Problem 14 (with suggested solution)
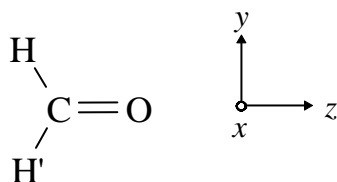
In its electronic groundstate, formaldehyde (H_2CO) is a planar molecule with C_{2v} symmetry:

$$
\begin{array}{c}
H \\
\quad \diagdown \\
\qquad C = O \\
\quad \diagup \\
H'
\end{array}
\qquad
\begin{array}{c}
y \\
\uparrow \\
\circ \!\!\longrightarrow z \\
x
\end{array}
$$

a) What are the symmetries (irreducible representations) of the 10 molecular orbitals (MOs) that can be constructed on the basis of the 10 valence atomic orbitals H(1s), H'(1s), C(2s, $2p_x$, $2p_y$, $2p_z$) and O(2s, $2p_x$, $2p_y$, $2p_z$)? Hint: Determine the characters of the reducible representation Γ based on the 10 atomic orbitals, and decompose Γ to irreducible representations.
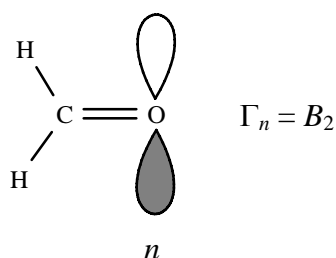
ANSWER:

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}'_v(yz)$	$h = 4$
A_1	1	1	1	1	z
A_2	1	1	−1	−1	R_z
B_1	1	−1	1	−1	x, R_y
B_2	1	−1	−1	1	y, R_x
Γ	10	0	4	6	n_i:
$\Gamma \times A_1$	10	0	4	6	$20/4 = 5$
$\Gamma \times A_2$	10	0	−4	−6	0
$\Gamma \times B_1$	10	0	4	−6	$8/4 = 2$
$\Gamma \times B_2$	10	0	−4	6	$12/4 = 3$

Check: $\sum_i n_i = 5 + 0 + 2 + 3 = 10$
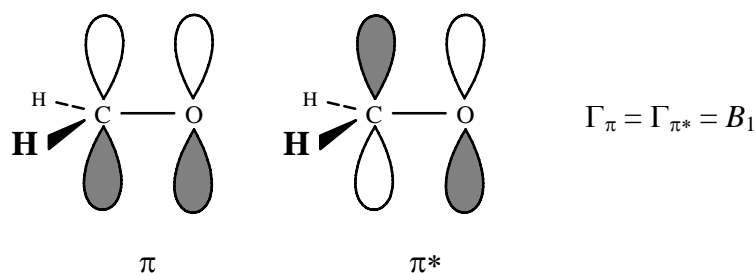
$$\Rightarrow \quad \Gamma = 5A_1 + 2B_1 + 3B_2$$

b) The highest occupied MO in the groundstate (HOMO) can be characterized as a "lone pair" orbital, largely localized in the $2p_y$ orbital of the oxygen atom. This MO contributes very little to the chemical bonding in the molecule; such an orbital is often called an n orbital ("n" for "non-bonding"). What is the symmetry Γ_n of formaldehydes n orbital?
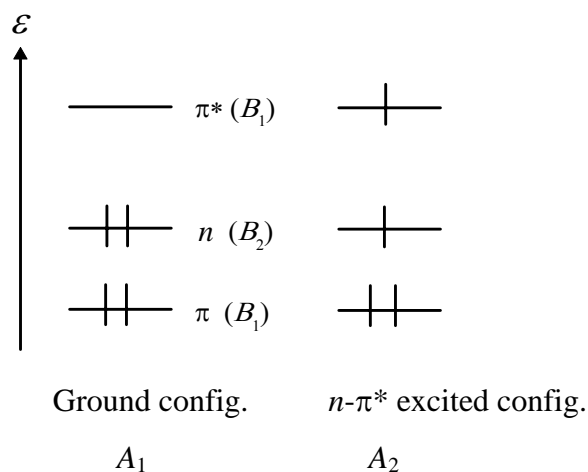
ANSWER:

$\Gamma_n = B_2$

n

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c) The second highest MO (SHOMO) and the lowest unoccupied MO (LUMO) are the π and $\pi*$ MOs, respectively, of the C=O double bond. Indicate the shape of these orbitals (you may compute them with the Hückel model, see Problem 12). What are their symmetries?

