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: \( E = hv \) \quad Schrödinger: \( \hat{H}\psi = E\psi \) \quad de Broglie: \( \lambda = h/p \)

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

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

\( E_n = (n + 1/2)h \) \quad \( \nu = (k/\mu)^{1/2}/(2\pi) \) \quad Beer-Lambert: \( I_r = I_0 \exp(-\alpha l) \)
\( g_J = 2J + 1 \) \quad \( B = h/(8\pi^2T) \) in Hz \quad \( E_J = BhJ(J+1) \)

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

\[ \int_0^\infty x^n \exp(-ax) = \frac{n!}{a^{n+1}} \]

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}.

\[ |L^2| = l(l + 1)h^2/(4\pi^2) \quad L_z = m_l h/(2\pi) \]
1. 30 points
Sea water partially absorbs visible light. The molar absorption coefficients of red and green light are $9 \times 10^5$ mol$^{-1}$ dm$^3$ cm$^{-1}$ and $6 \times 10^5$ mol$^{-1}$ dm$^3$ cm$^{-1}$, respectively. Taking the ratio of red to green light in sunlight to be 1, what ratio would you expect 10 m below the surface of the water? Note: 1 dm$^3$ of water contains about 55 mol H$_2$O.

\[ L > 1000 \text{ cm} \]

For red light, \( I_{kr} = \frac{9 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \times 55 \text{ mol dm}^{-3} \times 1000 \text{ cm}}{I_0 \times 10} \]
\[ = I_0 \times 10^{-4.95} \]

For green light, \( I_{kg} = \frac{6 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \times 55 \text{ mol dm}^{-3} \times 1000 \text{ cm}}{I_0 \times 10} \]
\[ = I_0 \times 10^{-3.30} \]

The ratio \( \frac{\text{red}}{\text{green}} = \frac{10^{-4.95}}{10^{-3.30}} = 10^{-1.65} = 0.022 \)
2. 50 points
Consider iodine (I\textsubscript{2}) molecules in their ground or X state exposed to light. Absorption has been measured at 12000, 13000, 13900, 14700, 15400, 16000, 16500, 16900 and 17200 cm\textsuperscript{-1}. Assume the first transition corresponds to the transition from the X (v=0) to the excited A state in v=0.
This information is graphed below in a Birge-Sponer plot. The difference in wavenumber between successive transitions is plotted against v+1/2 where v represents the vibrational quantum number in the upper state. It is known from atomic spectroscopy that the products of A state dissociation are 55 kJ mol\textsuperscript{-1} above those of X state dissociation to two ground state iodine atoms.

i) Why do the lines get closer together? (10 pts)
ii) Deduce the dissociation energy D\textsubscript{0} of the A state, in kJ mol\textsuperscript{-1}. (20 pts)
iii) Deduce the dissociation energy D\textsubscript{0} of the X state, in kJ mol\textsuperscript{-1}. (20 pts) If you have no answer to (ii) you may assume 90 kJ mol\textsuperscript{-1}. This is not the correct value.

\begin{itemize}
  \item i) Because of anharmonicity in the upper state, the v levels get closer in energy.
  \item ii) Area under plot: \( \frac{1}{2} \times 10^{-4} \times 1050 \text{ cm}^{-1} = 5250 \text{ cm}^{-1} \)
     This is D\textsubscript{0} for the A state. Convert to kJ mol\textsuperscript{-1}:
     \[ D_0 = 5250 \text{ cm}^{-1} \times 2.418 \times 10^{-3} \text{ cm} \times \frac{6.626 \times 10^{-34} \text{ J s}}{6.022 \times 10^{23} \text{ mol}^{-1}} \div 1000 \]
     \[ = 65.3 \text{ kJ mol}^{-1} \]
  \item iii) \[ D_0 + 55 = 12000 \text{ cm}^{-1} + 65.3 \]
     \[ D_0 = 1055 \text{ kJ mol}^{-1} + 12000 \text{ cm}^{-1} \]
     \[ = 153.8 \text{ kJ mol}^{-1} \]
\end{itemize}
3. 20 points
Carbon dioxide molecules are linear and have no dipole moment. Explain how they can nevertheless absorb infra-red radiation.

IR absorption requires a change in dipole moment during the normal mode of vibration.

Asymmetric stretching of CO₂ involves such a dipole moment change:

```
  O -- C -- O
     S+   S-
```

as does degenerate bending

```
     C
O -- C -- O
     S+   S-
```

By contrast, the dipole remains zero for symmetric stretching

and this mode is not IR-active.

```
  O -- C -- O
     S+   S-
```
4. **20 points**
The spacing between successive lines in the rotational Raman spectrum of $^1\text{H}^1\text{F}$ is 80 cm$^{-1}$. Deduce the bond length.

\[
\text{Spacing} = 48 \text{ from } \Delta J = \pm 2 \text{ selection rule}
\]
\[
\Rightarrow p = 20 \text{ cm}^{-1} = 5 \times 10^{-10} \text{ Hz}
\]
\[
\Rightarrow \mu = \frac{h}{8\pi^2 I}
\]
\[
\Rightarrow I = 1.40 \times 10^{-47} \text{ kg m}^2 = \mu r^2
\]
\[
\Rightarrow M = \frac{1 \times 10^{-21} \text{ amu}}{1 + 19} = 0.95 + 1.66 \times 10^{-27} \text{ kg} = 1.577 \times 10^{-27} \text{ kg}
\]
\[
r^2 = 8.88 \times 10^{-21} \text{ m}^2 \Rightarrow r = 0.94 \times 10^{-10} \text{ m or } 0.94 \text{ Å}
\]