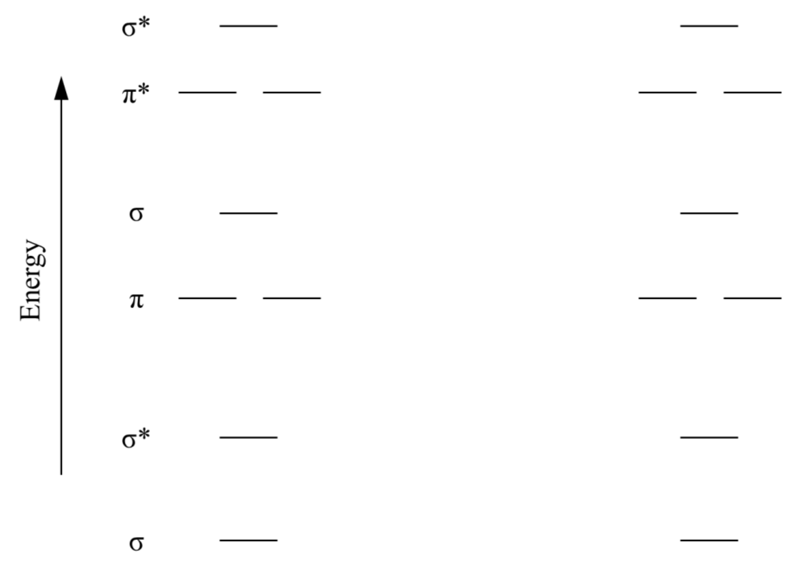
Marks
4

- 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.

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?

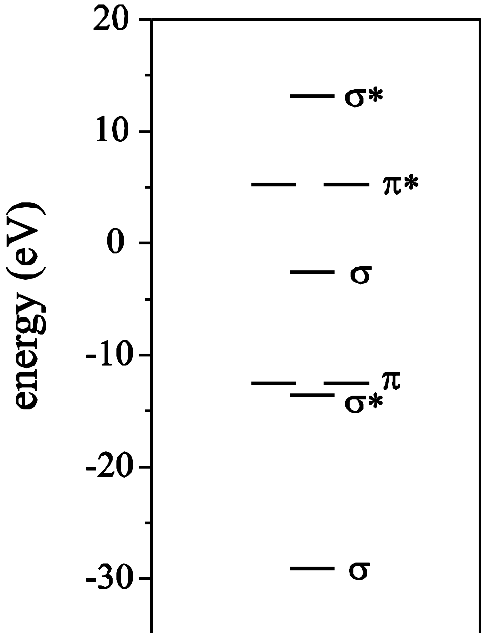
Answer:

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?

  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?

Is this state paramagnetic? Give reasoning.

What is the bond order of the ground state of C_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?

Answer:

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

Answer:

THIS QUESTION CONTINUES ON THE NEXT PAGE.

Marks
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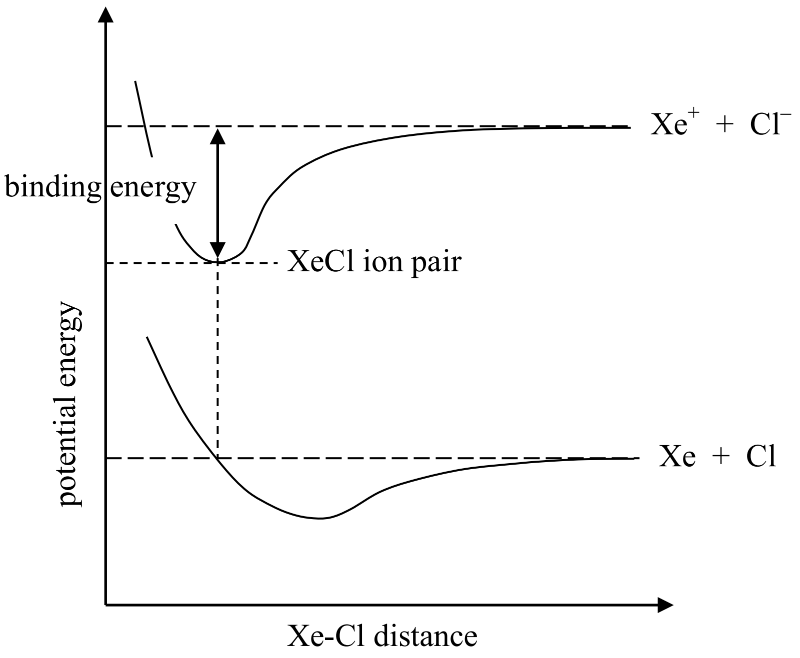


What is the binding energy (in J) of the XeCl ion pair?

