

Marks
3

- Determine an electronic transition involving the $n = 5$ level of the He^+ ion that emits light in the visible region (400–700 nm) of the electromagnetic spectrum.

Using Planck's relationship between wavelength and energy, $E = hc / \lambda$, visible light corresponds to the range:

$$E(400 \text{ nm}) = 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1} / 400 \times 10^{-9} \text{ m} = 4.97 \times 10^{-19} \text{ J}$$

$$E(700 \text{ nm}) = 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1} / 700 \times 10^{-9} \text{ m} = 2.84 \times 10^{-19} \text{ J}$$

For a 1-electron ion like He^+ , the orbital energies are given by $E_n = -Z^2 E_R / n^2$ where $Z = 2$ for He^+ and E_R is the Rydberg constant, $2.18 \times 10^{-18} \text{ J}$. For a transition from $n = 5$ to another level n_f , the energy difference is:

$$\Delta E = -4 \times 2.18 \times 10^{-18} \times (1/n_f^2 - 1/5^2)$$

With $n_f = 11$, the transition is just outside the visible range. As n_f must be an integer, the lowest value of n_f is 12. Any value of n_f above this will also be in the visible.

- Describe one piece of experimental evidence supporting the conclusion that electrons have wave-like character.

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Examples include:

- The diffraction of electron beams. Electrons can be diffracted just like light waves.
- The standing wave structure of atoms leading to atomic line spectra. Electrons can only exist in discrete orbits with certain energies, leading to absorption and emission at certain wavelengths rather than at every wavelength.

- An “excimer laser” is a type of ultraviolet laser used for lithography, micromachining and eye surgery. In one type of laser, an electrical discharge through HCl and Xe in a helium buffer gas yields metastable XeCl molecules, described like an ion pair. These then emit 308 nm light and dissociate into Xe and Cl atoms.

element	Ionisation energy / kJ mol ⁻¹	Electron affinity / kJ mol ⁻¹
Xe	1170.4	–
Cl	1251.1	–349

What energy, in eV, is required to convert a pair of Xe and Cl atoms into Xe⁺ and Cl⁻ ions?

To form Xe⁺ requires 1170.4 kJ mol⁻¹ and in forming Cl⁻, 349 kJ mol⁻¹ is released. The total energy change is therefore:

$$\text{total energy change} = [(+1170.4) + (-349)] \text{ kJ mol}^{-1} = +821.4 \text{ kJ mol}^{-1}$$

or

$$\begin{aligned} \text{total energy per pair of atoms} &= (+821.4 \text{ kJ mol}^{-1}) / (6.022 \times 10^{23} \text{ mol}^{-1}) \\ &= 1.364 \times 10^{-18} \text{ J} \end{aligned}$$

As 1 eV = 1.602 × 10⁻¹⁹ J, this corresponds to:

$$\begin{aligned} \text{total energy per pair of atoms} &= (1.364 \times 10^{-18}) / (1.602 \times 10^{-19}) \text{ eV} \\ &= 8.51 \text{ eV} \end{aligned}$$

Answer: **8.51 eV**

What energy (in eV) is released when the XeCl molecules emit ultraviolet light?

A wavelength of 308 nm corresponds to an energy of:

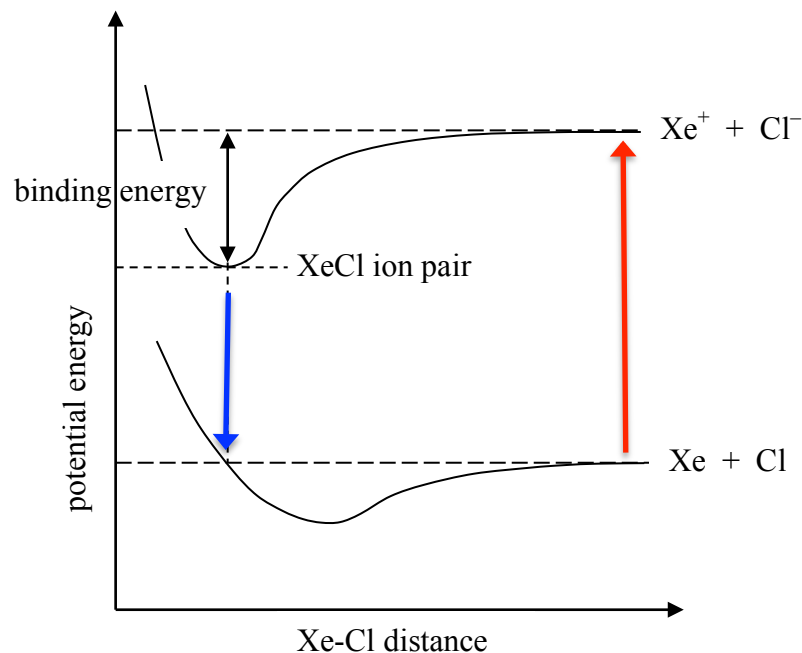
$$\begin{aligned} E &= hc / \lambda \\ &= (6.626 \times 10^{-34} \text{ J s}) \times (2.998 \times 10^8 \text{ m s}^{-1}) / (308 \times 10^{-9} \text{ m}) \\ &= 6.45 \times 10^{-19} \text{ J} \end{aligned}$$

