Phys 330 Spring 2020

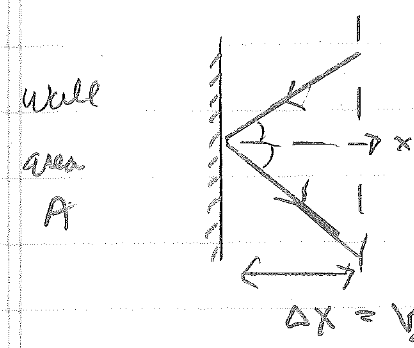
Lec 15: Statistical Physics I: Classical

Empirical ideal gas Law

ideal - non-interacting molecules a good approximation

At normal T,P molecules have large separation compared to de Broglie wavelength.

Kinetic theory: molecules undergo perfectly elastic collisions



momentum change

$$\Delta p_x = 2 m v_x$$

$$f_x = \frac{\Delta p_x}{\Delta t} = \frac{2 m v_x^2}{\Delta x}$$

Force by molecules with number density $\frac{N}{V}$

$$F = \left(\frac{N}{V}\right) A \Delta x \left(\frac{1}{2}\right)\left(\frac{2m \langle v_x^2 \rangle}{\Delta x}\right)$$ average

↑ on average $\frac{1}{2}$ toward wall

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle$$

pressure $P = \frac{F}{A} = \left(\frac{N}{V}\right) \frac{m}{3} \langle v^2 \rangle$

$$\frac{PV}{N} = \frac{m}{3} \langle v^2 \rangle = kT$$ from empirical

therefore $\langle E_k^{tr} \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$

translational kinetic energy, 3 translational degrees of freedom.

internal energy of monatomic gas

$$U_{mono} = N\langle E_k^{tr}\rangle = \frac{3}{2}NkT = \frac{3}{2}nRT$$

equipartition between degrees of freedom
diatomic molecule has 3 transl. + 2 rotational = 5

$$U_{diatomic} = \frac{5}{2}NkT = \frac{5}{2}nRT$$

Heat capacity @ fixed volume $C_V = \frac{f}{2}RT$ $f = 3, 5$

k = Boltzmann constant = 8.617×10^{-5} eV/K

N_A = Avogadro's number

$n = \frac{N}{N_A}$ = # moles $\equiv 6.022\times10^{23}$

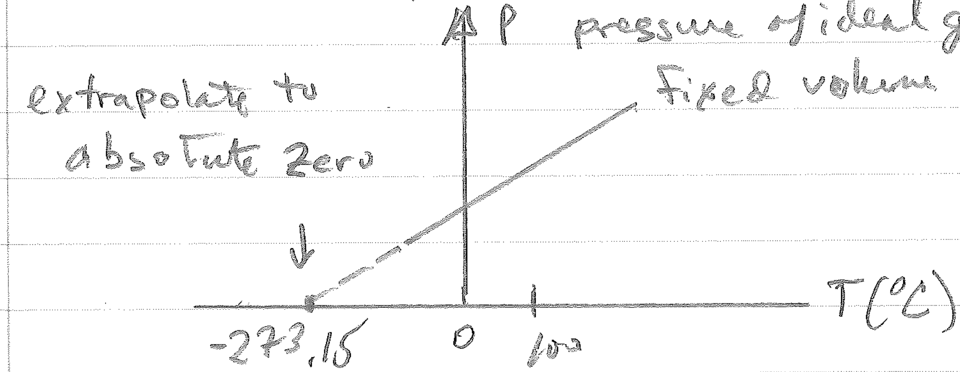
$R = kN_A$ empirical gas constant

"Degree of freedom" quadratic term in kinetic energy. Harmonic oscillator

$E = \frac{m}{2}\dot{x}^2 + \frac{1}{2}m\omega^2x^2$ has two 1 kinetic + 1 potential

EM field has 2 per frequency mode.

