Interstellar Medium (ISM)

Lecture 13
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Stochastic Heating of Very Small Grains

- Temperature History:
  - Two effects become increasingly important with diminishing grain size: (1) **the heat capacity of the dust becomes sufficiently small** that single-particle hits can cause large spikes in the dust temperature and (2) **the absorption rate with photons becomes sufficiently low** that the cooling of the dust between successive collisions becomes important.
  - ***Therefore, it is clear that one cannot speak of a representative grain temperature under these conditions - one must instead us a temperature distribution function.***
  - ***As the grain size is increased, however, photon absorption events occur more frequently, the temperature rise at each event is reduced by the increased heat capacity, and temperature varies over only a small range.***

- Energy content:
  - Heat capacity = heat energy required to raise the temperature of a material
  - When a grain is at a temperature T, the vibrational (internal) energy content of the grain (per unit volume) is

$$\frac{U(T)}{V} = \int_0^T C(T)dT$$

  where $C(T)$ is the heat capacity of the grain (per unit volume) at temperature T.
  - Small grains are subject to temporal fluctuations in temperature, because their steady state internal energies are small compared with the energies of absorbed UV photons.

$$U_{\rm steady}(T) \ll h\nu$$

$$VC\Delta T = h\nu: \ \Delta T \uparrow \ \text{as} \ VC \downarrow \ \text{for a given absorbed energy h}\nu$$

(1) Peak Temperature

- ***Peak Temperature***

  - ***Heat Capacity:*** We need to know the ***heat capacity*** for dust grains to estimate the peak temperature.

    In the low temperature limit: For a plausible grain material, the expected grain temperature would be in general lower than the Debye temperature; we may then use the *Debye approximation* for the heat capacity:

$$C(T) \approx \frac{N_a}{V} k_{\rm B} \frac{12\pi^4}{5} \left(\frac{T}{\theta_D}\right)^3$$

$V = (4\pi/3)a^3$ = volume of a grain particle

N_a = number of atoms forming the grain particle

$n_a = N_a/V$ = number density of atoms in the grain.

$$\left(n_a = \frac{\rho}{\mu m_{\rm H}}, \quad N_a = \frac{\rho}{\mu m_{\rm H}} \frac{4\pi}{3} a^3\right)$$

Here, **Debye temperature θ_D ~ temperature at which the highest-frequency mode is excited.**

For graphite, $\rm C \Rightarrow 6 \times 2$

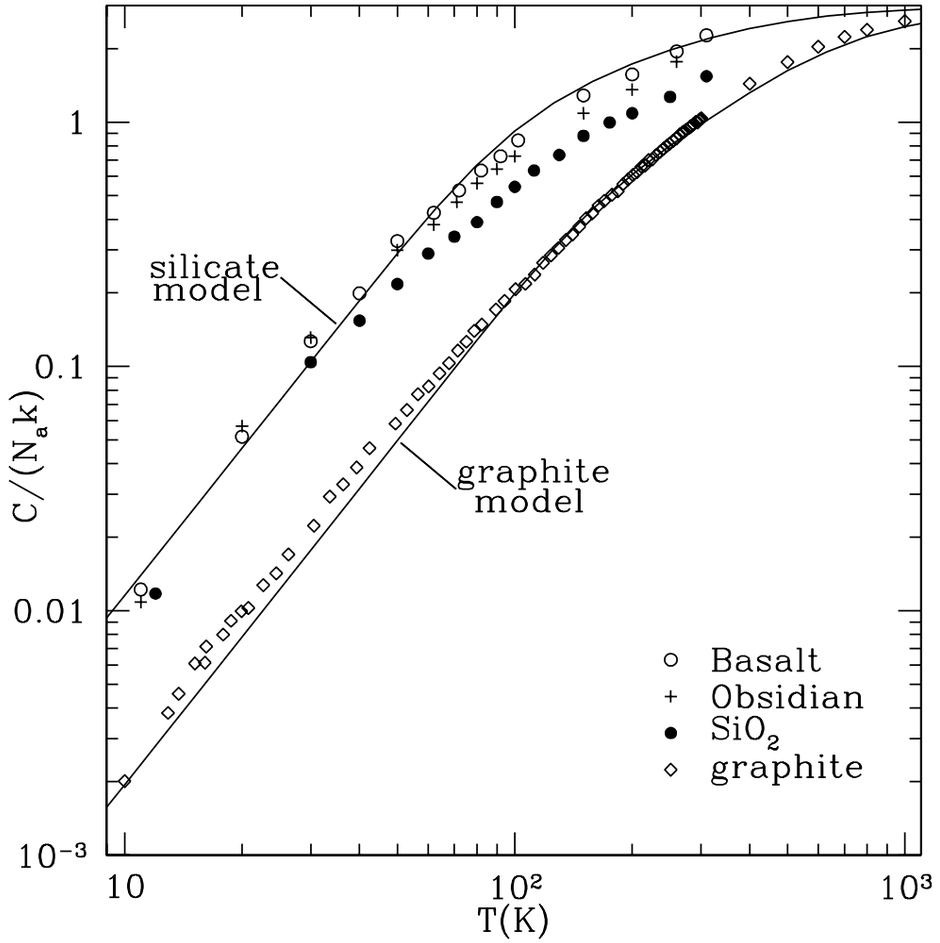
$$\mu = 12, \ \rho = 2.24\,{\rm g\,cm^{-3}}, \ \theta_D = 420\,{\rm K}$$

For silicate (olivine),

$$\mu = 170, \ \rho = 3.8\,{\rm g\,cm^{-3}}, \ \theta_D = 665\,{\rm K}$$

$\rm Mg_2SiO_4 \Rightarrow 12 \times 2 \times 2 + 14 \times 2 + 8 \times 2 \times 4$

Heat capacity of graphite and silicate
Fig 2 of Draine & Li (2001, ApJ, 551, 807)



In the high temperature limit: the heat capacity is given by *the rule of Dulong-Petit*:

$$C(T) \simeq 3\frac{N_a}{V}k_{\rm B}$$

- ***Internal Energy***: The internal energy at T is then given by

$$U(T) \equiv V\int_0^T C(T')dT'$$

$$U(T) \approx \frac{3\pi^4}{5}N_a k_{\rm B}T\left(\frac{T}{\theta_D}\right)^3 \quad \text{at low temperature}$$

$$\approx 3N_a k_{\rm B}T \quad \text{at high temperature}$$

The internal energy in the low temperature limit,

$$U(T) \approx \frac{4\pi^5}{5}k_{\rm B}\frac{a^3\rho}{\mu m_{\rm H}}\frac{T^4}{\theta_D^3}$$

$$\approx 5.1\times10^{-16}\,[\rm erg]\left(\frac{a}{10\,\text{Å}}\right)^3\left(\frac{12}{\mu}\right)\left(\frac{\rho}{2.24\,\rm g\,cm^{-3}}\right)\left(\frac{420\,\rm K}{\theta_D}\right)^3\left(\frac{T}{10\,\rm K}\right)^4$$

$$\approx 1.5\times10^{-17}\,[\rm erg]\left(\frac{a}{10\,\text{Å}}\right)^3\left(\frac{170}{\mu}\right)\left(\frac{\rho}{3.8\,\rm g\,cm^{-3}}\right)\left(\frac{665\,\rm K}{\theta_D}\right)^3\left(\frac{T}{10\,\rm K}\right)^4$$

Therefore, ***the internal energy of a very small grain is much smaller than the absorbed photon energy.***

$$h\nu = 1.0 \times 10^{-11}\,[\mathrm{erg}] \left(\frac{2000\,\text{Å}}{\lambda}\right) \longrightarrow \begin{array}{ll} U(T_0) \ll h\nu & \text{for } a \ll 270\,\text{Å} \\ U(T_0) \gg h\nu & \text{for } a \gg 270\,\text{Å} \end{array}$$

Now, the peak temperature can be estimated from:

$$h\nu = U(T_p) - U(T_0)$$

The peak temperature can be estimated as follows:

$$h\nu = U(T_p) - U(T_0) \longrightarrow U(T_p) \simeq h\nu$$

$$T_p \simeq 118\,\mathrm{K} \left(\frac{2000\,\text{Å}}{\lambda}\right)^{1/4} \left(\frac{a}{10\,\text{Å}}\right)^{-3/4} \left(\frac{\mu}{12}\right)^{1/4} \left(\frac{\rho}{2.24\,\mathrm{g\,cm^{-3}}}\right)^{-1/4} \left(\frac{\theta_D}{420\,\mathrm{K}}\right)^{3/4}$$

The peak temperature for a small grain is in general much higher than the equilibrium temperature.

However, the internal energy of a large grain is much larger than the absorbed photon energy.
Therefore, **large grains will stay in a steady state with an equilibrium temperature.**

(2) Heating and Cooling Time Scales

- Time Scales
  - There are three time scales to understand the temperature fluctuation of very small grains.
    - **Absorption time scale** : How often a grain will absorb a photon?
    - **Diffuse time scale** : How fast the absorbed energy is distributed over the whole grain?
    - **Cooling time scale** : How fast the excited vibration modes radiates back the energy to the interstellar space?

- ***Absorption Time Scale***:
  - The absorption rate of starlight photons by very small grains is

$$\left(\frac{dN_{\rm ph}}{dt}\right)_{\rm abs} = \int \frac{u_\nu d\nu}{h\nu} c\, Q_{\rm abs}(\nu)\pi a^2 = \int d\nu \frac{4\pi J_\nu}{h\nu} Q_{\rm abs}(\nu)\pi a^2$$

B. T. Draine does not provide an approximate formula for the absorption rate, but we can roughly estimate it from the heating rate.

$$\left(\frac{dN_{\rm ph}}{dt}\right)_{\rm abs} \approx \frac{1}{\langle h\nu\rangle}\left(\frac{dE}{dt}\right)_{\rm abs} = (\pi a^2)\,\langle Q_{\rm abs}\rangle_*\,\frac{u_* c}{\langle h\nu\rangle}$$

Here, $\langle h\nu\rangle$ is a typical photon energy of the ISRF.
We will take $\langle h\nu\rangle \approx 1\times10^{-11}\,\mathrm{erg}$ for $\lambda \approx 2000\,\text{Å}$.

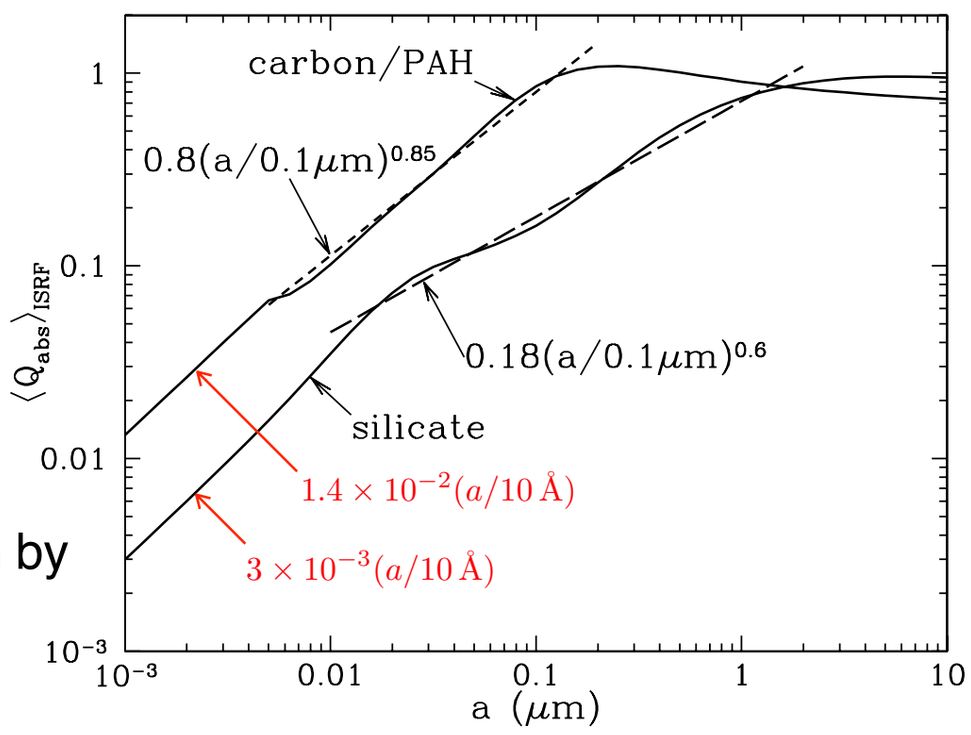
$$u_*/\langle h\nu\rangle \approx 1\times10^{-1}\,U\ [\mathrm{cm}^{-3}]$$

From the right figure, we take

$$\langle Q_{\rm abs}\rangle_* \approx 1\times10^{-2}(a/10\,\text{Å})\,[\mathrm{cm}^2]$$

Recall that the absorption efficiency is proportional to the grain size in the Rayleigh limit.

[Fig 24.2, Draine]



Hence, the photon absorption rate for small grains is given by

$$\left(\frac{dN_{\rm ph}}{dt}\right)_{\rm abs} \approx 1\times10^{-6}\,U(a/10\,\text{Å})^3\ [\mathrm{s}^{-1}]$$

- Absorption Rate for Large grains (using the absorption cross-section in the figure)

$$\left(\frac{dN_{\rm ph}}{dt}\right)_{\rm abs} \approx (\pi a^2)\,\langle Q_{\rm abs}\rangle_*\,\frac{u_* c}{\langle h\nu\rangle}$$
$$\approx 0.17\,U(a/0.1\mu{\rm m})^{2.6}\,[{\rm s}^{-1}], \quad \text{for silicate}$$
$$\approx 0.75\,U(a/0.1\mu{\rm m})^{2.85}\,[{\rm s}^{-1}], \quad \text{for graphite}$$

  - Absorption time scale:

$$t_{\rm abs} \equiv (dN_{\rm ph}/dt)^{-1}_{\rm abs}$$
$$\approx 1\times 10^6\,U^{-1}\ \ [{\rm s}]\ \ a\sim 10{\rm \AA} \quad \text{small grain}$$
$$\approx 1.3-5.9\,U^{-1}\,[{\rm s}]\ \ a\sim 0.1\mu{\rm m} \quad \text{large grain}$$

  - ***In diffuse interstellar space, the smaller component of interstellar dust will absorb star light photons once in two hours (for a ~ 50Å) - 11 days (for a ~ 10Å). Large dust grains (a ~ 0.1μm) will absorb photons once in a couple of seconds.***

- ***Diffuse Time scale***: How long does it take to heat up the whole grain?
  - The macroscopic diffuse equation:

$$\boxed{\frac{\partial T}{\partial t} = D\nabla^2 T \quad \text{where } D = \text{diffusion coefficient}}$$

$$t_{\rm diff} \approx a^2/D$$
$$\approx 10^{-12}\,[{\rm s}]\,(a/10\,{\rm \AA})^2(10^{-2}\,{\rm cm^2\,s^{-1}}/D)$$

a typical *D* value from (Duley 1973, Ap&SS, 23, 43)

  - Sound crossing time: Energy disturbance in a solid is transmitted to its lattice vibrational modes (photons) and phonons travel at the speed of sound, which is about a few 10^5 cm/s.

$$t_{\rm diff} \approx 2a/c_s$$
$$\approx 2\times 10^{-12}\,[{\rm s}]\,(a/10\,{\rm \AA})(10^5\,{\rm cm\,s^{-1}}/c_s)$$

$c_s \sim 1\ {\rm km\,s^{-1}}$ in a cold material.

