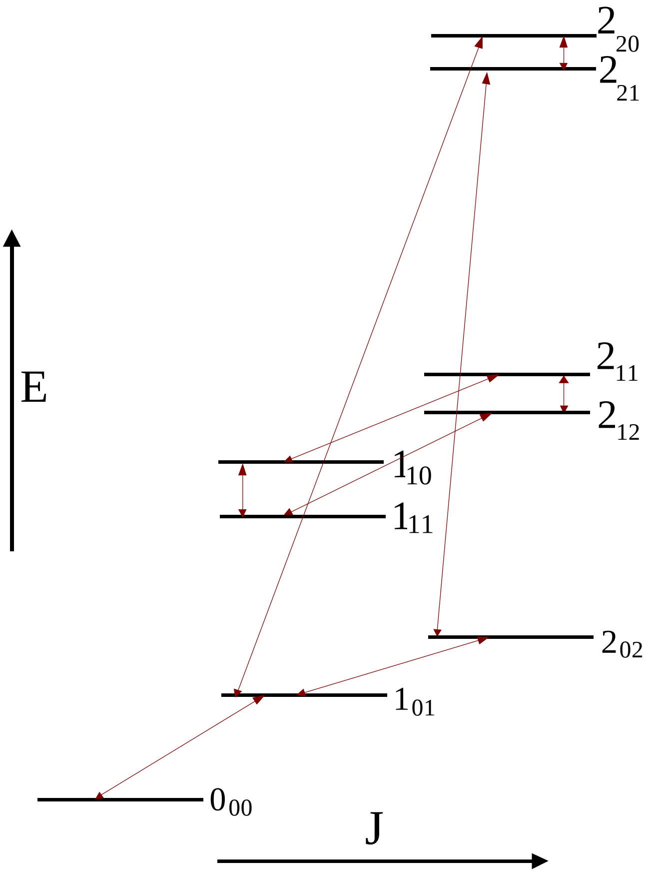
Ge/Ay 132
Problem Set #3 Solutions

1)a) From table 8.4 in the class notes and using

A=291291.641 MHz B=17699.628 MHz C=16651.83 MHz

$E(0_{00}) = 0.0$
$E(1_{01}) = B+C = 34351.5$ MHz
$E(1_{11}) = A+C = 307944.0$ MHz
$E(1_{10}) = A+B = 308991.0$ MHz
$E(2_{02}) = 2A+2B+2C-2*\{(B-C)^2+(A-C)(A-B)\}^{½} = 103051.0$ MHz
$E(2_{12}) = A+B+4C = 375599.0$ MHz
$E(2_{11}) = A+4B+C = 378742.0$ MHz
$E(2_{21}) = 4A+B+C = 1.199518\text{x}10^6$ MHz
$E(2_{20}) = 2A+2B+2C+ 2*\{(B-C)^2+(A-C)(A-B)\}^{½} = 1.199521\text{x}10^6$ MHz

The energy level diagram would look like:



b) For a near-prolate top, the selection rules are

$\Delta J = 0, \pm 1$ (for an assymetric top)

and since the molecule's dipole moment is directed along the symmetry axis only a-type transitions are seen,

$\Delta K_p = 0, \pm 2, \ldots$ and $\Delta K_o = \pm 1, \pm 3, \ldots$

The allowed transitions are shown in the diagram above.

