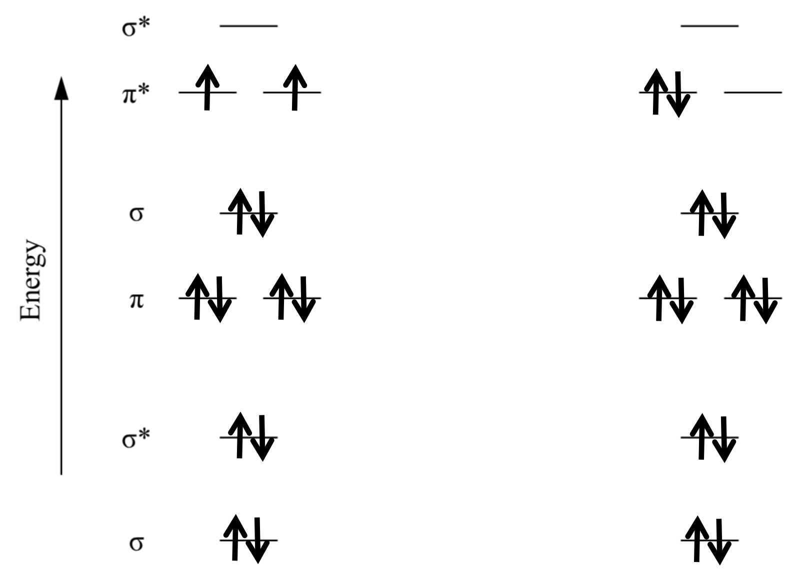
Marks
4

• Oxygen exists in the troposphere as a diatomic molecule.



(a) Using arrows to indicate relative electron spin, fill the left-most **valence** orbital energy diagram for O_2, obeying Hund's Rule.

(b) Indicate on the right-most **valence** orbital energy diagram the lowest energy electronic configuration for O_2 which has no unpaired electrons.

Suggest a heteronuclear diatomic species, isoelectronic with O_2, that might be expected to have similar spectroscopic behaviour.

NO^-, NF

The blue colour of liquid O_2 arises from an electronic transition whereby one 635 nm photon excites two molecules to the state indicated by the configuration in (b) *at the same time*. What wavelength photon would be emitted by one molecule returning from this state to the ground state?

635 nm excites two molecules. The energy emitted by one molecule will be half as much required to excite two molecules.

Energy, *E*, is inversely related to the wavelength, λ, through Plank's equation:

$$E = hc / \lambda.$$

Hence, if the energy is halved, the wavelength is *doubled*: 2 × 635 nm = 1270 nm.

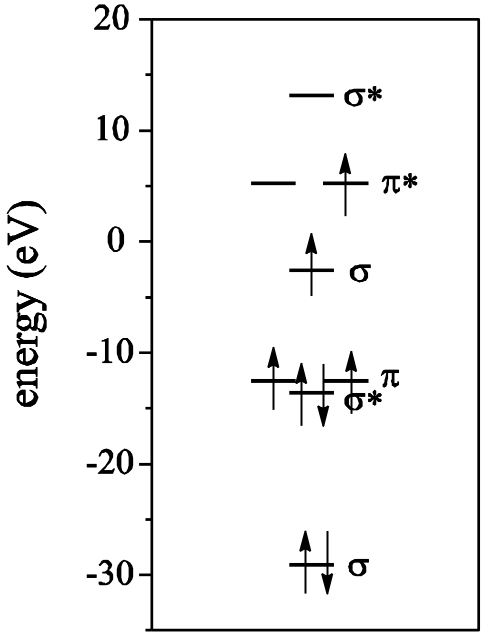
Answer: **1270 nm**

Marks
5

- C_2 is a reaction intermediate observed in flames, comets, circumstellar shells and the interstellar medium. In 2011, a new state of C_2 was observed with 4 parallel spins.

How many *valence* electrons are there in C_2? **8**

Complete the calculated MO diagram for the lowest energy state of C_2 *with 4 parallel spins* by inserting the appropriate number of electrons into the appropriate orbitals.