  - We may conclude that ***the grain is heated to a peak temperature instantaneously upon the absorption of a photon***, which is determined by:

$$h\nu = \frac{4\pi a^3}{3}\int_{T_0}^{T_p} C(T')dT'$$

$C(T)$ = heat capacity per unit volume

where T_0 is the temperature just prior to the absorption event.

- *The cooling time scale*

- The time evolution of grain temperature can be calculated by solving

$$\frac{dU}{dt} = -(4\pi)(\pi a^2)\int Q_{\rm abs} B_\nu d\nu = -4\pi a^2 \left\langle Q_{\rm abs}\right\rangle_T \sigma_{\rm SB} T^4$$

$$\frac{dT}{dt} = -\frac{3}{aC(T)}\left\langle Q_{\rm abs}\right\rangle_T \sigma_{\rm SB} T^4 \quad \longleftarrow \quad dU = \frac{4\pi a^3}{3} C(T) dT, \quad \int Q_{\rm abs} B_\nu d\nu = \frac{\sigma_{\rm SB}}{\pi} T^4$$

- The initial cooling time scale can be estimated by

$$t_{\rm cool} \approx \frac{U(T_p)}{|dU/dt|} \approx \frac{h\nu}{\Lambda}$$

$$h\nu = 1.0\times 10^{-11}\,[{\rm erg}]\left(\frac{2000\,{\rm \AA}}{\lambda}\right)$$

$$\Lambda = \left|\frac{dU}{dt}\right|_{T_p} = 4\pi a^2 \left\langle Q_{\rm abs}\right\rangle_T \sigma_{\rm SB} T_p^4$$

- We will assume an approximate, absorption efficiency, following S. S. Hong (홍승수, 1979, JKAS):

$$Q_{\rm abs}(\nu) = \frac{4\pi a}{\lambda} = Q_0(\lambda_0/\lambda) \quad \longleftarrow \quad Q_{\rm abs}(\nu) = 4\frac{2\pi a}{\lambda}{\rm Im}\left(\frac{m^2-1}{m^2+2}\right)$$ Rayleigh limit

Here, $Q_0 \approx 6.283\times 10^{-2}\,\chi(a/10\,{\rm \AA})$

$\lambda_0 = 2000\,\mu{\rm m}$

$\beta = 1$ $\qquad\qquad$ $\chi \simeq 1$

From the previous formula for $Q_{\rm abs}(\nu) = Q_0(\lambda_0/\lambda)^{-\beta}$

the planck-averaged absorption efficiency is given by

$$\begin{aligned}\langle Q_{\rm abs}\rangle_T &= \frac{15}{\pi^4}\Gamma(4+\beta)\zeta(4+\beta)Q_0\left(\frac{kT}{h\nu_0}\right)^\beta \\ &= 3.83220\,Q_0\left(\frac{kT}{h\nu_0}\right) \qquad \text{for } \beta = 1 \\ &\approx 3.950\times10^{-2}\,\chi\,(a/10\,\text{Å})(\lambda/2000\text{Å})(T/118\,\text{K})\end{aligned}$$

One may want to use the following formula for $\beta = 2$:
$\left\langle Q_{\rm abs}\right\rangle_T \approx 1\times10^{-6}\left(a/0.1\,\mu\text{m}\right)(T/\text{K})^2$

The cooling rate is:

$$\begin{aligned}\Lambda &= 4\pi a^2\,\langle Q_{\rm abs}\rangle_T\,\sigma_{\rm SB}T^4 \\ &= 5.46\times10^{-11}\,[\text{erg s}^{-1}]\,\chi(a/10\,\text{Å})^3(\lambda/2000\,\text{Å})(T/118\,\text{K})^5\end{aligned}$$

The cooling time scale at the peak temperature is:

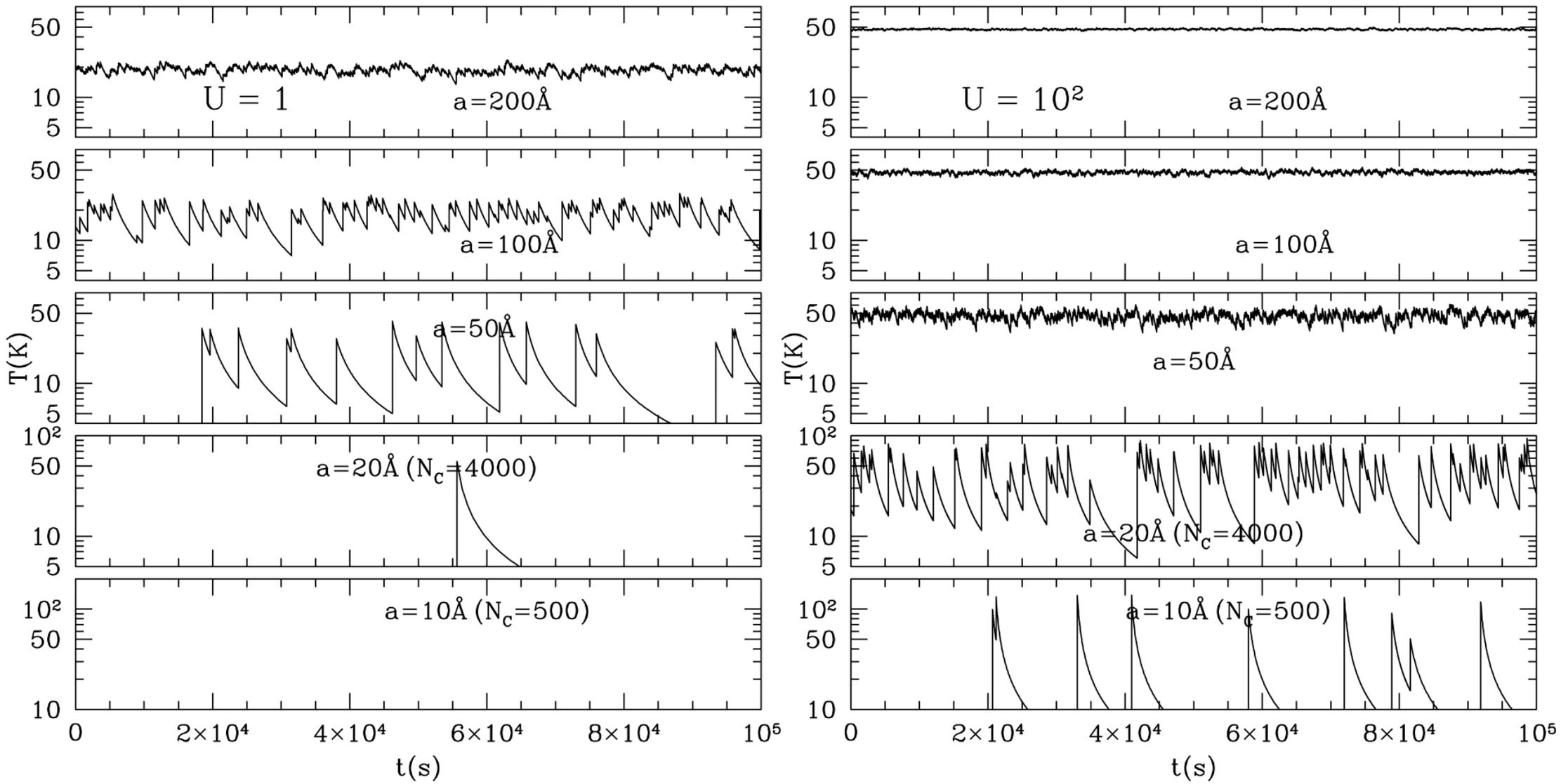
$$\begin{aligned}t_{\rm cool} &\approx \frac{U(T_p)}{|dU/dt|} = \frac{h\nu}{\Lambda} \\ &\approx 0.18\,[\text{s}]\,\chi^{-1}(10\,\text{Å}/a)^3(118\,\text{K}/T)^5\end{aligned}$$

Because of the strong temperature dependence of the cooling rate, **the grain actually needs much longer time (up to 10^4 sec) to radiate its excess (absorbed) energy back** to the interstellar space.

In summary, $t_{\rm abs} \gg t_{\rm diff},\quad t_{\rm abs} \gg t_{\rm cool},\quad t_{\rm cool} \gg t_{\rm diff}$

The Stochastic Time Evolution of Grain Temperature

Monte-Carlo simulations of the temperature fluctuation:
See Draine & Anderson (1985, ApJ, 292, 494) and Krugel (The Physics of Interstellar Dust, IoP).



Temperature versus time during 10^5 s (~1 day) for five carbonaceous grains in two radiation fields: the local starlight intensity (U = 1; left panel) and 10^2 times the local starlight intensity (U = 10^2; right panel). The importance of quantized stochastic heating is evident for the smallest sizes.

[Fig 24.5, Draine]

- Temperature History:
  - Two effects become increasingly important with diminishing grain size: (1) the heat capacity of the dust becomes sufficiently small that single-particle hits can cause large spikes in the dust temperature and (2) the absorption rate with photons becomes sufficiently low that the cooling of the dust between successive collisions becomes important.
  - ***For very small dust grains, one cannot speak of a representative grain temperature under these conditions - one must instead us a temperature distribution function.***

- Temperature Distribution Function:
  - Consider a large ensemble of identical grains in some interstellar environment. Let use define:

$P(T)dT$ = the probability that its temperature lies in the interval from *T* and *T + dT*.

The probability density is of course normalized: $\int_0^\infty P(T)dT = 1$

  - The temperature distribution will depend on grain size, composition, and the intensity (and spectrum) of the radiation illuminating the grains.

- **For normal interstellar grains of average size**, the temperature oscillates only a little around an equilibrium value $T_{\rm eq}$ and in the limit of large grains, the distribution density function approaches the delta-function:

$$P(T) \rightarrow \delta(T - T_{\rm eq})$$

where the equilibrium temperature follows from the steady-state balance between emission and absorption:

First, calculate the equilibrium temperature.

$$\int Q_\nu^{\rm abs} J_\nu d\nu = \int Q_\nu^{\rm abs} B_\nu(T_{\rm eq}) d\nu$$

Second, the emissivity (per solid angle per area per time)

$$\rightarrow \quad \epsilon_\nu = \pi a^2 Q_\nu^{\rm abs} B_\nu(T_{\rm eq})$$

- **Even for a very small particle** we will assume that its radiation obeys at any time Kirchhoff's law, so in the case of a sphere of radius a, we can express the average monochromatic emission per solid angle by

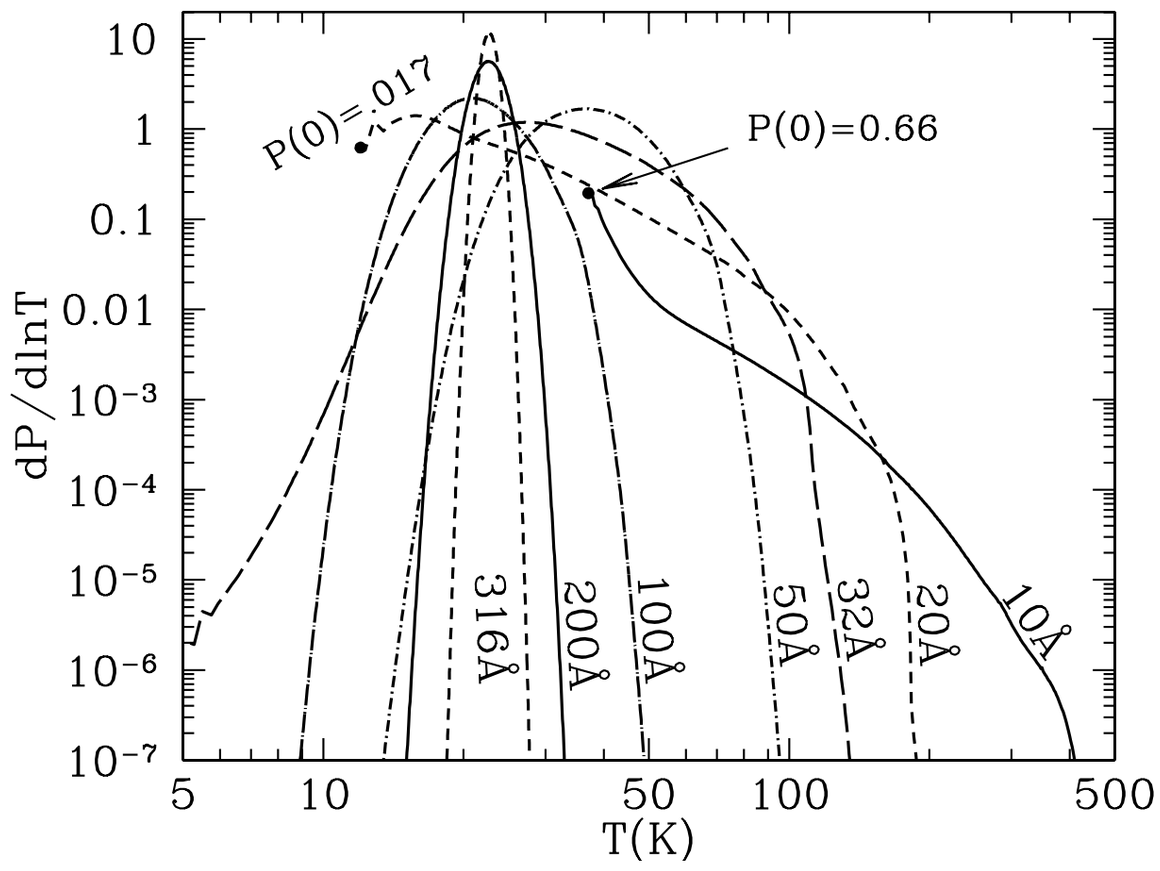
$$\epsilon_\nu = \pi a^2 Q_\nu^{\rm abs} \int B_\nu(T) P(T) dT$$

Although the emission of a single such grain is not time-constant, the whole ensemble radiates at any frequency at a steady state.

- The following figure shows temperature distribution functions calculated for graphite/ PAH dust grains of selected radii, exposed to the ISRF of Mathis et al. (1983).
  - We see that the distribution function for a grain with a = 10Å extends to T = 400 K - this is the temperature that this grain will be heated to when it absorbs a single photon with energy just below the Lyman limit cutoff at 13.6 eV.
  - Most of the energy radiated by the grain is radiated while it is at temperature above 100 K - the typical absorbed photon raises the grain temperature to T > 200 K. Such grains radiate strongly in the PAH features at 7.7, 8.6, and 11.3 μm.

Temperature distribution function for seven carbonaceous grains in ISRF with U = 1. Curves are labeled by grain radius. For a = 10 and 20Å curves, the dot indicates the first excited state and P(0) is the fraction in the ground state.

