Marks 7

Explain in terms of bond order why the upper state of the violet system exhibits a shorter bond length (1.15Å) than the ground state (1.17Å).

The bond order is an indication of the bond strength and bond length. A higher bond order leads to a strong and shorter bond. It can be calculated as:

bond order = ½ (number of bonding electrons – number of antibonding electrons)

The upper state in the violet system has 8 bonding electrons (2 × σ, 4 × σ* and 2 × σ) and 1 antibonding electron (1 × σ*):

bond order = ½ (8 – 1) = 7/2

The upper state in the red system has 7 bonding electrons (2 × σ, 3 × σ* and 2 × σ) and 2 antibonding electron (2 × σ*):

bond order = ½ (7 – 2) = 5/2

The upper state in the violet system has a higher bond order and this is consistent with it having a shorter bond (i.e. it has more bonding and fewer antibonding electrons).

Also indicated in Huggin's spectrum are the Fraunhofer absorption features labelled K, H and G, which arise from calcium. Explain the appearance of these features. (Hint: they would also appear in the spectrum of moonlight.)

Blackbody emission from the sun is absorbed by Ca in the sun's atmosphere. the solar spectrum is then reflected by the comet.

The Fraunhofer feature labelled 'h' is due to atomic hydrogen. What is the electronic transition responsible for this absorption feature? (Hint: one of the energy levels involved is $n = 2$.)

The feature occurs at 41 nm. This corresponds to an energy of:

$$E = (hc/\lambda) = (6.626 \times 10^{-34}\text{ J s} \times 2.998 \times 10^{8}\text{ m s}^{-1}) / (41 \times 10^{-8}\text{ m}) = 4.85 \times 10^{-19}\text{ J}$$

The energy of a level in hydrogen is given by $E_n = -E_R(1/n^2)$. The transition energy is the difference in the energies of the two levels involved:

$$\Delta E = \frac{-E_R}{n_f^2} - \frac{-E_R}{n_i^2} = E_R\left[\frac{1}{n_i^2} - \frac{1}{n_f^2}\right]$$ **where E_R is the Rydberg constant.**

As $n_i = 2$,

$$\Delta E = (2.18 \times 10^{-18}\text{ J})\left[\frac{1}{2^2} - \frac{1}{n_f^2}\right] = 4.85 \times 10^{-19}\text{ J}$$ **which gives $n_f = 6$.**