What is the bond order of this state of C_2? **1**

Is this state paramagnetic? Give reasoning.

Yes. It has 4 unpaired electrons.

What is the bond order of the ground state of C_2? **2**

Marks 6

- 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:

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

or

total energy per pair of atoms = (+821.4 kJ mol^{-1}) / (6.022 × 10^{23} mol^{-1})
= 1.364 × 10^{-18} J

As 1 eV = 1.602 × 10^{-19} J, this corresponds to:

total energy per pair of atoms = (1.364 × 10^{-18}) / (1.602 × 10^{-19}) eV
= 8.51 eV

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:

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

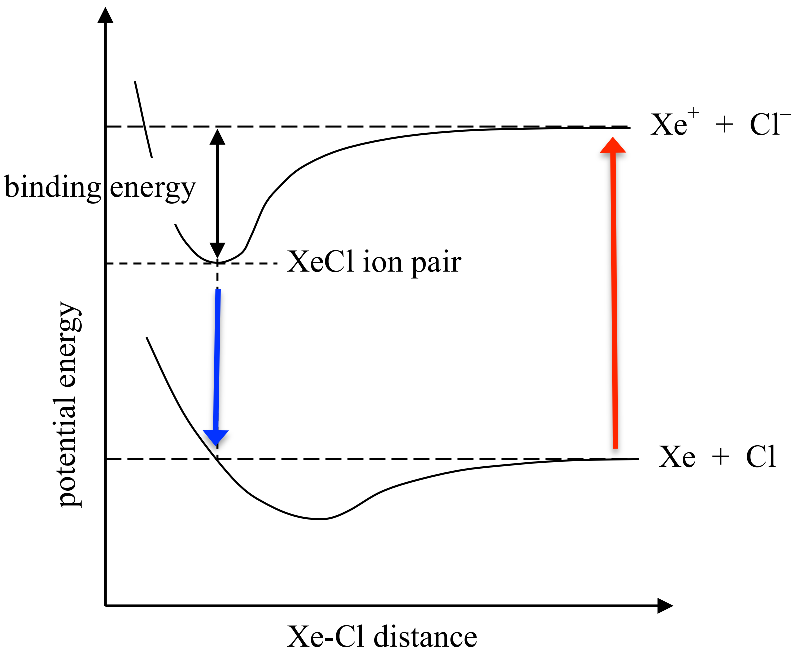
As 1 eV = 1.602 × 10^{-19} J, this corresponds to:

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

Answer: **4.03 eV**

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
4



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).

Binding energy = (8.51 – 4.03) eV = 4.48 eV

As 1 eV = 1.602×10^{-19} J, this corresponds to:

Binding energy = $(4.48 \times 1.602 \times 10^{-19})$ eV
= 7.18×10^{-19}

Answer: **7.18×10^{-19} 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: $E = \dfrac{q_1 q_2}{4\pi\varepsilon_0 r}$?

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

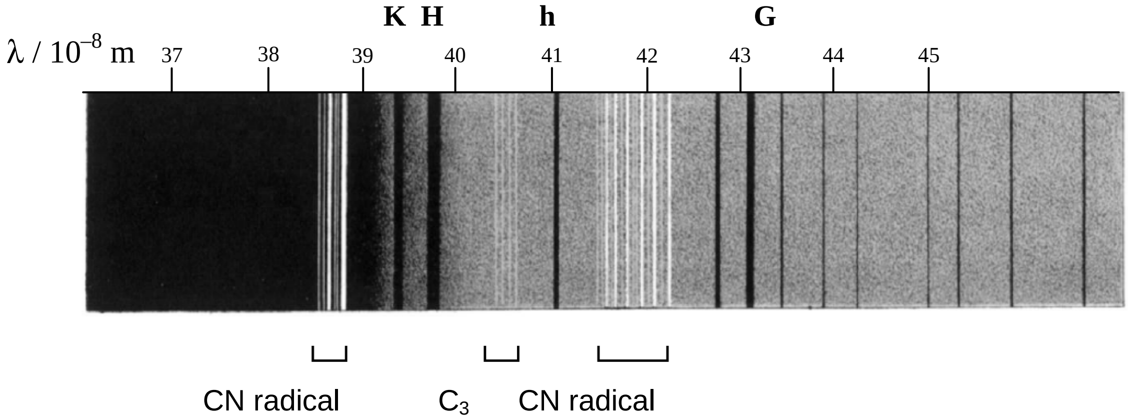
Using $\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 J^{-1} m^{-1} and $E = 7.18 \times 10^{-19}$ J:

