6. Spectroscopy fundamentals

This chapter provides a broad overview of the spectroscopic principles required in order to perform quantitative spectroscopy of atmospheres and to couple the details of the atmospheric spectroscopy with the radiative transfer processes and also with the assessment of spectroscopic measurements of atmospheres.

6.1 Einstein A and B coefficients

These provide the relationship between spontaneous emission by atoms or molecules that are in quantum states above the ground state, including the thermal emission by atmospheres (Einstein A coefficient) and induced absorption and emission, (Einstein B coefficient). The blackbody flux density (eq. 4.7, converted to emitted photons)

is $R_n(\sigma)d\sigma = \dfrac{2\pi c\sigma^3 d\sigma}{e^{c_2\sigma/T}-1}$, and the radiation density (eq. 4.8)

is $\rho(\sigma)d\sigma = \dfrac{8\pi hc\sigma^3 d\sigma}{e^{c_2\sigma/T}-1}$.

Figure 6.1. A 2 quantum-level system at equilibrium where, by definition, the number of transitions in absorption equals the number in emission.

Consider a macroscopic two quantum-level system, perhaps a volume of a simple gas, at equilibrium as shown in **Figure 6.1**. At equilibrium, the number of molecules in each of the two states does not change macroscopically, although individual molecules may change state at any time. The populations in each state are determined by Boltzmann statistics:

$$N_1 = N_0 e^{-c_2\sigma/T}. \tag{6.1}$$

At equilibrium, $dN_1/dT = dN_2/dT = 0$, implying

$$N_0\rho(\sigma)B_{01} = N_1\rho(\sigma)B_{10} + N_1 A_{10}. \tag{6.2}$$

Applying the Boltzmann factor

$$\frac{N_0}{N_1}\rho(\sigma)B_{01} = \rho(\sigma)e^{c_2\sigma/T}B_{01} = \rho(\sigma)B_{10} + A_{10}, \tag{6.3}$$

or

$$\rho(\sigma) = \frac{A_{10}}{B_{01}e^{c_2\sigma/T} - B_{10}} = \frac{8\pi hc\sigma^3}{e^{c_2\sigma/T}-1}. \tag{6.4}$$

Therefore

$$B_{01} = B_{10} \tag{6.5a}$$

$$A_{10} = 8\pi hc\sigma^3 B_{10}. \tag{6.5b}$$

This establishes the ratios among the absorption and emission rates for given radiation densities. Absolute values are given in Section 6.2.
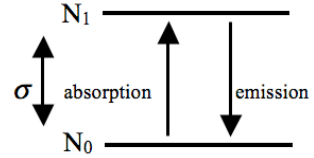
Note the very strong wavenumber/frequency σ^3 (or v^3) dependence of A_{10}; emission at short wavelengths is very fast, and the upper states have very short lifetimes (and broad line shapes (Section 7.2).

If the upper and lower state degeneracies are different, $A_{10} = 8\pi hc\sigma^3 B_{10}$ as before, but $g_0 B_{01} = g_1 B_{10}$.

6.2 Rotational spectroscopy

6.2.1 Diatomic molecules

Figure 6.2. Schematic of a diatomic molecule with internuclear distance r and atomic masses m_1 and m_2.
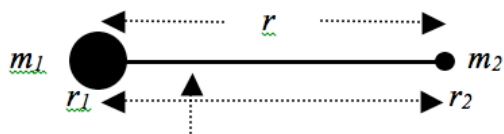
$COM \equiv$ center of mass (or inertia): $m_1 r_1 = m_2 r_2$

The moment of inertia I for rotation about the center of mass is given by

$$I = \sum_i m_i r_i^2 = m_1 r_1^2 + m_2 r_2^2. \tag{6.6}$$

since

$$r_1 = \frac{rm_2}{m_1 + m_2}; r_2 = \frac{rm_1}{m_1 + m_2}, \tag{6.7}$$

$$I = \frac{r^2 m_1 m_2^2}{(m_1 + m_2)^2} + \frac{r^2 m_1^2 m_2}{(m_1 + m_2)^2} = r^2 \frac{m_1 m_2}{m_1 + m_2} \equiv \mu r^2, \tag{6.8}$$

where μ is the *reduced mass* for rotation (reduced masses for other degrees of freedom of motion are also possible; reduced masses for modes of vibration are particularly notable). Note the common case of "hydrogenic" reduced mass: For HX molecules (X=F, Cl, Br, I, O, …) molecules, the reduced mass for rotation is small, similar to the mass of the hydrogen atom.

In general, for axis i of a three-dimensional object, $I_i = \int r_i^2 dm_i$, where r_2 is the distance from the axis and dm_i the differential in mass.

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The *moment of inertia tensor* has diagonal elements, *e.g.*, $I_{xx} = \sum_i m_i(y_i^2 + z_i^2)$ and off-diagonal elements, *e.g.*, $I_{xy} = I_{yx} = -\sum_i m_i x_i y_i$. The *principal axes* are the choice of axes that diagonalize the moment of inertia tensor for an object: $I_{xy} = I_{xz} = I_{yz} = 0$.

The *rotational energy* $E = I\omega^2/2$, classically, and the rotational angular momentum $L = I\omega$, or, $E = \dfrac{L^2}{2I}$. ***However***, quantum mechanics says that L must be quantized in units of $\hbar = \dfrac{h}{2\pi}$, where h is Planck's constant: $L = \dfrac{nh}{2\pi};\quad E = \dfrac{(nh/2\pi)^2}{2I}$

The Hamiltonian expression for rotation about one axis is

$$\frac{\hat{J}^2\Psi}{2I} = E\Psi = \frac{J(J+1)\hbar^2\Psi}{2I}, \tag{6.9}$$

with solution at energies $E = BJ(J+1)$, where $B = \dfrac{h^2}{2I} = \dfrac{h^2}{8\pi^2 I}$. B is the *rotational constant*. Nonlinear *polyatomic* molecules have 2 or 3 rotational constants, depending on the symmetry of the molecule. Expressing B in cm^{-1}:

B (H^{35}Cl)	10.59	← **hydrogenic**
B (HF)	20.94	← **hydrogenic**
B (OH)	18.87	← **hydrogenic**
B (O$_2$)	1.446	← **not hydrogenic**

The spectroscopic consequences of having small, hydrogenic, moments of inertia, with corresponding large rotational constants, are that such molecules (or the corresponding rotational degrees of freedom in polyatomic molecules having one or more hydrogenic reduced masses about rotational axes) 1. have smaller rotational partition functions, and thus distribute the rotational spectra into fewer, stronger transitions; 2. have Boltzmann population distributions that extend to higher energies. This corresponds to the far infrared (submillimeter, terahertz) spectral region, where intensities also are stronger because of the σ^3 factor in the blackbody expression. This spectral region is thus particularly useful for the measurements of gases that are important in stratospheric chemistry, including OH, H_2O, HO_2, H_2O_2, HCl, HF, and HBr. These are *not* hydrides. In hydrides, the hydrogen atom has a formal negative charge (*e.g.*, NaH, LiH, LiAlH$_4$).

