

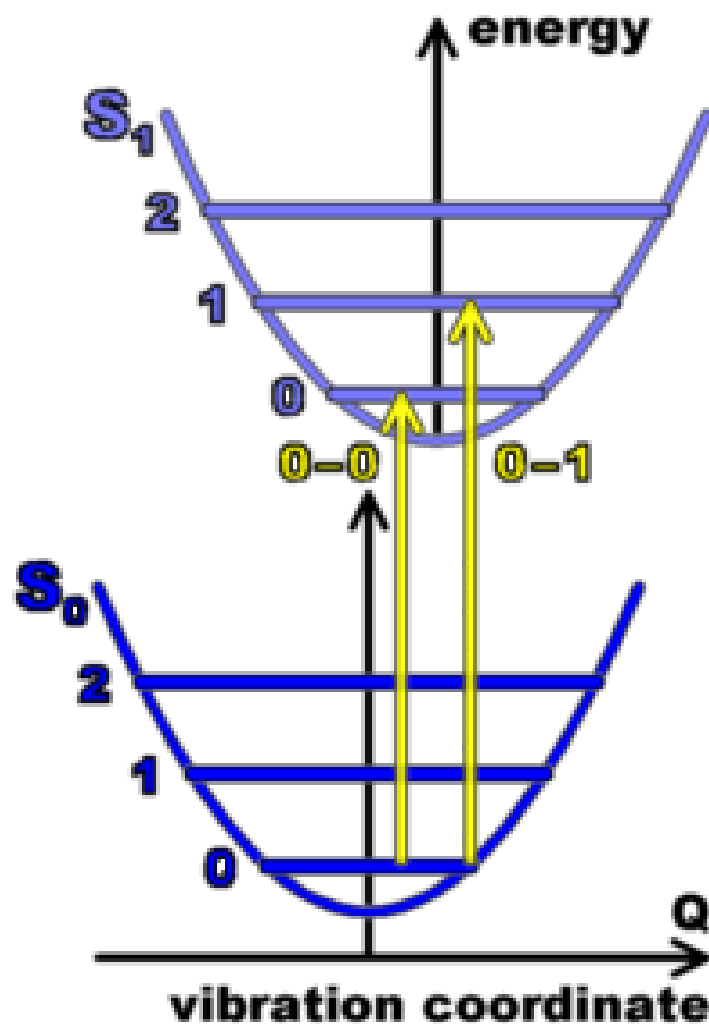
Comparação de Estruturas Calculadas por CIS e EOM-CCSD para Estados Adiabaticamente Excitados

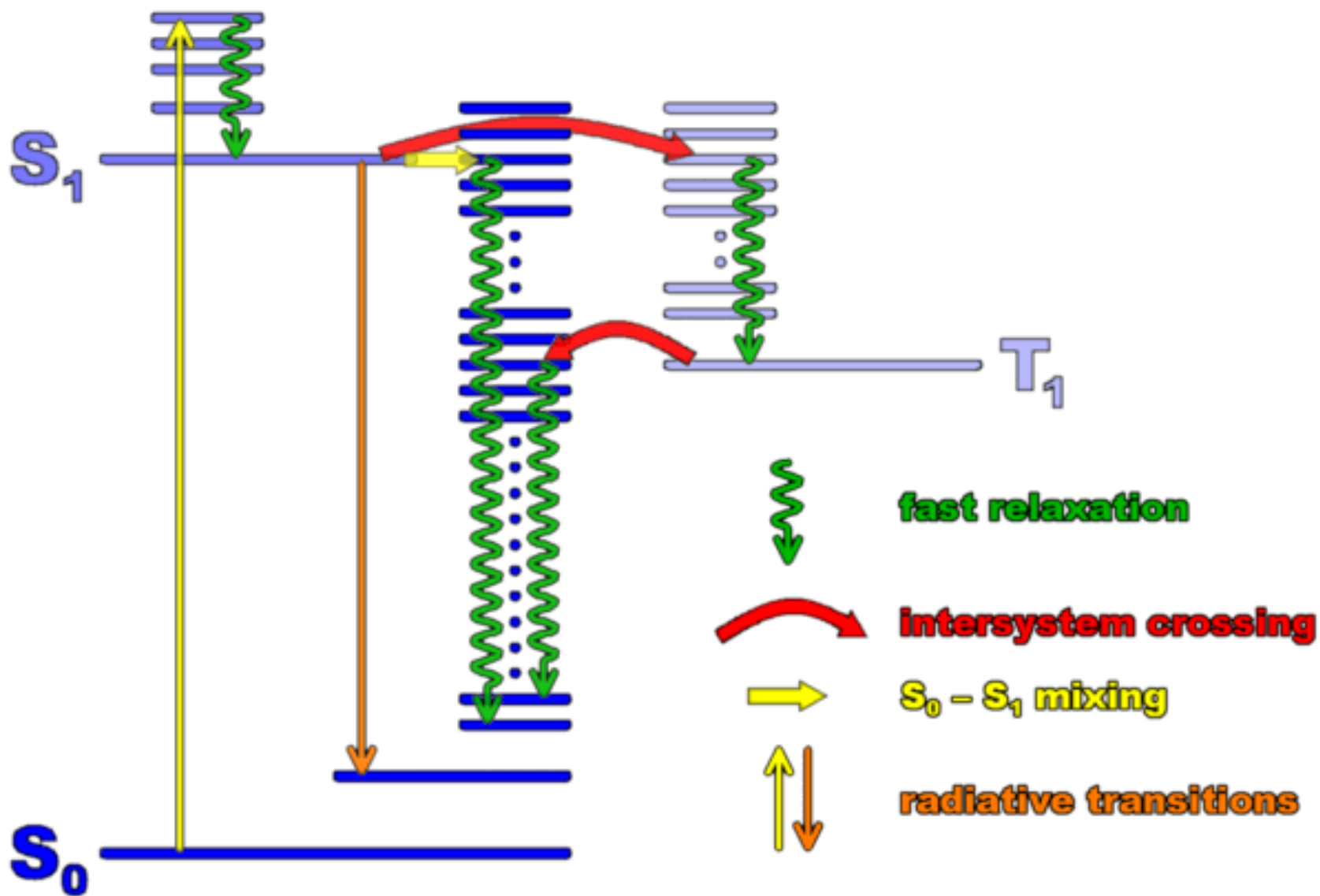


Anselmo Elcana de Oliveira

elcana@quimica.ufg.br

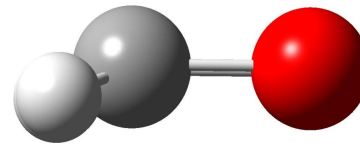
Introdução - Transição Eletrônica



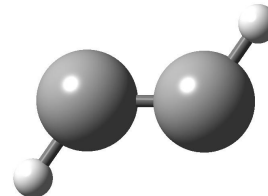


estados eletronicamente excitados apresentam estruturas diferentes dos estados fundamentais

formaldeído : $n \rightarrow \pi^*$ estrutura piramidal



acetileno: $\pi \rightarrow \pi^*$ estrutura distorcida



Problemática

- **Experimental**
 - **Atribuição de bandas nos espectros de VUV**
- **Teórica**
 - **Método de Cálculo**

• **CIS** { **Computacionalmente barato**
Otimização de geometria para os estados excitados e frequências vibracionais

● **EOM-CCSD** { **Computacionalmente caro**
Ótima reprodução das energias das transições experimentais

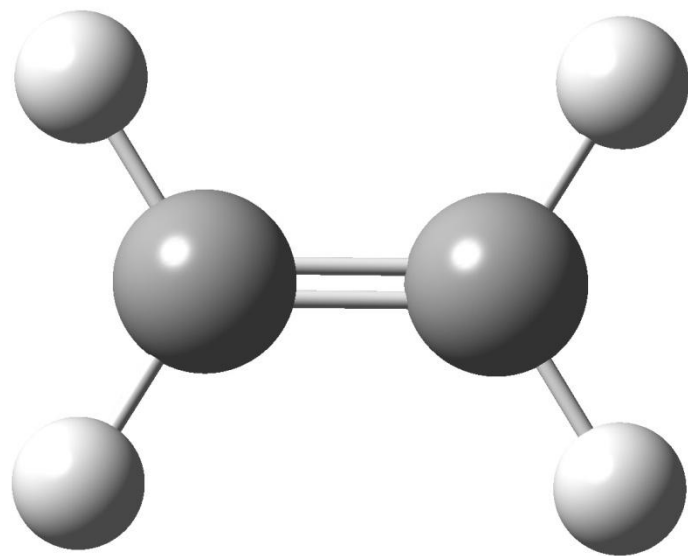
Objetivo

- **Estruturas otimizadas por CLS para os estados adiabaticamente excitados seriam adequadas como ponto de partida para otimizações de geometria com EOM-CCSD?**