$$\begin{aligned} r &= q_1 q_2 / 4\pi\varepsilon_0 E \\ &= (1.602 \times 10^{-19}\ \text{C})^2 / (4\pi \times 8.854 \times 10^{-12}\ \text{C}^2\ \text{J}^{-1}\ \text{m}^{-1} \times 7.18 \times 10^{-19}\ \text{J}) \\ &= 3.21 \times 10^{-10}\ \text{m} = 321\ \text{pm or } 3.21\ \text{Å} \end{aligned}$$

Answer: **321 pm or 3.21 Å**

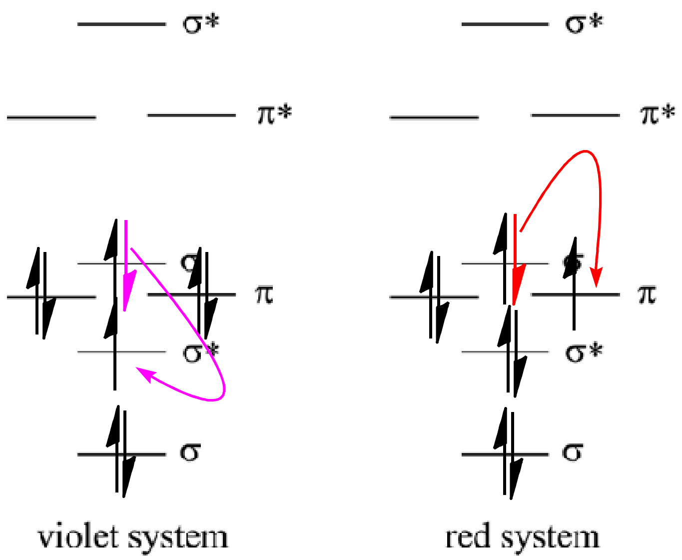
Marks
4

- The "Great Comet of 1881" was discovered by Tebbutt from his observatory at Windsor, NSW. Observations by Huggins of the comet's emission spectrum (pictured) revealed the presence of what was later determined to be the CN radical.



This emission system of CN is known as the "violet system", and results from a radical returning to the ground state as an electron makes a transition from a σ orbital to a σ* orbital. The "red system" of CN results from a radical returning to the ground state as an electron makes a transition from a σ orbital to a π orbital.

On the diagram below, indicate the orbital occupancy, using arrow notation, of the upper electronic states of the "violet" and "red" systems of CN. Also indicate how the excited electron relaxes when the radical emits light (use a curved arrow).



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.**

Marks
6

- The electronic energies of the molecular orbitals of diatomics consisting of atoms from H to Ne can be ordered as follows (with energy increasing from left to right):

$$\sigma\ \sigma^*\ \sigma\ \sigma^*\ 2\times\pi\ \sigma\ 2\times\pi^*\ \sigma^*$$

(the '2×' denotes a pair of degenerate orbitals)

Use this ordering of the molecular orbitals to identify the following species.

(i) The lowest molecular weight diatomic ion (homo- or heteronuclear) that has **all** of the following characteristics:

a) a single negative charge,
b) a bond order greater than zero *and*
c) is diamagnetic.

HBe^- has 6 electrons (1 from He, 4 from Be and 1 from the negative charge) so has a configuration $\sigma^2\ \sigma^{*2}\ \sigma^2$. It has a bond order of 1 and is diamagnetic.

(ii) A diatomic species that has the same electronic configuration as O_2.

There are many: simply substitute one or both O by a cation with the same number of electrons (F^+, Ne^{2+} etc) or an anion with the same number of electrons (N^-, C^{2-} etc). For example:

NO^-, OF^+, NF, F_2^{2+}, CN^{3-}, N_2^{2-} .....

