right)^{\frac{1}{2}} S(T, T_d)\, \eta(T_d)\, n n_{\mathrm{H}} \ \ \mathrm{cm}^{-3}\,\mathrm{s}^{-1} \tag{107}$$

    - ▲ At low, but not too low, temperature (5K < T < 75K), $S \sim 1, \eta \sim 1$

- ▲ Here is a complicated expression from Thielens for η

$$\eta = \left[\frac{\mu r_H}{2k_{ev}(\mathrm{H_2})} + 1 + \frac{k_{ev}(\mathrm{H})}{k_{pc}} \right]^{-1} \tag{108}$$

I. H_2 Destruction

- Photodisassociation is the primary channel via FUV photons (11–13.6 eV)
  - ◇ But, the absence of a direct route inhibits the process
  - ◇ Only 10–15% of absorbed FUV phtons result in an H_2 disassociation via a bound electronic state
- H_2 is very effective at self-shielding
  - ◇ This requires only $10^{14}\,\mathrm{cm}^{-2}$ H_2 molecules
  - ◇ The disassociation rates interior to this column are greatly reduced
- Estimating the rate
  - ◇ Complicated calculation requiring one to sum the opacity of <u>all</u> lines in the Lyman-Werner transitions
  - ◇ Then, one calcualtes the rates of spontaneous decays to the (unbound) vibrational continuum above the ground state
  - ◇ Good luck!
- A crude estimate

$$\Gamma^0_{\mathrm{H_2}} \approx 4 \times 10^{-11} G_0 \ \ \mathrm{s}^{-1} \tag{109}$$

  - ◇ G_0 is Habing's constant, an estimate of the FUV flux density in the Galaxy
  - ◇ Current estimates are 1.7 higher than Habing's 1968 estimate

$$G_0 = 1.7 \times 1.6 \times 10^{-3} \ \ \mathrm{erg\ cm^{-2}\, s^{-1}} \tag{110}$$

- One can compare the formation rate with the photodisassociation rate to estimate the H_2 abudances as a function of total column N
  - ◇ From Tielens, Sec 8.7.1 (ignoring dust, which may be wrong)

$$X(\mathrm{H_2}) = \frac{4N(\mathrm{H_2})}{N} = 4 \left(\frac{R_d n}{4\Gamma^0_{\mathrm{H_2}}} \right)^4 \left(\frac{N}{10^{14}\,\mathrm{cm}^{-2}} \right)^3 \tag{111}$$

  - ◇ Equation $X(\mathrm{H_2}) = 1/4$ with the HI/H_2 interface, the cloud is half molecular and half atomic when

$$N = N_{DF} \approx 3.7 \times 10^{22} \left(\frac{G_0}{n} \right)^{4/3} \quad \mathrm{cm}^{-2} \tag{112}$$

    - ▲ This is valid for $G_0/n < 4 \times 10^{-2}\,\mathrm{cm}^3$ where H_2 is the dominant FUV opacity
    - ▲ For higher radiation fields (e.g. near a bright FUV source), dust opacity will be more important

- ▲ In thic case, $N_{DF} \approx 4 \times 10^{21}\,\mathrm{cm}^{-2}$ corresponding to $A_V = 2$ (see also Krumholz et al. 2008a)
- ◇ Figure from Draine & Bertoldi 1996, ApJ, 468, 269

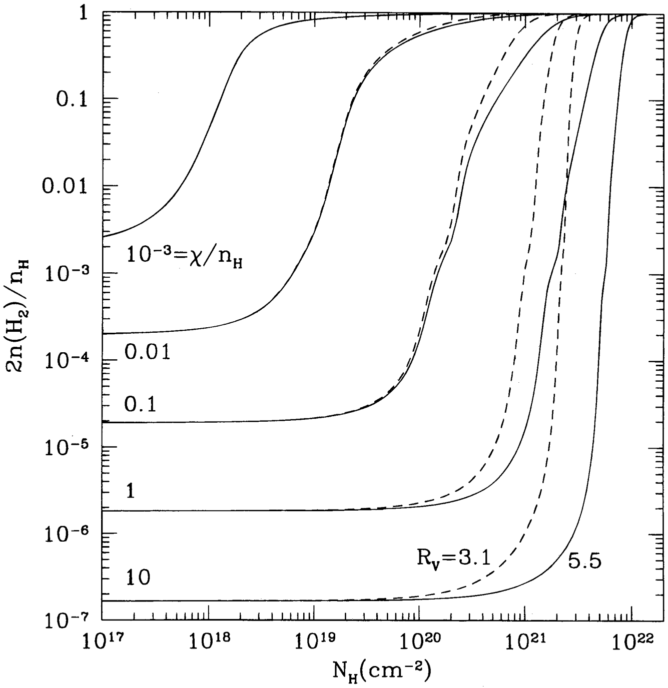

FIG. 8.—H_2 fractions in stationary, plane-parallel photodissociation fronts for $n_H = 10^2\ \mathrm{cm}^{-3}$ and $T_0 = 200$ K, for selected values of χ/n_H (cm^3) and dust with $R_V = 3.1$ ($\sigma_{d,1000} = 2 \times 10^{-21}\ \mathrm{cm}^2$) and $R_V = 5.5$ ($\sigma_{d,1000} = 6 \times 10^{-22}\ \mathrm{cm}^2$). $\lambda > 912$ Å radiation with $u_\nu \propto \nu^{-2}$ is propagating in the $+x$ direction at $N_H = 0$. N_H is the total column density of H nucleons. Self-shielding of the H_2 is computed for 27,983 lines using eq. (30) with $W_{\max} = 0.2$.

