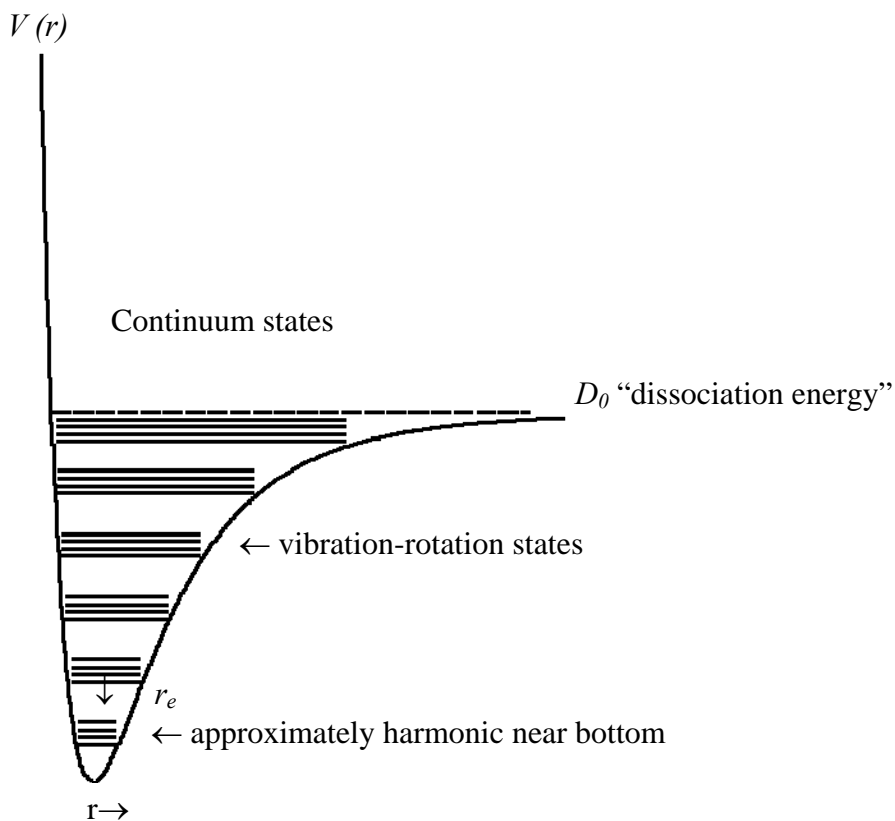


10. Diatomic molecules

Suggested reading: **Bernath** Chapter 6 and Chapter 7, Section 1 (vibrations of diatomics). See **Herzberg**, *Diatomics* for great detail.

Potential energy curves:



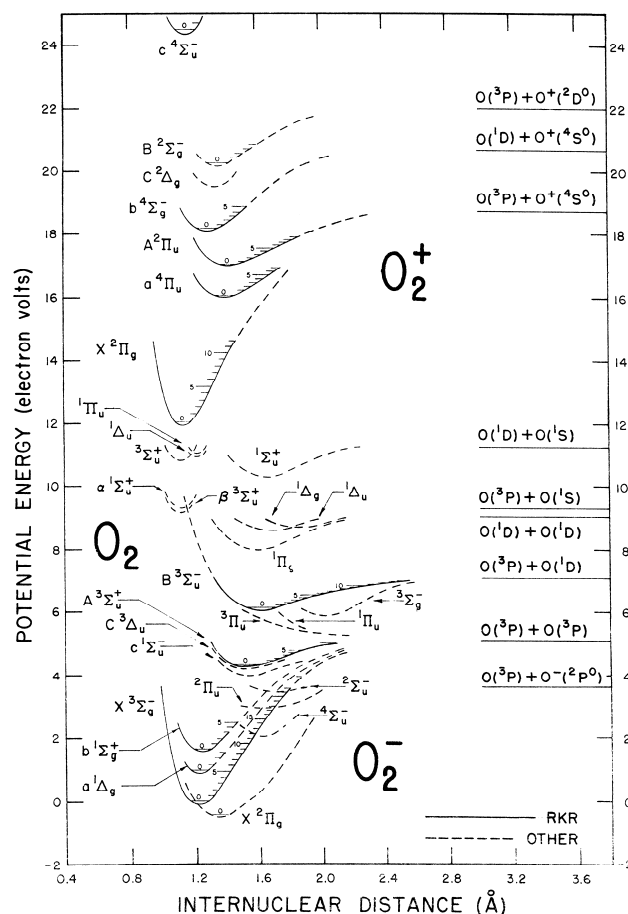
The potential curve is approximately harmonic (*i.e.*, a parabola) near the bottom. A better, and still analytic, potential is the Lennard-Jones (or 6-12) potential:

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

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

$V(r) = D(1 - e^{-\beta(r-r_e)})^2$. 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 O₂ from P.H. Krupenie, The spectrum of molecular oxygen, *J. Phys. Chem. Reference Data* **1**, 423-543, 1972.