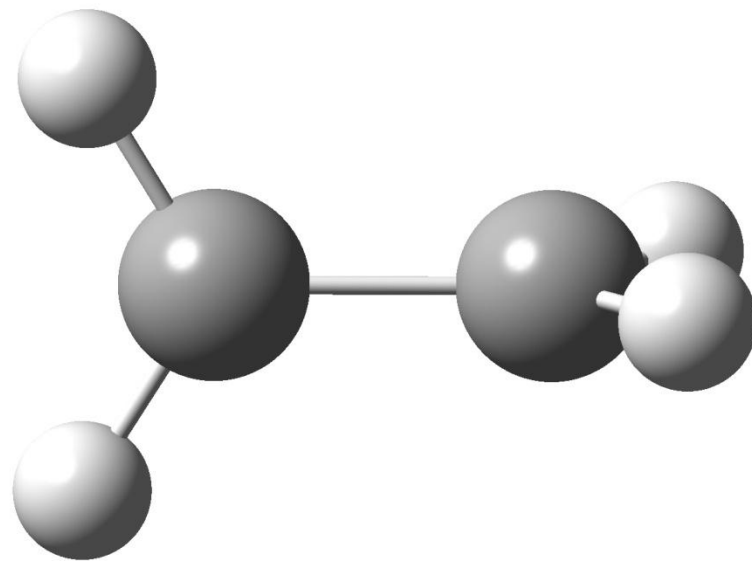
Cálculos

- **6-311++G****
 - **Bons valores para as energias de transição com EOM-CCSD**
 - **Estados de valência**
 - **Estados de Rydberg de menor energia**
- **SAC-CI, CIS: Gaussian03**
- **EOM-CCSD: ACES2, PSI3**

Eteno

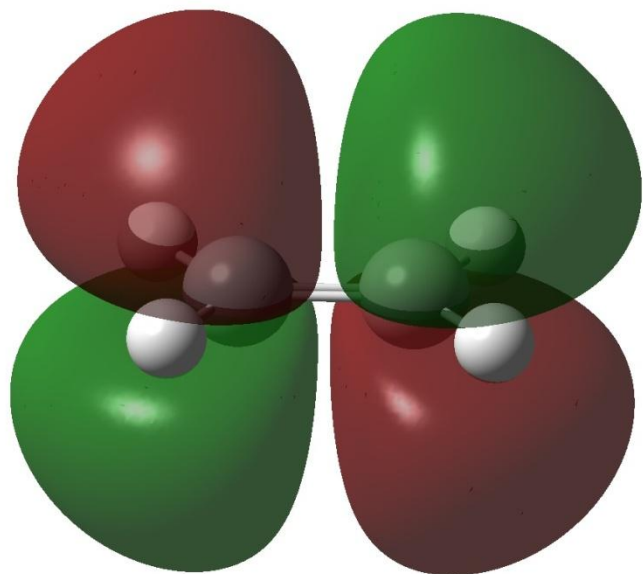


Estado Fundamental

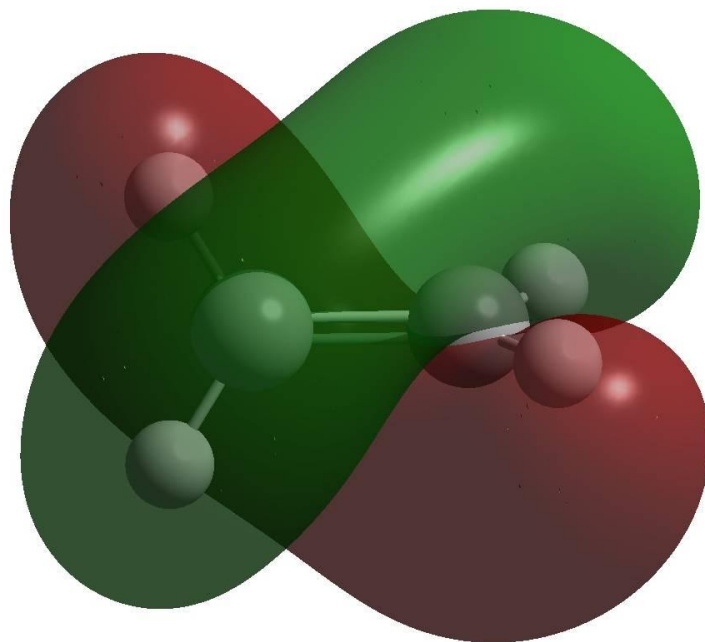
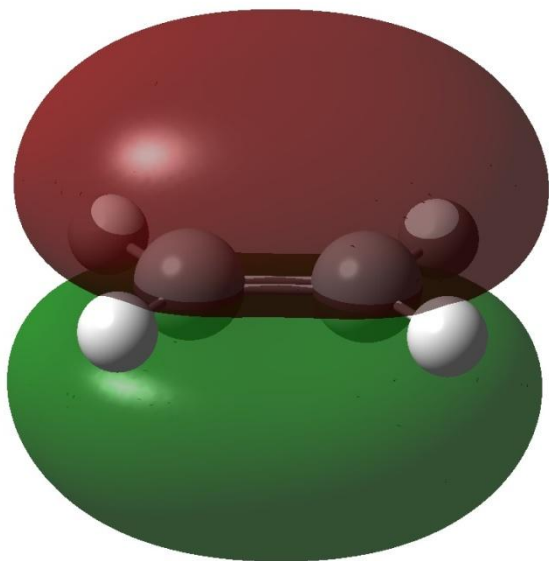


$\pi \rightarrow \pi^*$ (1^3B1u)

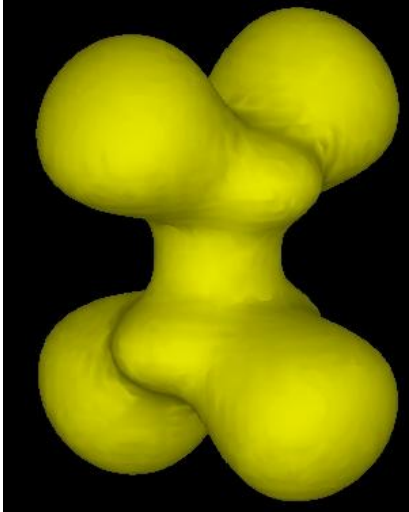
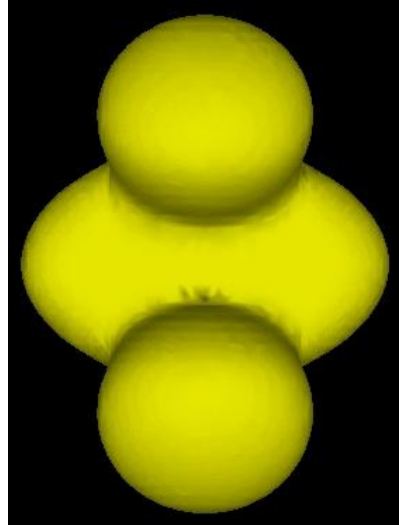
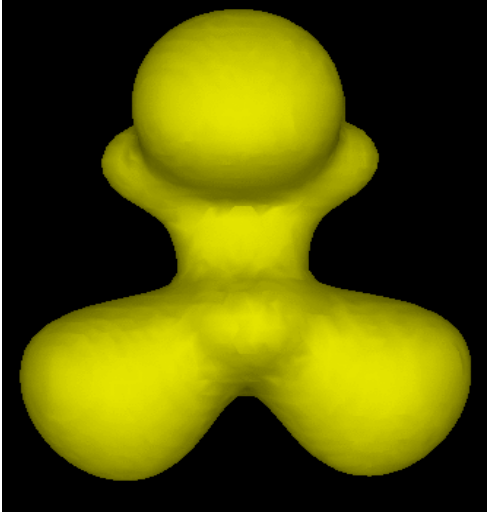
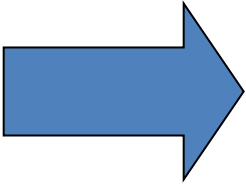
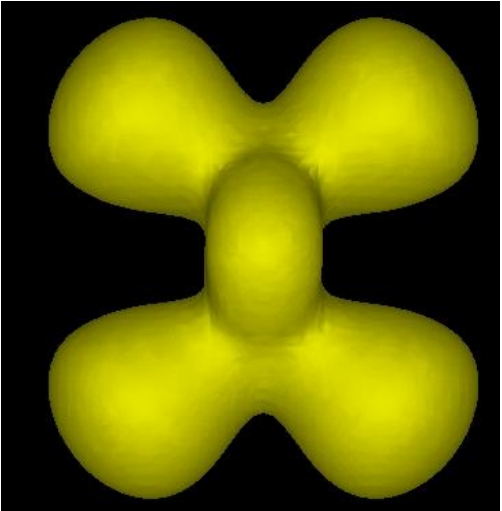
π^*



