Please write neatly and clearly, and show all working. Allocate time to each question in proportion to the available credit. Keep explanations brief and to the point.

Your name: SOLUTIONS

SOME POSSIBLY USEFUL INFORMATION:

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

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

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

\( E_K \) operator is \( -h^2/(8\pi^2 m) \text{ d}^2/\text{d}x^2 \)
\( V \) operator is multiply by \( V \)

\( E_{\nu} = (\nu + 1/2) h\nu \)
\( \nu = (k/\mu)^{1/2}/(2\pi) \)

\( g_J = 2J + 1 \)
\( B = h/(8\pi^2 l) \text{ in Hz} \)
\( E_J = BhJ(J+1) \)

\( \sin^2 x = (1 - \cos 2x)/2 \)
\( \cos^2 x = (1 + \cos 2x)/2 \)

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

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

\( |L|^2 = l(l + 1) h^2/(4\pi^2) \)
\( L_z = m_l h/(2\pi) \)
1. 50 points

Successive lines in the infra red spectrum of HCl (specifically, $^1\text{H}^3\text{Cl}$) are observed at 2840, 2860, 2900, 2920 and 2940 cm$^{-1}$.

a) Deduce the stretching force constant for HCl in N m$^{-1}$.

b) How do you expect the bond dissociation energy of DCl (that is, $^2\text{H}^3\text{Cl}$) to compare to that of HCl? Is it larger, smaller or the same? Be as quantitative as possible, to the nearest 0.1 kJ mol$^{-1}$.

\[ \nu = \frac{1}{2\pi} \sqrt{k/\mu} \]

\[ \mu = \frac{m_1 \cdot m_2}{m_1 + m_2} \]

\[ k = 4\pi^2 \nu^2 \mu = 4\pi^2 \times (8.63 \times 10^{12}) \times 1.61 \times 10^{-27} \text{ Nm}^{-1} \]

\[ = 475 \text{ Nm}^{-1}. \]

\[ \nu \approx \frac{1}{\sqrt{\mu}} \]

\[ \nu_{\text{HCl}} = 2880 \text{ cm}^{-1} \sqrt{\frac{0.972}{18.92}} = 2064 \text{ cm}^{-1} \]

\[ \nu_{\text{DCl}} = \frac{1}{2} \times 2064 \text{ cm}^{-1} = 1032 \text{ cm}^{-1} \]

\[ \text{Do for DCl is greater by } 1440 - 1032 = 408 \text{ cm}^{-1}. \]

\[ \text{In kJ mol}^{-1}, \text{ this difference is } 408 \times 2.998 \times 10^{10} \times 6.626 \times 10^{-24} \times 6.022 \times 10^{23} \]

\[ \text{=} \quad 41,888 \text{ kJ mol}^{-1}. \]
2. 40 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

a) The most populated rotational level, \( J_{\text{max}} \), satisfies the relation \( (2J_{\text{max}} + 1)^2 = 2k_B T / (B h) \) where \( T \) is the temperature, \( k_B \) is Boltzmann’s constant and \( h \) is Planck’s constant.

b) Successive lines in the rotational Raman frequency spectrum are 4B apart.

a) Probability \( P = \int_{-\infty}^{\infty} e^{-\frac{E}{k_B T}} \)

\[ P = (2J+1) \exp \left( -\frac{\hbar J (J+1)}{k_B T} \right) \]

Maximized when

\[ 0 = \frac{dP}{dJ} = e^{-\frac{\hbar J (J+1)}{k_B T}} \cdot 2 - (2J+1) e^{-\frac{\hbar J (J+1)}{k_B T}} \cdot \frac{\hbar J (J+1)}{k_B T} \]

so

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

\[ \therefore (2J_{\text{max}} + 1)^2 = \frac{2k_T}{\hbar} \]

b) For Raman spectroscopy, \( \Delta J = \pm 1 \).

\[ \Delta E = E_{J+1} - E_J = \frac{\hbar}{2} (J+1)(J+2) - \frac{\hbar}{2} J (J+1) \]

\[ = \frac{\hbar}{2} (J^2 + 5J + 6 - J^2 - J) \]

\[ = \frac{\hbar}{2} (4J + 6) \]

so \( \nu = \frac{2k_B T}{\hbar} \)

...With \( J = 0, 1, 2, 3 \ldots \)

...Observed will be at \( 6B, 10B, 14B, 18B \ldots \)

so the separation is 4B.
3. **10 points**

Two excited singlet oxygen molecules, $^1\text{O}_2$, can collide and emit red light at 630 nm while forming a pair of ground state triplet oxygen molecules, $^3\text{O}_2$:

$^1\text{O}_2 + ^1\text{O}_2 \rightarrow ^3\text{O}_2 + ^3\text{O}_2 + \nu$

Use this observation to deduce the energy difference between $^3\text{O}_2$ and $^1\text{O}_2$, in kJ mol$^{-1}$.

\[
\text{Photon energy } \nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^8}{6.20 \times 10^{-9}} \text{ J} = 3.15 \times 10^{-19} \text{ J}
\]

or 190 kJ mol$^{-1}$.

This comes from **two** $^1\text{O}_2$ molecules,

so the energy difference for single molecules is \(\frac{190 \text{ kJ mol}^{-1}}{2} = 95 \text{ kJ mol}^{-1}\).