$\dfrac{\hat{J}^2\Psi}{2I} = E\Psi$ has the set of solutions $\Psi = P_{JM}(\cos\theta)e^{iM\phi}$, which are *spherical harmonics*, where $J = 0, 1, 2, \ldots$ and $|M| \le J$. There are thus $2J + 1$ "states" of same energy for each J. Their *degeneracy* (in the absence of magnetic and electric fields $\vec{m}$ and $\vec{E}$ which may

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perturb these states from energy degeneracy when the molecules have magnetic or electric moments, Section 6.3) is $2J + 1$ (**Figure 6.3**).

This shows why we need to modify our statement for the Einstein coefficients from $B_{nm} = B_{mn}$ to $g_n B_{nm} = g_m B_{mn}$. The microscopic probabilities are the same but the summed quantities are not. *Detailed balance* requires the above relationship, *e.g.*, $1 \times B_{01} = 3 \times B_{10}$. Degeneracy in general is given by $2F + 1$, where F is the *total angular momentum* of the state (including rotation, orbital, spin, electronic, nuclear).
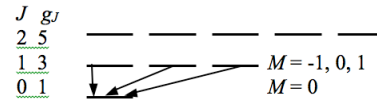

Figure 6.3. Illustration of the degeneracies of rotational energies for the lowest several rotational states of a diatomic molecule

Reminders: Blackbody radiancy $R_\sigma d\sigma = \dfrac{2\pi hc^2 \sigma^3 d\sigma}{e^{hc\sigma/kT} - 1}$

The radiation density $\rho(\sigma) = \dfrac{8\pi hc\sigma^3}{e^{hc\sigma/kT} - 1}$ erg cm^{-3}/cm^{-1} = erg cm^{-2}.

Since $\rho(\sigma) = \dfrac{hc\sigma}{c} F(\sigma)$ (F = flux), $F(\sigma) = \rho(\sigma)/h\sigma$ in cm^{-3} s^{-1}.

Dipole moments, transition moments, line strengths, and intensities

Spectroscopic transitions are effected by the interaction of electromagnetic radiation with electromagnetic moments in atoms and molecules. Important transitions giving rise to the spectra of atmospheres arise from electric dipole
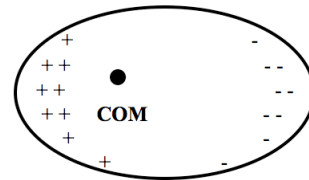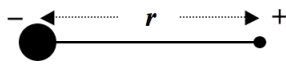

Figure 6.4. Left: a simpler arrangement of masses and charges, corresponding to a (hypothetical) purely ionically-bound molecule. Right: The more general case of an arbitrarily shaped molecule and charge distribution.

moments and (generally much weaker) magnetic dipole moments. Electric quadrupole and even higher moments can also contribute in limited cases (electric quadrupole-allowed transitions are significant in the near infrared A band of O_2).

The electric dipole moment of a molecule has between one and three components depending on the symmetry and arrangement of electric charges in the molecule (**Figure 6.4**). The components of the dipole moment are determined by taking integrals over the product of charge density and distance from the center of mass:

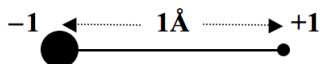$$\mu_r = \int e_r r \, dr, \quad r = x, y, z. \tag{6.10}$$

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Figure 6.5. An electric dipole moment of 1 Debye corresponds to unit plus and minus charges separated by 1 Å (10^{-10} m).

The *intensity* of a transition is proportional to μ^2: The square of the quantum-mechanical matrix element which governs intensity is

$$\left| \int \Psi_1 \mu \Psi_2 d\Omega \right|^2 = \mu_0^2 \times (\text{direction cosine matrix element})^2, \qquad (6.11)$$

where the direction cosine matrix elements describe the relative intensities for transition among different quantum states. Their squares are the *line strength factors*. (Additionally the Boltzmann statistics, Chapter 4, must be included for a complete description of line intensities.)

The standard unit of the electric dipole moment μ_e is the *Debye* (D, 1 Debye = 1 esu-Å, as illustrated in **Figure 6.5**). Magnetic dipole moments arise from circulating electronic charges in the atom or molecule, take on quantized values, and generally interact much more weakly with radiation. The standard unit of the magnetic dipole moment μ_B is the *Bohr magneton*. To gauge the relative ranges of strength of electric dipole allowed and magnetic dipole allowed transitions, $(1 \text{ Debye})^2 = 10^{-36}$ erg cm^3 and $(1 \text{ Bohr magneton})^2$ = 8.60×10^{-41} erg cm^3. For several important atmospheric molecules, as examples, μ_e (HCl) = 1.1 D, μ_e (OH) = 1.7 D, μ_e (O_2) = 0, but μ_B = 2 Bohr magnetons (quantized to almost exactly 2, with tiny corrections, including a relativistic correction).