As 1 eV = 1.602 × 10⁻¹⁹ J, this corresponds to:

$$\begin{aligned} E &= (6.45 \times 10^{-19}) / (1.602 \times 10^{-19}) \text{ eV} \\ &= 4.03 \text{ eV} \end{aligned}$$

Answer: **4.03 eV**

THIS QUESTION CONTINUES ON THE NEXT PAGE.



What is the binding energy (in J) of the XeCl ion pair?

The binding energy of the ion pair is shown by the double headed arrow on the diagram above. This is the *difference* between the energy needed to form a pair of Xe^+ and Cl^- ions (8.51 eV; red arrow above) and the energy released when XeCl molecules emit light (4.03 eV; blue arrow above).

$$\text{Binding energy} = (8.51 - 4.03) \text{ eV} = 4.48 \text{ eV}$$

As $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$, this corresponds to:

$$\begin{aligned} \text{Binding energy} &= (4.48 \times 1.602 \times 10^{-19}) \text{ eV} \\ &= 7.18 \times 10^{-19} \end{aligned}$$

Answer: $7.18 \times 10^{-19} \text{ J}$

If the binding is electrostatic, what is the approximate equilibrium bond length of

XeCl if the binding energy is given by the Coulomb formula: $E = \frac{q_1 q_2}{4\pi\epsilon_0 r}$?

For Xe^+ , $q = 1.602 \times 10^{-19} \text{ C}$. For Cl^- , $q = -1.602 \times 10^{-19} \text{ C}$.

Using $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$ and $E = 7.18 \times 10^{-19} \text{ J}$:

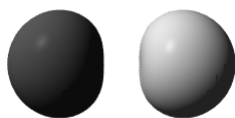
$$\begin{aligned} r &= q_1 q_2 / 4\pi\epsilon_0 E \\ &= (1.602 \times 10^{-19} \text{ C})^2 / (4\pi \times 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \times 7.18 \times 10^{-19} \text{ J}) \\ &= 3.21 \times 10^{-10} \text{ m} = 321 \text{ pm or } 3.21 \text{ \AA} \end{aligned}$$

Answer: 321 pm or 3.21 Å

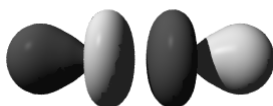
- In the spaces provided, explain the meaning of the following terms. You may use an example, equation or diagram where appropriate.

(a) antibonding molecular orbital

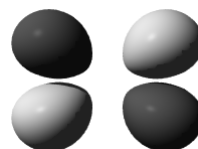
An orbital with a nodal plane perpendicular to the bond. Occupation of an antibonding orbital lowers the bond order and weakens a bond. The diagram below show the antibonding orbitals produced from overlap of s-orbitals (σ^* - A) and p-orbitals (σ^* - B and π^* - C):



σ^* - A



σ^* - B



π^* - C

(b) emission spectroscopy

The study of radiation emitted as an atom or molecule relaxes from an initial excited state. Because of the quantized nature of energy levels, emission occurs at particular wavelengths which are characteristic of the atom or molecule.

(c) band gap

The energy gap between the valence and conductance bands in a solid. The diagram below shows this schematically.

When this gap is large (as opposite), the solid is an insulator as there is insufficient energy to excite an electron from the filled valence band to the empty conductance band.



When this gap is small (as opposite), the solid is a semi-conductor as, except at very low temperatures, there is thermal excitation into the conductance band.



(d) a triple bond

A "bond" between two atoms involving the sharing of three electron pairs. It usually consists of 1 σ -bond and 2 π -bonds. The most common molecules containing triple bonds are N_2 and CO. Triple bonds are represented by drawing three lines between the atoms. For example, $N \equiv N$ and $C \equiv O$.