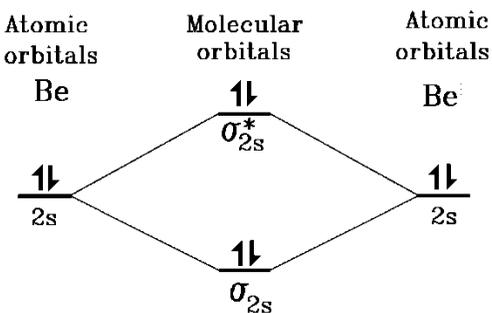


Chapter 3

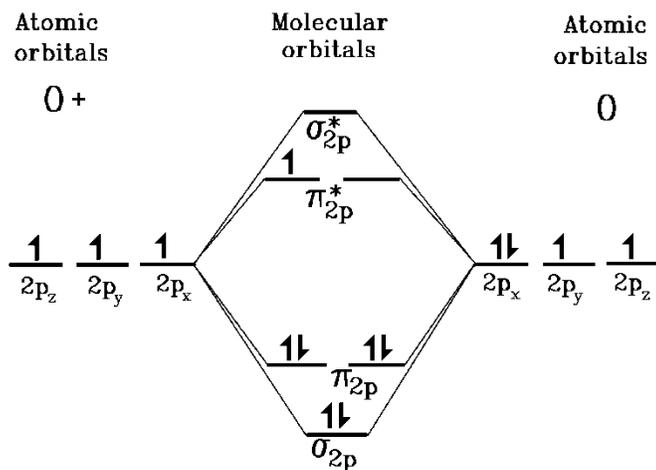
COVALENT BONDING

Exercises

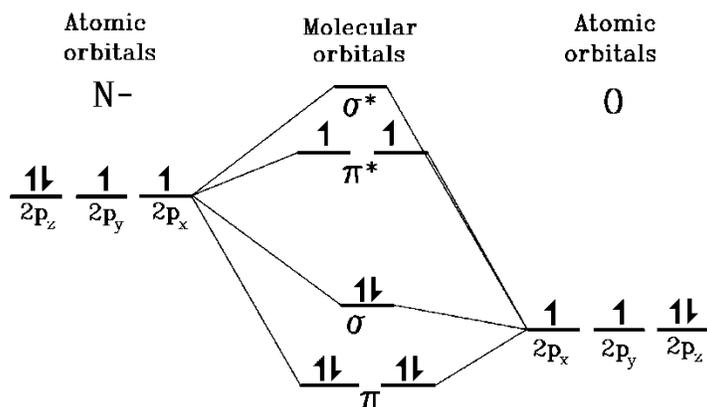
- 3.2 (a) Elements and compounds in which all atoms in a crystal are held together by covalent bonds; examples are diamond and silicon dioxide (quartz).
(b) Forces between neighboring covalent molecules, such as dispersion (London), dipole-dipole, and hydrogen bonding.
(c) Numerical value used to represent the relative attraction by an atom for a shared pair of electrons in a covalent bond.
(d) Strong attraction between a highly electronegative fluorine, oxygen, or nitrogen atom and a polar hydrogen atom on a neighboring molecule.
(e) A collection of symmetry elements that characterize a particular molecular shape and structure.
- 3.4 No, because there would be an equal number of antibonding and bonding pairs, hence a zero bond order.



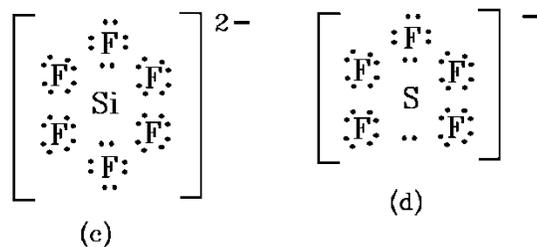
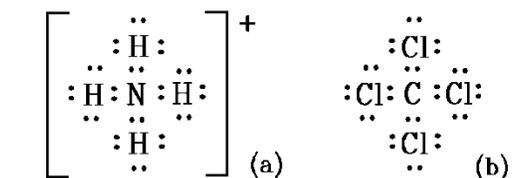
3.6 Bond order is $2\frac{1}{2}$. Electron configuration: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*)^1$.



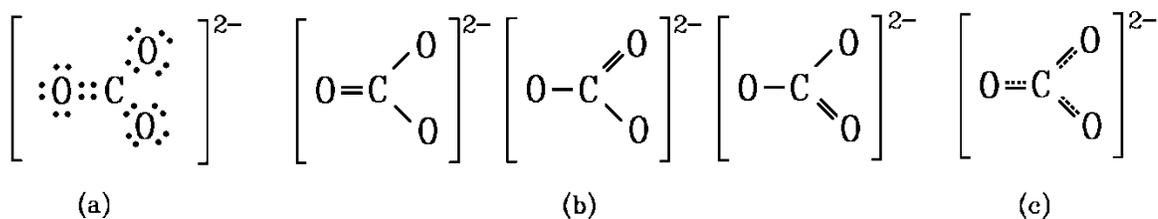
3.8 Double bond.