[Fig 24.6, Draine]



Method of Calculation

- **Monte-Carlo simulation** (Draine & Anderson 1985)
  - The cooling flux of low energy infrared photons and heating by photons with $\lambda > \lambda_c \ (= 1000\mu\mathrm{m})$ are assumed to be continuous. However, ***heating by photons with*** $\lambda < \lambda_c$ ***must be treated as a sequence of stochastic absorptions of single energetic photons.***
  - The probability a photon is absorbed by a grain in a time interval $(t, t + dt)$ is given by

$$P(t)dt = \dot{p}e^{-\dot{p}t}dt$$

$$\dot{p} = \int_0^{\lambda_c} \pi a^2 Q_\lambda^{\mathrm{abs}} \frac{u_\lambda c}{h\nu} d\lambda \quad [\mathrm{s}^{-1}] \longrightarrow$$

$$t = -\frac{1}{\dot{p}} \ln \xi \ (0 \le \xi < 1)$$

ξ = uniform random number

Heating of the grain by photons with $\lambda > \lambda_c = 1000\,\mu\mathrm{m}$ is modeled as continuous.

  - The energy (wavelength) of the absorbed photon is randomly determined according to

$$\frac{1}{\dot{p}} \frac{d\dot{p}}{d\lambda} d\lambda = \frac{Q_\lambda^{\mathrm{abs}} \left(u_\lambda c/h\nu\right)}{\int Q_\lambda^{\mathrm{abs}} \left(u_\lambda c/h\nu\right) d\lambda} d\lambda$$

  - The temperature of the grain is then assumed to be immediately increased to that estimated from:

$$\frac{hc}{\lambda} = \frac{4\pi a^3}{3} \int_{T_0}^{T} C(T')dT' \longleftarrow dU = \frac{4\pi a^3}{3} C(T)dT$$

Here, T_0 is the temperature just prior to the absorption event.

- For each grain type and size, the temperature evolution can be followed by solving the differential equation:

$$\frac{dU}{dt} = 4\pi^2 a^2 \left[\int_{\lambda_c}^{\infty} Q_\lambda^{\rm abs} J_\nu(t) d\lambda - \int_0^{\infty} Q_\lambda^{\rm abs} B_\lambda(T(t)) d\lambda \right]$$

continuous heating continuous cooling

Heating of the grain by photons with $\lambda > \lambda_c = 1000\,\mu\mathrm{m}$ is modeled as continuous.

$$\frac{dU}{dt} = \frac{4\pi a^3}{3} C(T) \frac{dT}{dt}$$

$$\longrightarrow \quad \frac{dT}{dt} = \frac{3\pi}{aC(T)} \left[\int_{\lambda_c}^{\infty} Q_\nu^{\rm abs} J_\nu(t) d\nu - \int_0^{\infty} Q_\nu^{\rm abs} B_\nu(T(t)) d\nu \right]$$

The right side describes the difference between the power absorbed from the radiation field J_ν and the cooling rate.

- Having followed $U(t)$ or $T(t)$ over a long period, one can obtain the probability density $P(T)$ from the fraction of time that the grain has spent in the temperature interval T and $T + dT$.

- Discretized steady state distribution function
  - It is far more efficient to solve directly for the discretized steady state distribution function.
    - **Guhathakurta & Draine (1989, ApJ, 345, 230)** developed a fast method to calculate the temperature distribution function.
      - **Draine & Li (2001, ApJ 551, 807)** presented a statistically exact, and quantum-mechanical treatment.
    - **Desert et al. (1986, A&A, 160, 295)** also developed a different method to compute the temperature distribution function, which is publicly available (**DustEM**; https://www.ias.u-psud.fr/DUSTEM/; Campiegne et al. 2010, A&A, 724, 44).
    - **Dwek (1986, ApJ, 302, 363)** presented a method to calculate the temperature fluctuations in dust particles when they collide with low-density, X-ray emitting electrons.
  - Guhathakurta & Draine (1989)
    - When a grain absorbs or emits a photon, its internal energy $U(T)$, which is a function of temperature, changes. We bin $U(T)$ into N states (bins) U_j of width ΔU_j.
      Let P_j the probability for a grain to be within the j th state.
      Let A_{fi} the transition probability that a single grain changes from state i to f.

- In statistical equilibrium, for each level j the number of populating and depopulating events must be equal.

$$\sum_{k \neq j} A_{jk} P_k = P_j \sum_{k \neq j} A_{kj}$$

population de-population

Note that P_j is proportional to the energy width ΔU_j

With the purely mathematical definition:

$$A_{jj} = -\sum_{k \neq j} A_{kj}$$

We can write the equilibrium equation as the following matrix equation:

$$\sum_{k=1}^{N} A_{jk} P_k = 0$$

- Only $N - 1$ of these N equations are linearly independent.

  One may first put $P_1 = 1$ (or $P_N = 1$) and then solve for $P_2, \cdots, P_N$ (or $P_1, \cdots, P_{N-1}$), and then rescale them:

$$\sum_{j=1}^{N} P_j = 1$$

- Matrix Elements
  - Heating:

$$A_{kj} = \frac{4\pi C_\nu^{\rm abs} J_\nu}{h\nu}\Delta U_k \quad \text{where } h\nu = |U_k - U_j| \;\; (j < k)$$

  - Cooling:

$$A_{kj} = \frac{4\pi C_\nu^{\rm abs} B_\nu(T_j)}{h\nu}\Delta U_k \quad \text{where } h\nu = |U_j - U_k| \;\; (j > k)$$

  - Above the main diagonal stand the cooling elements, below those for heating. The energy balance requires for the cooling and heating rate for each level j:

heating: $$\sum_{k>j} A_{kj}\,|U_k - U_j| = \int_0^\infty 4\pi C_\nu^{\rm abs} J_\nu d\nu$$

cooling: $$\sum_{k<j} A_{kj}\,|U_k - U_j| = \int_0^\infty 4\pi C_\nu^{\rm abs} B_\nu(T_j) d\nu$$

  - ***"Thermal Continuous" Cooling Approximation:*** As cooling proceeds via infrared photons which have low energy, their emission changes the grain temperature very little. ***This suggests that in cooling one needs to consider only the transitions to the levels immediately below*** ($k = j-1,\; j \to j-1$).

One can, therefore, put all matrix elements A_{fi} above the main diagonal to zero, except $A_{j-1,j}$. Then, in order to fulfill the energy equation, the ***cooling elements*** have to be written as:

$$\sum_{k>j} A_{kj} \left| U_k - U_j \right| = \int_0^\infty 4\pi C_\nu^{\rm abs} J_\nu d\nu$$

$$A_{j-1,j} \left| U_{j-1} - U_j \right| = \int_0^\infty 4\pi C_\nu^{\rm abs} J_\nu d\nu \quad \longrightarrow$$

$$A_{j-1,j} = \frac{1}{\left| U_j - U_{j-1} \right|} \int_0^\infty 4\pi C_\nu^{\rm abs} B_\nu(T_j) d\nu$$

$$A_{kj} = 0 \quad \text{if} \quad k < j-1$$

- However, ***heating should not be reduced to single transitions*** $j \rightarrow j+1$.
- Guhathakurta & Draine (1989) describe a simple trick to avoid numerical rounding errors in calculating the temperature distribution.

Setting $X_j = P_j / P_1 \quad (X_1 = 1)$, we can obtain the steady state solution for the distribution function:

$$\frac{d}{dt} \left(\sum_{j=1}^{j-1} P_j \right) = A_{f-1,f} P_f - \sum_{j=1}^{f-1} P_j \sum_{k=f}^{N} A_{k,j} \quad \longrightarrow$$

$$X_f = \frac{1}{A_{f-1,f}} \sum_{j=1}^{f-1} B_{f,j} X_j \quad \text{where} \quad B_{f,j} \equiv \sum_{k=f}^{N} A_{k,j} \ (f > j)$$

However, in practice, even adopting the trick, calculating the temperature distribution function is a bit tricky; it is hard to define a proper interval for U or T.

- Infrared Emission from Grains
  - In a typical spiral galaxy, perhaps 30-50% of the energy radiated by stars is absorbed by dust grains, and reemitted in the IR. The spectrum of this emission is determined by the temperatures and composition of the dust grains.
  - IR emission is a quantum process - a radiative transition between an upper and lower vibrational level of the grain. However, it has been shown (Draine & Li 2001) that a "thermal" approach provides an excellent approximation.
  - In the approximation, the emissivity of a population of grains can be written:

$$4\pi j_\nu = 4\pi \sum_i \int da \frac{dn_i}{da} \int dT \left(\frac{dP}{dT}\right)_{i,a} C_\nu^{\rm abs}(i,a) B_\nu(T)$$

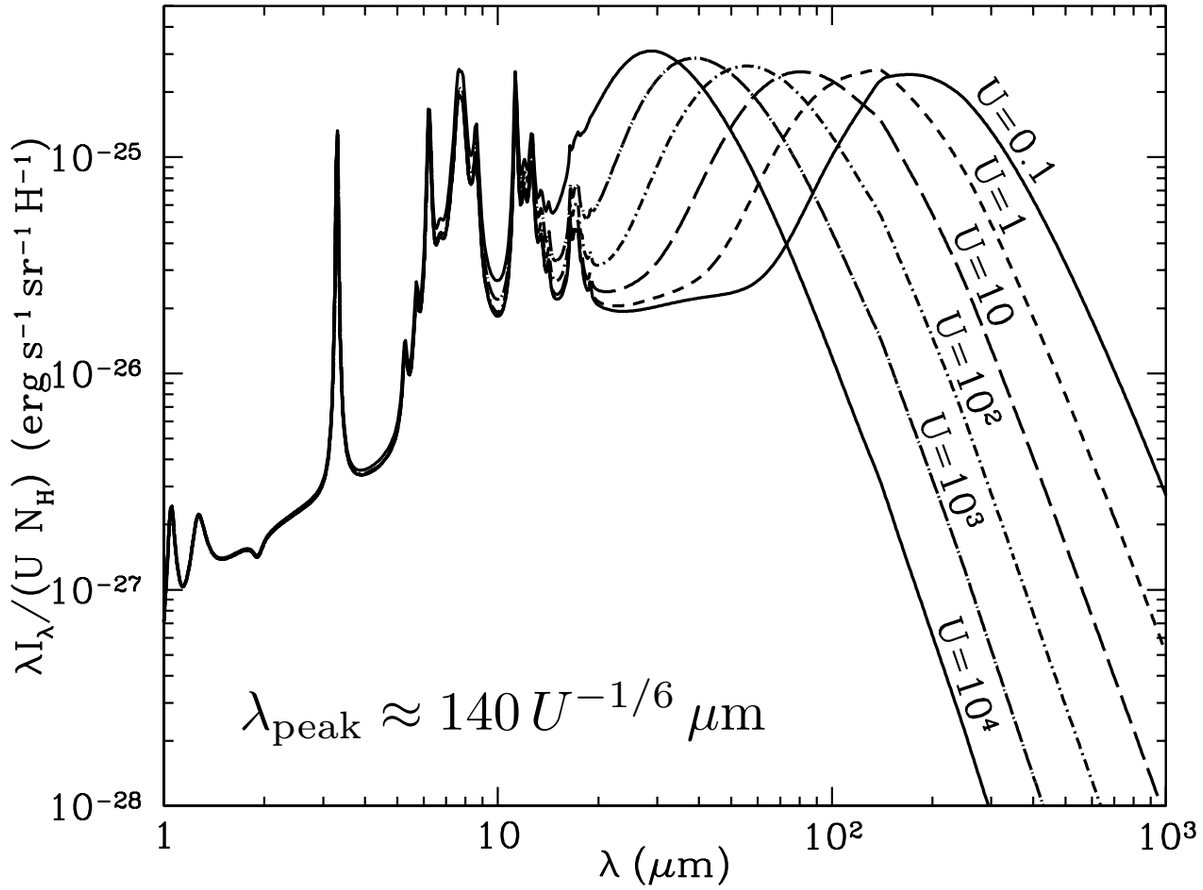
where $(dn_i/da)da$ is the number density of grains of type i with radii in $[a,\ a+da]$.

- We, therefore, need a grain model to provide the size distribution for each composition, the absorption cross sections and temperature distribution functions.
- For large grains, the temperature distribution is sufficiently narrow that it may be approximated by a delta function $dP/dT \rightarrow \delta(T - T_{\rm eq})$, where $T_{\rm eq}$ is the steady-state temperature for which the time-averaged cooling equals the time-averaged heating.
- But for $a \lesssim 0.01\,\mu{\rm m} = 100\,\text{Å}$, one should use a realistic temperature distribution dP/dT rather than a delta-function.

- Model IR emission spectra have been calculated by Draine & Li (2007).
  - The spectra shown in the following figure is normalized by the ISRF strength U.
  - The peak in the Far-IR corresponds to emission from “large” grains. The equilibrium temperature of the “large” grains are approximately:

$$T_{\rm eq} \approx 20\, U^{1/6}\,{\rm K}$$

  - The peak shifts toward shorter wavelength as U increases and the grains become warmer. the peak $(\lambda I_\lambda)_{\rm peak}$ occurs at $\lambda_{\rm peak} \approx 140\, U^{-1/6}\,\mu{\rm m}$.
  - The additional peaks at shorter wavelengths are due to vibrational modes of PAH grains; these features account for ~25% of the total power, but these features (normalized by the total power) hardly change as the radiation intensity is changed.
  - The PAH emission occurs following single-photon heating of very small grains.