For simple diatomic molecules, with electric dipole moments but without additional electronic or nuclear moments, we identify μ_e with μ_0 and find intensities proportional to

$$\left| \mu_{J \to J+1} \right|^2 = \mu_0^2 \frac{J+1}{2J+1}; \left| \mu_{J \leftarrow J+1} \right|^2 = \mu_0^2 \frac{J+1}{2J+3}. \qquad (6.11)$$

The usual *selection rules*, determining by symmetries of the quantum mechanic matrix elements as in Eq. 6.11 for rotational transitions of polar diatomics are $\Delta J = \pm 1$ (from the symmetry of $\int \Psi_a \mu \Psi_b$). Then, the rotational lines occur at energies of $\Delta E = 2B, 4B, 6B$ (**Figure 6.6**).
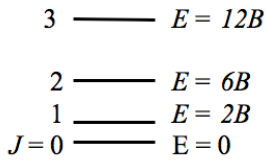
$$3 \quad\rule{1cm}{0.4pt}\quad E = 12B$$

$$2 \quad\rule{1cm}{0.4pt}\quad E = 6B$$
$$1 \quad\rule{1cm}{0.4pt}\quad E = 2B$$
$$J = 0 \quad\rule{1cm}{0.4pt}\quad E = 0$$

Figure 6.6. The lowest several rotational energy levels for polar diatomic molecules.

More generally, the rotational energy levels can be expanded as:

$$E = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3 + ...$$

Departures from the simple $BJ(J+1)$ are due to *centrifugal distortion*. By convention, only the first distortion term, $-DJ^2(J+1)^2$ has a negative sign. D is usually (perhaps always?) positive. Higher terms can in principle be positive or negative.

Rotational partition functions for diatomics are approximated by $Q_R \simeq T/c_2 B$, which is accurate for $B = kT$ and negligible centrifugal distortion. This is a very occasionally useful approximation but it is mostly a relic of pre-computer days. As an example, the HITRAN database of line parameters, which we will meet later, tabulates partition functions for every $1°K$. Interpolating assuming $Q_R \simeq T/c_2 B$ gives very accurate values in such a case.

The transition dipole moment between states m and n is proportional to the matrix element $\int \Psi_m \mu \Psi_n d\Omega$. It is independent of degeneracy as defined:
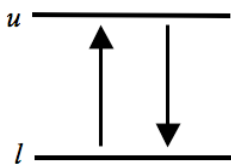
$$|R_{mn}|^2 = |\mu_{J \to J+1}|^2 (2J+1) = |\mu_{J \leftarrow J+1}|^2 (2J+3).$$

(6.12)

Then, quantum mechanics gives:

$$A_{mn} = \frac{64\pi^4 \sigma^3}{3h} |R_{mn}|^2 / g_m = \frac{64\pi^4 \sigma^3}{3h} \mu_{mn}^2, \text{ where } m \text{ is the upper state.}$$

$$B_{mn} = \frac{8\pi^3}{3h^2 c} |R_{mn}|^2 / g_m = \frac{8\pi^3}{3h^2 c} \mu_{mn}^2, \quad B_{nm} = \frac{8\pi^3}{3h^2 c} |R_{mn}|^2 / g_n = \frac{8\pi^3}{3h^2 c} \mu_{nm}^2.$$

The standard definition of intensity, S

Treating the induced absorption and emission, with N_0 as the total population, N_l as the population $N_0 f_l$ in the lower state and N_u as the population $N_0 f_u$ in the upper state:

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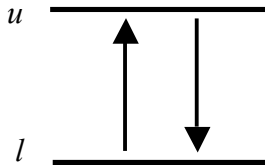$$-\dot{N}_l = N_0(f_l B_{lu} - f_u B_{ul})\rho(I_0,\sigma) \text{ in cm}^{-2}\text{ s}^{-1}, \text{ or}$$

$$-\dot{N}_l = N_0 f_l \frac{8\pi^3}{3h^2c}\mu_{lu}^2(1-e^{-c_2\sigma/T})\rho(I_0,\sigma)$$

$$-\dot{N}_l = N_0 f_l \frac{8\pi^3}{3hc}\mu_{lu}^2\sigma(1-e^{-c_2\sigma/T})F(I_0,\sigma)$$

$$\frac{-\dot{N}_l}{N_0 F} = f_l \frac{8\pi^3}{3hc}\sigma(1-e^{-c_2\sigma/T})\mu_{lu}^2 \equiv S.$$

The above version is in "absorption form." The entirely equivalent "emission form" can be derived from spontaneous emission using the Einstein A coefficient.

$$\frac{\dot{N}_u}{N_o} = f_u A_{ul}.$$

After normalizing to blackbody sterradiancy, the result is $S = \dfrac{8\pi^3}{3hc}\sigma(e^{c_2\sigma/T}-1)f_u\mu_{ul}^2$.

In general: $S = \dfrac{8\pi^3}{3hc}\sigma\dfrac{(e^{-c_2E_l/T}-e^{-c_2E_u/T})}{Q}|R|^2$.

f_l is the fraction of molecules in the lower state and f_u in the upper state. S is in cm (my preference), or in cm^{-1}/(molecules cm^{-2}), which is more standard usage.

Introduction to line shapes and spectral saturation

Multiplying S by the *column density n* of molecules, in cm^{-2}, gives the integral over the wavenumber-dependent optical thickness τ of the line or, in the weak limit of Beer-Lambert absorption or emission, the line's *equivalent width* (W) in cm^{-1} (**Figure 6.7**).
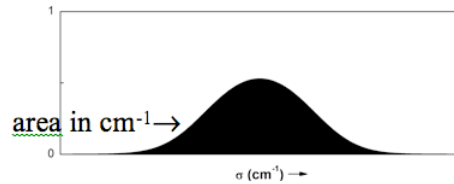

Figure 6.7. The integral of the optical thickness of a line is an area which is an upper limit to the line's equivalent width, it's actual area.

6.2.2 Polyatomic molecules

**Linear polyatomics - vibrational angular momentum, l-type doubling**

Degenerate bending modes of vibration in a linear polyatomic can occur in the two planes orthogonal to the linear axis. For bending vibrational quantum numbers of two or greater the interaction of rotation and vibration gives rise to a splitting of the degenerate vibrational levels known as l-type doubling. Splitting of lines in CO_2, for example,

increases its global warming potential since the lines become more efficient absorbers and emitters of radiation.

Symmetric top molecules

Two rotational constants are the same. This usually (not always) requires 4 atoms at minimum.

