3.2

From table 3.5

\[
\begin{align*}
\text{Si-O} & \quad 466 \text{ (KJ/mole)} \\
\text{Si-H} & \quad 318 \text{ (KJ/mole)} \\
\text{Si-Si} & \quad 266 \text{ (KJ/mole)} \\
\end{align*}
\]

\[
\begin{align*}
\text{C-H} & \quad 412 \text{ (KJ/mole)} \\
\text{C-O} & \quad 360 \text{ (KJ/mole)} \\
\text{C-C} & \quad 348 \text{ (KJ/mole)}
\end{align*}
\]

Si-O bonds have the highest enthalpy and therefore will be the most stable. Of the C-X bonds, C-H is the most stable.

3.7

UV photo electron spectrum of CO

\[
\begin{align*}
\text{UV photo electron spectrum of CO}
\end{align*}
\]
The author probably wanted something like this: The photoelectron spectra of SO is much more complicated. See the article (next 2 pages) for the actual photoelectron spectra of SO.
THE HIGH RESOLUTION PHOTOELECTRON SPECTRA
OF TRANSIENT SPECIES: SULPHUR MONOXIDE

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The first vacuum ultraviolet photoelectron spectrum of a transient free radical is reported. This enabled accurate measurements to be made of at least two ionization potentials of SO(3\Sigma^-). The results are compared with previous data from other techniques.

In recent publications [1, 2] we have reported the detection of atoms and electronically and vibrationally excited molecules by means of high resolution vacuum ultraviolet photoelectron spectroscopy (P.E.S.). We now wish to make a preliminary report of the first P.E. spectrum of a transient free radical.

The spectrometer was the same as that described previously and was equipped with a HeI 584 Å (21.21 eV) dc light source. Sulphur monoxide was produced by several methods including electrodeless discharge of inert gas/SO₂ mixtures and by the reaction of atomic oxygen and carbon disulphide.

Using the above techniques it was possible to locate several bands in the P.E. spectrum, which could be attributed to ionization of SO(3\Sigma^-). The ionization potentials were found to be 10.34 ± 0.02 eV and 14.86 ± 0.02 eV with the possibility of a third one at ca. 18 eV. All these bands together with the previously established peaks from atomic oxygen [2] were present in the P.E. spectrum of the SO₂/argon discharge products as shown in fig. 1 and the production of the same bands from the atomic oxygen/carbon disulphide reaction is clear evidence that they are due to photolization of sulphur monoxide. The P.E. spectrum of sulphur trioxide, the only possible reasonable alternative, was obtained in separate experiments and found to be entirely different.

![Fig. 1. Complete photoelectron spectrum of the products of SO₂/rare gas discharge. Ordinate: counts/sec, abscissa: ionization potential (eV).](image-url)
Conclusive proof of the assignment was given by the fact that addition of nitrogen dioxide to the products of the inert gas/SO₂ discharge caused the intensity of the bands to decrease rapidly. This is due to the fast reaction [5]:

$$\text{SO} + \text{NO}_2 \rightarrow \text{SO}_2 + \text{NO}. \quad (1)$$

A high resolution spectrum of the band arising from the lowest ionization potential of SO is shown in fig. 2. This is assigned to the SO($^3\Sigma^-$) → SO⁺($^2\Pi$) transition. The vibrational spacing is approximately 0.15 eV ($\approx 1210 \text{ cm}^{-1}$) compared with the ground state value of 1111 cm⁻¹ [4]. These figures are in line with the corresponding transition in molecular oxygen of $\approx 1890 \text{ cm}^{-1}$ and 1556 cm⁻¹ for the ion and molecule respectively [5]. The increase in vibrational frequency is as expected for removal of an electron from an antibonding orbital but only a small bond length change occurs on photolization as can be seen from fig. 1 in that the adiabatic and vertical ionization potentials coincide. This coincidence is not observed in the molecular oxygen case and hence a relatively smaller bond length change is indicated in the SO case.

The second positively identified band corresponding to a higher ionization potential of SO is at 14.96 eV and has the same contour as that of fig. 1. However, the vibrational spacing of $\approx 0.12 \text{ eV (} \approx 970 \text{ cm}^{-1})$ is smaller and is consistent with ionization involving an electron in a bonding orbital. Since to the best of our knowledge no state of SO⁺ has yet been identified by any spectroscopic technique, it is not feasible to make positive identification at this time although one may draw a comparison with the $^4\Pi_u$ and $^4\Sigma^-$ states of O₂ [6].

It is interesting to compare the value of the lowest ionization potential obtained in this work with previous data from other techniques. Values have ranged from 12.5 ± 0.3 eV [6], < 11.0 eV [7] to a more recent figure of 10.21 eV [8] which was calculated indirectly from photolization studies. The P.E.S. technique is capable of giving results of comparatively high accuracy and has particular potential value when applied to radicals because of the paucity of reliable data from other methods. There is the probability that in favourable cases such as SO one can build up an energy level diagram for the positive ion in a similar way as is now available for O₂ [5].

Attempts to obtain the P.E. spectrum of SO($^\Delta_g$) have so far been unsuccessful. This would be of particular value because not only would it establish the energy difference between the two electronic states of sulphur monoxide but it should also lead to new states of SO analogous to those we have recently found for O₂ from photolization of O₂($^\Delta_g$) [9].

The experimental work on both systems is continuing and attempts are being made to calculate approximate Franck-Condon factors and energies of states of the ion.