Absolute temperature:



$T = T(°C) + 273.15$ kelvin

* measured in kelvin absolute temperature

$$kT\Big|_{300K} \cong \left(\frac{1}{40}\right) eV$$ @ room temperature

molecular collisions perfectly elastic because minimum excitation energy $\sim 10 eV$

Boltzmann factor

Probability for system (e.g. molecule) in state i to have energy ε_i is

$$P_i = \frac{1}{Z} e^{-\varepsilon_i/kT}$$

Z is normalization $Z = \sum_{i \text{ all states}} e^{-\varepsilon_i/kT}$

so that $\sum_{i \text{ all states}} P_i = 1$

Collection of N molecules will have mean number with energy ε_i,

$$\bar{n}(\varepsilon_i) = N g_i P_i$$ $g_i \equiv$ degeneracy factor

$$\bar{n}_{MB}(\varepsilon_i) \equiv \frac{N g_i}{Z} e^{-\varepsilon_i/kT}$$

Maxwell-Boltzmann distribution
Classical (distinguishable molecules)

Classical statistics – counting of distinguishable molecules with fixed energy $E_{TOT} = m\Delta$ — Δ is unit of energy. m units

with N distinguishable objects

\# of arrangements =
(N ways to order 1st) x (N-1 ways to order 2nd) x ... x (1 way to order Nth) = N! ways

Consider system of N=4 molecules sharing m=3 units of energy.

$n(\varepsilon) \equiv$ # molecules with energy ε

state	$n(0)$	$n(\Delta)$	$n(2\Delta)$	$n(3\Delta)$	multiplicity	P_i
1	3	0	0	1	$4 = \frac{4!}{3!}$	4/20
2	2	1	1	0	$12 = 4!/2!$	12/20
3	1	3	0	0	$4 = 4!/3!$	4/20
					20	

↑ equivalent arrangements of energy

$$\text{multiplicity} = \frac{N!}{n(0)!\,n(\Delta)!\,n(2\Delta)!\,n(3\Delta)!}$$

Count mean number with energy ε_i

$$\bar{n}(\varepsilon_i) = \sum_{\text{states}=1,2,3} n(\varepsilon_i)\,P_i$$

$\varepsilon_i = 0, \Delta, 1\Delta, 2\Delta$

$\bar{n}(0) = 3\left(\frac{4}{20}\right) + 2\left(\frac{12}{20}\right) + 1\left(\frac{4}{20}\right) = 2$

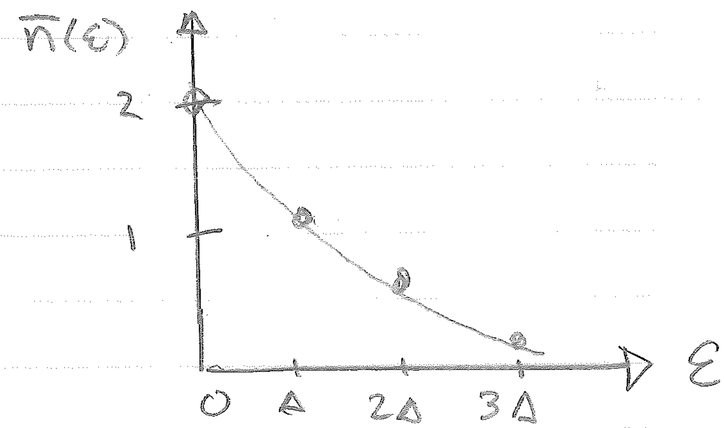
$\bar{n}(\Delta) = 1\left(\frac{12}{20}\right) + 3\left(\frac{4}{20}\right) = 1.2$

$\bar{n}(2\Delta) = 1\left(\frac{12}{20}\right) = 0.6$

$\bar{n}(3\Delta) = 1\left(\frac{4}{20}\right) = 0.2$

$2e^{-\varepsilon_i/\Delta}$
2
0.7
0.3
0.1

$\bar{n}(\varepsilon)$ is approximately exponential $e^{-\varepsilon_i/\Delta}$



extrapolate to large N, E_{TOT}:

$$\bar{n}(\varepsilon) = \left(\frac{N}{\varepsilon_0}\right) e^{-\varepsilon/\varepsilon_0}$$