3-fold axis

Symmetric top, but rare (astrophysical H_3^+)

Not symmetric tops
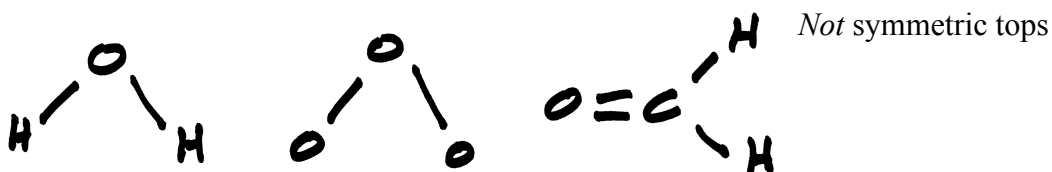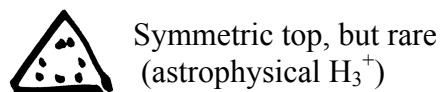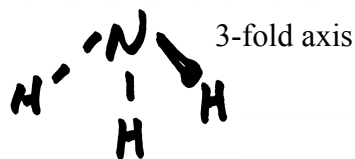
Prolate: $A > B = C$

Oblate: $A = B > C$ (much less common)

A is the largest rotational constant, C the smallest.

$$E \text{ (prolate)} = BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4 + ...$$

Selection rules: $\Delta J = \pm 1, \quad \Delta K = 0$ (The K-distributions are like discrete diatomic manifolds)

Partition function: $Q \cong \dfrac{\pi^{1/2}}{s} \left(\dfrac{T}{c_2 A} \right)^{1/2} \left(\dfrac{T}{c_2 B} \right), s \equiv symmetry\ number$ "the number of

different values of the rotational coordinates which all correspond to one orientation of the molecule, remembering that identical atoms are indistinguishable." (from Mayer and Mayer, as quoted by Davidson).

Asymmetric top molecules

The have quite complex energy expressions which are normally determined iteratively by diagonalizing a parameterized Hamiltonian expression in a basis set of symmetric top wave functions. The rotational partition function is approximated by:

$$Q \cong \pi^{1/2} \left(\frac{T}{c_2 A} \right)^{1/2} \left(\frac{T}{c_2 B} \right)^{1/2} \left(\frac{T}{c_2 C} \right)^{1/2}.$$

Some of the rotational degrees of freedom for nonlinear polyatomics can be hydrogenic, as for HX molecules. Examples include HO_2, H_2O, H_2O_2, HOCl, HOBr, and NH_3. For HO_2, the rotational constants are $A = 20.357$ cm^{-1}, $B = 1.118$ cm^{-1}, $C = 1.056$ cm^{-1}. A has a hydrogenic value.

A rigid planar molecule (or any rigid planar object) will have $I_C = I_A + I_B$ (easy to demonstrate using the Pythagorean theorem). The *inertial defect* measures the departure from this, defined as $\Delta = I_C - I_A - I_B$. Non-zero inertial defect is caused by vibrational averaging and/or (for tetratomic or greater molecules) out-of-plane bending vibrations.

6.3 Vibrational spectroscopy

6.3.1 Diatomic molecules
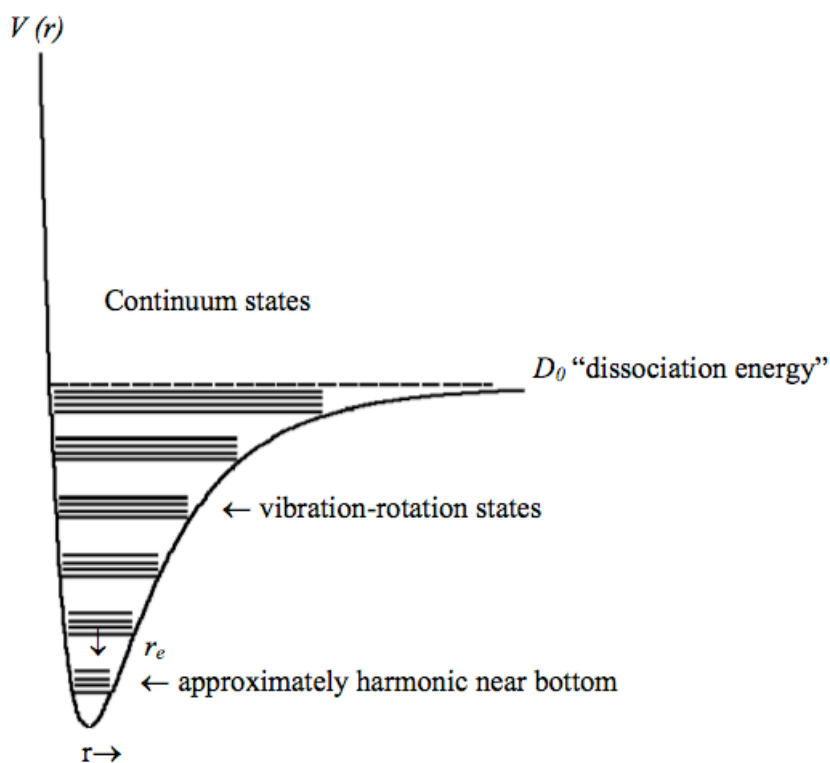
Potential energy curves:

Figure 6.8 Idealized potential energy curve for a bound electronic state of a diatomic molecule.

The potential well pictured in **Figure 6.8** is for a particular electronic state (a bound state in this case), which could well be the electronic ground state.

The bound-state potential curve is approximately harmonic (*i.e.*, a parabola) near the bottom. A better, and still analytic, potential is the Lennard-Jones (or 6-12) potential:

$$V(r) = 4a\left[\left(\frac{b}{r}\right)^{12} - \left(\frac{b}{r}\right)^6\right].$$

It has nice analytic properties for calculations of spectroscopic and thermodynamic properties. Also note the Morse potential, in Bernath:

$V(r) = D\left(1 - e^{-\beta(r-re)}\right)^2$. In general, though, accurate potentials are non-analytic, and are derived either from inversion of spectroscopic data or from complex theoretical calculations.