(iii) All of the atoms with atomic numbers less than or equal to 10 that cannot form stable, neutral, homonuclear diatomic molecules.

The neutral, homonuclear diatomic molecule would have a bond order of zero: He, Be and Ne.

He_2 $\sigma^2\ \sigma^{*2}$
Be_2 $\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}$
Ne_2 $\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}\ \pi^4\ \pi^{*4}\ \sigma^2\ \pi^{*4}\ \sigma^{*2}$

Given that there are three degenerate *p* orbitals in an atom, why are there only two degenerate π orbitals in a diatomic molecule?

One *p*-orbital on each atom overlaps end-on with the matching *p*-orbital on the other atom. This produces a *σ*-bond.

This leaves only two *p*-orbitals on each atom to overlap in the side-on manner required for π bonding.

- In a linear molecule consisting of a carbon chain with alternating double and single bonds, the HOMO and LUMO are often extended over the whole length of the molecule. What will happen to the size of the HOMO-LUMO gap as the length of such a molecule is increased?

2

As the wavelength associated with an electron is given by $\lambda = h/mv$, a longer wavelength is associated with a lower velocity and hence a lower energy. The gap is reduced.

Assuming that the molecule absorbs in the visible range, how will its colour change as the molecule length increases? Give a reason for your answer.

The colour will become more blue.

The energy of the light *absorbed* decreases as the band gap decreases, so its wavelength increases and it becomes more red. The colour of the compound is *complementary* to the light absorbed.

Marks
3

- The electronic energies of the molecular orbitals of homonuclear diatomics from the period starting with Li can be ordered as follows (with energy increasing from left to right):

  σ σ* σ σ* π σ π* σ*

  Using this ordering by energy of the molecular orbitals, how many unpaired spins do you expect in the ground state configurations of each of B_2, C_2, N_2, O_2 and F_2?

B_2	C_2	N_2	O_2	F_2
2	**0**	**0**	**2**	**0**

Consider the 15 species X_2^-, X_2 and X_2^+ where X is B, C, N, O or F. What is the maximum bond order found among these 15 species and which molecules or ions exhibit this bond order?

Maximum bond order = 3. This is exhibited by N_2

What is the minimum bond order found among these 15 species and which molecules or ions exhibit this bond order?

Minimum bond order = ½. This is exhibited by B_2^+ and F_2^-.

Marks
5

- The electronic configuration of the molecular oxygen dianion in its ground state is, in order (from left to right) of increasing energy: $\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}\ \sigma^2\ \pi^4\ \pi^{*4}$

What is the bond order of O_2^{2-}?

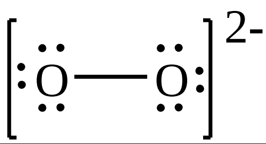
½ (8 – 6) = 1
(σ^2, σ^2 and π^4 are bonding, π^{*4} are antibonding)

Is O_2^{2-} paramagnetic or diamagnetic? Explain your answer.

All of the spins are paired as every orbital is full. It is therefore diamagnetic.

How many of the valence electrons in O_2^{2-} are in 'lone pairs' according to Lewis theory?

The Lewis structure gives 3 lone pairs on each oxygen atom so 12 electrons are in lone pairs in total.



On the electron configuration of O_2^{2-} below, indicate by arrows the molecular orbitals that contain the electron 'lone pairs'.

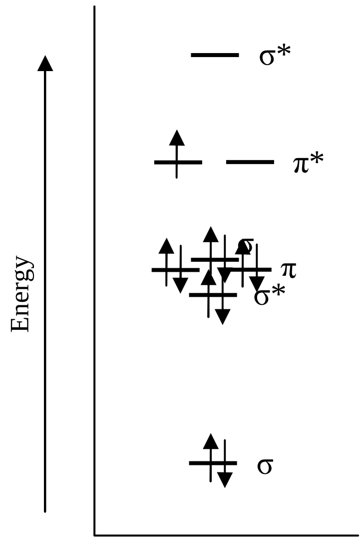
$$\sigma^2\ \sigma^{*2}\ \sigma^2\ \sigma^{*2}\ \sigma^2\ \pi^4\ \pi^{*4}$$