[Fig 24.7, Draine]

Evolution of Interstellar Dust in Galaxies

From B. T. Draine's keynotes

- ***Sources***
  - **Stellar sources**: AGB stars, Supernovae, Novae,…
  - **Interstellar**: Growth of solid material in the ISM by accretion of gas onto grain surfaces
    - If stellar injection dominates: then interstellar dust is mainly "stardust", with composition of stardust.
    - If interstellar growth dominates: then interstellar dust consists mainly of whatever materials can grow (and survive) in the ISM.
  - Both processes are active. ***Which is dominant in the Galaxy?***
- ***Sinks***
  - Destruction of solid material in ISM
    - sputtering (in shock waves and shock-heated gas)
    - grain-grain collisions $\Rightarrow$ vaporization
    - photodesorption
    - other (cosmic rays, Coulomb explosions, sublimation,…)
  - Incorporation into protostars
  - Removal in galactic outflow

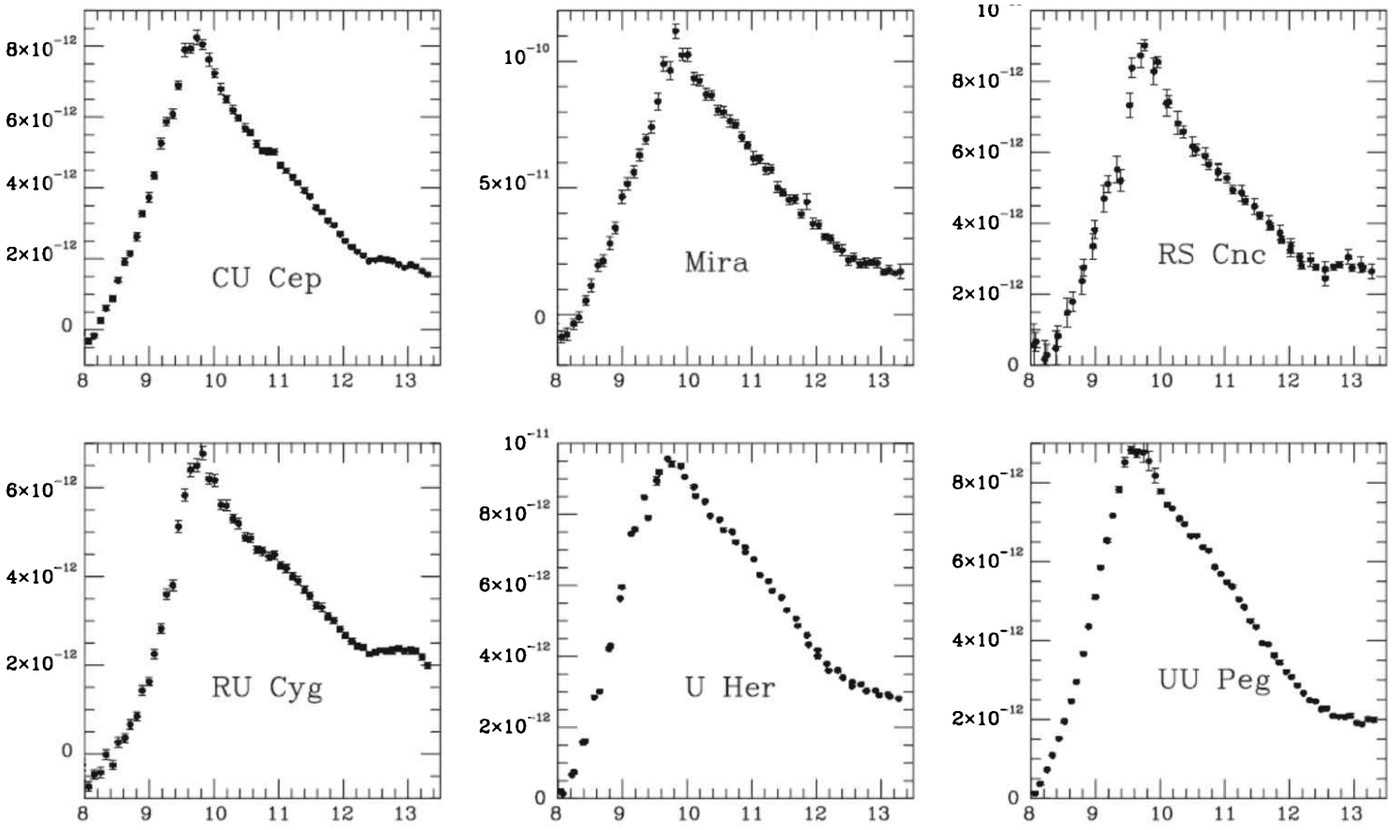
Sputtering: a phenomenon in which microscopic particles of a solid material are ejected from its surface, after the material is bombarded by energetic particles of a plasma or gas.

Coulomb explosion: the effect of a molecule moving at high speed striking a solid; binding electrons being torn off, and the resulting charged constituents separating due to Coulomb repulsion.

Photodesorption: a quantum effect whereby a single photon causes the desorption of an atom or molecule from a solid surface.

Stellar Sources - Example

- Observationally, it is seen that these “dust nurseries” exist in the dense, cool stellar winds of AGB stars, old planetary nebulae, and the cooling envelopes of novae. In these winds, the densities are as much as ~ 10^9 cm^{-3}, and the temperatures can drop below the condensation temperature of many heavy elements (~ 1000 K).
- For instance, Mira variable stars are AGB stars with substantial emission at mid-infrared wavelengths. In oxygen-rich Mira variables, most of carbon is locked up in gaseous CO, and the main condensates are silicates. Oxygen-rich Mira variables often have a strong silicate emission feature at λ ~ 9.7μm.



Continuum-subtracted spectra of oxygen-rich Mira variable stars.

The x-axis shows wavelength in μm and the y-axis flux in W m^{-2} $μm^{-1}$

[Speck et al. 2000]

- In carbon-rich Mira variables, the mid-IR thermal dust continuum is frequently accompanied by an emission feature at $\lambda \sim$ 11.3μm, due to the presence of SiC. However, in the winds of carbon-rich Mira variables, much of the carbon condenses out in the form of PAHs rather than silicon carbide grains, because of the scarcity of silicon relative to carbon.
- A typical mass loss rate for a Mira variable star is $\dot{M} \sim 10^{-6} M_\odot \, \mathrm{yr}^{-1}$. Given a dust-to-gas ratio of ~ 0.01 (by mass, considering only hydrogen), this implies that a Mira variable can produce as much as

$$\dot{M}_{\mathrm{dust}} \sim 10^{-8} M_\odot \, \mathrm{yr}^{-1}$$

of dust during its ~ Myr time scale for copious mass loss.

$$\boxed{M_{\mathrm{dust}} \approx \dot{M}_{\mathrm{dust}} \times \Delta t_{\mathrm{life}} \approx 0.01 M_\odot}$$

The newly formed $\sim 0.01 M_\odot$ of stardust is spread into the ISM, where it undergoes competing processes of growth and destruction.

Growth in ISM

- How dust grains form?
  - **Even in a fairly dense molecular cloud core**, with 3x10^4 atoms per cm^3, at cosmic abundances we expect **only 1 Si atom and 8 C atoms per cm^3**. How can we make such widely separated atoms to form a dense solid grain?
  - ***Gas accretion on grains*** - How fast dust grains can grow?
    - Let's imagine a solid spherical grain made of element X. The number density of X atoms in the interstellar gas is $n_{\rm X}$, and the rms thermal velocity of an X atom is

$$v_X = \left(\frac{3kT}{2m_X}\right)^{1/2}$$

T = the gas temperature
m_X = the mass of an X atom

    - If there exists a *"seed"* grain of radius a, it will accrete additional X atoms from the surrounding gas, and the grain's mass will grow at the rate

$$\frac{dM_{\rm gr}}{dt} = (n_X v_X)(\pi a^2) m_X \mathcal{P}_s$$

    - where $\mathcal{P}_s$ is the *"sticking probability"*; that is, the probability that an X atom striking the grain will stick instead of bouncing off. The mass of the spherical grain is

$$M_{\rm gr} = \frac{4\pi}{3} a^3 \rho_{\rm gr}$$

$\rho_{\rm gr}$ = the bulk density of element X.

- We can rewrite the mass growth rate as a radius growth rate:

$$\frac{da}{dt} = \frac{n_X v_X \pi a^2 m_X \mathcal{P}_s}{4\pi \rho_{\rm gr} a^2} = \frac{n_X v_X m_X \mathcal{P}_s}{4\rho_{\rm gr}}$$

- Thus, the growth rate da/dt is independent of the grain size a, unless the sticking probability $\mathcal{P}_s$ is a function of grain size. For carbon atoms in the cold neutral medium ($T \sim$ 100 K, $n_{\rm C}/n_{\rm H} \approx 3 \times 10^{-4}$.

$$\frac{da}{dt} = \frac{n_{\rm C}}{n_{\rm H}} \frac{n_{\rm H} m_{\rm C} \mathcal{P}_s}{4\rho_{\rm gr}} \left(\frac{3kT}{2m_{\rm C}}\right)^{1/2}$$

$$\approx 0.2\,[\mu{\rm m/Gyr}]\,\mathcal{P}_s \left(\frac{n_{\rm H}}{30\,{\rm cm^{-3}}}\right) \left(\frac{T}{100\,{\rm K}}\right)^{1/2}$$

$\rho_{\rm gr} = 2.24\,{\rm g\,cm^{-3}}$ for graphite

See slide 31, the residence time scale of atoms (grains) in the ISM.

  - This simple calculation suggests that ***grains can grow to the observed size during a time scale shorter than the age of our galaxy as long as atom-grain collisions are sticky***.
  - It becomes much easier to grow grains, if there exist seed grains produced in regions that are denser and/or cooler than typical regions of the ISM.

- ***Grain-Grain collisions***: Dust grains can grow as the result of grain-grain collisions. However, they can also be shattered into smaller fragments by high-speed collisions.

  [shattering: action of breaking something into small pieces]

Destruction of Grains: Sputtering in Hot Gas

- ***Sputtering***: Grains can be vaporized by shock heating in supernova blast wave.
  - Gas atoms moving at slow speeds can be accreted onto a dust grain. However, *in a hotter gas, the collision of high-speed ions can erode the grain*, chipping away one or more atoms at a blow. This process of erosion by high-speed atoms or ions is called sputtering.
  - The molecular bonds holds together the atoms in a dust grain. They typically have a bond energy $E_{\rm bond} \sim 5$eV. Thus, if a dust grain is surrounded by gas, the gas particles will cause sputtering if

$$\boxed{T \gg \frac{2B_{\rm bond}}{3k} \sim 40,000\,{\rm K}\left(\frac{E_{\rm bond}}{5\,{\rm eV}}\right)}$$

  - Detailed studies: For temperatures in the range 10^6 K < T < 10^9 K, the sputtering rate for a graphite or silicate grain can be approximated as

$$\boxed{\frac{da}{dt} \simeq -1\,\mu{\rm m}\,{\rm Myr}^{-1}\left(\frac{n_{\rm H}}{1\,{\rm cm}^{-3}}\right)}$$

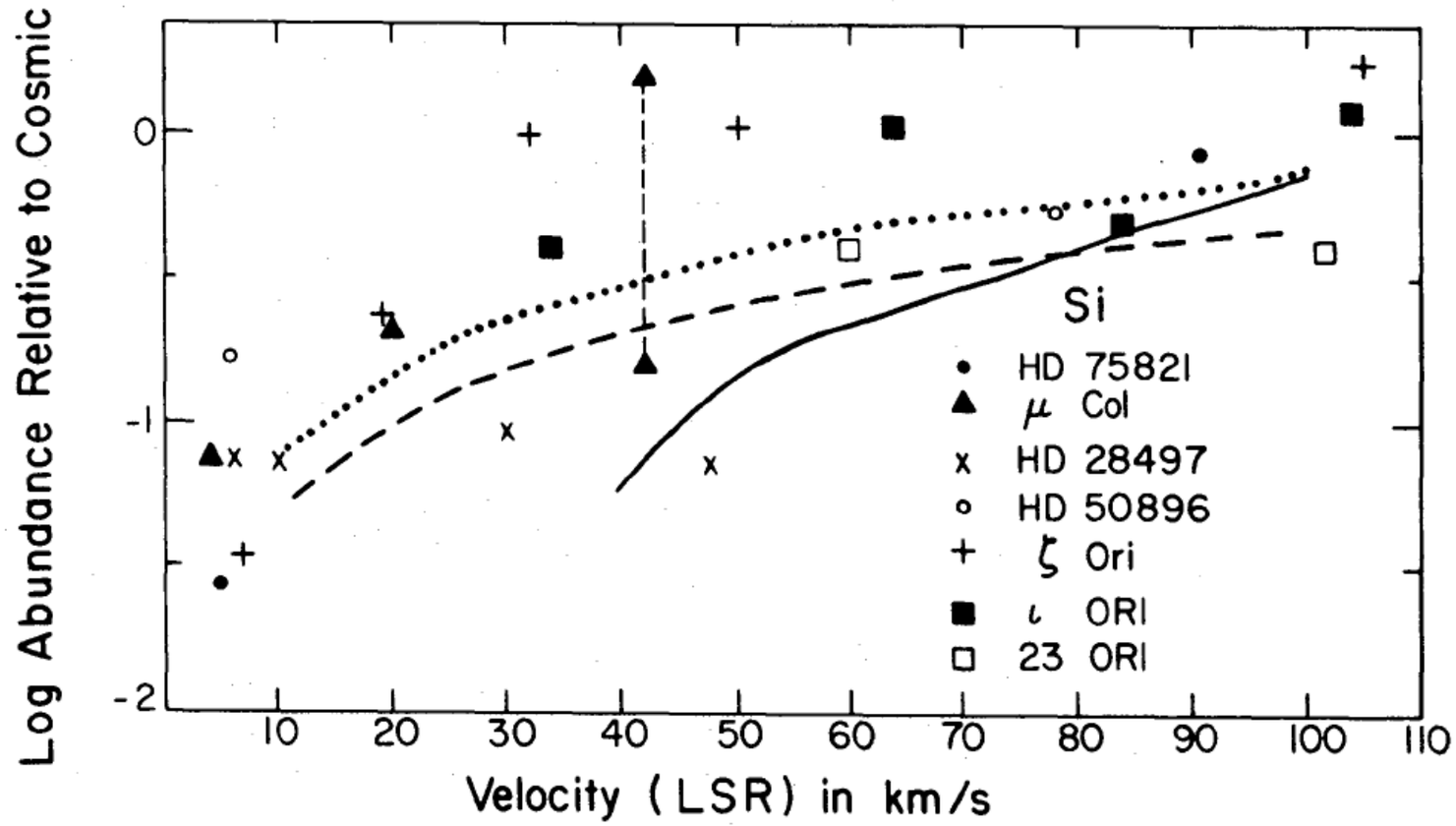
    This sputtering rate corresponds to a lifetime:

$$\boxed{t_{\rm sput} = \frac{a}{|da/dt|} \approx 0.1\,{\rm Myr}\left(\frac{a}{0.1\,\mu{\rm m}}\right)\left(\frac{n_{\rm H}}{1\,{\rm cm}^{-3}}\right)^{-1}}$$

    In a supernova remnant, $n_{\rm H} \sim 1\,{\rm cm}^{-3}$ and $T \gtrsim 10^6$ K, giving a lifetime of 0.1 Myr for a typical dust grain in the ISM.

  - In the intracluster medium of the Coma Cluster, $n_{\rm H} \sim 3 \times 10^{-3}\,{\rm cm}^{-3}$ and $T \sim 10^8\,{\rm K}$, the lifetime is ~ 30 Myr for a typical dust grain. Thus, we don't expect the intracluster medium to be dusty unless there are strong Galactic outflow sources.[However, there is indirect evidence of the existence of dust in intracluster medium, from the study of statistical reddening of background galaxies/quasars.]

- In low-velocity gas, Si is heavily depleted.
- Gas moving at high speeds in ISM
  - has been accelerated by a shock wave.
  - shows evidence of grain destruction: enhanced gas-phase abundances of Si and other species that are normally depleted.



