Question 1

(a) \(\text{TeF}_5^-\) 42 valence electrons, square pyramidal, \(C_{4v}\)

\(\text{ICl}_4^-\) 36 valence electrons, square planar, \(D_{4h}\)

trans-\(\text{Cl}_2\text{C}_2\text{H}_2\) planar, \(C_{2h}\)

\(\text{IO}_2\text{F}_2\) 34 valence electrons; axial fluorines, equatorial O's with 1 eq. lone pair, \(C_{2v}\)

\(\text{IF}_7\) pentagonal bipyramid, \(D_{5h}\)

\(\text{ICl}_2^+\) 20 valence electrons, bent, \(C_{2v}\)

(b) \(\text{B}_8\text{S}_{16}\) \(D_{4h}\)  

\((\text{NSCl})_3\) \(C_{3v}\)  

\((\text{Te}_6)^{4+}\) \(D_{3h}\)

(f) (i) Re, W, Sb, At  

(ii) Lanthanum, La  

(iii) Hg, or Br  

(iv) Indium  

(v) Astatine, At

(g) asymmetric—having no symmetry other than E  
dissymmetric—lacking an \(S_n\) axis

(h) Many possible answers. A molecule is chiral if it lacks an \(S_n\) axis—this is true in point groups \(C_1\), \(C_n\), and \(D_n\).  

\(C_1\), for example Si(H)(F)(Cl)(Br)  

\(D_3\), for example \([\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^3+\) as seen in class  

\(C_3\), for example \([\text{Cr}([\text{SCH}_2\text{CH}_2\text{NH}_2)_3]^3+\) as in the point group lab

(i) Again, many possible answers, including point groups \(C_1\), \(C_5\), \(C_n\), \(C_{nv}\). For example: \(C_{2v}\), H\(_2\)O \(C_{3v}\), NH\(_3\) \(C_{00v}\), HCl

Question 2

(a) \(\text{XeF}_4\) and \(\text{IF}_4^-\) are isoelectronic (36 valence electrons) but since Xe has larger nuclear charge than I, its F ligands should feel increased electrostatic attraction to the nucleus, hence we predict shorter Xe-F bonds.

(b) The nuclear charge of N is greater than that of C. Hence the N electrons are more tightly held to the nucleus and less easy to ionize.

(c) These are all isoelectronic (8 valence electrons) so sizes are controlled by nuclear charge (the bigger this is the more the electrons are pulled in to the nucleus and the smaller the size) so \(\text{N}^{3-} > \text{O}^{2-} > \text{Ne} > \text{Na}^+\)

(d) \(\text{H}_2\text{F}^+\) is isoelectronic with water, so it is bent, \(C_{2v}\), for the same reasons.

(e) Because of the large radial extent of the Si p orbitals, there is poor overlap of the \(\pi\) symmetry orbitals at the bond distance required by the size of the Si atoms and by the required sigma bonding. Therefore the \(\pi\) interaction which gives a double bond is weak and the \(\text{Si}_2\text{H}_4\) molecule oligomerizes. This is not a problem for smaller C atoms, where the needed overlap works fine.
Note however that the Si=Si bond can be protected by bulky groups as in the stable Mes₂Si=SiMes₂ \((\text{Mes} = 2,4,6-\text{Me}_3\text{C}_6\text{H}_2)\) 

(f)

Question 3
(a) The CO HOMO is a sigma antibonding MO, polarized on C. It looks like this

![CO HOMO](image1)

(c) Because of the polarization above, the 1st ionization energy of CO should be similar to that of C. We can crudely compare this to the first I. E. of N₂, which can be modelled (again crudely) by N. From nuclear charge considerations C should be easier to ionize.

(d) CF has 11 valence electrons. The one removed to make CF⁺ comes from the antibonding 2π MO, so the cation should have a stronger bond than the neutral (bond orders are 3 and 2.5 respectively)

(e) This is the same as the CF problem, again 11 and 10 valence electrons; removing the electron from NO's antibonding 2π MO is favorable energetically.

Question 4
(a) The HOMO of Cl₂ is the antibonding 2πg MO; removing an electron from this orbital will increase the Cl-Cl bond strength in the cation relative to the neutral, thus giving a stronger shorter bond.

(b) This question depends on the LUMO of these molecules, where the new electron will go. For O₂ the LUMO is the antibonding 2πg, so adding an electron is unfavorable, but for C₂ the LUMO is the bonding 3σg MO and adding an electron is more favorable.

(c) Be₂ with 4 valence electrons would have 2 electrons in a bonding MO and 2 in an antibonding MO, for a bond order of 0. Therefore you wouldn't expect to observe it.

(d) Removing an electron from the O₂ HOMO (2πg, antibonding) strengthens the O-O bond and leads to a shorter O-O distance. However removing an electron...
from the N₂ HOMO (3σg, bonding) weakens the N-N bond and increases the N-N distance.

(e) NH₃ has 8 valence electrons. Starting in the C₃ᵥ geometry, its 1st excited state will have the electron configuration (1a₁)²(1e)⁴(2a₁)¹(3a₁)¹. The HOMO, 3a₁, will be stabilized in the planar geometry (according to the Walsh diagram) so the 1st excited state should be planar.

(f) Umbrella inversion in ammonia interconverts 2 pyramidal structures; presumably the intermediate is planar. This is consistent with the MO description in part (e)--excitation of the C₃ᵥ ground state leads to a D₃h intermediate which can relax back to the pyramidal ground state.

(g) CH₃⁻ is like NH₃ with 8 valence electrons so it should be pyramidal and its HOMO is 2a₁ as shown on p. 11 of the exam. As expected from this it acts as a carbon-centered nucleophile/Lewis base in organic reactions.

(h) LiH₃ has 4 valence electrons so the Walsh diagram predicts the planar geometry to stabilize its 1e HOMO.

(i) To predict which AH₃ molecules will distort from trigonal planar D₃h to T-shaped C₂ᵥ geometry, we find from the Walsh diagram which orbitals will be stabilized by the geometry change (in C₂ᵥ these are 1b₂, 3a₁, and 4a₁).

Then find the right number of valence electrons for AH₃ to make these the HOMO (that is 3 or 4 for 1b₂; 9 or 10 for 3a₁; or 11 or 12 for 4a₁).

Finally count valence electrons to say what A is:
A needs 0 valence electrons for AH₃ to have 3, so that's impossible
A needs 1 to make 4 total, so A=Li (as hinted in part (h) above).
A needs 6 to make 9 total, so A = O
A needs 7 to make 10 total, so A = F
A needs 8 to make 11 total, so A = Ne
A needs 9 to make 12 total, but that's also impossible
Conclusion: AH₃ where A is Li, O, F, or Ne.