ε_0 energy constant

$$\int_0^\infty \bar{n}(\varepsilon)\, d\varepsilon = N \int_0^\infty e^{-x} dx = N$$

mean energy:

$$\bar{\varepsilon} = \frac{1}{N}\int_0^\infty \varepsilon\, \bar{n}(\varepsilon)\, d\varepsilon = \varepsilon_0 \int_0^\infty \left(\frac{\varepsilon}{\varepsilon_0}\right) e^{-\varepsilon/\varepsilon_0} \left(\frac{d\varepsilon}{\varepsilon_0}\right)$$

$$= \varepsilon_0 \int_0^\infty x e^{-x} dx = \varepsilon_0$$

<u>To connect to physics</u> (thermodynamics)

① $\varepsilon_0 = kT$ T in <u>Kelvin</u>

$k \equiv$ Boltzmann constant

② number of states increase with energy. <u>density of states</u> $\equiv \rho(\varepsilon)$

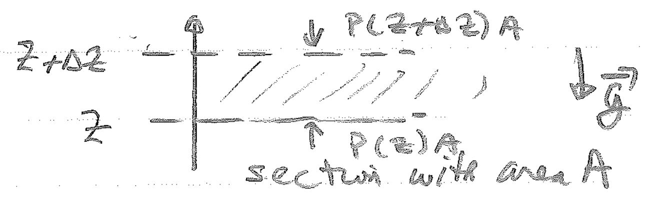
$\rho(\varepsilon)\Delta\varepsilon \equiv$ # states with ε to $\varepsilon + \Delta\varepsilon$

Then $$N = \int_0^\infty \rho(\varepsilon)\, \bar{n}_{MB}(\varepsilon)\, d\varepsilon$$

$$\bar{n}_{MB}(\varepsilon) = N\,(\text{const.})\, e^{-\varepsilon/kT}$$

Maxwell Boltzmann distribution function   Boltzmann factor

<u>Example: isothermal atmosphere, Pressure vs height</u>



mass of section $= \left(\frac{N}{V}\right) m A \Delta z$

m: molecular mass

P(z) pressure @ z

Newton II is $\quad -\left(P(z+\Delta z) - P(z)\right)A = \frac{N}{V} m A \Delta z\, g$

limit $\Delta z \to 0$

$$-\frac{dP}{dz} = \frac{N}{V} mg = \left(\frac{P}{kT}\right) mg$$

↑ ideal gas law

$$\frac{dP}{P} = -\frac{mg}{kT}\,dz \quad \text{integrate to}$$

$$P(z) = P(0)\, e^{-mgz/kT}$$

Boltzmann factor appears

Maxwell velocity distribution

molecular velocities of gas at temperature T

$d^3\vec{v} \equiv dv_x\, dv_y\, dv_z$

probability g to have speed $\vec{v}$ can only depend on v^2 by symmetry. Must have:

$v^2 = |\vec{v}|^2 = v_x^2 + v_y^2 + v_z^2$

$$g(v^2) = h(v_x^2)\, h(v_y^2)\, h(v_z^2)$$

Functional equation has solution

$$h(v_x^2) = \text{const } e^{-v_x^2/2\sigma^2}$$

$2\sigma^2$ some constant

$$g(v^2) = \left(\frac{1}{\sqrt{2\pi}\,\sigma}\right)^3 \exp\left\{-\frac{1}{2}\frac{v^2}{\sigma^2}\right\}$$

normalized Gaussian. Kinetic theory for 3 degrees of freedom

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT = \frac{1}{2} m\, 3\sigma^2$$

Gaussian: $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\sigma^2$

$\sigma^2 = kT/m$

$$g(v^2) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\left(\frac{\frac{1}{2} m v^2}{kT}\right)\right\}$$

Boltzmann factor

Molecular speed distribution

$$1 = \int_0^\infty g_s(v)\, dv = \int_0^\infty v^2 dv \int_0^\pi \sin\theta\, d\theta \int_0^{2\pi} d\phi\ g(v^2)$$