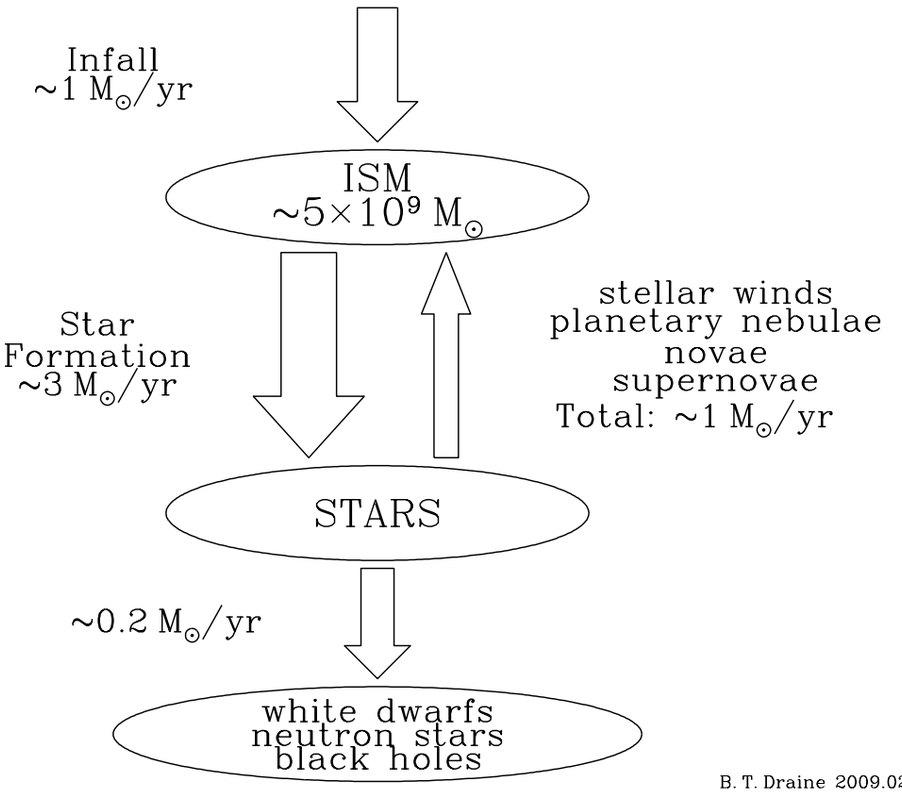
[Fig 1 in Cowie (1978, ApJ, 225, 887)]

- Survival time of random Si atoms in grain is $t_{\rm dest} \approx (3-5) \times 10^8\,{\rm yr}$.

  (Barlow 1978; Draine & Salpeter 1979; Dwek & Scalo 1979, 1980; Jones et al. 1994, 1996).

Stardust or Growth in ISM: (1) Dust Mass Balance in the ISM

Flow of baryons in the Milky Way.



B. T. Draine 2009.02.03.1337

Taken from B. T. Draine's keynotes

- MW: star formation more-or-less steady for past ~ 8 Gyr (Rocha-Pinto et al. 2000):

  $M > 1\,M_\odot$ stars are dying at ~ same rates as being formed.

- $M_{\rm ISM} \approx 5 \times 10^9 M_\odot$ in MW
- Sources and Sinks:

$$\begin{aligned} \dot{M}_{\rm ISM} &\approx +1 M_\odot/{\rm yr} \;:\; {\rm Infall} \\ &\approx -3 M_\odot/{\rm yr} \;:\; {\rm Star\ Formation} \\ &\approx +1 M_\odot/{\rm yr} \;:\; {\rm StellarOutflows} \\ \hline {\rm Net} \;&:\; -1 M_\odot/{\rm yr} \end{aligned}$$

- ISM declining on timescale $M_{\rm ISM} / \left| \dot{M}_{\rm ISM} \right| \approx 5\,{\rm Gyr}$
- Atom (or grain) in ISM incorporated in a star on timescale

$$\frac{M_{\rm ISM}}{\rm SFR} \approx \frac{5 \times 10^9 M_\odot}{3 M_\odot/{\rm yr}} \approx 1.5\,{\rm Gyr}$$

This is the Residence Time scale of atoms (grains) in the ISM. There is enough time that grain seeds can grow in the ISM.

(2) Stellar Sources

Injection of Gas and Dust ("Stardust") from Stellar Sources

gas ($M_\odot$/ yr)	dust ($M_\odot$/ yr)	stellar source
0.4	0.002	Planetary Nebulae (∼0.3/yr)
0.5	0.0025	Red Giant, Red Supergiant, C star winds
0.06	$< 0.0001?$	OB, WR, other warm/hot star winds
0.25	**0.0002?**	Sne (1/100yr, $\sim 10^{-2} M_\odot$ dust/SN?)
0.01	0.00001	Novae (100/yr, $10^{-7} M_\odot$ dust/nova?)
∼1.2	**∼0.005**	All stellar sources

- O-rich stars (O/C > 1) produce (mainly) silicate dust (C is in CO)
- C-rich stars (C/O > 1) produce (mainly) carbonaceous dust and SiC (O is in CO)

C and O combine to form CO, and the remaining atoms are consumed for dust grains.

Stardust Injection Rate

$$\dot{M}_{\rm dust} \approx 0.005\, M_\odot/{\rm yr}$$

Core-collapse SNe (e.g., Cas A, SN87a)

- Cas A: silicates, etc.
  $M_{\rm dust} \lesssim 0.14 M_\odot$ (Arendt et al. 2014)
  $M_{\rm dust} \approx 0.6 M_\odot$ (Priestley et al. 2019)
- SN87a:
  $M_{\rm dust} \approx 0.8 M_\odot$ (Matsuura et al. 2015)
- Cas A, SN87a: very young (pre-Sedov)
  much ejecta still unshocked
  reverse shock → grain destruction
  how much SN dust survives to mix into ISM?
  some does: presolar grains in meteorites.
- SN presolar grains in meteorites rare
  guess: $< 10\%$ of SN-formed dust enters ISM
- SN dust production: secondary importance today
  possibly important in first $\sim 10^8$ yr of galaxy

(3) Sputtering in Hot Gas

- Substantial grain destruction occurs in a shock of $V_s \gtrsim 220\,\mathrm{km\,s^{-1}}$ and $T_s = 7 \times 10^5\,\mathrm{K}$.
- A SN explosion ejects $\sim 10^{51}\,\mathrm{ergs}$ kinetic energy. The SNR blastwave shock-heats the ISM.
- In the energy-conserving Sedov-Taylor phase, the mass of the SNR would be

$$M_{\rm SNR} V_s^2 \approx 10^{51}\,\mathrm{ergs}$$

$$M_{\rm SNR} \approx 10^3 M_\odot \left(\frac{220\,\mathrm{km\,s^{-1}}}{V_s}\right)^2 \qquad V_s \gtrsim 220\,\mathrm{km\,s^{-1}}$$

- Detailed studies show that most dust grains materials are sputtered if $V_s \gtrsim 220\,\mathrm{km\,s^{-1}}$.
- Every $\sim 10^2$, the SN blastwave destroys grains in $\sim 10^3 M_\odot$ of the ISM.
- Therefore, the grain lifetime against destruction is:

Lecture 11: The SN frequency in the Galaxy is estimated to be one event every 30-50 yr.

$$t_{\rm dest} \approx \frac{5 \times 10^9 M_\odot}{10^3 M_\odot / 10^2\,\mathrm{yr}} \approx 5 \times 10^8\,\mathrm{yr}$$

- ***This lifetime is short compared to 1.5 Gyr residence time.***

MOST STARDUST WILL NOT SURVIVE

Balance of Formation and Destruction

Total dust mass in ISM: $M_{\rm dust} \sim 0.007 \times M_{\rm ISM} \approx 3.5 \times 10^7 M_\odot$

Balance:

Stardust Injection + Formation in ISM = Removal

$$\sim 0.005\, M_\odot\, {\rm yr}^{-1} \quad \text{+ Formation in ISM} = \frac{\sim 3.5 \times 10^7\, M_\odot}{\sim 5 \times 10^8\, {\rm yr}}$$

$$\frac{\text{Formation in ISM}}{\text{Stardust injection}} = \frac{\sim 0.07\, M_\odot\, {\rm yr}^{-1}}{\sim 0.005\, M_\odot\, {\rm yr}^{-1}}$$

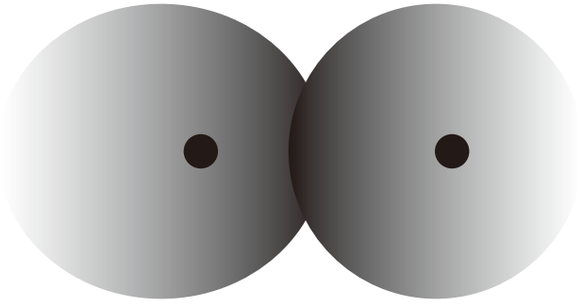
$$\frac{\text{Formation in ISM}}{\text{Stardust injection}} \approx 14$$

Conclusion: Stardust accounts for only ~ 5-10% of interstellar dust.
~ 90-95% is grown from gas in the ISM.

Molecular Clouds

[Born-Oppenheimer Approximation]

- **Born-Oppenheimer approximation:**
  - To a very good approximation, the motions of the electrons and nuclei could be treated separately. The electrons move much faster than the nuclei.
  - *This come about because of the great difference between the masses of the electron and a typical nuclei.*
  - The slowly moving nuclei only sense the electrons as a kind of smoothed-out cloud. As the nuclei move the electrons have sufficient time to adjust to adiabatically the new nuclear positions. (***It is like flies buzzing round an elephant - as the elephant moves the flies move with it.***) The nuclei then feel only an equivalent potential that depends on the internuclear distance and on the particular electronic state.

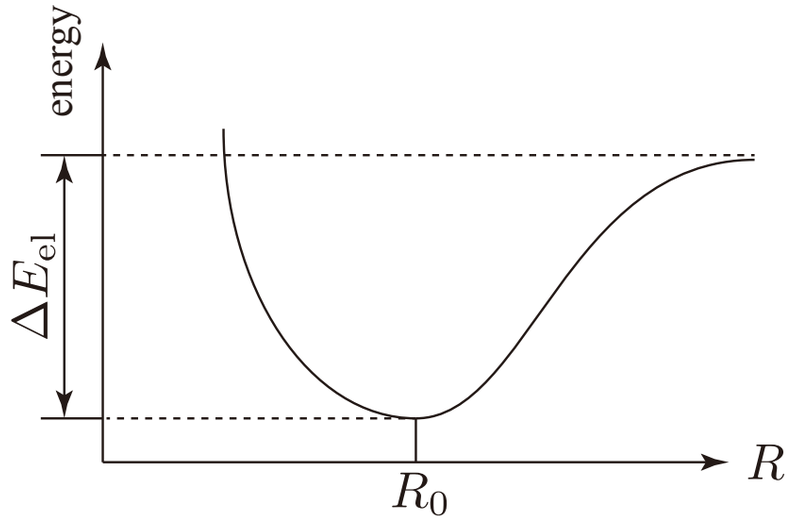


  - One separates the wavefunction for the motions of electrons from the wavefunction for the motions of the nuclei. One can then consider the electronic wavefunction separately for each position of nuclei, as if the nuclei are held fixed.
  - Due to very different energies of the electronic, vibrational, and rotational states, these interactions can be assumed to be decoupled. The separation of wavefunctions is referred to as the Born-Oppenheimer approximation. Under the Born-Oppenheimer approximation, the total wavefunction is a product of the nuclear, electronic, vibrational, and rotational wavefunctions.

$$\psi_{\text{tot}} = \psi_{\text{nuc}}\psi_{\text{el}}\psi_{\text{vib}}\psi_{\text{rot}}$$

- **Order of magnitude of energy levels**

  - ***Electronic energy:***



As the separation between the two atoms $R \to 0$ (at very small R), the overall interactions are strongly repulsive. There is repulsion due to nuclear-nuclear interaction whose potential depends on $Z_A Z_B/R$. There is also repulsion due to the electron-electron interactions, which also behave approximately as $1/R$. However, these repulsive interactions are largely cancelled by the attractive electron-nuclear interaction.

As $R \to \infty$, the molecule is pulled apart and it separates into atoms in a process known as dissociation. The energy of the system at dissociation is clearly just the sum of the atomic exchange.

At intermediate R, to get binding there must be some region of R where the molecular energy is less than the sum of the atomic energies. In this case, the electronic state is described as 'attractive' and there is a minimum in the potential energy curve.

For a diatomic molecule, a stable chemical bond can form between two atoms that approach within a distance of each other comparable to the Bohr radius $a_0 = \hbar^2/m_e c^2$. Then, the electron energy will be given by

$$E_{\rm elect} \sim m_e v^2 = \frac{p^2}{m_e} \sim \frac{\hbar^2}{m_e a_0^2} \quad (\leftarrow \quad p \times a_0 \sim \hbar, \text{ uncertainty relation}) \qquad \Longrightarrow \text{visible/UV (a few eV)}$$

$$(a \sim 1 \text{ Å})$$

- ***Vibrational energy:***

If the two nuclei are displaced from the equilibrium separation R_0 by a displacement comparable to $\xi \sim a_0$, they will vibrate about the equilibrium position with a frequency $\omega_{\rm vib}$ such that the vibrational energy contained in the motion and displacements of the two nuclei (of typical mass M) will be comparable to the depth of the electronic potential well.

$$M\omega_{\rm vib}^2 a_0^2 \sim E_{\rm elect}$$

where $\omega =$ frequency of vibration.
$M =$ mass of the molecule.