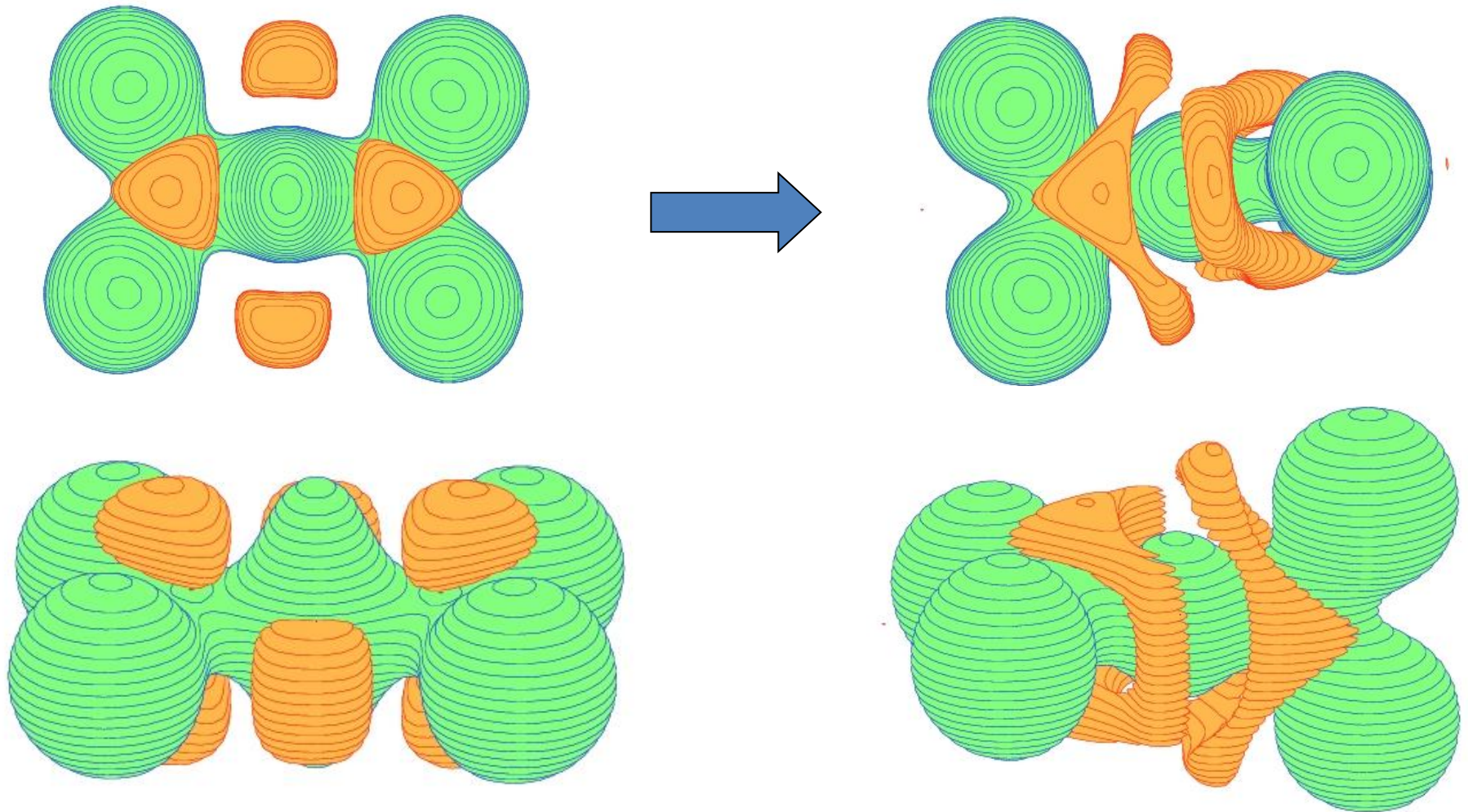
π

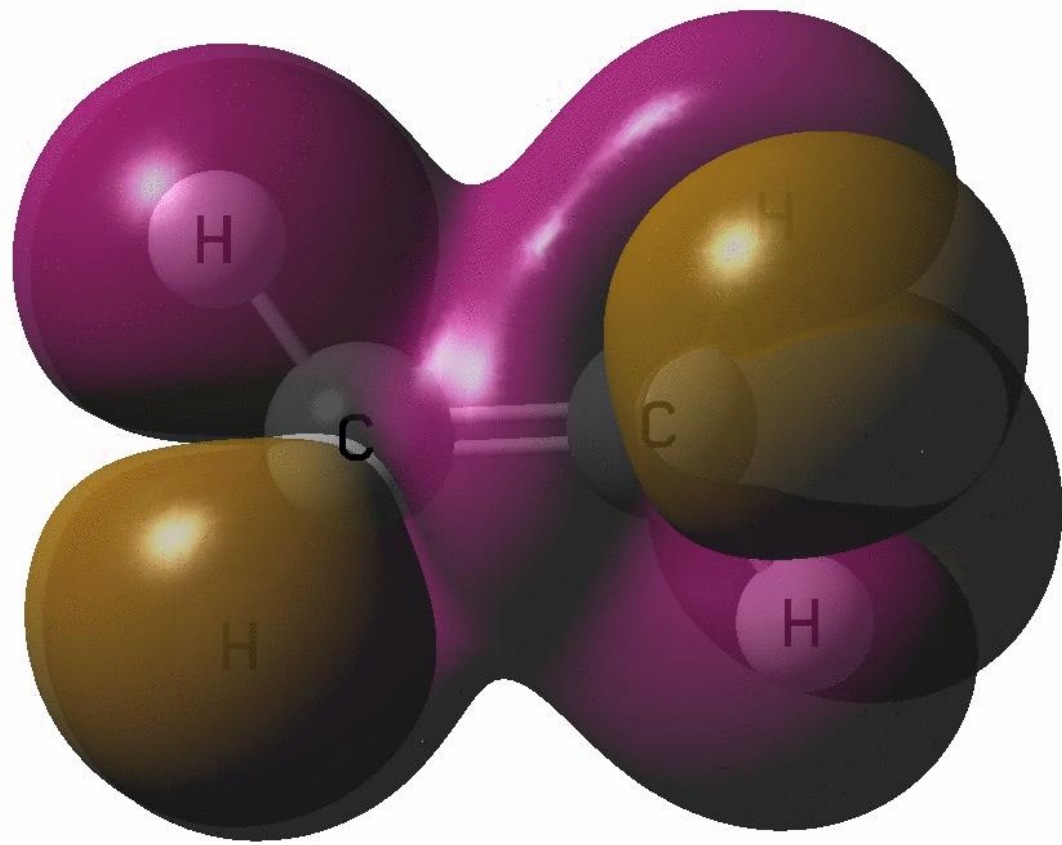


Função de Localização do Elétron (ELF)