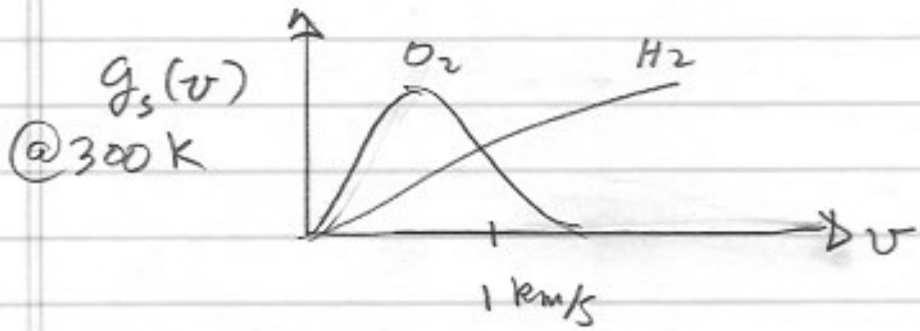
speed → g_s ; $v = \sqrt{|\vec{v}|^2}$

$$= \int_0^\infty 4\pi v^2 g(v^2)\, dv \qquad |\vec{v}|^2 = v^2$$

$$g_s(v) = 4\pi v^2 g(v^2)$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 e^{-\left(\frac{mv^2}{2kT}\right)}$$

Maxwell speed distribution (dependence on m)



light gases escape earth's gravity

$V_{esc} = 11.2$ km/s

Absence of H_2 in earth's atmosphere given age of earth's atmosphere > $\frac{1}{10}$ billion y

Density of states for gas

$$N = \int \rho(\varepsilon)\, \bar{n}_{MB}(\varepsilon)\, d\varepsilon$$

Maxwell speed change variables to

$$\varepsilon = \tfrac{1}{2} m v^2 \qquad \frac{d\varepsilon}{dv} = mv = \sqrt{2m\varepsilon}$$

$$N = \int_0^\infty N g_s(v)\, dv = \int_0^\infty \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi v^2 N \exp\left(\frac{-mv^2}{2kT}\right) dv$$

$$= \int_0^\infty \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi \left(\frac{2\varepsilon}{m}\right) N \exp\left(-\frac{\varepsilon}{kT}\right) \frac{d\varepsilon}{\sqrt{2m\varepsilon}}$$

$$= \int_0^\infty \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{4\pi\sqrt{2}}{m^{3/2}} \sqrt{\varepsilon}\, N \exp\left(-\frac{\varepsilon}{kT}\right) d\varepsilon$$

$$N = \int_0^\infty \underbrace{\frac{2}{\sqrt{\pi kT}} \sqrt{\varepsilon}}_{\rho(\varepsilon)} \;\; \underbrace{\left(\frac{N}{kT}\right) e^{-\varepsilon/kT}}_{\bar{n}_{MB}(\varepsilon)} d\varepsilon$$

where we have chosen to normalize $\bar{n}_{MB}(\varepsilon)$ as

$$N = \int_0^\infty \bar{n}_{BE}(\varepsilon)\, d\varepsilon = N \int_0^\infty e^{-x} dx = N$$

