SOME POSSIBLY USEFUL INFORMATION:

\[ N_A \text{ or } L = 6.022 \times 10^{23} \text{ mol}^{-1} \quad h = 6.626 \times 10^{-34} \text{ J s} \]
\[ k_B = 1.38 \times 10^{-23} \text{ J K}^{-1} \quad c = 2.998 \times 10^8 \text{ m s}^{-1} \]
\[ \text{H atom mass} = 1.66 \times 10^{-27} \text{ kg} \quad \text{electron mass} = 9.11 \times 10^{-31} \text{ kg} \]
\[ R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]

Planck: \( E = h \nu \)  
Schroedinger: \( \hat{H}\psi = E\psi \)  
de Broglie: \( \lambda = h/\rho \)

\( \hat{x} \) operator is multiply by \( x \)  
\( \hat{p} \) operator is \( h/(2\pi i) d/dx \)

\( \hat{E}_k \) operator is \( -h^2/(8\pi^2 m) d^2/dx^2 \)  
\( \hat{V} \) operator is multiply by \( V \)

\[ E_\nu = (\nu + 1/2) h\nu \quad \nu = (k/\mu)^{1/2}/(2\pi) \]
\[ g_J = 2J + 1 \quad B = h/(8\pi^2 I) \text{ in Hz} \quad E_J = Bh(J+1) \]
\[ \sin^2 x = (1 - \cos 2x)/2 \quad \cos^2 x = (1 + \cos 2x)/2 \]

\[ \int_0^\infty x^n \exp(-ax) = \frac{n!}{a^{n+1}} \quad \text{Relative population proportional to } g \exp(-E/(k_B T)) \]

I.P. of one-electron atom proportional to \( Z^2/\alpha^2 \). I.P. of H = 13.6 eV = 2.18 \times 10^{-18} \text{ J}.

\[ |L|^2 = l(l + 1) h^2/(4\pi^2) \quad L_z = m_l h/(2\pi) \]
Successive lines in the rotational Raman spectrum of H$_2$ are observed at values of 240, 480, 720, and 960 cm$^{-1}$ above the central frequency from Rayleigh scattering. The molar mass of H is 1 g mol$^{-1}$.

Deduce the bond length of H$_2$.

\[ \Delta J = \pm 2 \rightarrow \text{spacing is } \frac{4B}{9} \]

\[ 4B = 240 \text{ cm}^{-1} \rightarrow \tilde{B} = 60 \text{ cm}^{-1} \times 3 \times 10^{10} \text{ cm s}^{-1} \]

\[ B = 1.8 \times 10^{-12} \text{ s}^{-1} \]

\[ B = \frac{\hbar}{8\pi^2 I} \]

\[ I = \frac{\hbar^2}{8\pi^2 B} = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 (1.8 \times 10^{-12} \text{ s}^{-1})} \]

\[ = 4.66 \times 10^{-48} \text{ kg m}^2 = \mu r^2 \]

\[ \mu = \frac{1}{1+1} g \text{ mol}^{-1} = \frac{1}{2} g \text{ mol}^{-1} = 8.3 \times 10^{-28} \text{ kg} \]

\[ \frac{1000}{N_A} \]

\[ r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{4.66 \times 10^{-48} \text{ kg m}^2}{8.3 \times 10^{-28} \text{ kg}}} = 7.5 \times 10^{-11} \text{ m} \]

or 0.75 Å
2. **40 points**

The vibrational frequency of $\text{H}_2$ is 4200 cm$^{-1}$. Deduce the vibrational frequency of $\text{D}_2$ (that is, $^2\text{H}_2$).

How do you expect the observed bond dissociation energy $D_0$ of $\text{D}_2$ to compare to that of $\text{H}_2$? Is it larger, smaller or the same? If different, by how much?

Be as quantitative as possible, to the nearest 0.1 kJ mol$^{-1}$.

\[
U = \frac{1}{2\pi} \int \frac{k}{\mu} \quad k_{\text{H}_2} = k_{\text{D}_2} \quad \therefore \quad U_{\text{H}_2} = \frac{1}{2\pi} \int \frac{k}{\mu_{\text{H}_2}} = \frac{1}{2\pi} \sqrt{\frac{k}{2\mu_{\text{D}_2}}}
\]

\[
\mu_{\text{H}_2} = \frac{1 \times 1}{1 + 1} = \frac{1}{2} \text{ amu} \\
\mu_{\text{D}_2} = \frac{2 \times 2}{2 + 2} = \frac{4}{4} = 1 \text{ amu}
\]

\[
\therefore \quad U_{\text{D}_2} = \frac{1}{\sqrt{2}} U_{\text{H}_2} = 2969.8 \text{ cm}^{-1}
\]

\[
E_{v=0} = \frac{1}{2} h \nu
\]

\[
\text{Zpe for } \text{H}_2 = 2100 \text{ cm}^{-1} \\
\text{Zpe for } \text{D}_2 = 1484.9 \text{ cm}^{-1}
\]

\[
\Delta \text{Zpe} = 615.1 \text{ cm}^{-1} \times 2.998 \times 10^{10} \text{ cm/s} \\
= 1.849 \times 10^{13} \text{ s}^{-1} \times 6.626 \times 10^{-34} \text{ J s} \\
= 1.22 \times 10^{-20} \text{ J} \times \frac{N_A}{10200 \text{ J mols}^{-1}} \\
= 7.4 \text{ kJ mols}^{-1}
\]
3. 26 points

Starting with expressions for the degeneracy and energy of the Jth rotational level of a linear molecule whose rotational constant is B (in Hz), prove that the most populated rotational level, at J = J_{max}, satisfies the relation \((2J_{max} + 1)^2 = 2k_B T/(Bh)\) where \(T\) is the temperature, \(k_B\) is Boltzmann's constant and \(h\) is Planck's constant.

\[ g_J = 2J + 1 \]
\[ E_J = BhJ(J+1) \]
\[ \text{relative pop} = g e^{-\frac{E_J}{k_B T}} = (2J+1) e^{-\frac{BhJ(J+1)}{k_B T}} \]

\[ J_{max} \text{ where } \frac{d}{dJ} g e^{-\frac{E_J}{k_B T}} = 0 \]

\[ 0 = 2 e^{-\frac{Bh(J^2+J)}{k_B T}} + (2J+1) \left( -\frac{Bh(2J+1)}{k_B T} \right) e^{-\frac{Bh(2J+1)}{k_B T}} \]

\[ Z = (2J + 1) Bh \left( \frac{2J + 1}{k_B T} \right) \]

\[ \frac{2k_B T}{Bh} = (2J + 1)(2J + 1) = (2J_{max} + 1)^2 \]