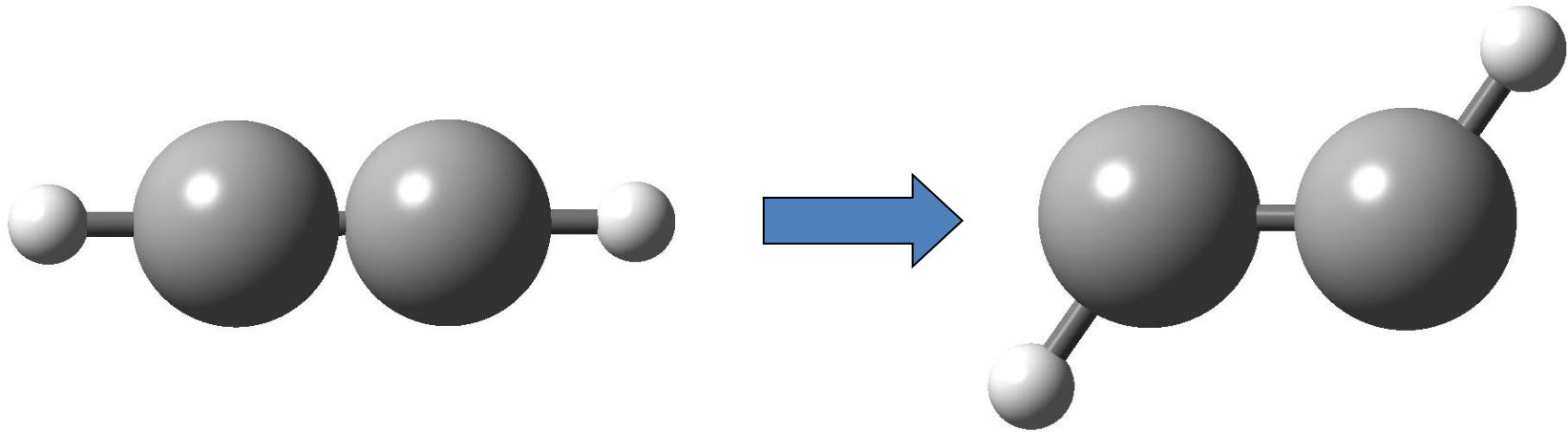
Deformação da Densidade Eletrônica





| <i>Estado</i> | <i>Nível</i> | <i>r(CC)</i> | <i>r(CH)</i> | <i>HCC</i> | <i>HCCH</i> | <i>ET</i> |
|------------------------|-----------------|--------------|--------------|--------------|--------------|--------------|
| <i>EF</i> | Exp. | 1,339 | 1,087 | 121,7 | 0,0 | |
| | CCSD | 1,337 | 1,086 | 121,5 | 0,0 | |
| | HF | 1,319 | 1,076 | 121,6 | 0,0 | |
| $\pi^* \leftarrow \pi$ | Exp. | 1,4 | | | 37-90 | |
| | EOM-CCSD | 1,344 | 1,090 | 123,9 | 87,0 | 5,86 |
| | CIS | 1,373 | 1,091 | 123,5 | 88,5 | 5,61 |
| <i>ET Planar</i> | EOM-CCSD | 1,480 | 1,085 | 120,4 | 0,0 | 7,62 |
| | CIS | 1,496 | 1,074 | 120,0 | 0,0 | 7,25 |
| $3s \leftarrow \pi$ | Exp. | 1,41 | 1,08 | 117,8 | ~37 | 7,11 |
| | EOM-CCSD | 1,412 | 1,093 | 119,8 | 27 | 7,075 |
| | CIS | 1,418 | 1,074 | 119,7 | 0,0 | 7,01 |
| <i>ET Planar</i> | EOM-CCSD | 1,388 | 1,089 | 119,9 | 0,0 | 7,064 |

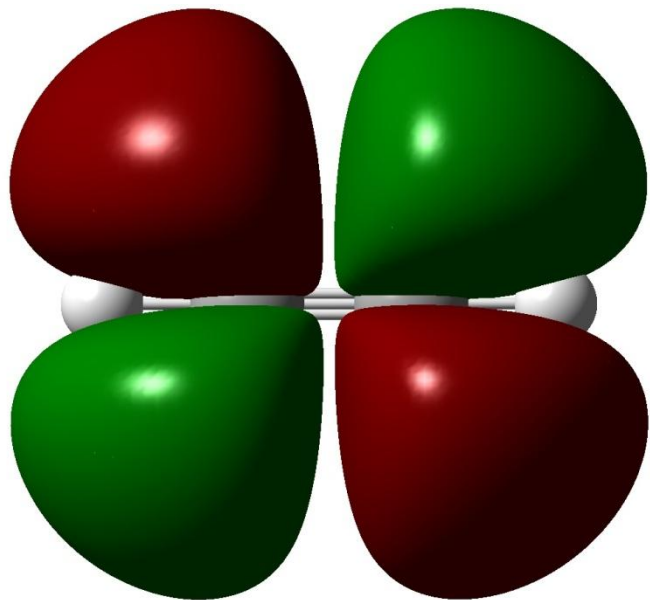
Acetileno



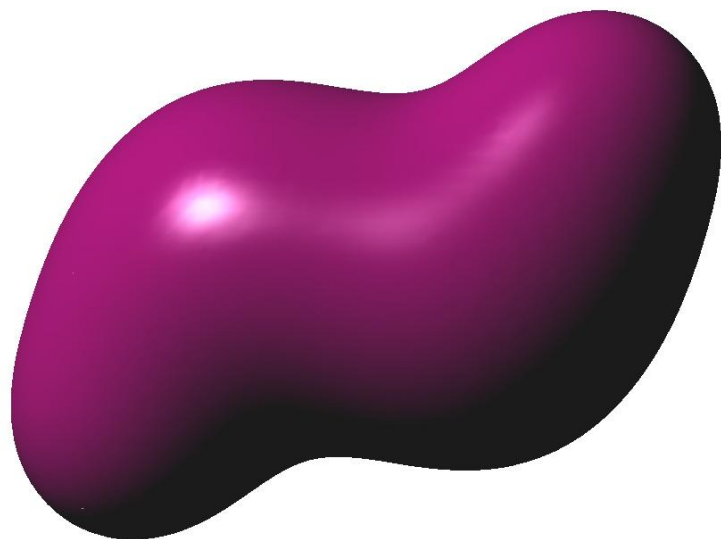
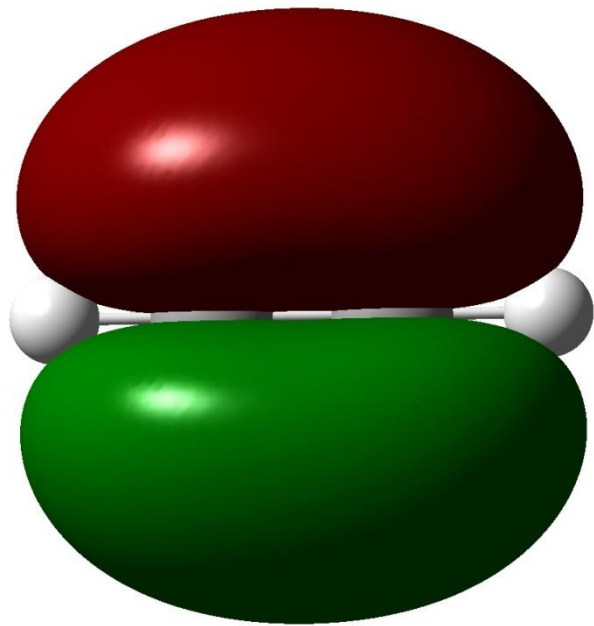
Estado Fundamental

$\pi \rightarrow \pi^*$ (1Au)

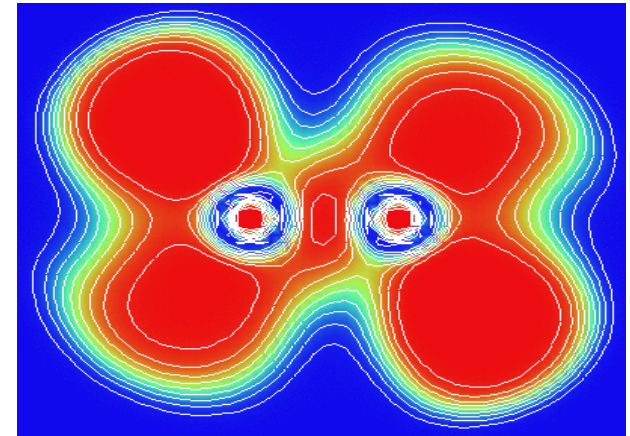
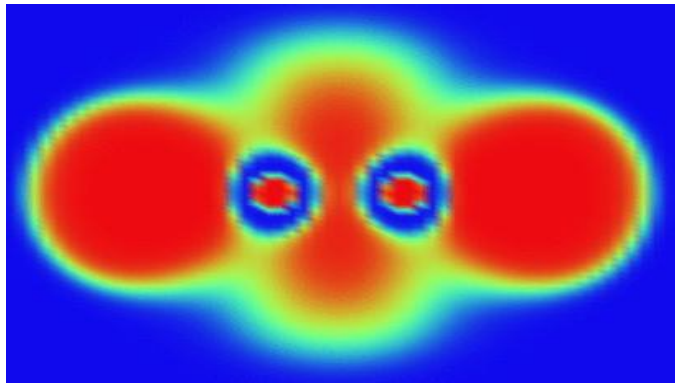
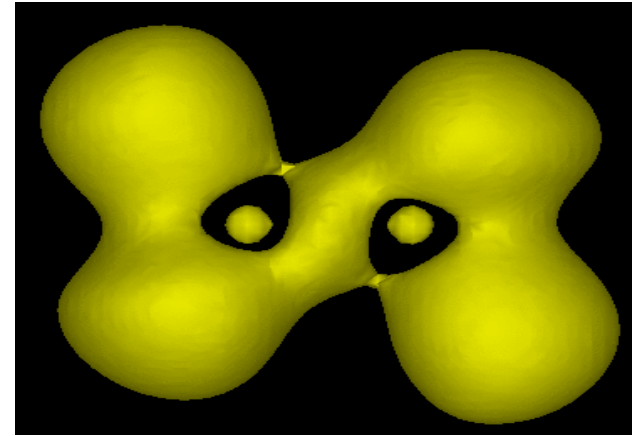
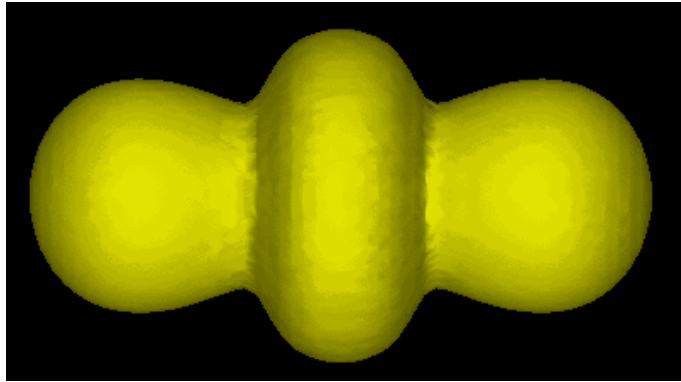
π^*