	Marks
• Describe two physical properties of liquid or solid water that distinguishes it from 'normal' liquids or solids.	3
The solid is less dense than the liquid. **The density of the liquid can decrease on cooling.** **The melting and boiling points are significantly higher than would be predicted from extrapolation of the other group 16 dihydrides.** **It is capable of dissolving ionic solids to a larger extent than most other liquids.**	
• Molecules with multiple resonance structures are said to be "resonance stabilised". Briefly explain the origin of this extra stability in terms of electron waves and molecular orbitals.	2
The presence of resonance Lewis structures indicates the presence of molecular orbitals that extend over more than a pair of atoms. This greater delocalisation of electrons produces lower energies and hence increased stabilisation of the molecule.	

Marks
4

- The molecular orbital energy level diagram below is for the valence electrons of the O_2^+ ion.

  Indicate the ground state electronic configuration of O_2^+ using the arrow notation for electron spins on the provided molecular orbital energy level diagram.



Calculate the bond order of O_2^+.

Bond order = ½ (8 – 3) = 2.5

Indicate the lowest energy electron excitation in this ion by identifying the initial and final molecular states of the electron undergoing the excitation.

The gap between the highest occupied σ and the π* is very similar to that between π* and σ*: either σ → π* or π* → σ*

Marks
4

- The electronic configuration of molecular nitrogen in its ground state is, in order (from left to right) of orbitals of increasing energy:

$$\sigma^2\sigma^{*2}\sigma^2\sigma^{*2}\pi^4\sigma^2$$

What is the bond order of N_2?

½ (8 – 2) = 3 – a triple bond

How many of the valence electrons in N_2 are in non-bonding 'lone pairs' according to Lewis theory?

Four electrons (2 lone pairs) $:N\equiv N:$

On the electron configuration of N_2 below, indicate by arrows the molecular orbitals that contain the non-bonding electrons.

$$\sigma^2\sigma^{*2}\sigma^2\sigma^{*2}\pi^4\sigma^2$$

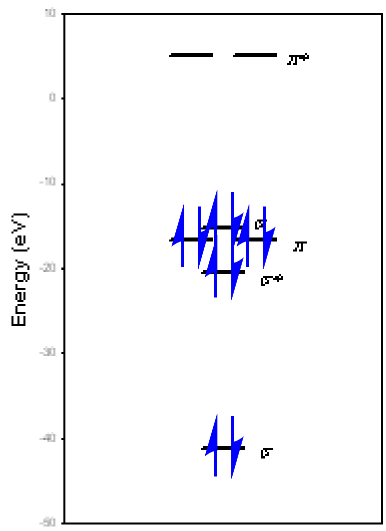
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

Marks

4

- Nitrogen gas constitutes about 78% of the Earth's atmosphere.

Complete the MO diagram for the valence electrons for the ground state electronic configuration of the nitrogen molecule by inserting the appropriate number of electrons into the appropriate orbitals.



Is N_2 paramagnetic or diamagnetic? Explain your answer.

The electrons in N_2 are all paired up – there are as many up as down-spin electrons so that there is no resultant spin. The molecule is diamagnetic.

The N_2^- anion can be generated as a transient species in an electrical discharge. What is the bond order of this molecular ion?

N_2^- has an additional electron in the π^* level. Overall there are 8 bonding electrons (a pair in each σ and two pairs in the π levels) and 3 antibonding electrons (a pair in σ^* and a single electron in π^*). Hence the bond order is:

½ (8 – 3) = 5/2

2

- Why is the H_2 molecule lower in energy than two isolated H atoms?

The electrons are delocalised over two nuclei in H_2, as opposed to being localised around one nucleus in the case of two isolated H atoms. This delocalisation results in an increase in their wavelength and hence a decrease in their momentum from the de Broglie relationship:

$$p = \frac{h}{\lambda}$$

The lower momentum is associated with a lower kinetic energy.