c) For the allowed transitions,

$E\ (1_{01} - 0_{00})$ = c / (34351.5 MHz) = 0.870413 cm = 8.7 mm
$E\ (1_{11} - 1_{10})$ = c / (307944.0 MHz - 34351.5 MHz) = 0.109287 cm = 1.09 mm
$E\ (2_{02} - 1_{01})$ = c / (103051.0 MHz - 34351.5 MHz) = 0.435229 cm = 4.35 mm
$E\ (2_{12} - 1_{11})$ = c / (375599.0 MHz - 307944.0 MHz) = 0.441948 cm = 4.44 mm
$E\ (2_{11} - 1_{10})$ = c / (378742.0 MHz - 34351.5 MHz) = 0.0868200 cm = 0.87 mm
$E\ (2_{11} - 2_{12})$ = c / (378742.0 MHz - 375599.0 MHz) = 9.51318 cm
$E\ (2_{20} - 1_{01})$ = c / (1.199521×10^6 MHz - 34351.5 MHz) = 25661.5 cm = 256.615 m
$E\ (2_{21} - 2_{02})$ = c / (1.199518×10^6 MHz - 103051.0 MHz) = 27269.3 cm = 272.693 m
$E\ (2_{20} - 2_{21})$ = c / (1.199521×10^6 MHz - 1.199518×10^6 MHz) = 10000 cm

These transitions are in the cm,mm and sub-mm parts of the spectrum.

2)Finding B_0, B_1, B_e, $\tilde{\nu}_o$, α, R_e, ωe and $\omega_e x_e$:

First, start with the equations for the frequencies of the P and R branches,

$$\tilde{\nu}_P = \tilde{\nu}_o - (B' + B'')\,J + (B' - B'')\,J^2$$
$$\tilde{\nu}_R = \tilde{\nu}_o + (B' + B'')(J+1) + (B' - B'')(J+1)^2$$

We can find B" and B', which are the same as B_0 and B_1 in this problem, by using similar equations for a few transistions.

For R(0) and P(1),

$$2242.087 = \tilde{\nu}_o + (B' + B'')1 + (B' - B'')(1)^2$$
$$2216.723 = \tilde{\nu}_o - (B' + B'')1 + (B' - B'')\,1^2$$

So,

$$4458.810 = 2*\tilde{\nu}_o + (B' - B'')*2 \quad \text{-->} \quad (B' - B'') = 2229.41 - \tilde{\nu}_o$$
$$25.3640 = (B' + B'')*2 \quad \text{-->} \quad (B' + B'') = 12.6820$$

For R(1) and P(2),

$$2254.257 = \tilde{\nu}_o - (B' + B'')2 + (B' - B'')(2)^2$$

$2203.541 = \tilde{\nu}_o + (B' + B'\ ')2 + (B' -^{2}B'\ ')\ 2$

So,

$4457.800 = 2*\tilde{\nu}_0 + (B' - B'\ ')*8$ --> $2228.90 = \tilde{\nu}_o + (B' - B'\ ')*4$

$50.7161 = (B' + B'\ ')*4$ --> $(B' + B'\ ') = 12.6790$

combining with the results above,

$2228.90 = \tilde{\nu}_o + (2229.41 - \tilde{\nu}_o)*4$

$3*\tilde{\nu}_o = 8917.64 - 2228.90$

$\tilde{\nu}_o = 2229.58\ cm^{-1}$

and

$B_0 = B'\ '\ \mp\ \tilde{\nu}_0 (\ - 2216.73)/2 = 6.42505\ cm^{-1}$

$B_1 = B' = 12.6820 - B'' = 6.25695^{1} cm$

To find B_e and α use the formulae

(1) $B_0 = B_e - 1/2\ \alpha = 6.42505\ cm^{-1}$

(2) $B_1 = B_e - 3/2\ \alpha = 6.25695\ cm^{-1}$

Then, multiplying (2) by negative one and add to (1) gives,

$\alpha = 0.168100$

And substituting back into (1) gives

$6.42505\ cm^{-1} = B_e - ½\ \alpha$ --> $B_e = 6.50910\ cm^{-1}$

To find R_e, use the relation:

$R_e = [h*10^{-2} / (8*\pi^2 *\mu*c*B_e)\ ]^{½}$

where μ = reduced mass = $m_1*m_2 / (m_1+m_2)$

For $^{1}H^{127}I$,

$\mu = (1*127)/(1+127) = 0.992188$ amu ~ $1.65955x10^{-24}$ g

$R_e = [6.626x10^{-27}$ erg s/ $(8*\pi^2*(2.99x10^{10}$ cm/s) $*1.65955x10^{-24}$ g$*6.50910\ cm^{-1}\ )]^{½}$