π

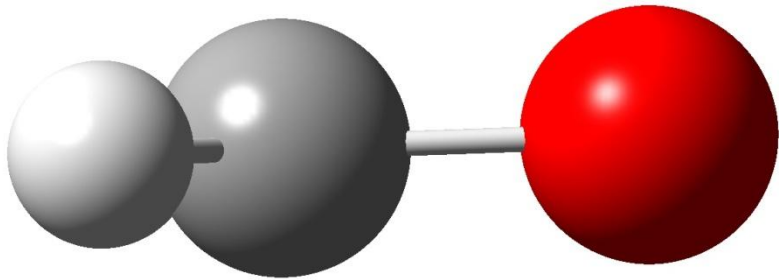


Função de Localização do Elétron (ELF)

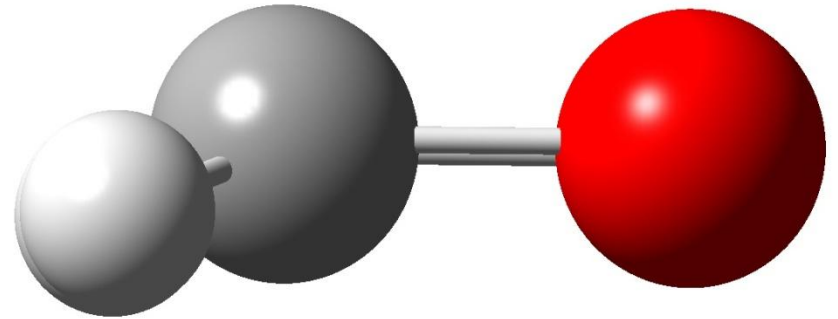


| <i>Estado</i> | <i>Nível</i> | <i>r(CC)</i> | <i>r(CH)</i> | <i>HCC</i> | <i>ET</i> |
|------------------------|-----------------|--------------|--------------|--------------|-------------|
| <i>EF</i> | Exp. | 1,208 | 1,057 | 180,0 | |
| | CCSD | 1,209 | 1,066 | 180,0 | |
| | HF | 1,184 | 1,055 | 180,0 | |
| $\pi^* \leftarrow \pi$ | Exp. | 1,4 | 1,097 | 122,5 | 5,23 |
| | EOM-CCSD | 1,364 | 1,099 | 123,6 | 5,53 |
| | CIS | 1,356 | 1,082 | 124,6 | 4,52 |