Then, the vibratinal energy is

$$E_{\rm vib} \sim \hbar\omega \sim \left(\frac{m_e}{M}\right)^{1/2} \frac{\hbar^2}{m_e a^2} \sim \left(\frac{m_e}{M}\right)^{1/2} E_{\rm elect} \qquad \Rightarrow \text{Near-IR / Mid-IR}$$

- ***Rotational energy:***

The nuclei can also rotate about each other. Then, the energy of rotation is

$$E_{\rm rot} \sim \frac{L^2}{2I} \sim \frac{\hbar^2 \ell(\ell+1)}{2I} \qquad \Rightarrow \text{radio}$$

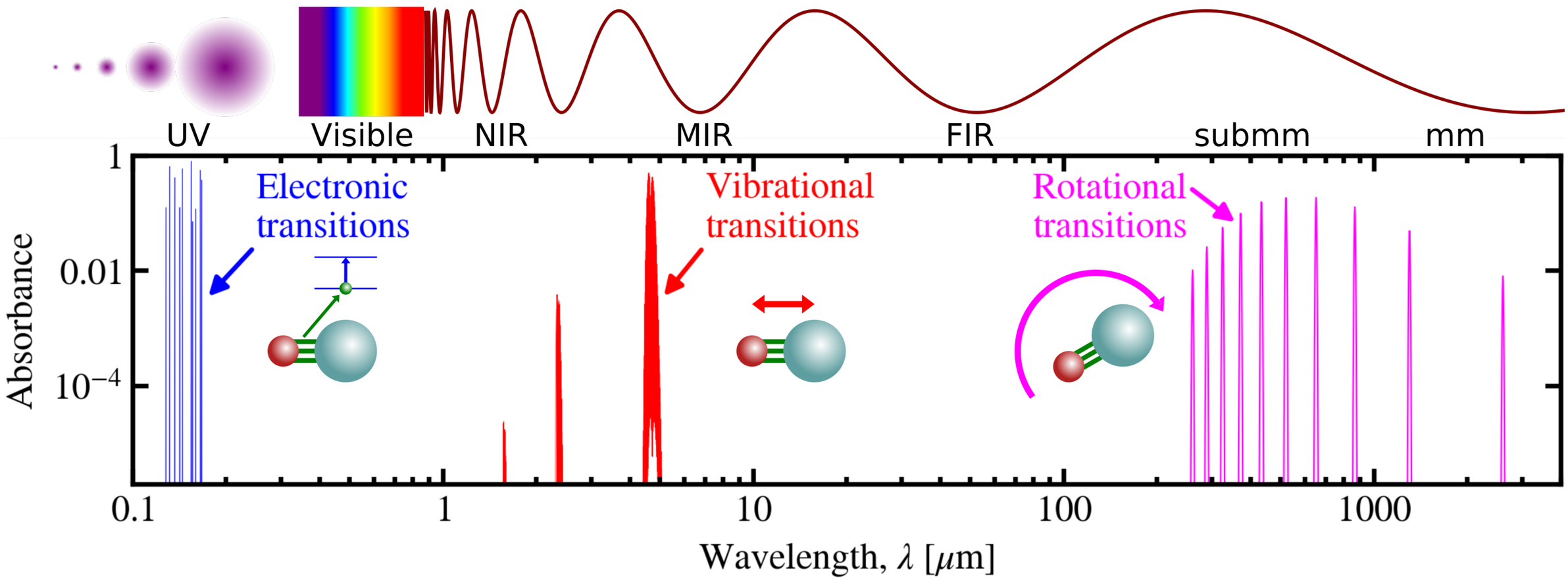
where I is the moment of inertia of the molecule: $I = Ma_0^2$. Therefore, we obtain

$$E_{\rm rot} \sim \left(\frac{m_e}{M}\right) E_{\rm elect}$$

In summary, $\boxed{E = E_{\rm elect} + E_{\rm vib} + E_{\rm rot}}$

$$E_{\rm elect} \ : \ E_{\rm vib} \ : \ E_{\rm rot} = 1 \ : \ \left(\frac{m_e}{M}\right)^{1/2} \ : \ \left(\frac{m_e}{M}\right)$$

for hydrogen ~ 0.02 ~ 0.0005



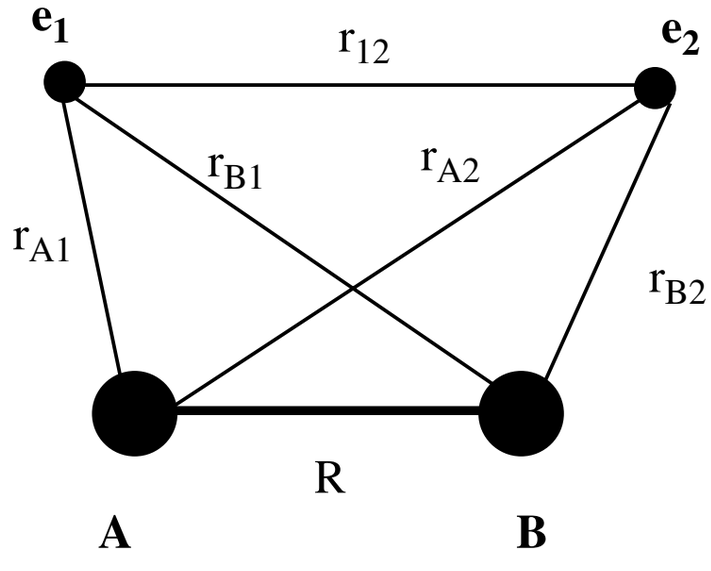
Molecular transitions.
The different types of transitions are illustrated with the CO molecule.

[credit: Frédéric Galliano]

Schrödinger equation for a diatomic molecule

For a diatomic molecule with N electrons,

$$\left(-\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 + V_e - E\right)\Psi(\mathbf{R}_A, \mathbf{R}_B, \{\mathbf{r}_i\}) = 0$$



The first two terms are the kinetic energy operators for the motions of nuclei A and B, the third term gives the kinetic energy operator for the electrons, V_e is the potential and E is the total energy of the system.

The potential is given by the various Coulomb interactions within the molecule:

$$V_e = -\sum_{i=1}^{N}\frac{Z_A e^2}{r_{Ai}} - \sum_{i=1}^{N}\frac{Z_B e^2}{r_{Bi}} + \sum_{i=2}^{N}\sum_{j=1}^{i-1}\frac{e^2}{r_{ij}} + \frac{Z_A Z_B e^2}{R}$$

(1) attraction of the electrons by nucleus A
(2) attraction of the electrons by nucleus B
(3) electron-electron repulsion
(4) nuclear-nuclear repulsion

- Born-Oppenheimer approximation: One can write the wave function as a product of electronic and nuclear wave functions.

$$\boxed{\Psi(\mathbf{R}_A, \mathbf{R}_B, \{\mathbf{r}_i\}) = \psi_e(\{\mathbf{r}_i\})\psi_n(\mathbf{R}_A, \mathbf{R}_B)}$$

Then the equation becomes

$$\left[\left(-\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 - E\right)\psi(\mathbf{R}_A,\mathbf{R}_B)\right]\psi(\{\mathbf{r}_i\}) + \left[\left(-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 + V_e\right)\psi(\{\mathbf{r}_i\})\right]\psi(\mathbf{R}_A,\mathbf{R}_B) = 0$$

- In this case the **electronic wavefunction** satisfies the following equation:

$$\boxed{\left(-\frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2 + V_e\right)\psi_e(\mathbf{r}_i) = E_e\psi_e(\mathbf{r}_i)}$$

This equation is solved separately for each value of the internuclear separation R.

Then, the resulting eigenvalue E_e is the electronic energy at R and gives the $\boxed{\text{electronic potential } V(R) = E_e}$ upon which the nuclei move.

The equation for the wavefunction of nuclei is obtained to be

$$\boxed{\left(-\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 + V(R) - E\right)\psi_n(\mathbf{R}_A,\mathbf{R}_B) = 0 \qquad \text{where } V(R) \equiv E_e.}$$

Here, E (the eigenvalue) is the total energy of the system.

- The Schrödinger equation for the nuclei:

$$\left(-\frac{\hbar^2}{2M_A}\nabla_A^2 - \frac{\hbar^2}{2M_B}\nabla_B^2 + V(R) - E\right)\psi_n(\mathbf{R}_A, \mathbf{R}_B) = 0 \qquad \text{where } V(R) \equiv E_e.$$

The equation deals with three types of motions of the nuclei: (1) translation of the whole system, (2) vibrations, and (3) rotations. The motions can be separated into the translational motion of the center-of-mass of the system plus the internal motion of one body in a 'central' potential, which depends on the distance between the particles. The effective mass of this one-body problem is the reduced mass:

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

The Schrödinger equation for nuclear motion, neglecting the translational motion, becomes:

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + V(R) - E\right]\psi_n(\mathbf{R}) = 0$$

where $\mathbf{R} = (R, \theta, \phi)$. R is the internuclear separation, (θ, ϕ) is the orientation of the molecular axis relative to the laboratory z-axis.

The vibrational and rotational motion cannot be separated rigorously. However, as a good first approximation, the vibration and rotational motion may be separated.

$$\psi_n(\mathbf{R}) = \psi_{\text{vib}}(R)\psi_{\text{rot}}(\theta, \phi)$$

Then, we obtain two equations for the rotational motion and vibrational motion:

angular equation: $$\left\{-\frac{\hbar^2}{2\mu R^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]-E_r\right\}\psi_{\rm rot}(\theta,\phi)=0$$

$\longrightarrow$ the angular part of the Laplacian operator ∇^2

radial equation: $$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+V(R)-E_v\right]\psi_{\rm vib}(R)=0$$

(1) The solution of the angular equation is:

$$\psi_{\rm rot}(\theta,\phi)=Y_{JM}(\theta,\phi) \quad \text{spherical harmonics}$$

$$E_r=\frac{\hbar^2}{2\mu R^2}J(J+1)$$

(2) The potential *V*(*R*) is not a simple function and thus the radial equation has no general algebraic solution. But, we can approximate *V*(*R*) about its minimum by a parabola:

$$V(R)=V(R_e)+\frac{1}{2}\left.\frac{d^2V}{dR^2}\right|_{R=R_e}(R-R_e)^2+\mathcal{O}\left((R-R_e)^3\right) \longleftarrow \frac{dV}{dR}=0 \ \text{ at } \ R=R_e$$

$$=V_0+\frac{1}{2}k(R-R_e)^2+\cdots$$

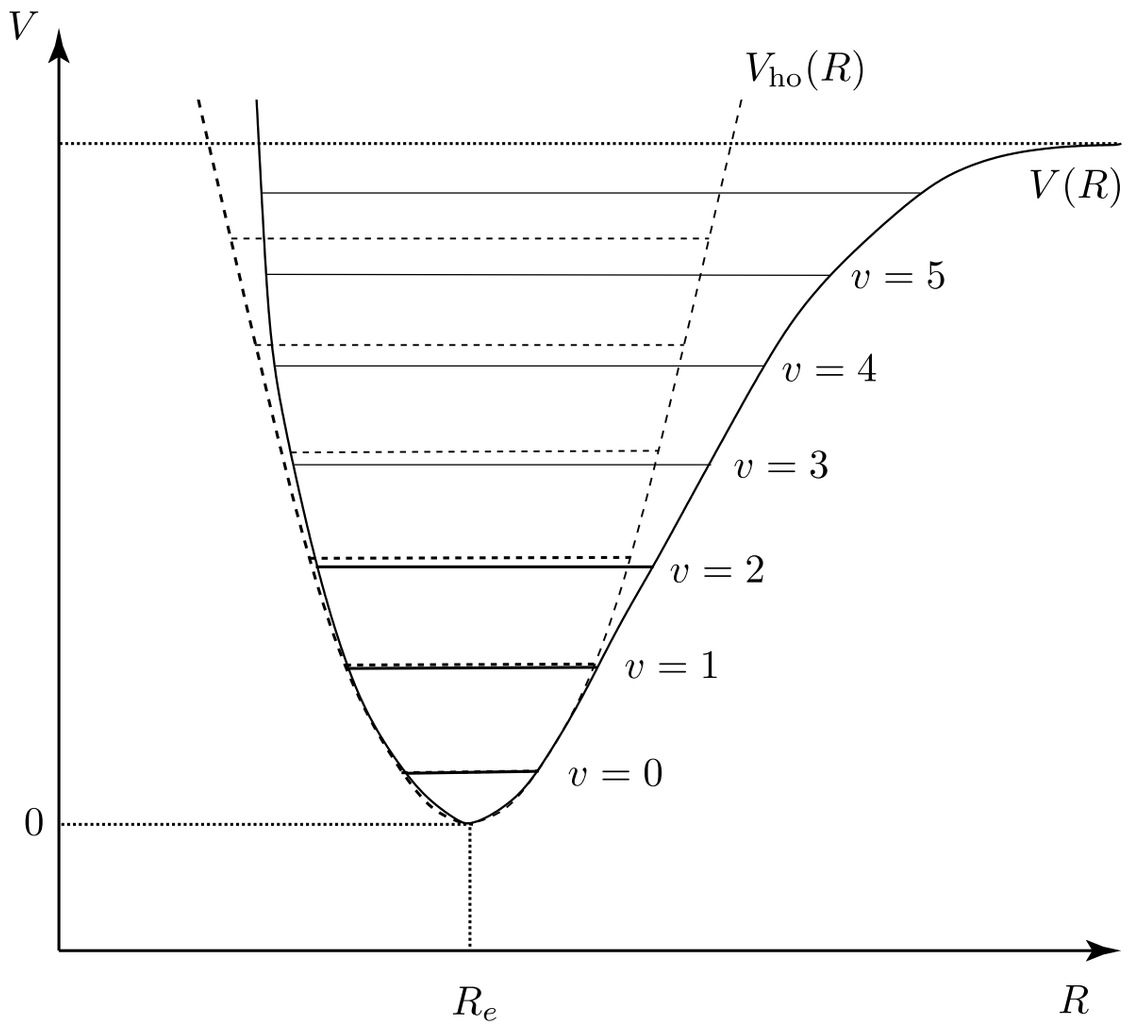
Setting the zero of energy at the minimum potential, $V_0 = V(R_e) = 0$, the radial equation becomes

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \frac{1}{2}k(R-R_e)^2 - E_v\right]\psi_{\rm vib}(R) = 0$$

This is the QM equation for the harmonic oscillator with the spring constant k. The energy levels of this equation are:

$$E_v = \hbar\omega\left(v+\frac{1}{2}\right)$$

where $\omega = \left(\frac{k}{\mu}\right)^2$, $\quad v = 0, 1, 2, \cdots$



[Energy Levels]

- **Energy Levels**

  An electronic transition consists of vibrational bands, which in turn are made up of rotational transitions.

$$E_q(v,J) = V_q(r_0) + h\nu_0\left(v+\frac{1}{2}\right) + B_v J(J+1)$$

$$\nu_0 \equiv \frac{\omega_0}{2\pi} \qquad B_v = \frac{\hbar^2}{2I} \qquad I = \mu r_0^2$$ = moment of inertia of the molecule.

  Here, q denotes an electronic state.

- **Angular Momentum**

  Molecules are not spherical and the orbital angular momentum of the individual electrons is no longer a conserved quantity.

  - *For diatomic molecules, the total orbital angular momentum L is strongly coupled to the nuclear axis.*
  - It is therefore necessary to consider the components of L, designated $\mathcal{L}$ (or Λ), along the diatomic nuclear axis which, by convention, is taken to define the z-axis of the system.
  - While the value of the total orbital angular momentum in a diatomic molecule can change, its projection onto the diatomic axis is conserved.
  - As the projection of L onto z-axis can be either positive or negative, states with $\mathcal{L} \neq 0$ are twofold degenerate while states with $\mathcal{L} = 0$ are singly degenerate.

[Labelling of Electronic States of Diatomic Molecules]

- ***Heteronuclear diatomic molecule*** (e.g., HD, OH, or CO): The notation of the electronic structure of a diatomic molecule is similar to that for atomic structure under *LS* coupling. Each electronic state is designated by the **term symbol**.

$$^{2S+1}\mathcal{L}_{J_{ez}}$$

In some literatures, the following symbol is used.

$$^{2S+1}\Lambda_{\Omega}$$

$S =$ total electronic spin

$\mathcal{L} =$ projection of the total electronic "orbital" angular momentum along the internuclear axis
$(\rightarrow \quad L_z)$

$J_{ez} =$ projection of the total electronic angular momentum onto the internuclear axis
$= |\mathcal{L} + S_z| \quad (\rightarrow \quad J_{ez} = L_z + S_z; \quad S_z = -S, -S+1, \cdots S-1, S)$

- The uppercase Greek letters to denote the total "orbital" angular momentum.

$$\mathcal{L} = \Sigma, \Pi, \Delta, \cdots \quad (\text{for } L_z = 0, 1, 2, \cdots)$$

Recall $S, P, D, \cdots$ in the atomic spectroscopy.