$= 1.61193x10^{-8}$ cm = 1.61193 Å

For $^{2}H^{127}I$, we are given

R_e = 1.607775 Å,

so $R_e\ (^{1}H^{127}I\ ) / R_e\ (^{2}H^{127}I\ ) = 1.00258$ --> almost the same

What should the relationship be? Well,

$R_e \; \alpha \; 1/(\mu * B_e)^{½}$

And

$\mu(^2H^{127}I) = (2*127)/(2+127) = 1.96899$ amu > $\mu(^1H^{127}I)$

And because $B_e \, \alpha \, 1/\mu$,

$B_e(^1H^{127}I) > B_e(^2H^{127}I)$

So, R_e should be about the same for the two isotopes.

To find ω_e and $\omega_e x_e$:

$G(Jv) = h\tilde{\nu}(v) = \omega_e (v + ½) - \omega_e x_e (v + ½)^2 + J(J+1)B_e - D_J J^2(J+1)^2 - (v + ½)J(J+1)$

In this case,

$G(Jv) = h\tilde{\nu}_0(v) = \omega_e (v + ½) + \omega_e x_e (v + ½)^2$ (because J=0)

So,

$\tilde{\nu}_0 (1\text{-}0) = G(1) - G(0) = \omega_e (3/2) - \omega_e x_e (9/4) - \omega_e (1/2) + \omega_e x_e (1/4)$

$\tilde{\nu}_0 (2\text{-}0) = G(2) - G(0) = \omega_e (5/2) - \omega_e x_e (25/4) - \omega_e (1/2) + \omega_e x_e (1/4)$

And

$\tilde{\nu}_0 (1\text{-}0) = \omega_e - \omega_e x_e (2) = 2229.58 \text{ cm}^{-1}$

$\tilde{\nu}_0 (2\text{-}0) = \omega_e (2) - \omega_e x_e (6) = 4379.00 \text{ cm}^{-1}$

Using these two equations and solving for ω_e and $\omega_e x_e$:

$\omega_e x_e = (4379.00 - 2 * 2229.58) / (4 - 6) = 79.5801/ 2 = 39.7901 \text{ cm}^{-1}$

$\omega_e = (2229.58 - 2*\omega_e x_e) = 2309.58 \text{ cm}^{-1}$

In summary,

$B_0 = 6.42505 \text{ cm}^{-1}$
$B_1 = 6.25695 \text{ cm}^{-1}$
$B_e = 6.50910 \text{ cm}^{-1}$
$\tilde{\nu}_0 = 2229.58 \text{ cm}^{-1}$
$\alpha = 0.168100 \text{ cm}^{-1}$
$R_e = 1.61193$ Å
$\omega_e = 2309.58 \text{ cm}^{-1}$
$\omega_e x_e = 39.7901 \text{ cm}^{-1}$

3)

a) For the CH_3CN transitions:

1. 220.539 GHz -- $12_{7,0} - 11_{7,0}$
2. 220.594 GHz -- $12_{6,0} - 11_{6,0}$
3. 220.641 GHz -- $12_{5,0} - 11_{5,0}$
4. 220.679 GHz -- $12_{4,0} - 11_{4,0}$
5. 220.709 GHz -- $12_{3,0} - 11_{3,0}$
6. 220.730 GHz -- $12_{2,0} - 11_{2,0}$
7. 220.742 GHz -- $12_{1,0} - 11_{1,0}$
8. 220.747 GHz -- $12_{0,0} - 11_{0,0}$

b) Beginning with the equation provided,

$$\int T_A\, dv = (hc^3/8\pi k\nu^2))\, A_{ul} g_u\, (N_T / Q\, (T_{ex}))\, *\, e^{-Eu/kTex}$$

rearranging and taking the natural log of both sides gives:

$$\ln\, [(8\pi k\nu^2/A_{ul}g_u hc^3)\int T_A\, dv] = \ln\, [N_T\ /\ Q\, (T_{ex})]\ - E_u /kT_{ex}$$

So if we plot $\ln\, [(8\pi k\nu^2/A_{ul}g_u hc^3)\int T_A\, dv]$ vs. E_u in Kelvin for each of the CH_3CN transitions, then the slope of the line is $1/T_{ex}$ and the intercept is $\ln\, [N_T\ /\ Q\, (T_{ex})]$.