Formaldeído

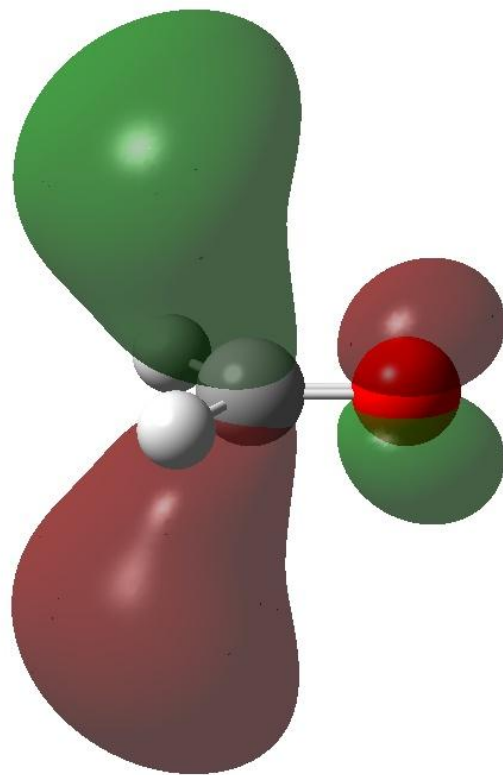


Estado Fundamental

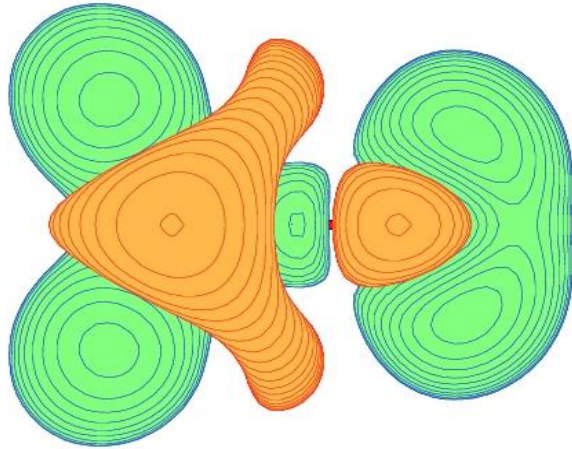


$n_y \rightarrow \pi^*(A'')$

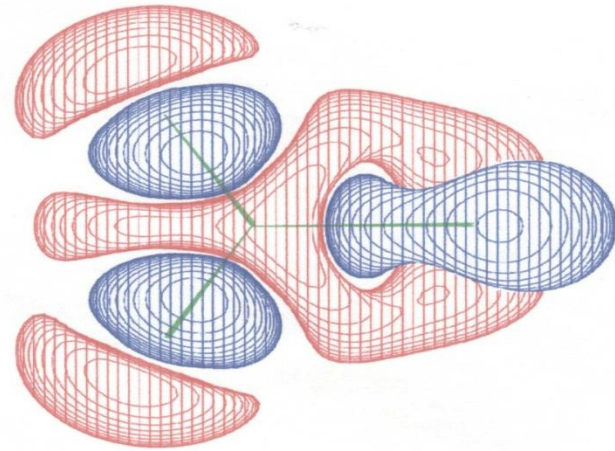
Orbital π^*



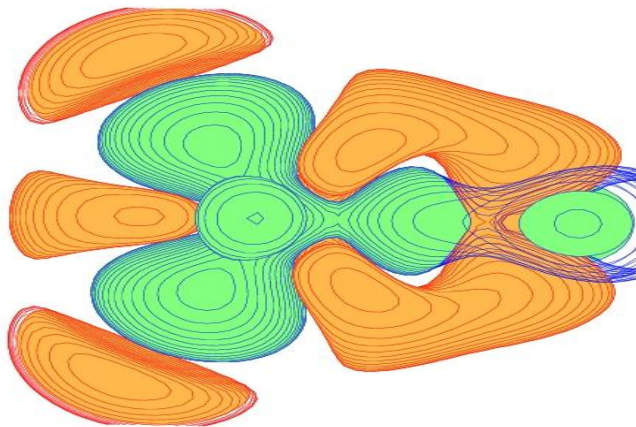
Deformação da Densidade Eletrônica



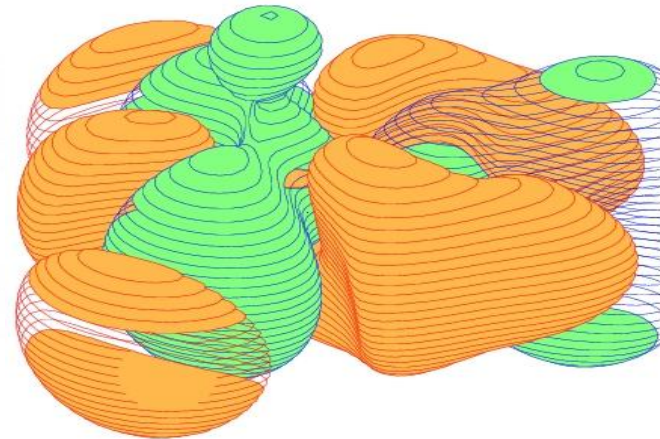
a



b



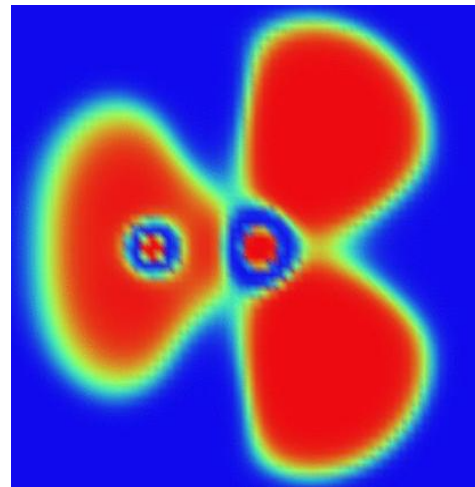
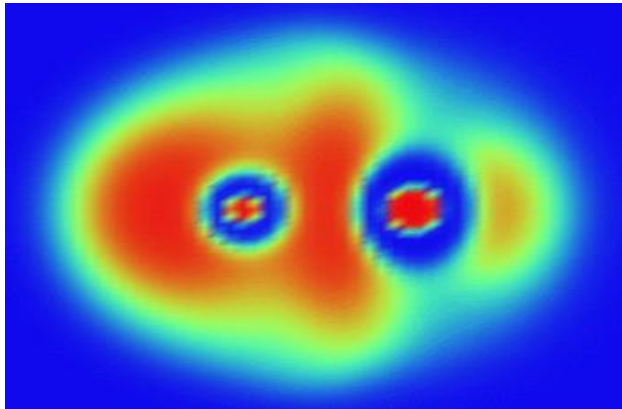
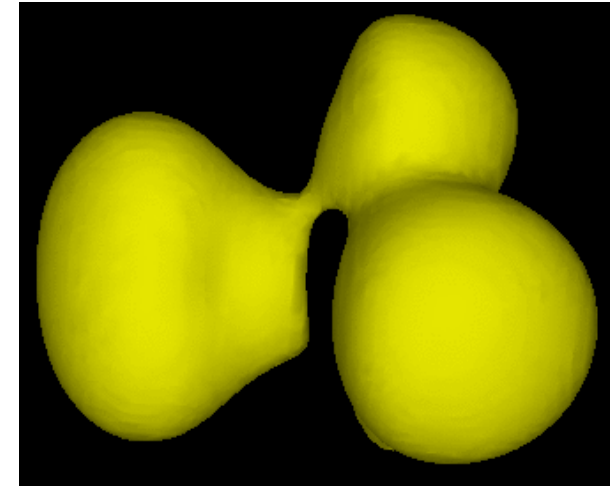
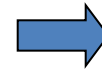
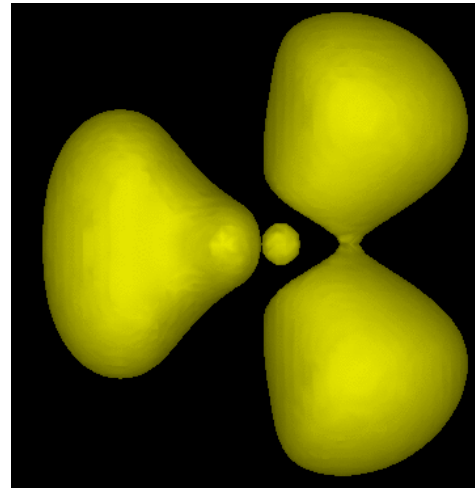
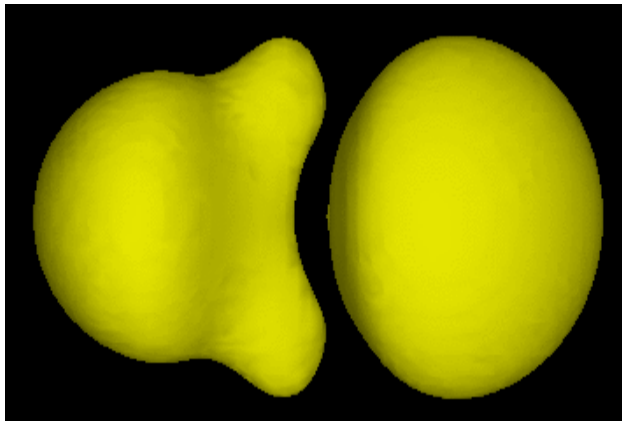
c



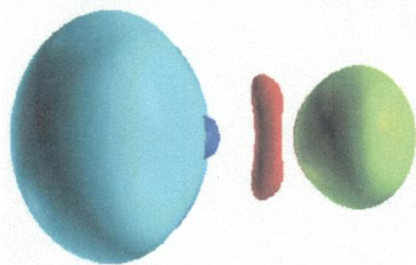
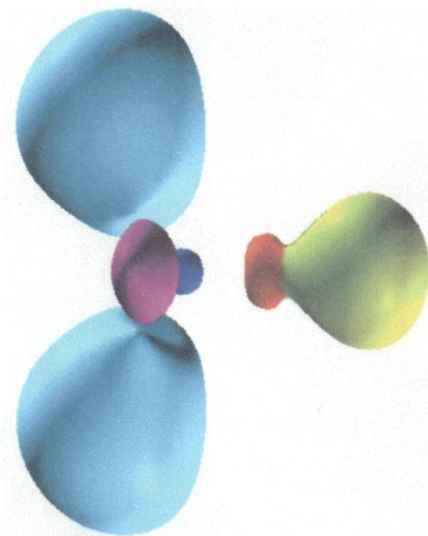
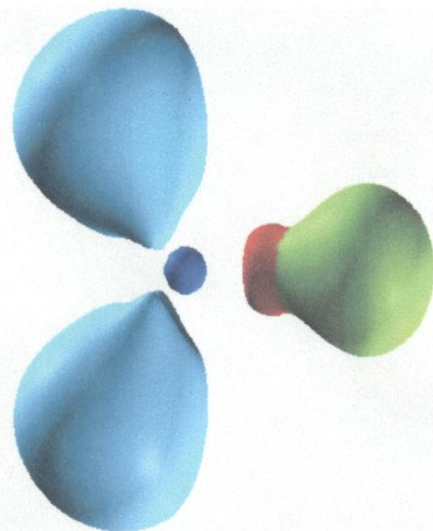
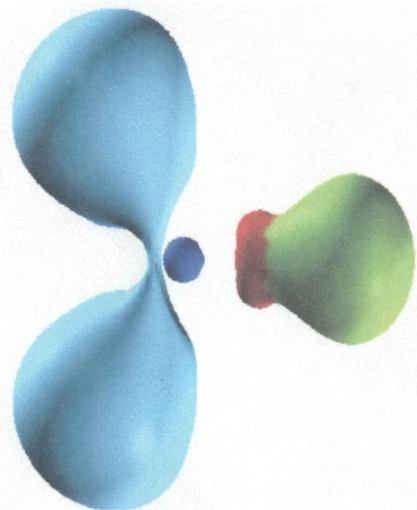
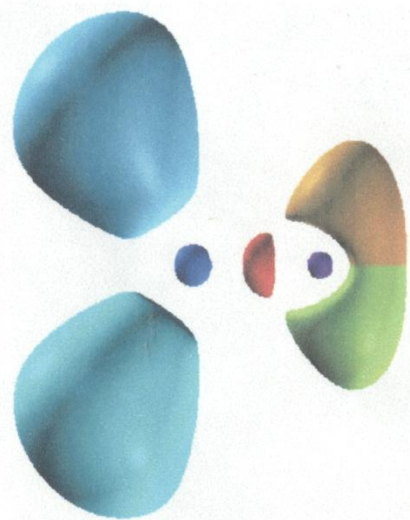
d

← visão lateral

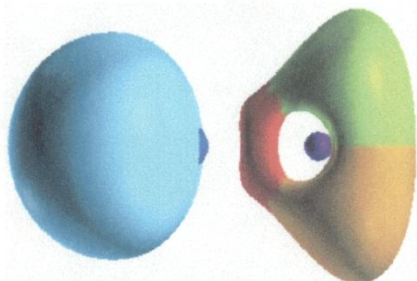
Função de Localização do Elétron (ELF)



