## Chemistry 2000 Spring 2019 Test 1 Version A SOLUTIONS

1. (a)

2.

(a)



- (b) According to valence-bond theory, the hybridization of carbon  $\mathbf{1}$  is  $\underline{\mathbf{sp}}^2$  while the hybridization of carbon  $\mathbf{2}$  is  $\mathbf{sp}^3$ .
- (c) According to valence-bond theory, the carbon-oxygen sigma bond is made by overlapping a carbon  $sp^2$  orbital with an oxygen 2p orbital.



- (b) To use a p-n junction as a solar (photovoltaic) cell, the  $\underline{\mathbf{n}}$  side of the junction is exposed to light. This causes electrons to be transferred from the <u>valence</u> band to the <u>conduction</u> band. These electrons can then flow to the  $\underline{\mathbf{p}}$  side of the junction where they can be collected to power an external circuit.
- 3. Yes, nitric oxide is a greenhouse gas. It has a dipole moment, and this dipole moment will change during a vibration, so it can absorb IR radiation.



Note that there is more bonding than antibonding character (bond order  $=\frac{1}{2}$ ), so this molecule could exist. Like many other exotic molecules we have seen this term, this one is found in space and can be made in certain experiments.

5.  $O_2$  has 12 valence electrons, and s-p mixing is (relatively) negligible in this molecule. The MO diagram is therefore as follows:



The Lewis diagram of oxygen is of course

The MO diagram predicts a bond order of

bond order 
$$=\frac{1}{2} \{ \text{bonding} - \text{anti} \} = \frac{1}{2}(8-4) = 2.$$

This agrees with the Lewis diagram.

All the electrons are paired in the Lewis diagram, but not in the MO diagram. Indeed, oxygen is known to be paramagnetic.

Our rules for counting  $\pi$  electrons in Lewis diagrams would indicate that O<sub>2</sub> has just 2  $\pi$  electrons, but the MO diagram shows a total of 6. Interestingly though, the  $\pi$  bond orders agree (1 in either case).

There is not a clear correspondence between the lone pairs and the MO diagram.

6. (a)



(b) From the Lewis diagram, we count 4  $\pi$  electrons (two in double bond, one lone pair). The filled MO diagram is therefore the following:



(d) A Lewis acid accepts electrons into its LUMO, here the  $3\pi^*$ . The  $3\pi^*$  is closest

in energy to the sulfur 3p orbital, so it will have a larger contribution from this orbital than from the oxygen 2p orbitals. (Note that the pictures of the  $3\pi^*$  above agree with this reasoning.) This would mean that SO<sub>2</sub> would preferentially accept electrons at the sulfur atom.

7. The two lowest-energy peaks correspond to ionization of  $H_2$  to the two lowest vibrational levels of the molecular ion  $H_2^+$ . Reading off the graph, we find these ionization energies to be approximately

IE<sub>1</sub> 
$$\approx 126700 \,\mathrm{cm}^{-1}$$
,  
and IE<sub>2</sub>  $\approx 128800 \,\mathrm{cm}^{-1}$ 

The difference between these two values is the vibrational frequency of  $H_2^+$ :

$$\tilde{\nu}(\mathrm{H}_2^+) \approx 128\,800 - 126\,700\,\mathrm{cm}^{-1} = 2100\,\mathrm{cm}^{-1}.$$

The ground-state electronic configuration of  $H_2$  is  $(1\sigma)^2$ . Ionizing  $H_2$  therefore leaves just one electron in a bonding orbital, so it weakens the bond, which is reflected in the decreased vibrational frequency of the ion. Note, in fact, that the vibrational frequency of  $H_2^+$  is almost exactly half the vibrational frequency of  $H_2$ , which makes sense given that, in this very simple molecule, we have lost exactly half of the bonding character by removing an electron from the  $1\sigma$  orbital.