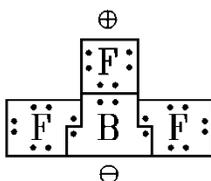
3.12 Electron-dot diagrams:



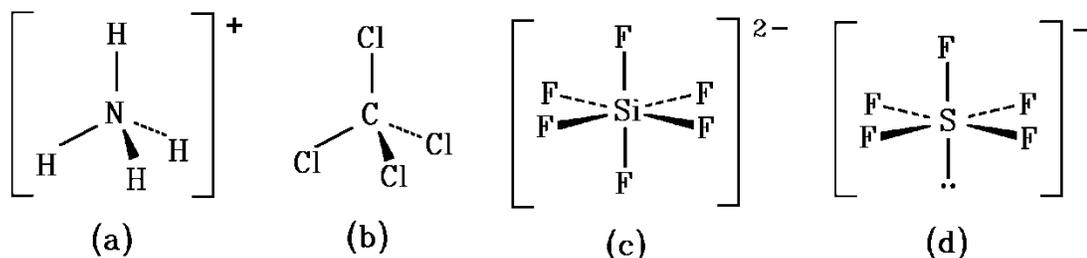
3.14 (a) Electron-dot diagram; (b) resonance structures; (c) partial bond representation.



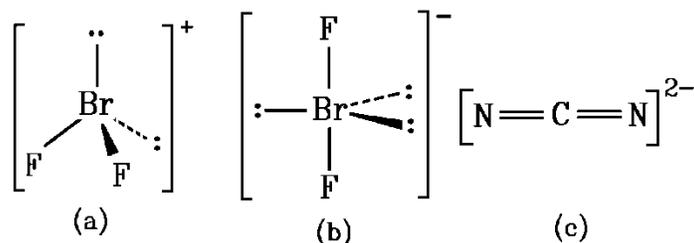
3.16 Using the single-bond structure, there are no formal charges in the bonding. The following multiple-bond representation results in a formal charge with a positive fluorine atom (highly unlikely).



- 3.18 (a) tetrahedral, tetrahedral; (b) tetrahedral, tetrahedral; (c) octahedral, octahedral; (d) octahedral, square-based pyramid.



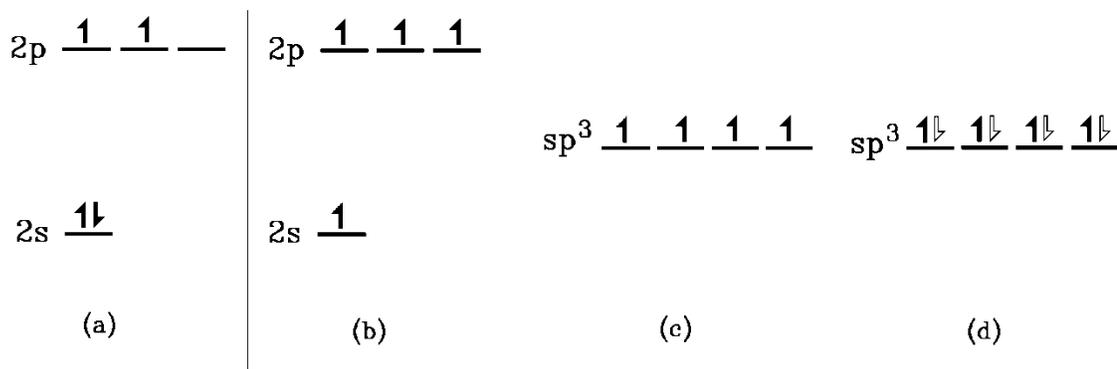
- 3.20 Linear: BrF_2^- and CN_2^- ; V-shaped: BrF_2^+ ($< 109\frac{1}{2}^\circ$).



- 3.22 Only the pentafluorosulfate, SF_5^- , ion. The equatorial S–F bonds will be bent up from the equatorial position as a result of the expansion of the lone pair beneath the plane.

- 3.24 (a) sp^3 ; (b) sp^3 ; (c) sp^3d^2 ; (d) sp^3d^2 .

- 3.26 The hybrid orbitals used would be sp^3 , providing the tetrahedral arrangement.