We can estimate Gaussian line shape integrated line intensities by:

$$\int T_A dv\ \sim\ T_A * \Delta\nu * 1.064$$

And for a line width which is dominated by Doppler broadening:

$$\Delta\nu\ /\ \nu = \Delta v\ /\ c$$

So,

$$\int T_A dv \sim 1.064\ T_A\ \Delta\nu\ /\ c$$

Additionally, because the spectrum has a finite resolution, the FWHM for all of the CH_3CN transitions should be roughly the same, and estimating from line #5 gives

$$\Delta v \sim 1\ \text{GHz} = 1\text{x}10^9\ \text{Hz}$$

And one can calculate the E_u from the transistion frequencies (FREQ) and lower state energies (ELO) given in the JPL line catalog.

Use the equation provided

$$A_{ul} = 1.748\text{x}10^{-9}\ I_{cat}(T_0)\ Q(T_0)/g_u\ e^{-Eu/kTo}$$

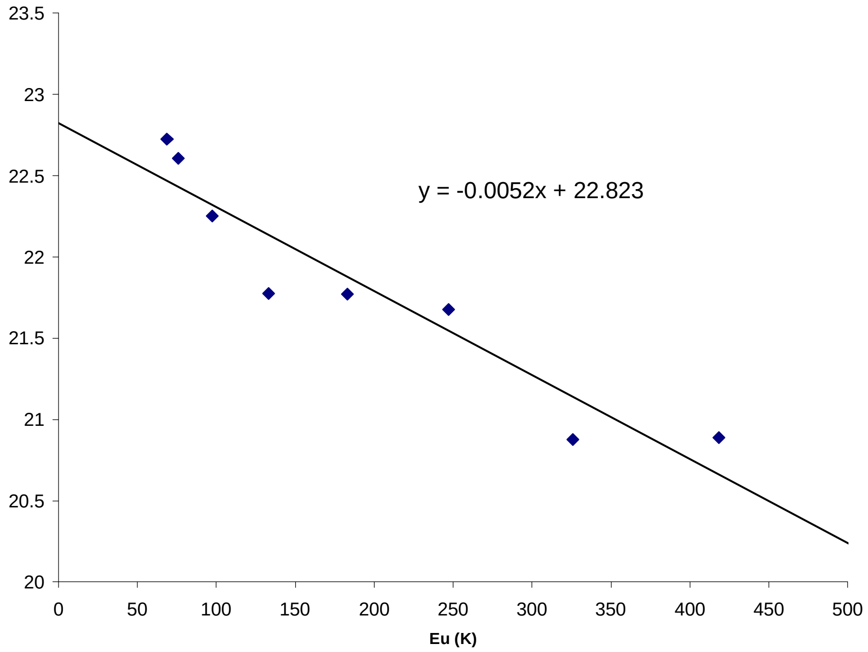
to get the quantity $A_{ul}g_u$.

We can get I_{cat} from the LGINT values listed in the catalog

$$I_{cat} = 10^{LGINT(1)} + 10^{LGINT(2)} + 10^{LGINT(3)} + \ldots$$

Further details of the calculation (such as tricky conversion factors and other subtleties) can be found in the excel spreadsheet, which is available both in excel format and converted to a pdf file. When all of the bookkeeping is over we find the data below, which can be plotted in a rotation diagram:

ln term	Eu (K)
20.88791243	418.4728627
20.87691821	325.7763247
21.67800418	247.3051477
21.77172341	183.077023
21.77438536	133.1067639
22.25224295	97.40543843
22.60701446	75.98153685
22.72594135	68.83966151