The potential well pictured on the previous page is for a particular electronic state (a bound state), which could well be the electronic ground state (see O₂, just above, for a more complex system of potentials). The **rotational energy levels** corresponding to this state can be expanded as:

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

Departures from the simple $BJ(J+1)$ are due (primarily) 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 $Q_R \approx T/c_2B$, which is accurate for $B \ll kT$ 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 $Q_R \approx T/c_2B$ gives very accurate values in such a case.

The **vibrational energy levels** (Hermite polynomials are the wave functions for the harmonic approximation to the vibrational potential) are approximately $E = \omega(v + 1/2), v = 0, 1, 2, \dots$ where ω is the *vibrational constant*. It is related to the Hooke's law restoring force and the reduced mass for vibration, μ_v : $\omega \propto \sqrt{k / \mu_v}$. Note that 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 (*Bernath*, Eq. 7.28):

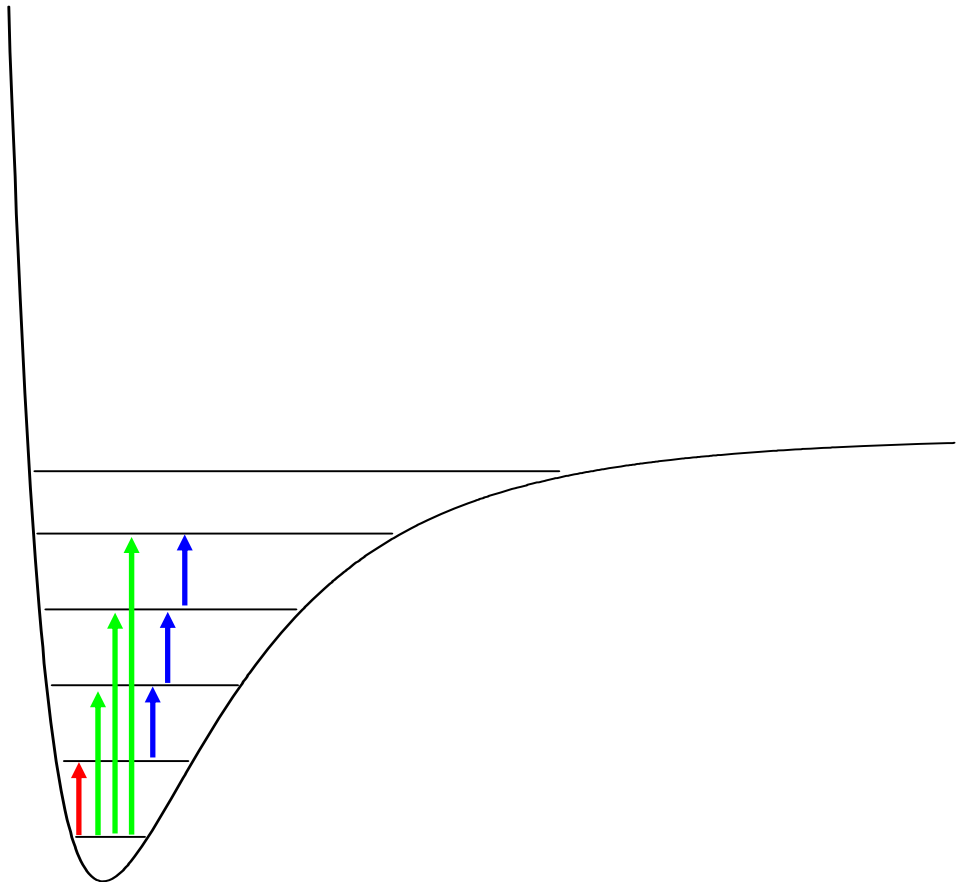
$$E = \omega(v + 1/2) - \omega_e X_e (v + 1/2)^2 + BJ(J + 1) - DJ^2(J + 1)^2 - \alpha_e (v + 1/2)J(J + 1) + \dots$$

Vibrational transitions

Torquing between vibration states is accomplished through $d\mu/dr$ instead of μ (see

why?) and intensities are $\propto \left. \frac{d\mu}{dr} \right|_{r_e}^2$ + 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).



Vibration band types: The *fundamental* transition is $\nu = 0 \rightarrow 1$ in absorption, $\nu = 0 \leftarrow 1$ in emission. *Overtone* transitions have $\Delta\nu > 1$. *Hot band* transitions are between states with $\nu \geq 1$. 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 $Q_\nu = 1 + e^{-c_2\omega/T} + e^{-2c_2\omega/T} + \dots$, 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 $Q_\nu \approx \frac{1}{1 - e^{-c_2\omega/T}}$. 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).