How complicated does it get? These are potential energy curves for O_2 and its molecular ions from P.H. Krupenie, The spectrum of molecular oxygen, *J. Phys. Chem. Reference Data* **1**, 423-543, 1972. States can be bound or purely repulsive (for example the $^3\Pi_u$ state of O_2). States dissociate to atomic species in different atomic electronic states. Dissociation of the $B\,^3\Sigma_g^-$ state, for example, leads to a ground state (^3P) atom plus an $O(^1D)$ atom, a significant driver of photochemistry in the upper stratosphere and mesosphere through the formation of OH through $O(^1P) + H_2O \rightarrow 2OH$. ($O(^1D)$ at lower altitudes is predominantly from O_3 photolysis.)
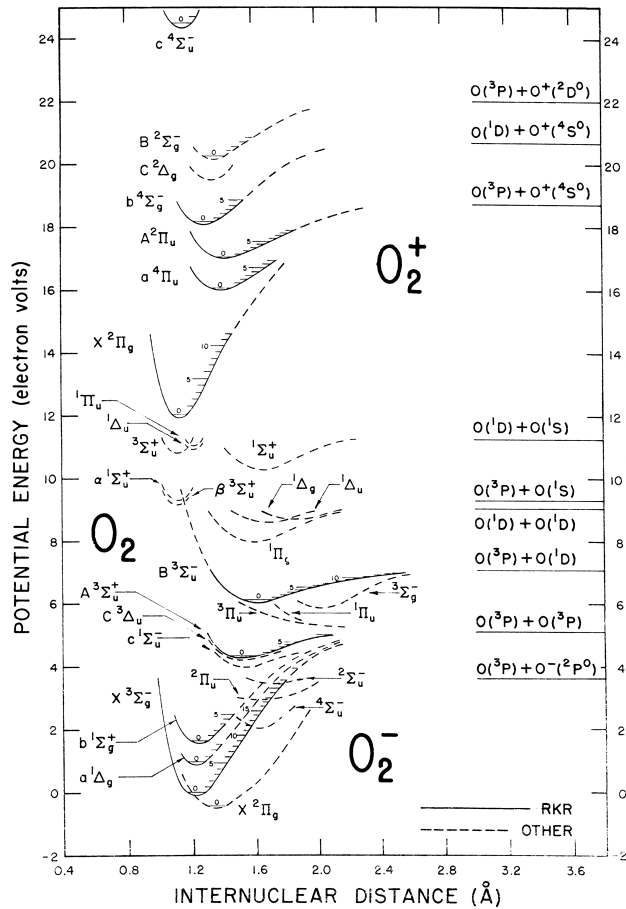

Figure 6.9. Potential curves for O_2 and its ionic forms from P.H. Krupenie, The spectrum of molecular oxygen, *J. Phys. Chem. Reference Data* **1**, 423-543, 1972.

The *vibrational energy levels* (Hermite polynomials are the wave functions for the harmonic approximation to the vibrational potential) are approximately

$E = \omega(v+1/2), v = 0,1,2,...$, where ω is the *vibrational constant*. It is related to the Hooke's law restoring force and the reduced mass for vibration, μ_v: $\omega \propto \sqrt{k/\mu_v}$. The lowest vibrational state, for $v = 0$ has energy $\omega/2$; this is the vibration *zero-point energy*, required by the Heisenberg uncertainty principle. In general, vibrations also have distortions and terms coupling vibration to rotation (*cf. Bernath*, Eq. 7.28):

$$E = \omega(v+1/2) - \omega_e X_e (v+1/2)^2 + BJ(J+1) - DJ^2(J+1)^2 - \alpha_e(v+1/2)J(J+1) + \cdots$$

Vibrational transitions: Fundamentals, overtones and hot bands

Torqueing between vibration states is accomplished through $d\mu/dr$ instead of μ (see why?) and intensities are $\propto \left|\dfrac{d\mu}{dr}\right|_{r_e}^2$ + higher-order terms (μ here is dipole moment; sorry about any confusion with the μ_v of vibrational energy levels). This explains, for example, why OH vibrational transitions are weak while rotational transitions are strong: μ is large, while $d\mu/dr$ is small near r_e (it has zero derivative near r_e).
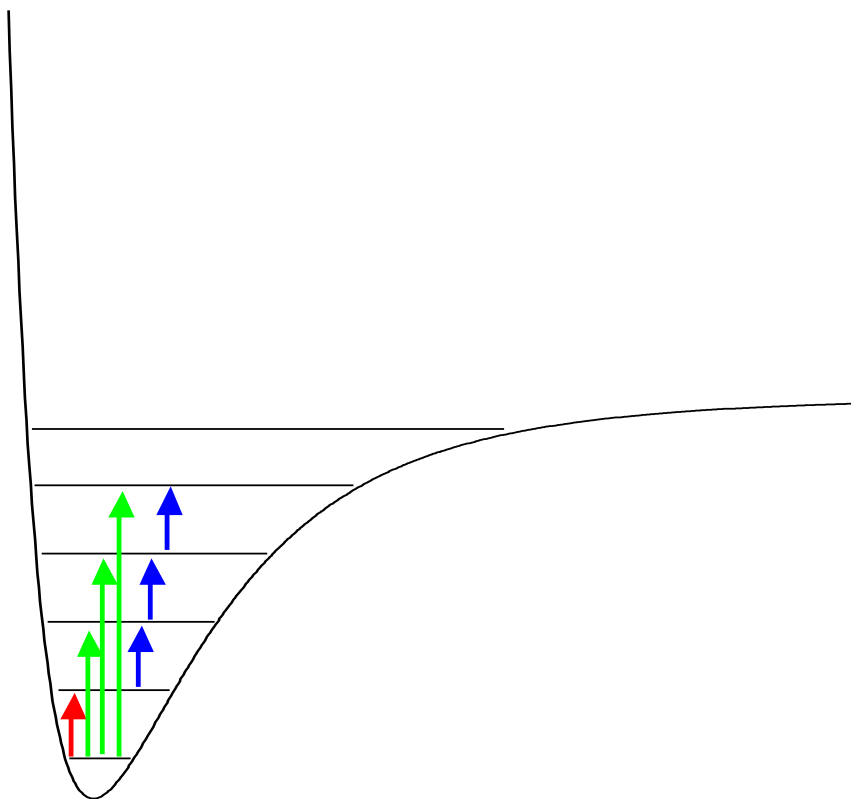

Figure 6.10 Schematic of the vibrational band types for a diatomic molecule.

Vibration band types: The ***fundamental*** transition is $v = 0 \rightarrow 1$ in absorption,

$v = 0 \leftarrow 1$ in emission. ***Overtone*** transitions have $\Delta v > 1$. ***Hot band*** transitions are between states with $v \geq 1$. This gets much more complicated very quickly with polyatomics (discussed later) since the number of fundamentals goes as $3N - 6$ ($3N - 5$ for linear molecules), where N is the number of atoms in the molecule.