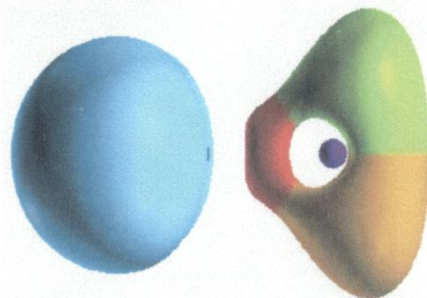
visão de topo



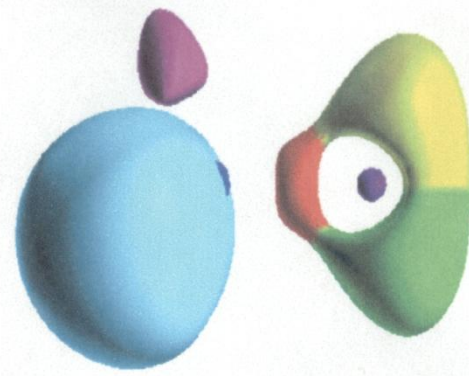
a



b



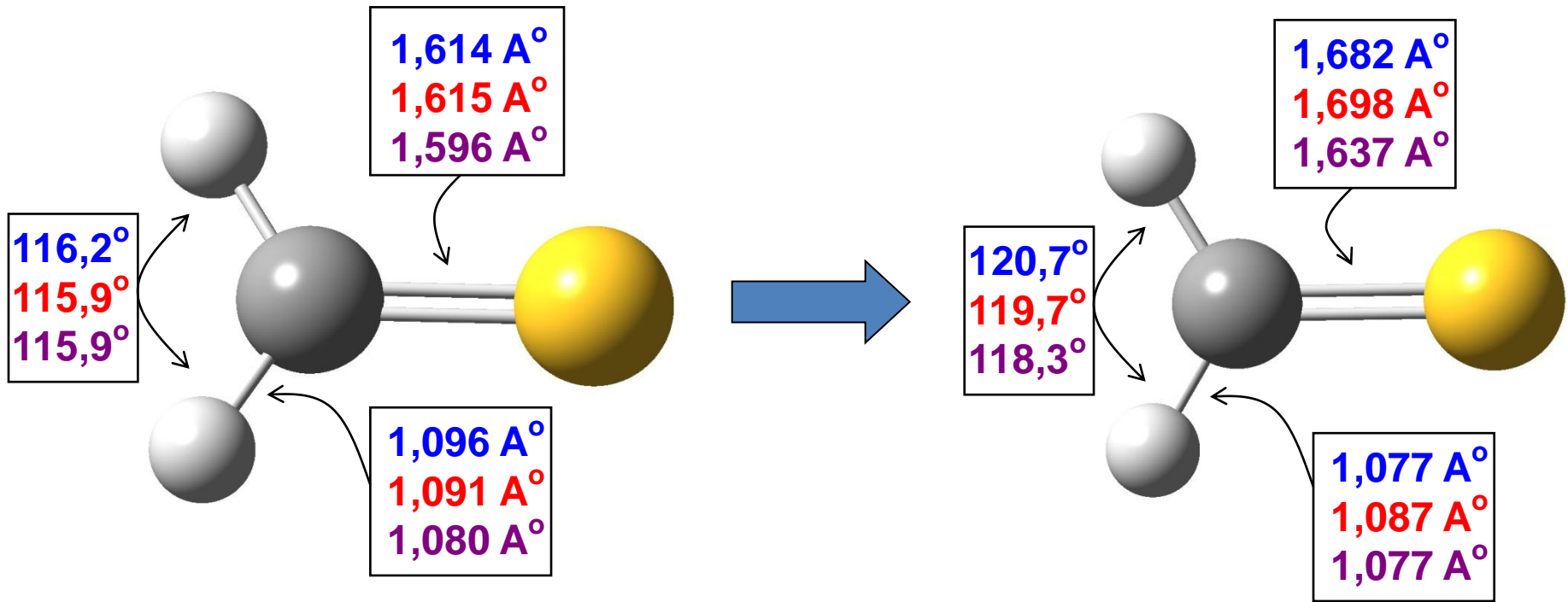
c



d

| <i>Estado</i> | <i>Nível</i> | <i>r(CO)</i> | <i>r(CH)</i> | <i>HCCH</i> | α | <i>ET</i> |
|-----------------------------|-------------------|--------------|--------------|--------------|-------------|-------------|
| <i>EF</i> | Exp. | 1,203 | 1,101 | 116,3 | 0,0 | |
| | CCSD(full) | 1,205 | 1,106 | 116,1 | 0,0 | |
| | HF | 1,180 | 1,094 | 116,2 | 0,0 | |
| $n_y \leftarrow \pi^*$ | Exp. | 1,323 | 1,098 | 118,4 | 34 | |
| | EOM-CCSD | 1,311 | 1,095 | 118,8 | 32,5 | |
| | CIS | 1,248 | 1,087 | 118,2 | 25,7 | |
| $n_z \leftarrow \pi^* (A')$ | EOM-CCSD | 1,430 | 1,084 | 137,2 | 0,0 | 8,05 |
| | CIS | 1,481 | 1,069 | 142,6 | 0,0 | 8,30 |

Tioformaldeído



Estado Fundamental

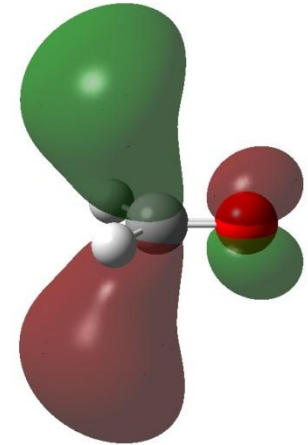
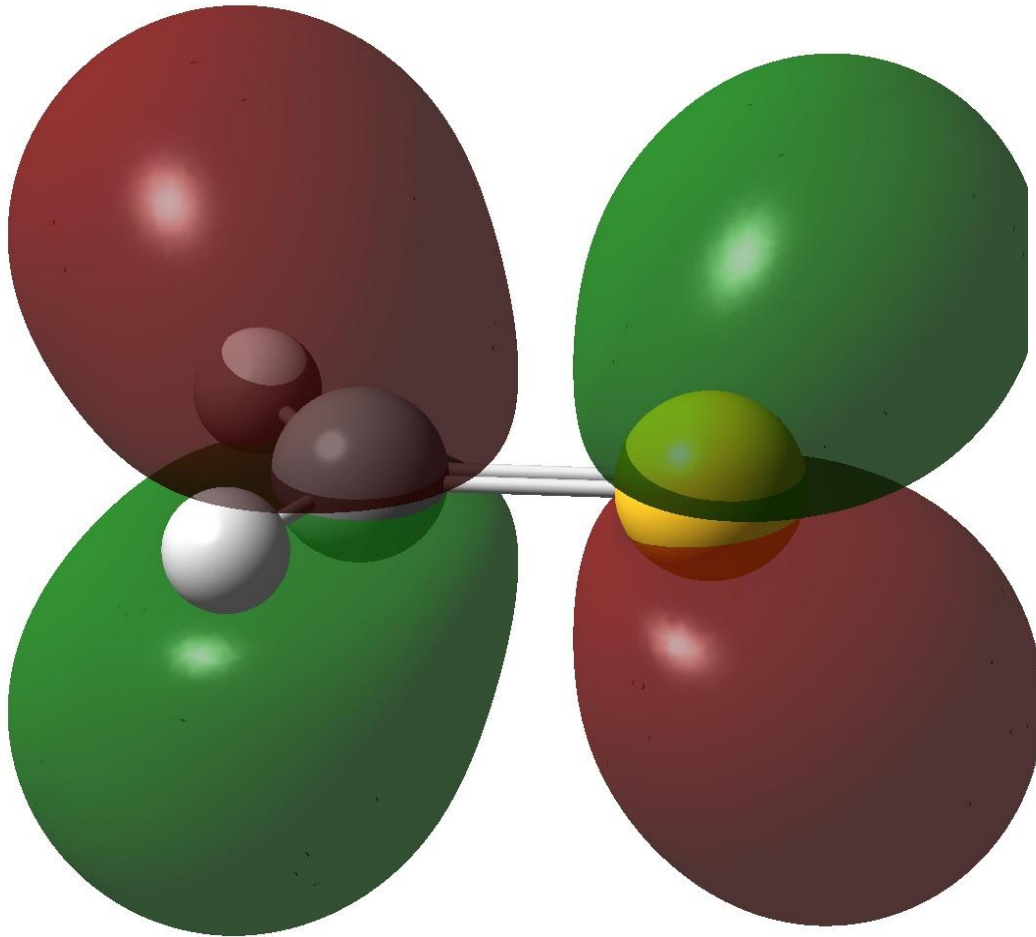
$n_y-\pi^*(A'')$

Experimental

CCSD(completo)/EOM-CCSD

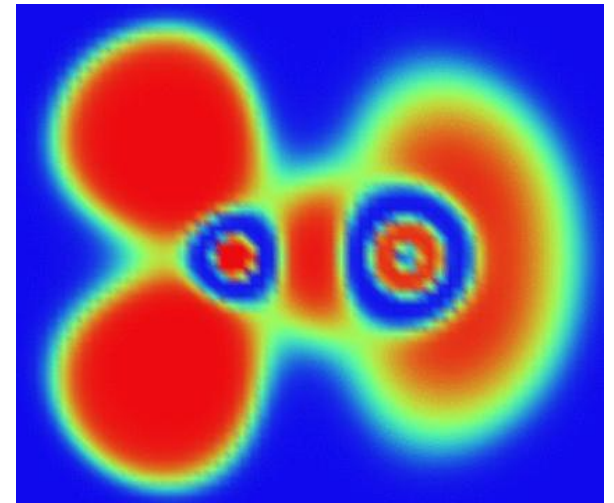
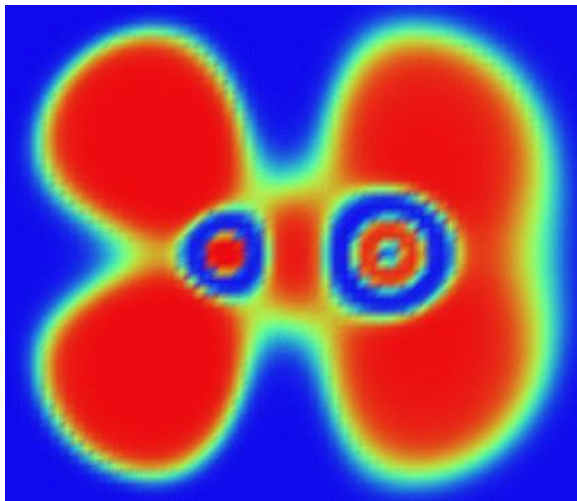
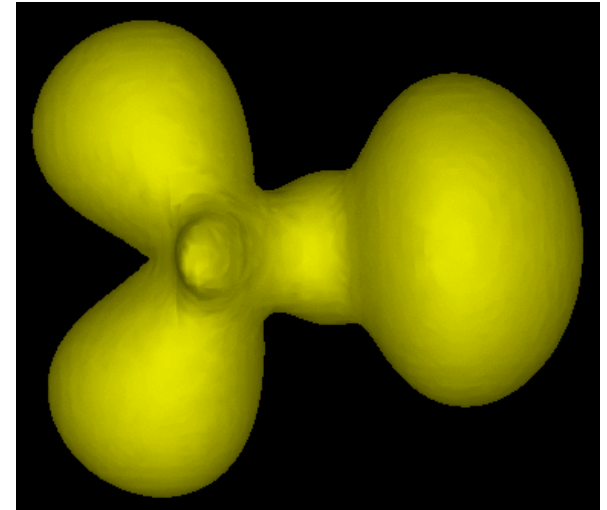
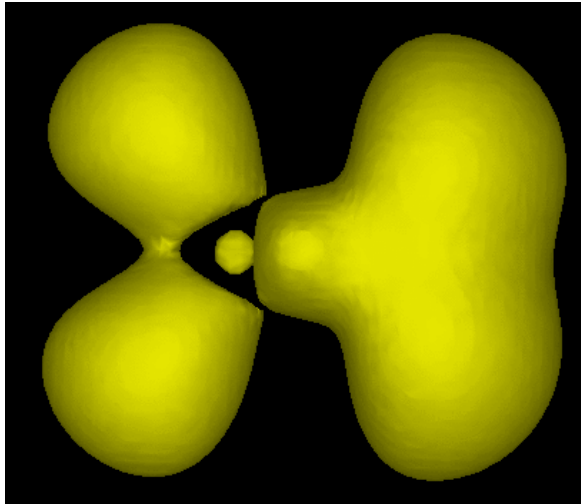
HF/CIS