and

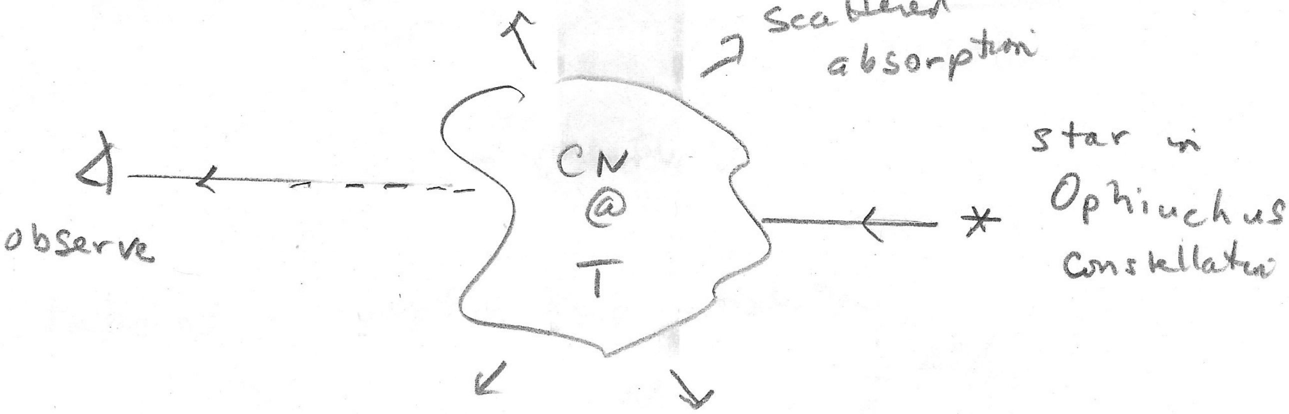
$$N = \int_0^\infty \frac{2}{\sqrt{\pi}} \sqrt{\frac{\varepsilon}{kT}}\, N e^{-\varepsilon/kT} d\left(\frac{\varepsilon}{kT}\right)$$

$$= N \frac{2}{\sqrt{\pi}} \int_0^\infty \sqrt{x}\, e^{-x} dx = N$$

Maxwell-Boltzmann example

McKellar 1940

Absorption (dark) line observed in interstellar Cyanogen (CN) molecule

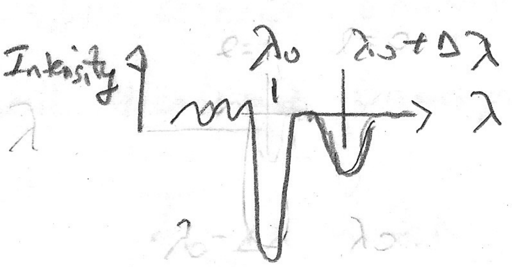


molecular rotation energies

$$E_\ell = \frac{\langle L^2 \rangle}{2I} = \frac{\hbar^2}{2I}\,\ell(\ell+1)$$ multiplicity $2\ell+1$

$$N_\ell(T) = N_0\,(2\ell+1)\,e^{-E_\ell/kT}$$ population at level ℓ

ratio $$\frac{N_1(T)}{N_0(T)} = \frac{3}{1}\,e^{-\Delta E/kT} \qquad \Delta E = \frac{\hbar^2}{2I}$$



molecular absorption lines

$E_0 = hc/\lambda_0 \qquad \lambda_0 = 387.5\ \text{nm}$

$\Delta\lambda = 0.061\ \text{nm}$

In high dispersion spectra of distant stars a few exceedingly sharp lines occur which have been shown to be due to absorption in interstellar space.... While some of these lines were readily identified... several others remained unidentified until it was realized... that they are due to interstellar molecules in their