The vibrational partition function is $Q_v = 1 + e^{-c_2\omega/T} + e^{-2c_2\omega/T} + ...$, ignoring distortion. (Where did the $\omega/2$ zero-point energy go? Got it? *The choice of the zero of energy for Boltzmann statistics is arbitrary, as long as it is consistent, since any offset occurs in both numerators and denominators*.) Often there is only one upper vibrational state that is thermally accessible (*i.e.*, which has a non-negligible Boltzmann factor).[*] Then

$Q_v \; ; \; \dfrac{1}{1 - e^{-c_2\omega/T}}$. Again, this is now mostly a pre-computer curiosity, except for narrow range interpolation.

[*]This is less true for polyatomics, with ozone and CO_2 being important cases. It is also less true for hot conditions (astrophysical, combustion, plasmas).

6.3.2 Polyatomic molecules

For a nonlinear *N*-atomic molecule there are 3*N*-6 vibrational *degrees of freedom* (= number of vibrational fundamentals). This comes from 3 degrees of freedom, for the 3 spatial directions, from each atom, -3 for molecular translation, -3 for molecular rotations. For a linear polyatomic there are 3*N*-5, plus vibrational angular momentum, which gives rise to *l-type doubling*.

Example for triatomic isosceles XY$_2$ molecule (C$_{2v}$ symmetry) $S_1 = v_1$: symmetric stretch; $S_2 = v_2$: bend; $S_3 = v_3$: asymmetric stretch (From Herzberg, *Infrared and Raman Spectra*).

Examples (*HITRAN*2008):

	v_1	v_2	v_3
H_2O	3652 cm^{-1}	1595 cm^{-1}	3756 cm^{-1}
O_3	1103 cm^{-1}	701 cm^{-1}	1042 cm^{-1}

also, O_3 $2v_1$ @ 2201; $2v_1 + v_2$ 2886; $3v_1$ @ 3278 ʟ

CO$_2$ has 4 fundamentals (since it is linear): symmetric and asymmetric stretch and *doubly-degenerate* bending:

v_1 (symmetric) 1286 cm^{-1}
v_2 (greenhouse) 667 cm^{-1}; doubly degenerate
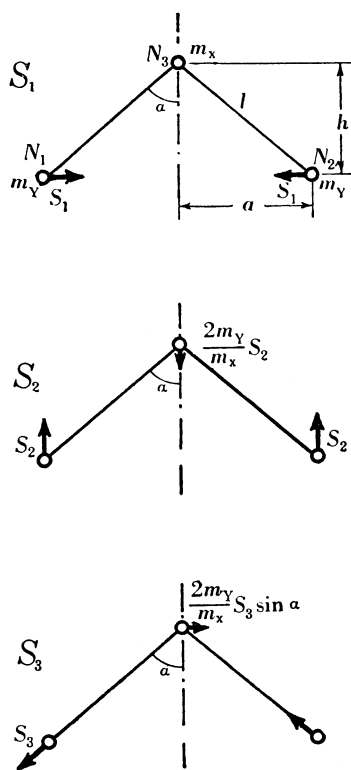v_3 (strong, asymmetric) 2349 cm^{-1}

Figure 6.11. Vibrations for a triatomic molecule with C$_{2v}$ symmetry, from Herzberg, Infrared and Raman Spectra.

The symmetric stretch is *Raman* active rather than infrared active, that is, the transition is allowed by the anisotropy of the polarizability rather than by a dipole moment derivative (since it is, by symmetry, non-existent). The polarizability is responsible for molecular (Rayleigh) scattering. Its anisotropy causes part of the scattering (4% for air) to be *inelastically* scattered. The scattered photons gain or lose energy (becoming bluer or redder) while the molecules lose or gain rovibrational energy, respectively. More later on the atmospheric importance (you could check out our paper *Ring effect studies: Rayleigh scattering, including molecular parameters for rotational Raman scattering, and the Fraunhofer spectrum*, K. Chance and R.J.D. Spurr, *Appl. Opt.* **36**, 5224-5230, 1997, available at http://cfa-www.harvard.edu/atmosphere/publications.html).

The full story for CO_2 is, of course, much more complicated. See, for example, Herzberg, *Infrared and Raman Spectra*, Table 56 and Figure 84.

For a list of *characteristic vibrational band frequencies* – see Table 7.5 in *Bernath* (*e.g.*, $CO \sim 1700$ cm^{-1}).

(Potential surfaces - later)

6.4 Nuclear spin

Definitions
Nuclear spin I = integral: Bosons; they obey Bose-Einstein statistics
Nuclear spin I = half-integral: Fermions; they obey Fermi-Dirac statistics

The total wave function Ψ must be either symmetric or antisymmetric with respect to the interchange of the coordinates of the two identical (in type and molecular location) nuclei, for bosons (integral nuclear spin, I) or fermions (half-integral nuclear spin), respectively. This is a consequence of the *Pauli exclusion principle*, which states that two fermions may not simultaneously occupy the same quantum state. Bosons may, leading to some interesting physical consequences (neutron stars, Bose-Einstein condensates – BECs). Half-integral spin values were discovered, accidentally, in 1922 by *Stern and Gerlach* during magnetic deflection studies of a beam of (nuclear spin ½) silver atoms.

Nucleus	Spin (I)
H	½
D ($=^2$H)	1
^{14}N	1
^{12}C	0
^{16}O	0
^{35}Cl	3/2
^{37}Cl	3/2

Bosons: $P_{AB}\Psi = +\Psi$
Fermions: $P_{AB}\Psi = -\Psi$,

Where P_{AB} is the permutation operator and Ψ is the wave function, which is the product of an electronic, a vibrational, a rotational, and a nuclear spin wave function:

$$\Psi = \Psi_{elect}\Psi_{vib}\Psi_{rot}\Psi_{spin}.$$

Ψ_{elect} is symmetric with respect to the permutation for the electronic ground state of H_2 (the more usual case); Ψ_{vib} is symmetric (always), and Ψ_{rot} are symmetric with respect to permutation of A and B for even J and asymmetric for odd J.