ANSWER:

$$\Gamma_\pi = \Gamma_{\pi*} = B_1$$

d) The lowest electronic transition of formaldehyde corresponds to the HOMO $\rightarrow$ LUMO transition, $n \rightarrow \pi*$. What is the symmetry of the excited state?

ANSWER:

Ground config. $n\text{-}\pi*$ excited config.
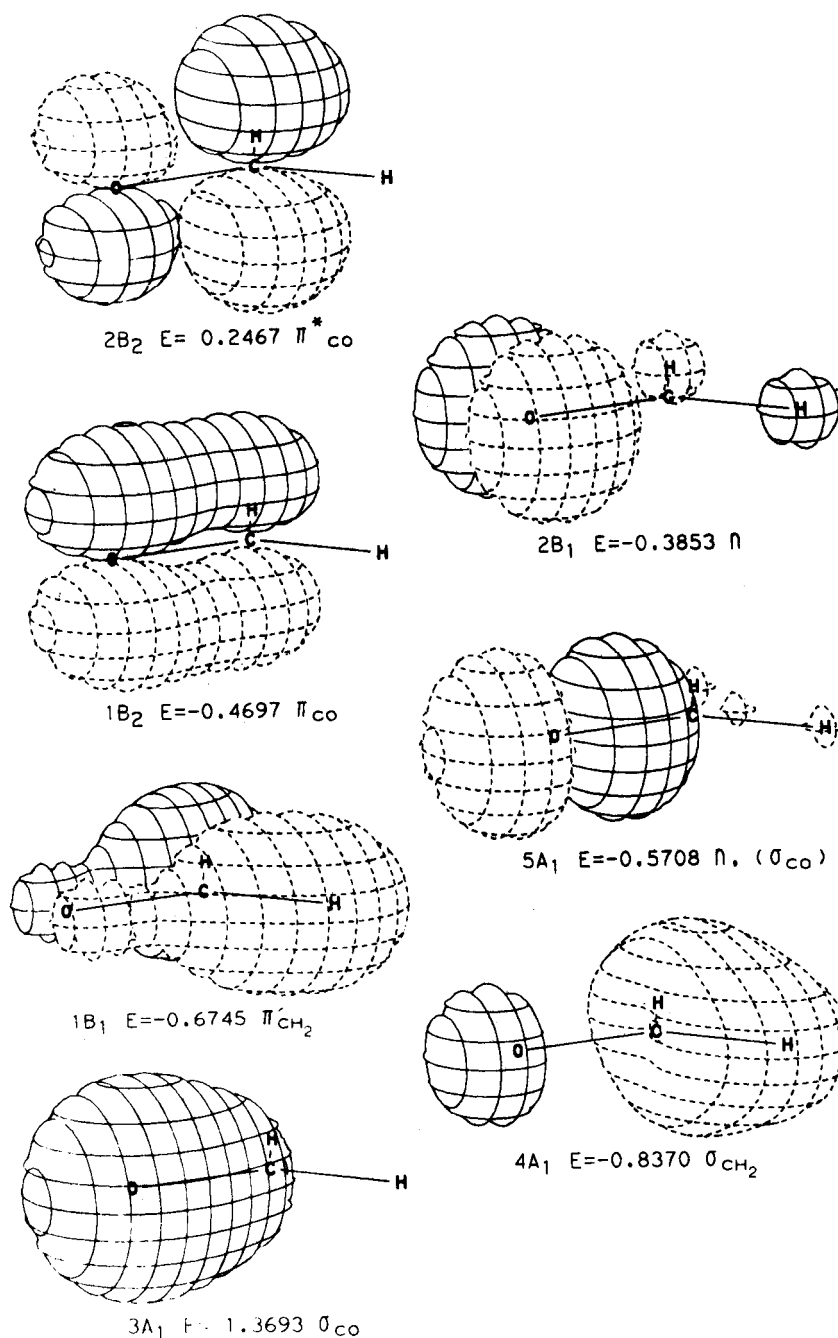
A_1 A_2

The symmetry of the $n\text{-}\pi*$ excited configuration is $B_2 \times B_1 = A_2$

e) This transition is observed as an extremely weak absorption band near 30000 cm^{-1}. Why is the transition so weak?