- <u>If the term symbol $\mathcal{L}$ is **Σ**</u> ($L_z = 0$), then additional superscript $\pm$ is applied.

$$\pm = \begin{cases} + & \text{if symmetric under reflection through (all) planes containing the nuclei,} \\ - & \text{if antisymmetric under reflection through a plane containing the nuclei.} \end{cases}$$

Nearly all **Σ** states are + state Σ^+.
One exception is O_2, of which the lowest electronic state is $^3\Sigma_g^-$.

- ***Homonuclear diatomic molecule***: Diatomic molecules with identical nuclei (H_2, N_2, O_2, C_2) are referred to as homonuclear. The energy levels of homonuclear diatomic molecules are designated by

$$^{2S+1}\mathcal{L}_{u,g} \qquad \boxed{^{2S+1}\Lambda_{u,g}}$$

$$u, g = \begin{cases} g & (\text{“gerade”}) \text{ if symmetric under reflection through the center of mass,} \quad \Rightarrow \text{even} \quad (\text{게하드}) \\ u & (\text{“ungerade”}) \text{ if antisymmetric under reflection through the center of mass.} \quad \Rightarrow \text{odd} \quad (\text{운게하드}) \end{cases}$$

For the special case of Σ state, a superscript + or - is added.

$$^{2S+1}\sum\nolimits^{\pm}_{u,g}$$

- The ***electronic states*** of diatomic molecules are also labelled with one of the following letters, appearing in front of the term symbol.

X labels the ground electronic state
A, B, C, … label states of same spin multiplicity as the ground state
a, b, c, … label states of different spin multiplicity to the ground state

- Examples:

  ${}^1\Sigma$ denotes a state with $S = 0$ and $\mathcal{L} = 0$

  ${}^3\Pi$ denotes a state with $S = 1$ and $\mathcal{L} = 1$, etc

S $\rightarrow \Sigma$
P $\rightarrow \Pi$
D $\rightarrow \Delta$
F $\rightarrow \Phi$
G $\rightarrow \Gamma$

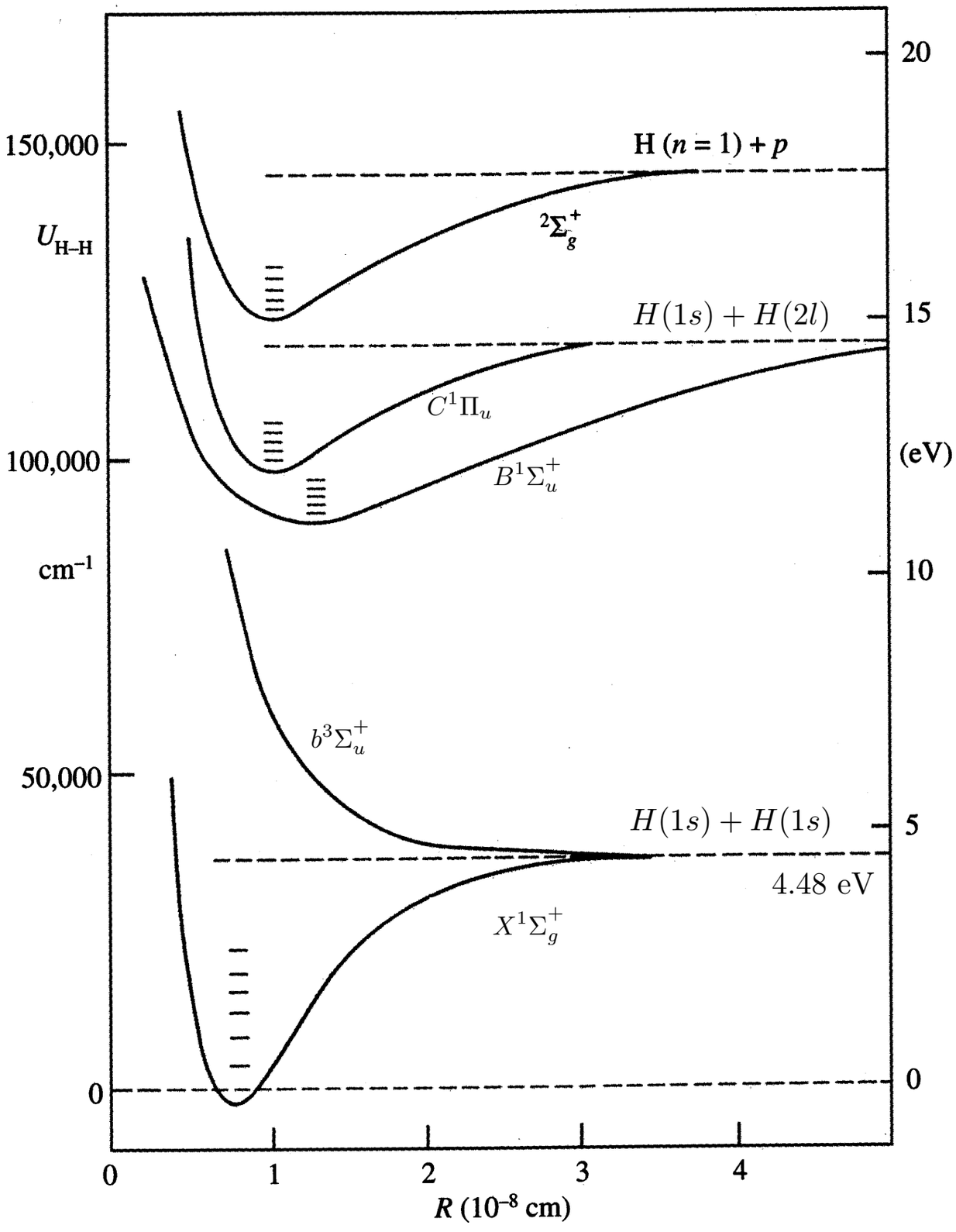
H: $1s^1$
C: $1s^2 2s^2 2p^2$
N: $1s^2 2s^2 2p^3$
O: $1s^2 2s^2 2p^4$

- For most (stable) diatomics, the electronic ground state is a closed shell, meaning that it is ${}^1\Sigma$.
  - Examples include H_2, N_2 and most other homonuclear diatomics. The exception is O_2 which has a ${}^3\Sigma$ ground state. (Each O has 4 valence electrons, and thus S = 1)
  - CO and many other heteronuclear diatomics with an even number of electrons also have ${}^1\Sigma$ ground states.
- Diatomics with an odd number of electrons usually have S = 1/2. For example, H_2^+, CH^+, and CN all have ${}^2\Sigma$ ground state.
- CH, OH and NO all have $\mathcal{L} = 1$ and thus their ground states are ${}^2\Pi$. These molecules have extra lines in their spectra due to a process called Λ-doubling.

$\mathcal{L} =$	0	1	2	3	4 ...
Orbitals	σ	π	δ	ϕ	γ ...
States	Σ	Π	Δ	Φ	Γ ...
Degeneracy	1	2	2	2	2 ...

Letter designations for projected total orbital angular momentum.

[Energy levels of Molecular Hydrogen]



- The short horizontal lines in each of the bound states indicate the vibrational levels.

- The transition from the ground state $X^1\Sigma_g^+$ to the excited states $B^1\Sigma_u^+$ and $C^1\Pi_u$ are called **Lyman and Werner bands.**

Werner band: $C^1\Pi_u - X^1\Sigma_g^+$ at $\lambda \approx 970 - 1650$Å

Lyman band: $B^1\Sigma_u^+ - X^1\Sigma_g^+$ at $\lambda \approx 930 - 1240$Å

In principle, states are labelled alphabetically in ascending energy order. However, there are many exceptions.

The lowest triplet state of H_2 is the $b^3\Sigma_u^+$ with the $a^3\Sigma_g^+$ lying somewhat higher.

Other molecules

	Ground term
H_2	$^1\Sigma_g^+$
CH	$^2\Pi_{1/2,3/2}$
CH^+	$^1\Sigma_0^+$
OH	$^2\Pi_{3/2,1/2}$
CN	$^2\Sigma_{1/2}^+$
CO	$^1\Sigma_0^+$
SiO	$^1\Sigma_0^+$
CS	$^1\Sigma_0^+$

H(1): $1s^1$
C(6): $1s^2 2s^2 2p^2$
N(7): $1s^2 2s^2 2p^3$
O(8): $1s^2 2s^2 2p^4$
Si(14): $1s^2 2s^2 2p^6 3s^2 3p^2$
S(16): $1s^2 2s^2 2p^6 3s^2 3p^4$

The electronic ground state of H_2 (two electrons) has zero electronic orbital angular momentum ($L_e = 0$), has zero electron spin ($S_e = 0$), is symmetric under reflection through the center of mass (g), and is symmetric under reflection through planes containing the nuclei (+). The ground state is $X^1\Sigma_g^+$.

CO has two (2) p electrons contributed by C and four (4) p electrons contributed by O; together these six (6) p electrons fill the $2p$ subshell, and as a result, the ground electronic state of CO has zero electronic angular momentum and zero electronic spin: $^1\Sigma_0^+$, just like H_2.

OH is an example of a molecule with the ground electronic state having nonzero electronic orbital angular momentum: with seven electrons, the OH ground state has $L_{ez} = 1$ and $S_{ez} = 1/2$, and is therefore designated by $^2\Pi_{1/2,3/2}$. The electron spin and orbital angular momenta can couple to give $J_e = 1/2$ or $3/2$, with energies that are separated due to spin-orbit coupling (i.e., fine-structure splitting in atoms or ions); the $J_e = 3/2$ state has the lower energy.

[Pure rotational & ro-vibrational transitions]

- **Energy Levels**

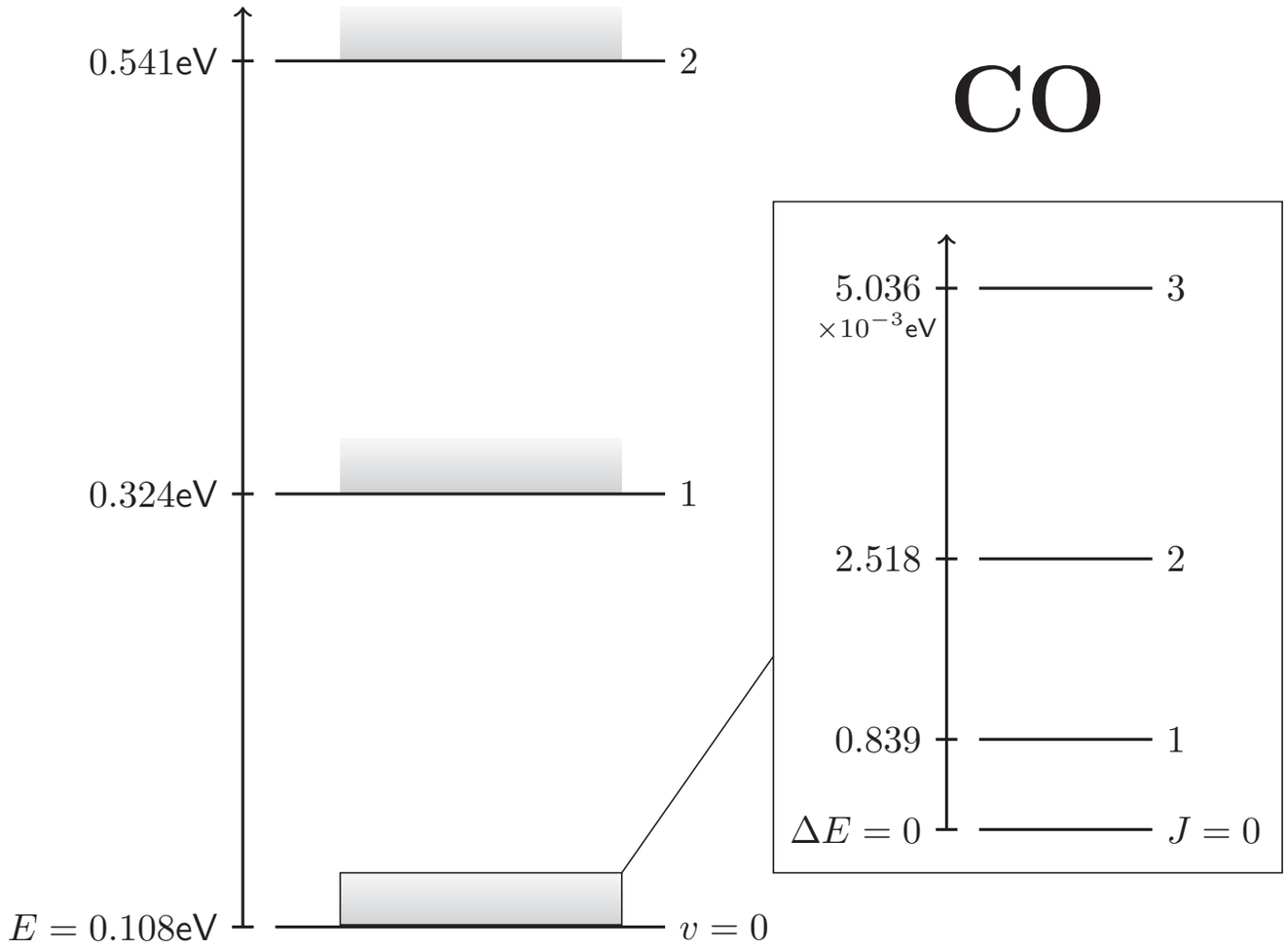
  An electronic transition consists of vibrational bands, which in turn are made up of rotational transitions.

$$E_q(v, J) = V_q(r_0) + h\nu_0 \left(v + \frac{1}{2}\right) + B_v J(J+1)$$

$$\nu_0 \equiv \frac{\omega_0}{2\pi} \qquad B_v = \frac{\hbar^2}{2I} \qquad I = \mu r_0^2 \quad = \text{moment of inertia of the molecule.}$$

  Here, q denotes an electronic state.

- **Pure rotational spectrum**: In the lowest vibrational and electronic states, it is possible to have transitions solely among the rotational states. Such transitions give rise to a pure rotational spectrum.
- **Rotational-vibration spectrum**: Because the energies required to excite vibrational modes are much larger than those required to excite rotation, it is unlikely to have a pure vibrational spectrum in analogy to the pure rotational spectrum. The transitions then yield a rotation-vibrational spectrum, in which both the vibrational state and the rotational state can change together.



The rotational and vibrational energy levels for CO. The left side show the vibrational energy for each level ν. The rotational transitions are illustrated by the gray shading at each level. The rotational energies are about 100 times smaller than the vibrational and the inset on the right hand side shows a zoomed-in region of the J-ladder.

[J. Williams, Introduction to the interstellar medium]

[Selection Rules]

- Electric-dipole selection rules for electronic transitions in a diatomic molecule.