For H_2, where the nuclei (protons) A and B have spins of $I = 1/2$ (and are thus fermions), the two possible spin wave functions for each proton may be called α and β, where α (A) is the state where proton A has angular momentum $+1/2$ (in units of $\hbar$) along the axis of quantization (the internuclear axis), and β (A) has angular momentum $-1/2$ along the axis. Possible nuclear spin wave functions for the molecule are:

$\alpha(A)\alpha(B)$
$\beta(A)\beta(B)$
$[\alpha(A)\beta(B) + \beta(A)\alpha(B)]/\sqrt{2}$
$[\alpha(A)\beta(B) - \beta(A)\alpha(B)]/\sqrt{2}$

The first three are symmetric with respect to permutation of A and B and the last one asymmetric with respect to permutation of A and B. To make $P_{AB}\Psi = -\Psi$, required for fermions, asymmetric nuclear spin wave functions (1-fold degenerate) may only go with symmetric rotational wave functions (even J). Conversely, symmetric nuclear spin wave functions (3-fold degenerate) may only go with asymmetric rotational wave functions (odd J).

The states of higher spin degeneracy are called *ortho* states, and those of lower spin degeneracy are called *para* states. Thus for H_2, the nuclear spin degeneracies are:

$g_N = 1$ for even J (para)
$g_N = 3$ for odd J (ortho).

For homonuclear diatomics in general, both bosons and fermions, the ortho/para ratio is $(I+1)/I$. When $P_{AB}\Psi_{elect} = +\Psi_{elect}$ (the more usual case), this is the ratio of even J to odd J spin degeneracies for bosons and of odd J to even J spin degeneracies for fermions. Thus $^{14}N_2$ ($I = 1$) has $g_N = 2$, J even and $g_N = 1$, J odd.

When $P_{AB}\Psi_{elect} = -\Psi_{elect}$, $(I+1)/I$ is the ratio of odd J to even J spin degeneracies for bosons and of even J to odd J spin degeneracies for fermions. Thus $^{16}O_2$ ($I = 0$), which has a $^3\Sigma_g^-$ ground state, has *only* odd rotational states ($^{16}O^{17}O$ and $^{16}O^{18}O$ have both).

Thus, there are ortho and para forms of H_2, and of other molecules as well. This affects the rotational parts of the spectrum very significantly. The nuclear spin degeneracies must be included in the Boltzmann factors and partition functions:

$$b_J = g_N(2J+1)e^{-c_2 E_J/T}$$

$$Q_{rot} = \sum_{J=0}^{\infty} b_J.$$

Polyatomics have a straightforward continuation of these permutation principles (*e.g.*, for CO_2, H_2O, O_3, NH_3), but we will not develop them here.

In general, ortho and para states of molecules behave as independent species, unconnected to one another by electromagnetically-allowed transitions. If an equilibrium mixture changes temperature, equilibrium may only be re-established by other, chemical, means, where dissociation and reformation is permitted.

Hyperfine structure is due to nuclear spins $\geq 1/2$ and gives (small) additional corrections to the energy levels. This includes "dipolar" contributions due to the interaction of the nuclear spin magnetic moments with internal magnetic fields. Hyperfine structure also includes contributions from nuclear *quadrupole* moments: Nuclear spins ≥ 1 have nuclear quadrupole moments, Q, giving rise to somewhat larger (but still small) energy corrections through $Q : \nabla E$.

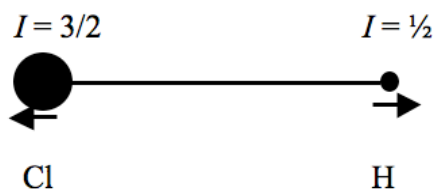Nuclear spins *always* add to the total angular momentum.

$I = 3/2$ $I = \frac{1}{2}$

Cl   H

Figure 6.12. Cartoon of the nuclear spins associated with the HCl molecule.

6.5 Electronic spectroscopy

6.5.1 Electronic orbital angular momentum, electronic spin angular momentum

For a diatomic molecule, the electronic state is given by $^{2S+1}\Lambda$, *e.g.*, $^2\Pi$, $^3\Sigma$, $^1\Delta$, etc. Λ is the quantized *orbital* angular momentum projected onto the intermolecular axis. $\Lambda = 0 \Rightarrow$ Σ state, $\Lambda = 1 \Rightarrow \Pi$ state, $\Lambda = 2 \Rightarrow \Delta$ state, etc. No half-integral orbital angular momentum values are allowed. L is the total electron orbital angular momentum. S is the electron spin angular momentum (half-integral spin angular momentum values are allowed; the electron has spin $\frac{1}{2}$). $2S + 1$ is the *multiplicity*. There may be additional complexities (due to additional symmetries), *e.g.*, the O_2 ground state is $^3\Sigma_g^-$, where g stands for *gerade* (German for *even*, as opposed to *ungerade*). A *gerade* state is even with respect to *inversion*. A state may only (and must be) g or u only if it is a state of a homonuclear diatomic molecule. The superscript "-" refers to reflection in a plane containing both nuclei. This symmetry only applies to molecules in Σ states, because they are non-degenerate.

Hund's coupling cases

How do angular momenta couple? In diatomic molecules, they couple according to *Hund's cases*. Angular momenta must be positive quantities. Angular momenta A and B ($A \geq B$) couple to give resulting totals $A - |B|$ to $A + |B|$, in integer steps (e.g., $1 + 1/2 = 1/2$ or $3/2$). **Figures 6.13** and **6.14** illustrate the two most common of the numerous Hund's cases. In Hund's case (a) the orbital angular momentum and the spin angular momentum are strongly coupled to the molecular axis with quantized projections Λ and Σ (which exists only for $\Lambda > 0$). The vector sum $\Omega = |\Lambda + \Sigma|$ couples to the rotational angular momentum O to give the total angular momentum J. Λ, Σ, and Ω give, *e.g.*, the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ states of OH and ground rotational NO. In Hund's case (b), the spin angular momentum is uncoupled from the molecular axis and is coupled to the vector sum of Λ and the rotational angular momentum O to give the total angular momentum J. With increasing O, the spin angular momentum in NO, for example, rapidly uncouples from the molecular axis to approach case (b).

$$\Lambda + \Sigma = \Omega$$
$$\Omega + O = J$$

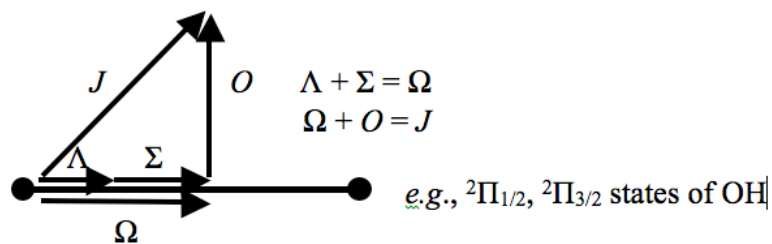e.g., $^2\Pi_{1/2}$, $^2\Pi_{3/2}$ states of OH

Figure 6.13. Hund's case (a), where the orbital angular momentum and the spin angular momentum are strongly coupled to the molecular axis with quantized projections Λ and Σ. The vector sum $\Omega = |\Lambda + \Sigma|$ couples to the rotational angular momentum O to give the total angular momentum J.