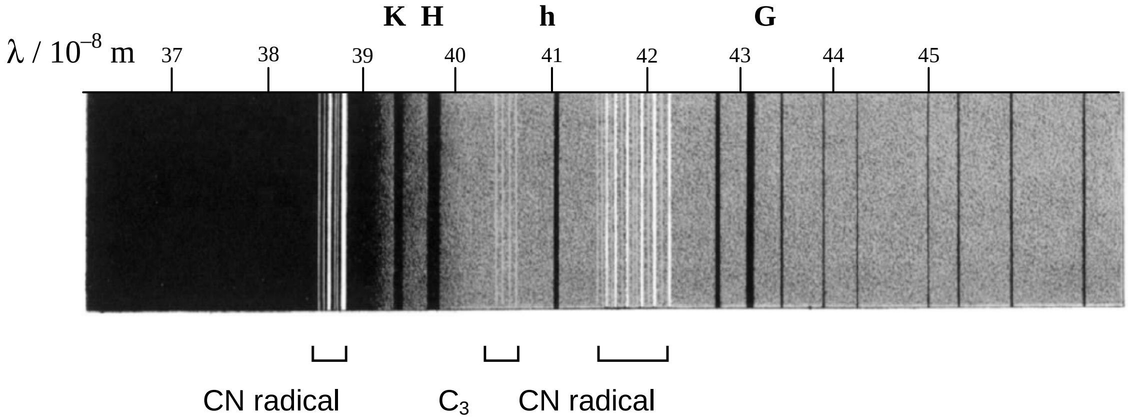
Answer:

If the binding is electrostatic, what is the approximate equilibrium bond length of XeCl if the binding energy is given by the Coulomb formula: $E = \dfrac{q_1 q_2}{4\pi\varepsilon_0 r}$?

Answer:

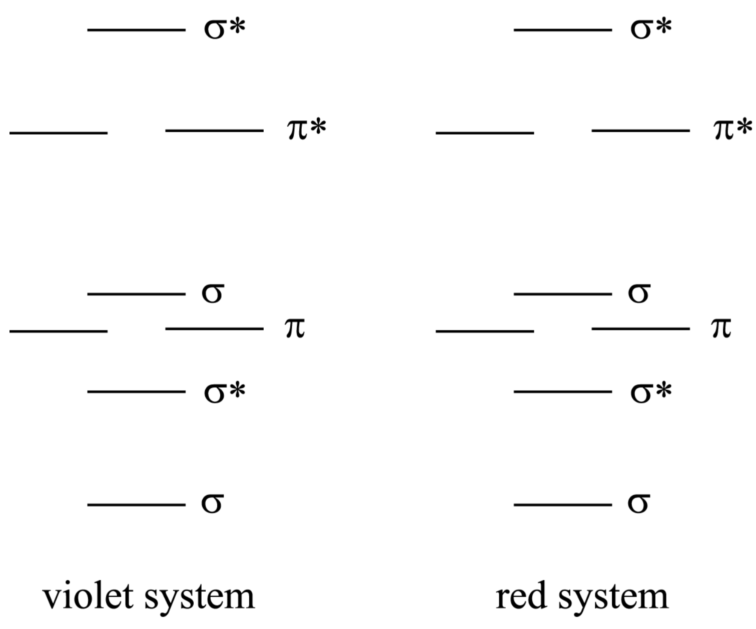
Marks
4

- 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).

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.)

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 $n = 2$.)

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.

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

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

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

- 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**

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.

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

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?

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

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-}?

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

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

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

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

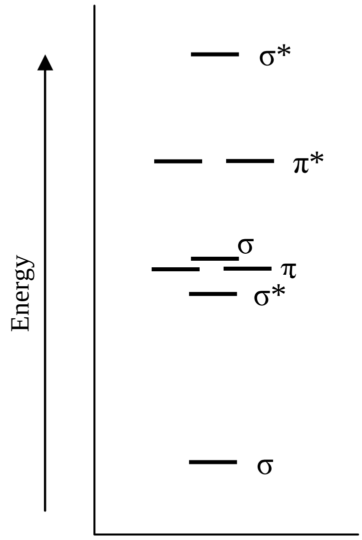
THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

- 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**

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^+.

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

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY

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?

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

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

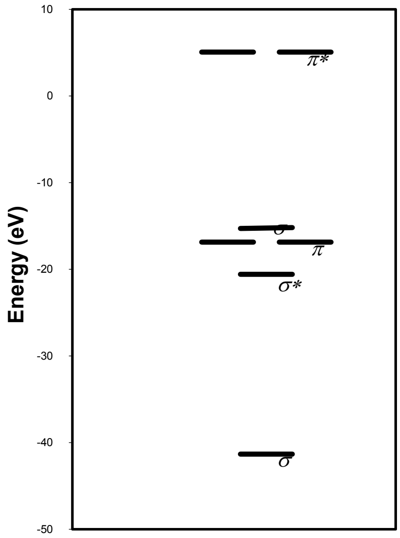
$$\sigma^2\sigma^{*2}\sigma^2\sigma^{*2}\pi^4\sigma^2$$

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

2

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