(1) $\Delta\mathcal{L} = 0, \pm 1$, e.g., $\Sigma - \Sigma$, $\Pi - \Sigma, \Delta - \Pi$, etc.
(2) $\Delta S = 0$
(3) $\Delta J_z = 0, \pm 1$
(4) $\Sigma^+ - \Sigma^+$, $\Sigma^- - \Sigma^-$, but not $\Sigma^+ - \Sigma^-$
(5) $g \longleftrightarrow u$

- $\Delta\Lambda = 0, \pm 1$, e.g., $\Sigma - \Sigma$, $\Pi - \Sigma$, $\Delta - \Pi$, etc.
- $\Delta S = 0$
- $\Delta\Omega = 0, \pm 1$
- $\Sigma^+ - \Sigma^+$, $\Sigma^- - \Sigma^-$, but not $\Sigma^+ - \Sigma^-$
- $g \leftrightarrow u$

- Electric-dipole selection rule for ro-virational transitions:

$\Delta v =$ any
$\Delta J = 0, \quad \pm 1 \quad$ not $\quad J = 0 \leftrightarrow 0$

- **Note that H_2 has no permanent electric-dipole moment.**

The electric-quadrupole are allowed for $\Delta J = \pm 2$ within the ground electronic state.

O, P, Q, R, and S transitions

- The rotational levels of diatomic molecules are specified by a single vibrational quantum number v and rotational quantum number J.
  - **Transitions will change J by either $0, \pm 1, \pm 2$.**
  - It is customary to identify transitions by specifying the upper and lower electronic states, upper and lower vibrational states, and one of the follows: $O(J_\ell),\ P(J_\ell),\ Q(J_\ell),\ R(J_\ell),\ S(J_\ell)$
  - The usage of the symbols are shown in the following table.

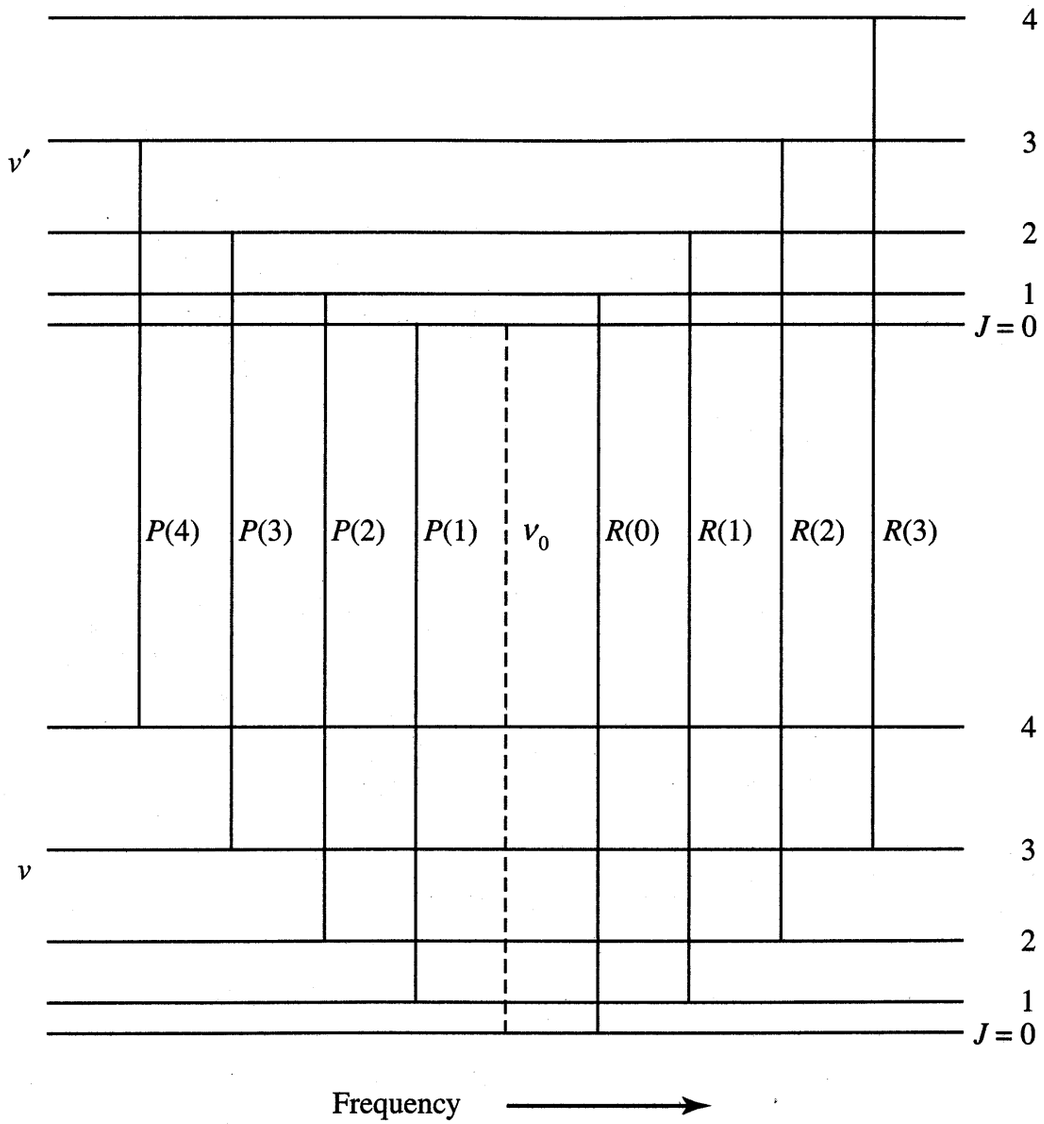
Do not be confused with **electronic** transitions.

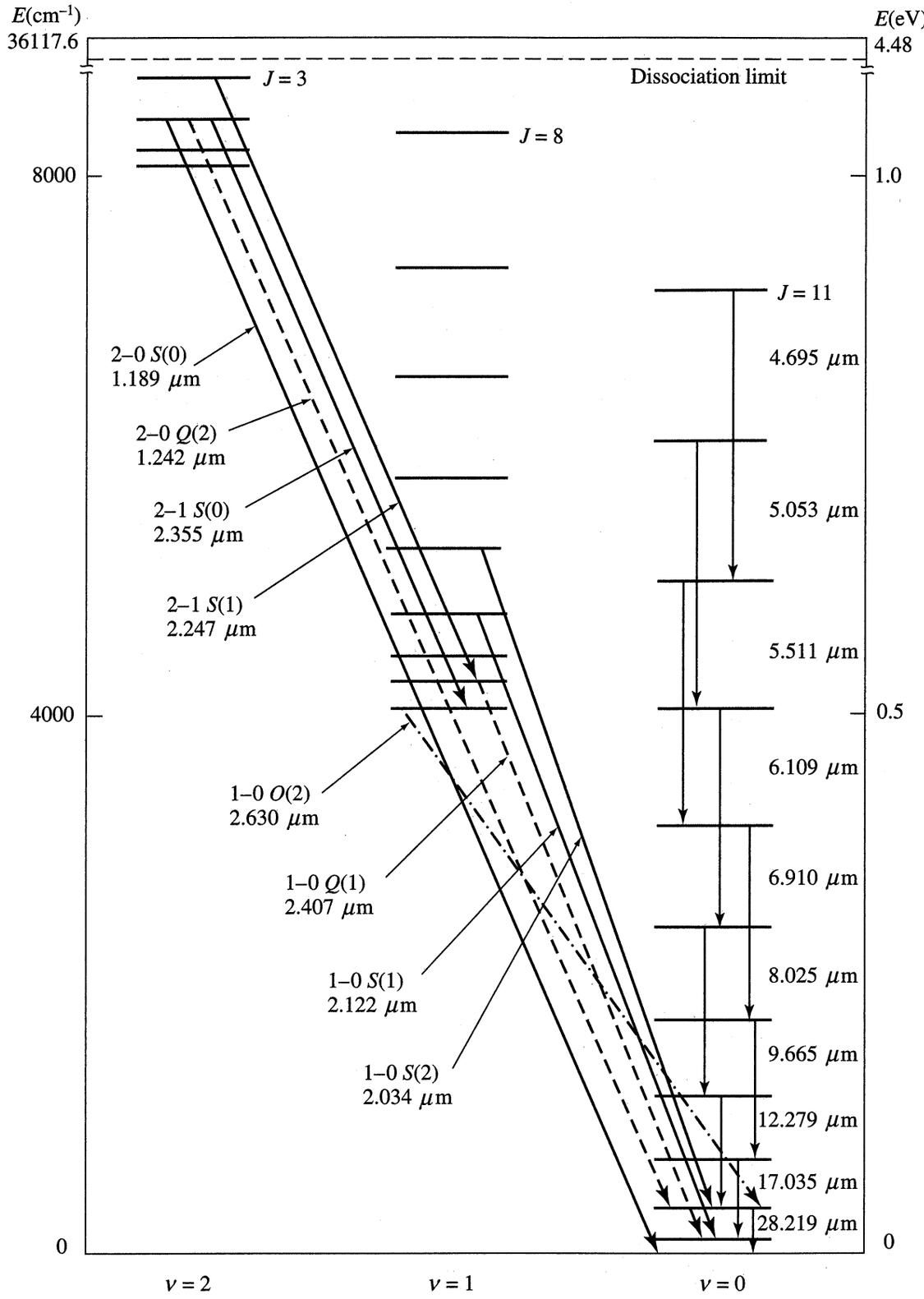
$$J_u \rightarrow J_\ell$$

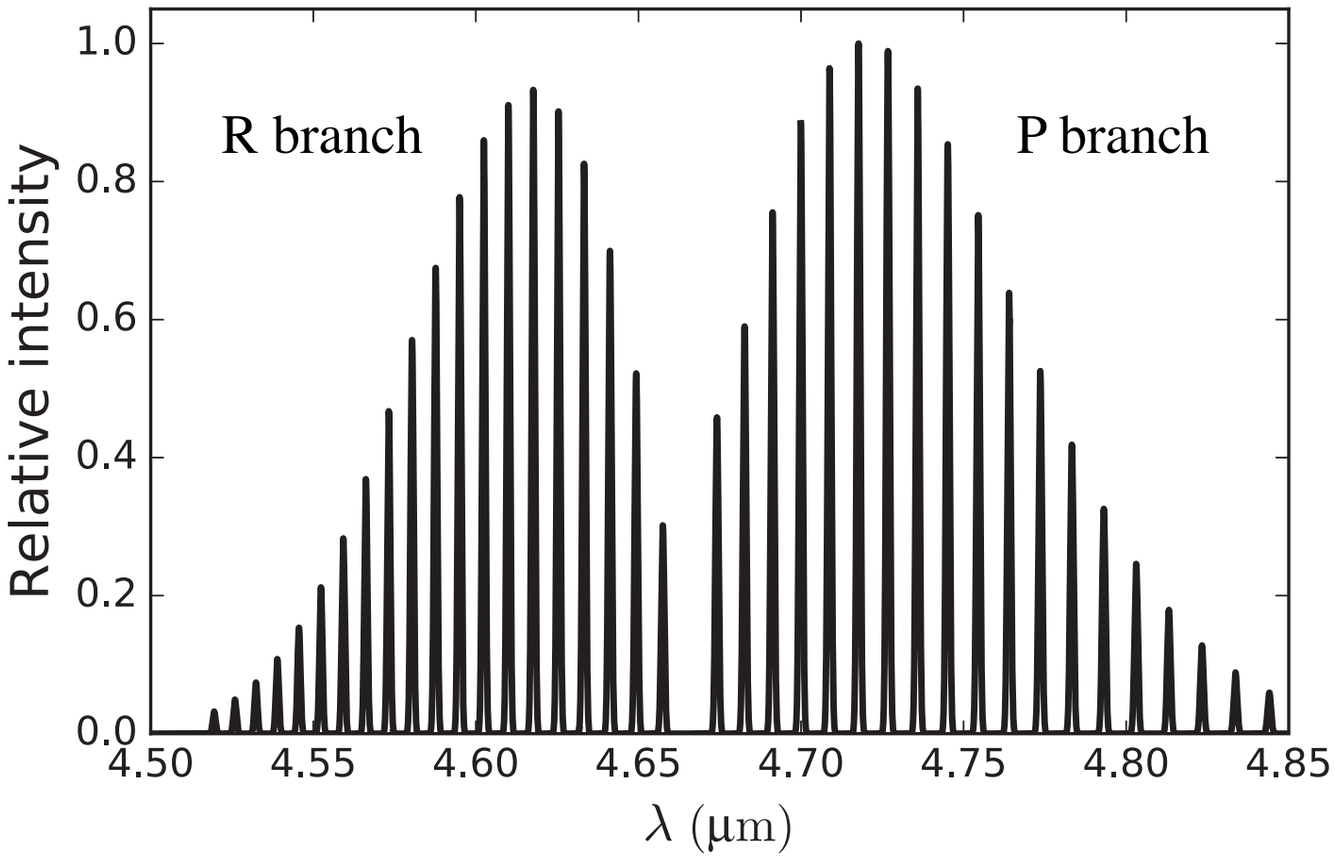
Designation	$(J_u - J_\ell)$	Note
$O(J_\ell)$	-2	Electric quadrupole transition
$P(J_\ell)$	-1	Electric dipole transition
$Q(J_\ell)$	0	Electric dipole or electric quadrupole; $Q(0)$ is forbidden
$R(J_\ell)$	$+1$	Electric dipole transition
$S(J_\ell)$	$+2$	Electric quadrupole transition

- For instance, a transition from the the $v_\ell = 0,\ J_\ell = 1$ level of the ground electronic state to the $v_u = 5,\ J_u = 2$ level of the first electronic excited state would be written to be

B-X 5-0 *R*(1)


v′
4
3
2
1
J = 0
P(4)
P(3)
P(2)
P(1)
ν0
R(0)
R(1)
R(2)
R(3)
v
4
3
2
1
J = 0
Frequency


E(cm⁻¹)
36117.6
8000
4000
0
E(eV)
4.48
1.0
0.5
0
Dissociation limit
J = 3
J = 8
J = 11
2–0 S(0)
1.189 μm
2–0 Q(2)
1.242 μm
2–1 S(0)
2.355 μm
2–1 S(1)
2.247 μm
1–0 O(2)
2.630 μm
1–0 Q(1)
2.407 μm
1–0 S(1)
2.122 μm
1–0 S(2)
2.034 μm
4.695 μm
5.053 μm
5.511 μm
6.109 μm
6.910 μm
8.025 μm
9.665 μm
12.279 μm
17.035 μm
28.219 μm
v = 2
v = 1
v = 0



Model spectrum of ro-vibrational lines for CO $\nu = 1 - 0$, illustrating the two branches corresponding to a positive or negative change in J and a central gap at $\Delta J = 0$.

The R branch corresponds to a higher energy jump, $J \rightarrow J - 1$, and lies at shorter wavelengths. The P branch is a smaller energy jump, $J \rightarrow J + 1$, and is at longer wavelengths.

The envelope shape arises from the population level distribution that is small at low levels due to the degeneracy, $g_J = 2J + 1$, and at high levels due to the Boltzmann exponential, $e^{-E/kT_{\rm ex}}$. The difference between the relative intensity of the P and R branches is due to different value of the Einstein A coefficient.