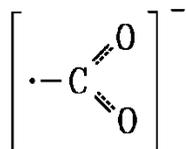
- 3.28 Iodine monochloride because it is polar; dibromine is nonpolar. The two molecules have the same number of electrons. Hence the contribution of induced dipoles (dispersion forces) would be the same in both cases, but iodine monochloride would have a permanent dipole, providing a stronger interaction.
- 3.30 Polar: the pentafluorosulfate ion; nonpolar: the ammonium ion, carbon tetrachloride, the hexafluorosilicate ion.
- 3.32 Arsine, because the greater number of electrons will lead to stronger dispersion forces than in the case of phosphine (the slightly weaker dipole-dipole interaction of arsine than that of phosphine is a less important factor).
- 3.34 One possible reason is that the chloride atom being larger than the fluoride atom “forces” the bond angle open. An alternative hybridization explanation is that the bonding in arsenic trifluoride involves more p character on the central arsenic atom, resulting in the bond angle being closer to 90° .
- 3.36 For a vibration to be infrared active, the bond must be polar and there must be a change in dipole moment of the bond during the vibration. For a vibration to be Raman active, there must be a change in polarizability of the molecule during the vibration.
- 3.38 For Figure 3.38(a), there will be one C_3 axis, three σ_v planes, one improper S_6 axis, and three S_2 axes. The molecule would have C_{3v} symmetry.
For Figure 3.38(b), there will be one C_2 axis, two σ_v planes, and one improper S_2 axis. The molecule would have C_{2v} symmetry.
- 3.40 (a) Linear. One C_∞ axis and an infinite number of σ_v planes. The point group will be $C_{\infty v}$.
(b) Tetrahedral. Four C_3 axes, three C_2 axes, and six σ_v planes. The point group will be T_d .
(c) Linear. One C_∞ axis, an infinite number of C_2 axes, an infinite number

of σ_v planes, one σ_h plane, and a center of symmetry. The point group will be $D_{\infty h}$.

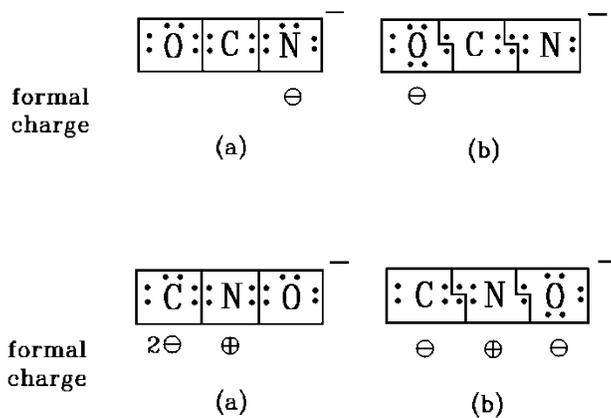
(d) V-shape. One C_2 axis and two σ_v planes. The point group will be C_{2v} .

Beyond the Basics

3.42 The ion would be V-shaped with a bond angle greater than 120° .

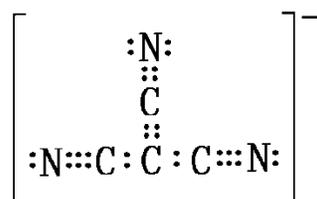
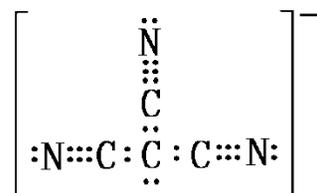


3.44 The two feasible formal charge electron arrangements for the cyanate ion, OCN^- , have only one single formal charge. The electron arrangements for the isocyanate ion, CNO^- , have at least two negative and one positive formal charge. This is a much less favorable arrangement.



3.46 The methyl radical should be distorted tetrahedral with the bond angles slightly greater than $109\frac{1}{2}^\circ$ because the single electron will occupy less space than a lone pair. The carbon free radical compound with fluorine will be planar. This will be isoelectronic with and hence isostructural with boron trifluoride. We infer that there is a π -bonding system using filled p_z orbitals on the carbon atom and an empty p_z orbital on the carbon atom.

- 3.48 The first figure shows the conventional bonding representation for the molecule. On this basis, there should be a tetrahedral arrangement of electron pairs around the central atom, resulting in a trigonal pyramidal geometry for the molecule. The linear arrangement indicates that the π -bonding system extends throughout the molecule. The second figure shows one resonance structure having a conjugated π system.



- 3.50 With 14 electrons around the xenon (eight from the xenon, one from each fluorine, plus the negative ion charge), there will be seven electron pairs around the xenon. Hence the shape should be based on the pentagonal bipyramid with five bonding pairs and two lone pairs. Because the two lone pairs will occupy the most space, the actual shape should be pentagonal planar.
- 3.52 There are $(3N-6)$ allowable vibrational modes for a nonlinear molecule. With five atoms, there will therefore be nine vibrational modes. Being square planar, the molecule possesses a center of inversion. Thus there will be no absorptions common to the infrared spectrum and the Raman spectrum.
- 3.54 In **amorphous silicon**, instead of the diamond-type tetrahedral arrays present in crystalline silicon, the atoms form a continuous random network. Not all the atoms within amorphous silicon are four-fold coordinated and it is the unoccupied sites or 'dangling bonds' that makes the surface of amorphous silicon more reactive than that of crystalline

silicon.

Nano-crystalline silicon is similar to that of amorphous silicon, but it has tiny 'islands' of crystalline structure within the amorphous network. It is sometimes called microcrystalline silicon.

Polycrystalline silicon consists solely of tiny crystalline silicon grains, separated by grain boundaries.

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