From the linear fit, we find:

$$\text{slope} = -0.0052 = -1 / kT_{ex}$$

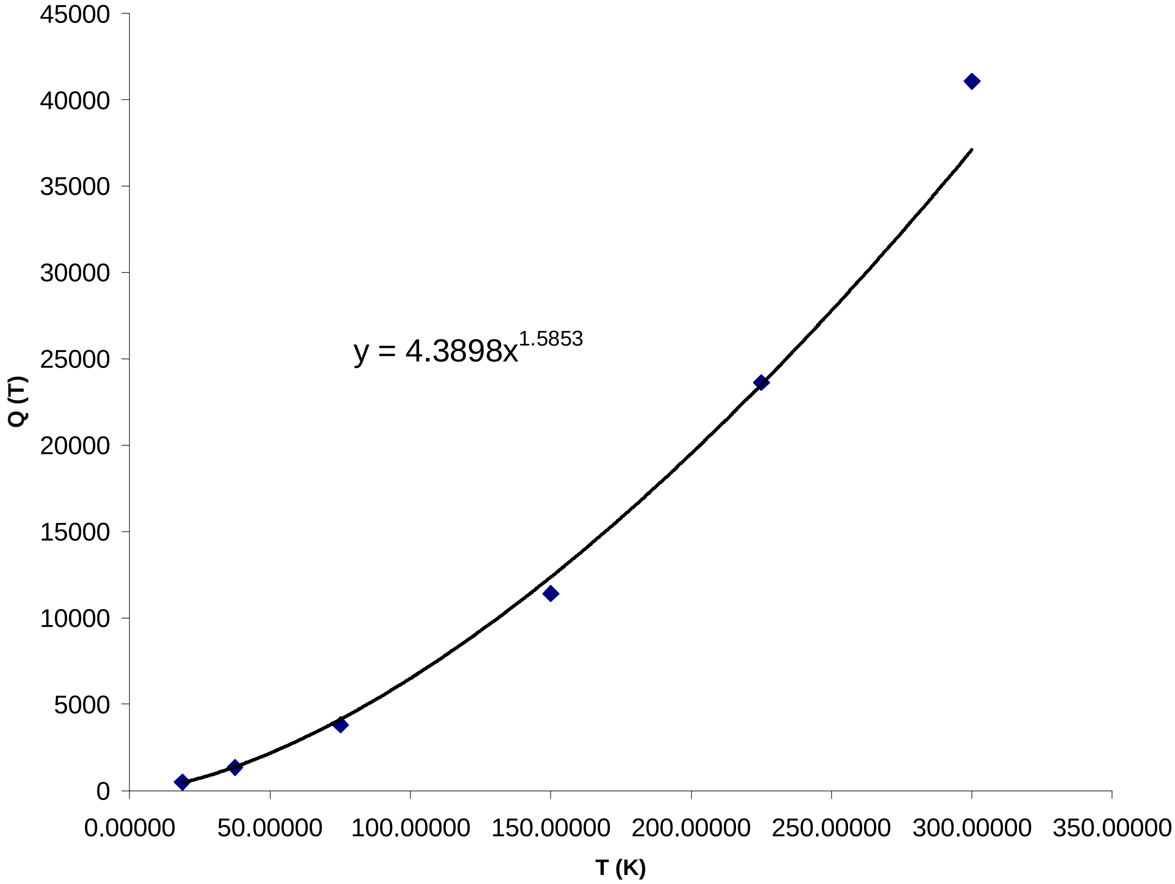
$$\Rightarrow \qquad T_{ex} = 192.31 \text{ K}$$

c) To find the total column density (N_T) :

From part b, we know that:

$$\text{intercept} = 22.823 = \ln [N_T / Q(T_{ex})]$$

We can plot the partition function data from the catalog as a function of T and fit it to a power law:



This yields Q (T_{ex})] = 18334.31267 at 192.31 K, the temperature derived in part b.

So solving for the total column density (N_T) gives:

$$N_T = e^{22.823} * 18334.61267$$

$$N_T = 1.5x10^{14} \text{ cm}^{-2}$$