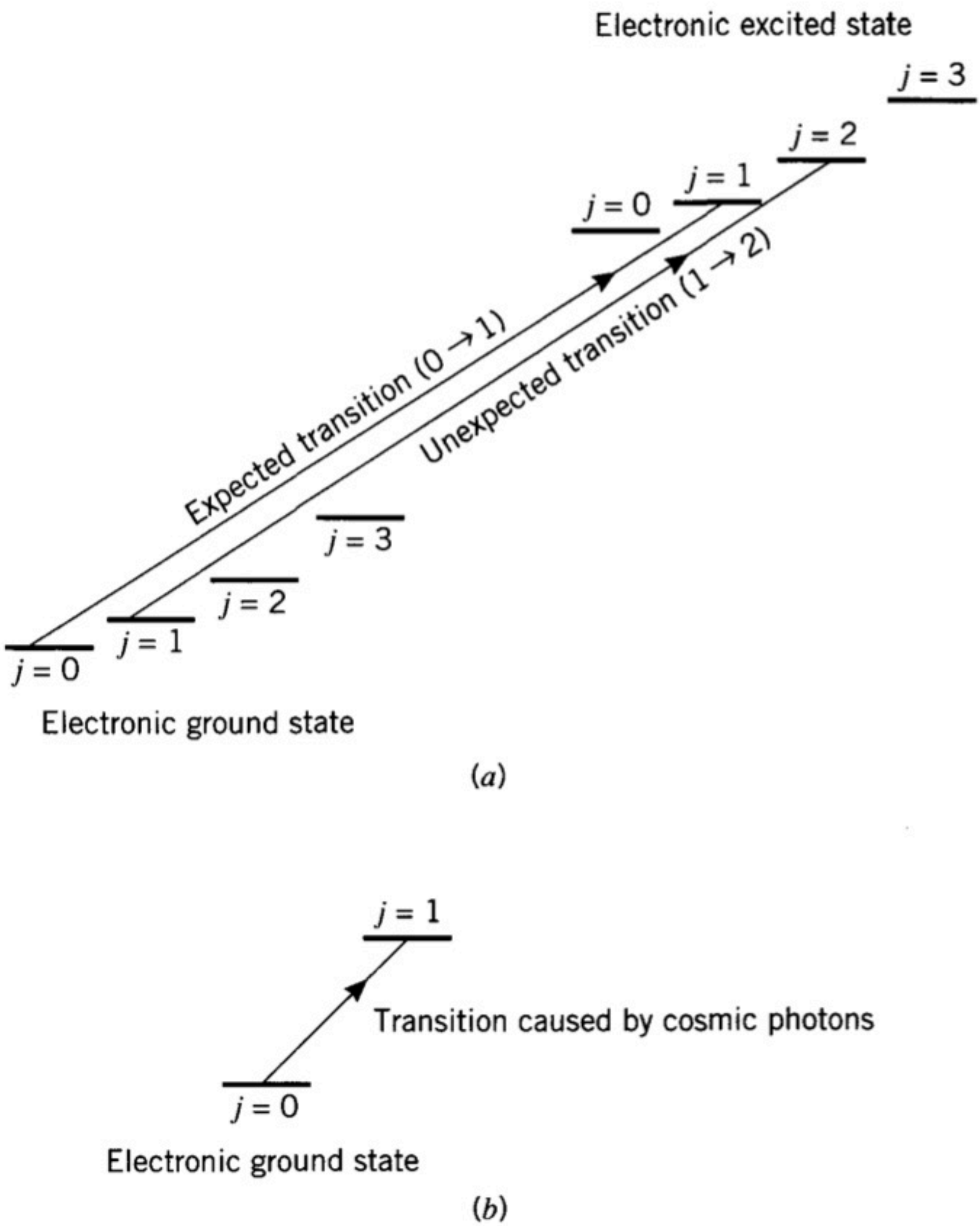


FIGURE 10-14 Energy levels of the CN molecule.
(*a*) Observed transitions from ζ Ophiuci, and (*b*) transition caused by cosmic photons.

$$\frac{\Delta E}{E} = \frac{\Delta\lambda}{\lambda} \qquad \Delta E = E\,\frac{\Delta\lambda}{\lambda} = \frac{hc\,\Delta\lambda}{\lambda^2}$$

$$\Delta E = \frac{hc\,\Delta\lambda}{\lambda_0^2} = (1240\ \text{eV}\cdot\text{nm})\,\frac{0.061\ \text{nm}}{(387.5\ \text{nm})^2}$$

$\Delta\lambda << \lambda$

$$= 5\times10^{-4}\ \text{eV}$$

ratio of absorption line intensities

$$\frac{I_1}{I_0} = \frac{1}{4} = \frac{N_1}{N_0} = 3\,e^{-\Delta E/kT}$$

$$e^{\Delta E/kT} = 4(3) = 12$$

$$T_{obs} = \frac{\Delta E}{k\ln(12)} = \frac{5\times10^{-4}\ \text{eV}}{\ln(12)\ 8.617^{-5}\ \text{eV/K}}$$

$$= 2.3\ \text{K}$$

Before direct observation of the Cosmic Microwave Background (CMB)

$$T_{CMB} = 2.7\,\text{K}$$