CHEMISTRY 3BB3 1999/2000

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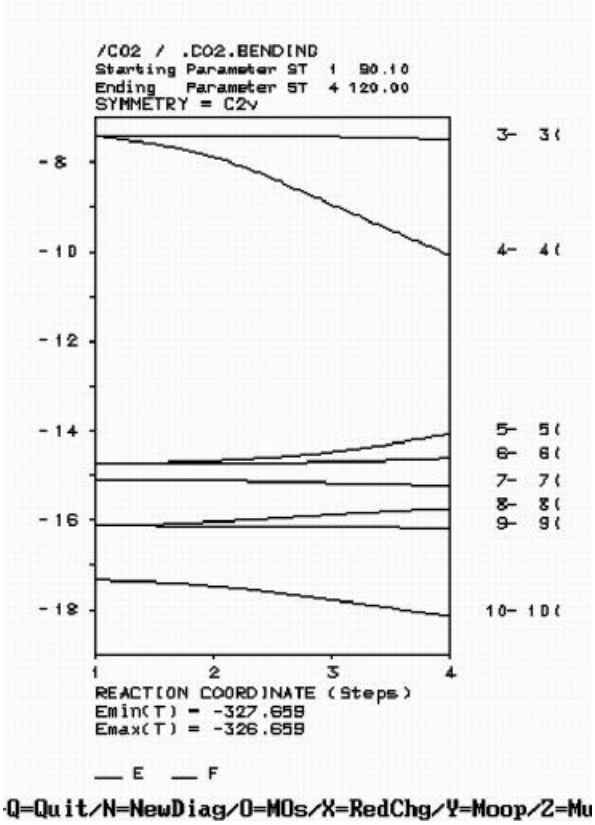
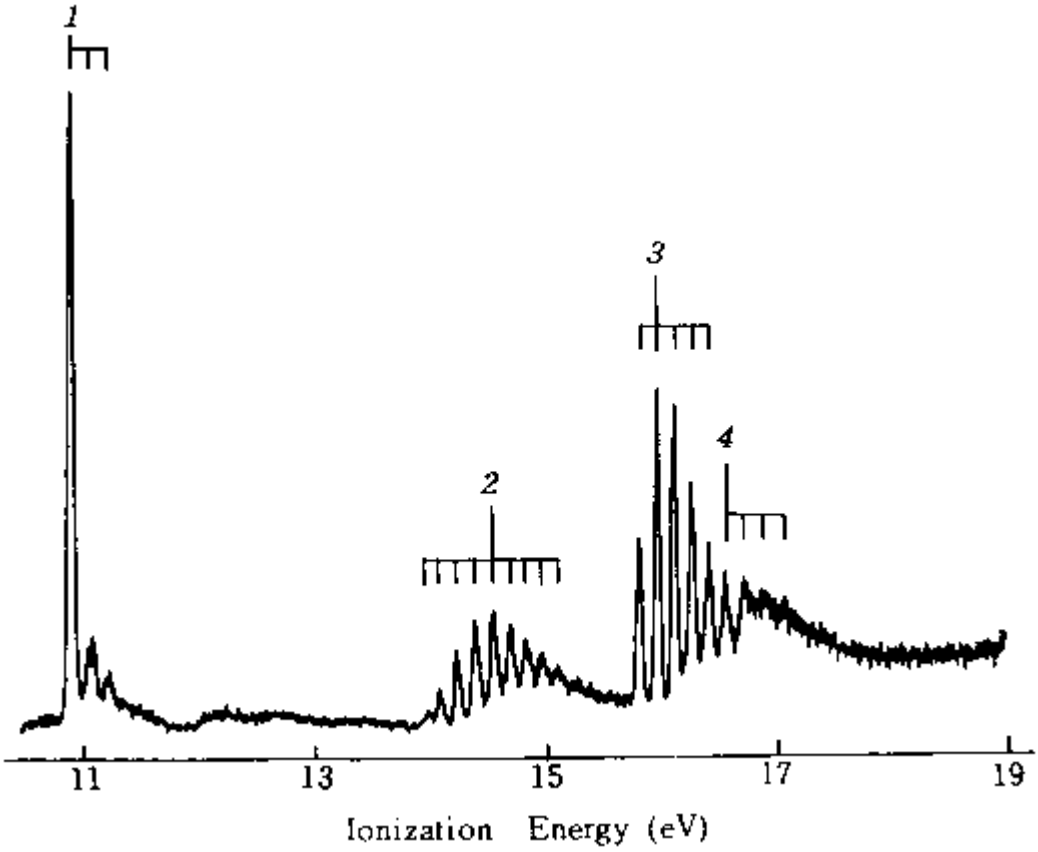
SOLUTIONS TO ASSIGNMENT 7

1. Below is a Walsh diagram, showing the effect of bending on the orbitals of a CO_2 molecule. Two valence orbitals are not shown, since they have much lower energy and do not change with the O-C-O angle. Use this diagram to rationalize the geometry of CO_2. Do you predict that the first electronically excited state is linear or bent? Justify your answer.



Remember we calculate the total energy as the sum of all the energies of the electtrons in their orbitals. CO_2 has 16 valence electrons, but 4 are in the orbitals not shown in the diagram, so we have 12 electrons to put into the orbitals shown. They will therefore go into the orbitals labeled 10, 9, 8, 7, 6 and 5. Since 5, 6 and 8 increase in energy as the molecule bends, it is not surprising that the molecule is linear. However, in the first excited electronic state, there is one electron in orbital 5, and one in orbital 4. Orbital 4 is strongly stabilized by the bending, so we have lost some of the resistance to bending (only one electron in 5, rather than two), and gained considerable energy from the electron in 4. Therefore, the excited state will be bent.



2. Above is the photoelectron spectrum of formaldehyde. The ionization potentials (in order of increasing IP) correspond to ionization from a b_2, a b_1, an a_1 and a b_2 orbital. Classify the orbitals according to whether they are σ or π symmetry. Also, explain why some peaks have pronounced vibrational structure and some do not. Which vibration of the molecule does this vibrational structure belong to?

In a Lewis structure, there are three σ bonds (two C-H bonds and one C-O), a π bond, and two oxygen lone pairs. The b_2 and b_1 orbitals correspond, respectively, to an in-plane lone pair, mainly centred on an oxygen p orbital, and the carbon-oxygen π bond (remember, I prefer the convention for the C_{2v} point group that has the out-of-plane orbitals as b_1). The other a_1 corresponds to a combination of the σ bonds, and the other (formal) oxygen lone pair, and b_2 is the antisymmetric combination of the C-H bonds. Vibrational structure occurs if an electron is removed from an orbital strongly involved in bonding. This means that the positive ion has less bonding, so the geometry is quite different from the neutral. The Franck-Condon principle (see Harris and Bertolucci), then predicts vibrational structure. In this case, only the b_2 oxygen lone pair does not contribute to bonding.