We wish to thank the Science Research Council for their generous support of this work in the form of equipment grants and a Studentship (to D.J.S.).

REFERENCES

Orbitals:

1σ

2σ

1π

F - H

H

H
3.10
a) semiconductor
b) conductor

3.11

Walsh diagram for $XH_2$

\[ \text{Linear} \quad \text{Bent} \]

$\Delta E_b < \Delta E_L$ so first excited state will be bent

3.12

\[ \rho = \frac{1}{e^{\Delta E/kT} + 1} \]

$\Delta E = 1.14 \text{ eV}$

$K = 8.613 \times 10^{-5} \text{ eV/K}$

@ $T = 373 K \quad \rho = 7.971 \times 10^{-6}$

@ $T = 273 K \quad \rho = 2.965 \times 10^{-11}$
Looking at figure 3.34, the HOMO are non-bonding orbitals and the LUMO are anti-bonding orbitals. By stretching the 6 F atoms equally, the LUMO will drop in energy and the HOMO will remain the same. The HOMO-LUMO gap will decrease in energy.

Additional problems set #1

3) \[ \text{SeF}_2 \text{O}_2 \text{SeF}_2 \text{ original pyramidal} \]

\[ \text{SnCl} \]

\[ \text{bent} \]

\[ \text{I}_3^- \text{ linear} \]

\[ \text{I}_2 \text{O}_2 \text{F}_2^- \text{ See saw} \]
Problem 6:

Walsh diagrams predict the degree of bending w/ the # of valence electrons present.

BH₂ favors a bend but not a strong one b/c the Homo is half filled. The difference in angle between CH₂ + SiH₂ involves the promotion energy from a singlet to triplet state in the molecule. If they were singlets, their angles would tend toward 90°. 7-8 e⁻ in NH₂ + OH₂ have similar angles b/c you are filling up a non-bonding orbital. For PH₂ + SH₂ + AlH₂ the molecules are more bent b/c the orbitals have more p-character b/c the s-orbital is more contracted.

YeF₂ is linear b/c it has the least amount of antibonding Homo.
Problem Set 2
Due September 22, 2004

For the purposes of self-study, you should be able to do any of the Exercises on p. 140 of your text.

Problems from SA, Chapter 4, p. 141: 4.1, 4.2, 4.3, 4.5, 4.6, 4.7, 4.9, 4.10

Additional problems:

1. Character tables for selected point groups are given in Appendix 3 of your text. Of those point groups, identify all for which a molecule can have a permanent dipole moment.

2. Determine the symmetry elements and assign the point groups for (a) NH₂Cl, (b) CO₃²⁻, (c) SiF₄, (d) HCN, (e) SiFCIBr₁, (f) BF₄⁻.

3. For each of the molecules in problem 2, determine the number of vibrational degrees of freedom.

4. Assign point group symmetries to the molecules and shapes depicted here and on the next page.

(H-atoms are above BO₃ plane)
Problem set #2
ch 4 pg 141

4.1) $\tilde{O} = I \quad F \quad \text{highest E}$

$\tilde{O} = I \quad F \quad \text{second highest}$

$F - I \quad F \quad \text{lowest in energy}$

because the distance between $\pi$ bonds is maximized.

4,2) a) yes, there are $E$ (double degenerate) states and $T$ (triple degenerate) states for the $Td$ point group.

b) no, there are no degenerate states possible.
4.3

a.) Point group is $D_{3h}$

\[ \frac{1}{\sqrt{3}} (\phi_{1sa} + \phi_{15b} + \phi_{1sc}) - \text{Hydrogen} \]

$\phi_{2sc}$ - Carbon
only 2s.

Hydrogen
\[ \frac{1}{\sqrt{6}} (2\phi_{1s3} - \phi_{1s1} - \phi_{1s2}) \]
\[ \frac{1}{\sqrt{2}} (\phi_{1s1} - \phi_{1s2}) \]

Carbon: $\phi_{2p_y}$ and $\phi_{2p_x}$

Carbon $\phi_{2p_z}$
No Hydrogen
$a_2''$ linear combination

The unoccupied orbitals above the $a_2''$ are strongly antibonding so the carbon will not be hypervalent.

$D_{3h} \rightarrow C_{3v}$
4.6) a) \[ \begin{array}{c}
H \quad \text{H}_3\text{O}^+ \\
B \quad \text{O}^- \\
H \\
\end{array} \]

b) \[ \begin{array}{c}
\text{H} \\
\text{O}^- \\
\text{H} \\
\text{B} \\
\text{H} \\
\text{C}_3 \quad \text{chiral} \end{array} \]
Additional problems

1) $C_1, C_3, C_2, C_1, C_4, C_{2v}, C_{3v}, C_{4v}, C_{5v}, C_{6v}, C_{3m}$

2) a) $E, \sigma_c, C_5$

   $3N - 6 = 6$

   $E_1, C_3, O_h, 3\sigma_v, i, 3C_2$

   $D_{3h}$

b) $3N - 6 = 6$

   $3N - 6 = q$
d) $H - C = \mathbb{N}$, $E, C_\infty$, $\infty$ $\Rightarrow C_\infty$

$3N - 5 = 4$

---

3) see above

---

e) $I_{\infty} D_4$

$E \quad C_1$

$3N - 6 = 9$

---

f) $D_4$

$3N - 6 = 9$