ANSWER: Transition from the ground state, $A_1 \rightarrow A_2$, is forbidden by symmetry!

Supplementary material is given below!

$2B_2$ E= 0.2467 π^*_{CO}

$2B_1$ E=-0.3853 n

$1B_2$ E=-0.4697 π_{CO}

$5A_1$ E=-0.5708 n, (σ_{CO})

$1B_1$ E=-0.6745 π'_{CH_2}

$4A_1$ E=-0.8370 σ_{CH_2}

$3A_1$ E= 1.3693 σ_{CO}

Drawings of some of the MOs of formaldehyde computed with *ab initio* Hartree-Fock theory (W.L. Jorgensen & L. Salem: "The Organic Chemist's Book of Orbitals"). – Note that relative to the usage in Problem 14, the symmetry labels B_1 and B_2 are reversed. This is because the authors have reversed the labeling of the coordinate axes x and y. It is important that the definition of the coordinate system is given; otherwise the designation of symmetry labels may become ambiguous. – The numbers in front of the symmetry labels indicate the energy ordering of MOs with the same symmetry: $1A_1$, $2A_1$, $3A_1$, etc. The numbering starts with the inner orbitals, *i.e.*, the MOs based on C(1s) and O(1s), which are not considered in Problem 14.
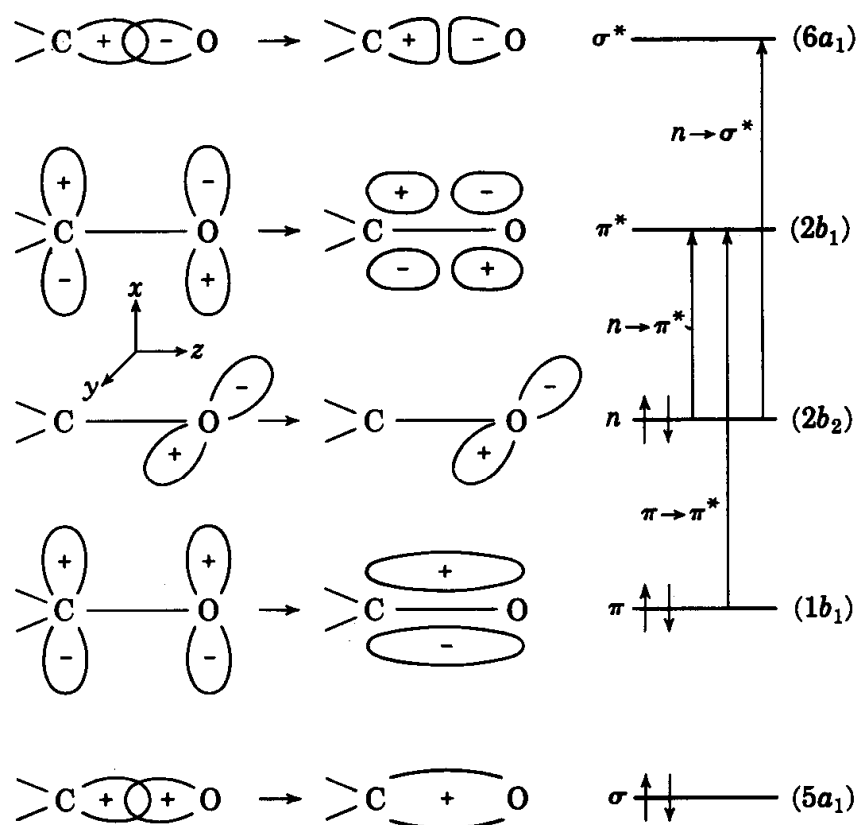
Fig. 10.21. Localized MO's and electronic transitions for the carbonyl group. The symmetry species on the far right apply to the formaldehyde molecule.

Qualitative representation of some of the MOs of formaldehyde (G. W. King: "Spectroscopy and Molecular Structure"). AO basis orbitals are indicated to the left, and the resulting MOs are given to the right. – Note that "small letters" are used in the MO symmetry labels, like a_1, b_1, etc. It is common practice in the spectroscopic literature to use "small letters" in the symmetry designation of one-electron functions like MOs, while capital letters (A_1, B_1, etc.) are used for the wavefunctions of many-electron states.

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