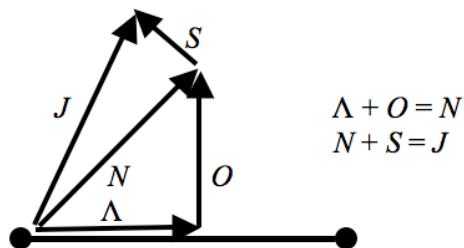$$\Lambda + O = N$$
$$N + S = J$$

Figure 6.14. Hund's case (b). The spin angular momentum is uncoupled from the molecular axis and is coupled to the vector sum of Λ and the rotational angular momentum O to give the total angular momentum J.

There is no perfect coupling except when symmetry requires it; otherwise only total angular momentum is an exact quantum number. Also, for a given molecule in a given electronic state, the closest Hund's case may change as rotational state changes as angular momenta uncouple and recouple as strengths of interactions change.

Where are angular momentum coupling and perturbations in the spectra due to them important? In free radicals: OH, O_2 (!), NO, HO_2, ClO, …. In OH (B = 18.87 cm^{-1}), the *spin-orbit* interaction is so strong that the first transitions are at 61 cm^{-1} rather than at 38 cm^{-1} (except for fine structure "maser" transitions, as seen in astrophysical OH masers). Also, the OH spectrum looks totally unlike that of an evenly-spaced diatomic spectrum.

6.5.2 Electronic transitions

Electronic transitions often, although not always, occur in the visible and ultraviolet portions of the spectrum because of the larger energy levels, and thus energy level differences encountered for electronic states as compared to vibrations and rotations.
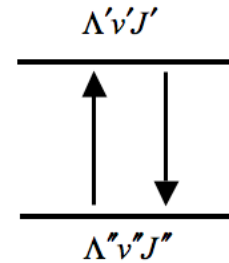
For electronic transitions
$|\mu_{u\to l}|^2 = q_{v'v''} |R_e|^2 S_{J''}/(2J'+1)$, and $|\mu_{l\to u}|^2 = q_{v'v''} |R_e|^2 S_{J''}/(2J''+1)$, where $S_{J''}$ is a *rotational line strength* term (*Bernath*) $\Rightarrow$ *Hönl-London factor*.

$S_{J''}$ is like earlier rotational terms, but now involving Λ', Λ''.

Remember $|\mu_{J\to J+1}|^2 = \mu_0^2 (J+1)/(2J+1)$ and
$|\mu_{J\leftarrow J+1}|^2 = \mu_0^2 (J+1)/(2J+3)$ for simple rotational spectra.
$J+1$ is the Hönl-London factor in this simple case

$\Lambda'v'J'$

$\Lambda''v''J''$

$q_{v'v''}$ is the *Franck-Condon Factor* or *vibrational overlap*: $|\int \Psi_{v'}^* \Psi_{v''} d\tau|^2$ **(show vertical transition here)**

R_e is the electronic transition dipole moment: $R_e = \int \Psi_{el}' \mu_e \Psi_{el}'' d\tau$. See *Bernath* chapters 9 and 10 for copious details.

Then, S (cm) $= \dfrac{8\pi^3}{3hc}\sigma \dfrac{(e^{-c_2 E_l/T} - e^{-c_2 E_u/T})}{Q(T)} g_l |\mu_{l\to u}|^2$

$= \dfrac{8\pi^3}{3hc}\sigma \dfrac{(e^{-c_2 E_l/T} - e^{-c_2 E_u/T})}{Q(T)} q_{v'v''} |R_e|^2 S_{J''}$.

Sum rule: $\sum_{J'} S_{J''} \propto 2J''+1$

"Sums of the line strengths of all transitions to or from a given rotational level are proportional to the statistical weight of that level." Herzberg, *Spectra of Diatomic Molecules*, pp. 208-209.

Finally, what we mostly do with electronic spectra is to use cross sections $\Sigma(\sigma)$, in cm^2, often with temperature dependence and occasionally with pressure dependence, to calculate spectra.

References

6.1 Bernath, Section 5.2 for development of the quantum mechanical Hamiltonian operator (total energy operator for a conservative system) for angular momentum problems (developed for atomic spectra, but just as applicable to rotational angular momentum) and its solutions.

6.2.1 Bernath; For incredible detail, go to Herzberg, *Spectra of Diatomic Molecules*.

6.2 Bernath, Chapter 6; Townes and Schawlow and Herzberg, *Infrared and Raman Spectra* (for much detail) on linear polyatomics - vibrational angular momentum, and l-type doubling.

Bernath, Chapters 6 and 7; Davidson, Chapter 11, for more detail; Herzberg, *Infrared and Raman Spectra*, for yet more detail on symmetric top molecules; also Mayer, J.E., and M.G. Mayer "Statistical Mechanics," Wiley, New York, 1940 for symmetry number definition.

6.3 Bernath Chapter 6 and Chapter 7, Section 1 (vibrations of diatomics); Herzberg, *Diatomics* for great detail.

6.4 Bernath, Sections 7.2 and 9.4. Fuller treatment can be found in a standard statistical mechanics reference. I use Davidson *Statistical Mechanics*, which is now very old, but still excellent.

Townes and Schawlow: Chapter 8 for magnetic hyperfine and Chapter 6 for nuclear electric quadrupole.

6.51 Bernath, Chapter 9, Townes and Schawlow Chapter 7.

Problems

6.1. In class: Demonstrate that $g_0 B_{01} = g_1 B_{10}$ using detailed balance of populations.