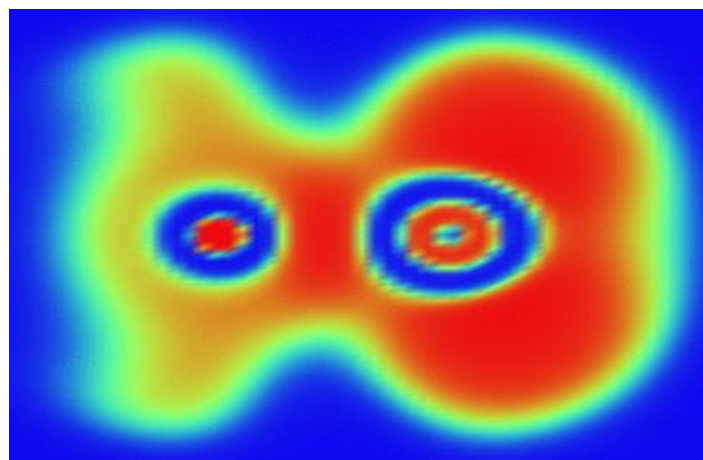
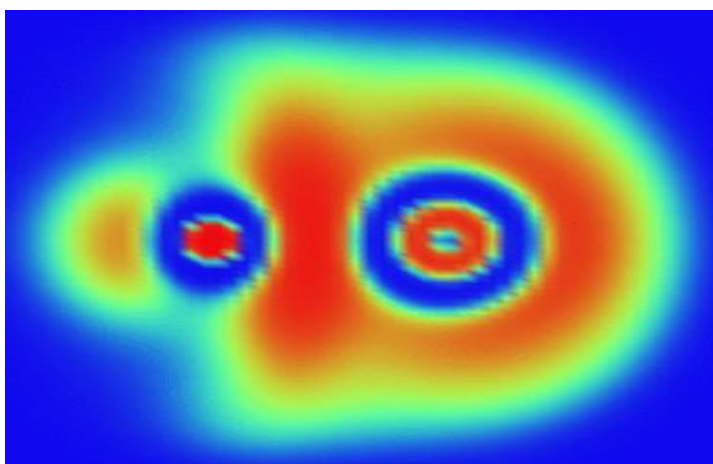
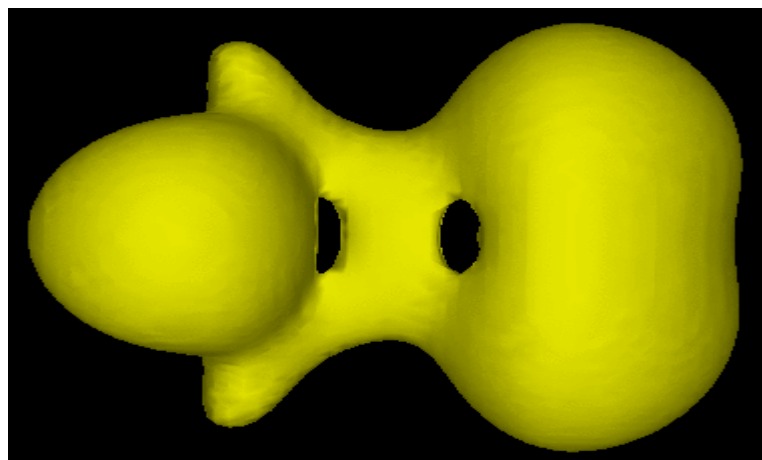
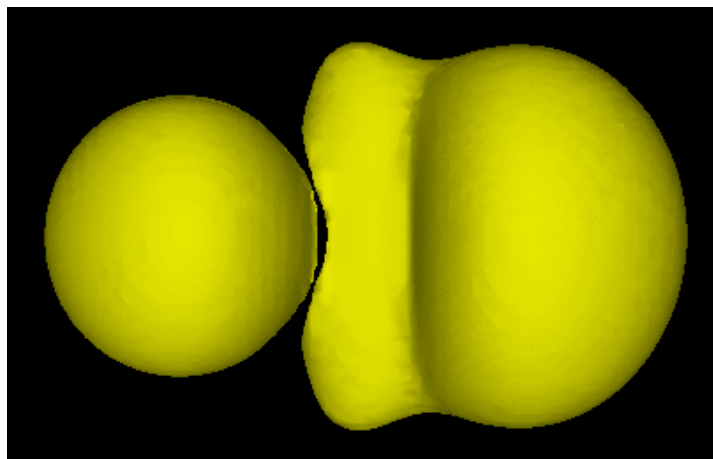
Orbital π^*



Formaldeído

Função de Localização do Elétron (ELF)





| <i>Estado</i> | <i>Nível</i> | <i>r(CS)</i> | <i>r(CH)</i> | <i>HCCH</i> | α | <i>ET</i> |
|------------------------------|-------------------|--------------|--------------|--------------|-------------|-------------|
| <i>EF</i> | Exp. | 1,614 | 1,096 | 116,2 | 0,0 | |
| | CCSD(full) | 1,615 | 1,091 | 115,9 | 0,0 | |
| | HF | 1,596 | 1,080 | 115,9 | 0,0 | |
| $n_y \leftarrow \pi^* (A'')$ | Exp. | 1,682 | 1,077 | 120,7 | 0,0 | 2,04 |
| | EOM-CCSD | 1,698 | 1,087 | 119,7 | 0,0 | 2,20 |
| | CIS | 1,637 | 1,077 | 118,3 | 0,0 | 2,68 |
| $n_z \leftarrow \pi^* (A')$ | EOM-CCSD | 1,936 | 1,094 | 115,3 | 35,1 | 6,03 |
| | CIS | 1,919 | 1,082 | 117,3 | 46,9 | 5,71 |

Dióxido de Carbono

| <i>Estado</i> | <i>Nível</i> | <i>r(CO)</i> | <i>OCO</i> | <i>ET</i> |
|-----------------------|-------------------|--------------|--------------|-------------|
| <i>EF</i> | Exp. | 1,162 | 180,0 | |
| | CCSD(full) | 1,160 | 180,0 | |
| | HF | 1,136 | 180,0 | |
| 1B₂ | Exp. | 1,246 | 122,0 | 5,8 |
| | EOM-CCSD | 1,238 | 120,9 | 5,81 |
| | CIS | 1,210 | 124,4 | 7,35 |
| 1A₂ | EOM-CCSD | 1,266 | 176,0 | 8,20 |
| | CIS | 1,229 | 174,1 | 9,39 |

Dióxido de Enxofre

| <i>Estado</i> | <i>Nível</i> | <i>r(CS)</i> | <i>OSO</i> | <i>ET</i> |
|-----------------------|-------------------|--------------|--------------|-------------|
| <i>EF</i> | Exp. | 1,556 | 180,0 | |
| | CCSD(full) | 1,557 | 180,0 | |
| | HF | 1,543 | 180,0 | |
| 1B₂ | Exp. | 1,640 | 131,9 | |
| | EOM-CCSD | 1,634 | 131,9 | 3,64 |
| | CIS | 1,595 | 144,5 | 4,29 |
| 1A₂ | EOM-CCSD | 1,616 | 175,6 | 3,92 |
| | CIS | 1,579 | 173,6 | 4,36 |

Colaboração

- **Yale University**
 - **Kenneth B. Wiberg**
 - **Patrick H. Vaccaro**
 - **Yi-gui Wang**

Agradecimentos