J. H_2 in the Milky Way and Neighbors

- Locally, we can probe H_2 directly in absorption
  - ◇ Need a bright, UV background source
  - ◇ And a space telescope for the FUV (*Copernicus, FUSE*)
- Molecular fractions in diffuse clouds
  - ◇ Measure $N(H_2)$ from Lyman-Werner absorption lines
  - ◇ Estimate $N_{\rm HI}$ from 21cm observations

$$f(H_2) = \frac{N(H_2)}{N_{\rm HI} + 2N(H_2)} \tag{113}$$

  - ◇ Plot.. (Tumlinson et al. 2002, ApJS)

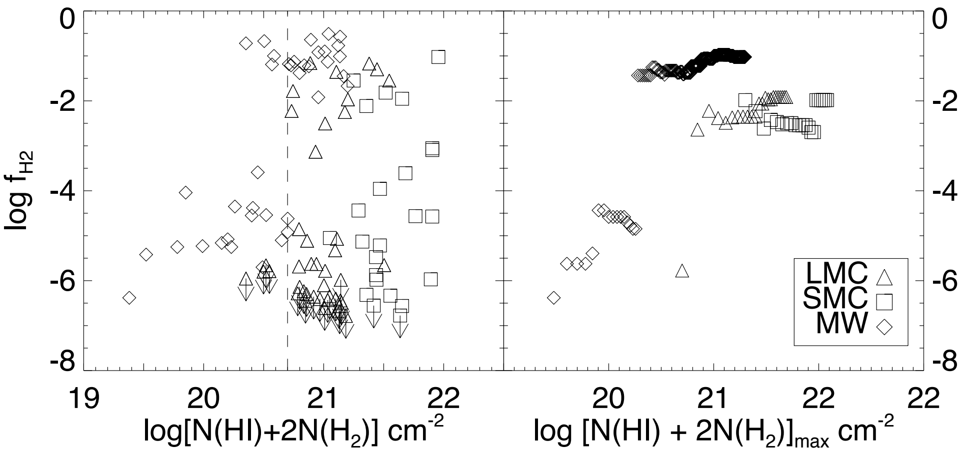

Fig. 8.—*Left panel:* Molecular fraction vs. total H column density for the 44 LMC and 26 SMC sight lines and the S77 sample. *Right panel:* Cumulativ average molecular fraction for the LMC, SMC, and S77 samples, as a function of the maximum value of the total gas content, $N(\mathrm{H}) = N(\mathrm{H\ I}) + 2N(\mathrm{H}_2$ considered in the average. The LMC and SMC are more gas-rich than the Galaxy, but they have a lower molecular fraction.

  - Results for the Galaxy
    - In the Galaxy, the gas becomes molecular at columns of $\log N_H \approx 20.7$
    - At lower values, the molecular fraction is negligible because of the ambient radiation field
  - Results for the SMC, LMC
    - One requires $\log N_H > 21$
    - The metallicity is $2 - 3\times$ lower
    - And the FUV radiation field is higher

- Excitation temperature T_{ex}
  - The relative populations of the J-levels are a function of the gas temperature and FUV radiation field
  - For a negligible radiation field (i.e. collisions alone), the J-levels will be populated by the Boltzman distribution

$$\frac{n_J}{n_0} = \frac{g_J}{g_0} \exp\left[-\Delta E / kT \right] \tag{114}$$

    - Most of the time, collisions will dominate the first few J levels at least
    - Therefore, T_{Ex} will give T_{kin}
  - Radiation excites the J-levels indirectly
    - H_2 absorbs a FUV photon (Lyman-Werner)
    - Then de-excites to the ground-state in an different J-level
    - This is referred to as UV pumping
  - Example from the distant universe (the Galaxy shows similar behaviours)
    - Noterdaeme et al. 2007
    - The low J levels trace the kinetic temperature which is $T_{kin} \approx 90$K

- ▲ The higher J levels trace the radation field, characterized by an excitation $T_{Ex} \approx 500\text{K}$

K. Molecular Gas Beyond the Galaxy

- Problem: Because it is homonuclear, H_2 has very weak emission
  - ◇ Rotational transitions are forbidden!
  - ◇ Also, the rotational constant for H_2 is VERY large
    - ▲ $B(\text{H}_2) = 87\text{K}$
    - ▲ Excitation is difficult in most astrophysical environments
  - ◇ Absorption works
    - ▲ But is limited to a small sample of galaxies
    - ▲ And, sparse sampling of those galaxies
- Solution
  - ◇ Use another molecule to trace H_2
  - ◇ CO is the preferred molecule, observationally
- $^{12}\text{C}^{16}\text{O}$ – surrogate tracer for molecular clouds
  - ◇ Properties
    - ▲ Robust molecule
    - ▲ Most abundant after H_2 and H_2O
    - ▲ Rotational constant $B = 2.77\text{K}$
  - ◇ $J = 1 \rightarrow 0$ transition occurs at 2.6mm (115GHz)
  - ◇ Small dipole moment
    - ▲ Small spontaneous coefficient

$$A_{10} = 6 \times 10^{-8}\text{s}^{-1} \tag{115}$$

    - ▲ Only a minimal number of collisions are needed to populate the excited level
    - ▲ $J = 1$ is populated for $n_H \gtrsim 10^3\,\text{cm}^{-3}$
  - ◇ Radio observations with high angular resolution trace the kinematics of molecular clouds
    - ▲ Optically thick
    - ▲ Observe typical kinetic temperature of $T_K \approx 10\text{K}$
    - ▲ ^{12}CO does not directly trace CO gas mass, however
- $^{13}\text{C}^{16}\text{O}$, $^{12}\text{C}^{16}\text{O}$
  - ◇ Optially thin
  - ◇ Gas mass and temperature diagnostics