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# Chemiluminescence

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## 1,2-dioxetanedione driven chemiluminescence

### Overview

*1,2-dioxetanedione* is a planar molecule with the conventional chemical structure shown at right. The molecule is essentially an unstable dimer of two $CO_2$ molecules.
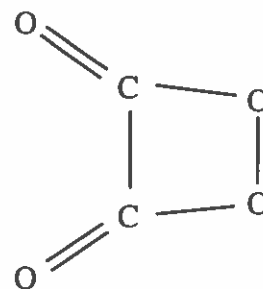


The process of interest is the dissociation of the dimer into two $CO_2$ molecules, for this produces a $CO_2$ molecule in an electronically excited state. In the *firefly* or the *glostick*, the excitation energy of the excited $CO_2$ molecule is transferred to a dye molecule which subsequently fluoresces in the visible.

### Geometry

To describe the geometry of the dissociation, let us embed the molecule in a Cartesian coordinate system in which all the atoms lie in the $x, z$-plane. Subscripts have been added to distinguish the different atoms.
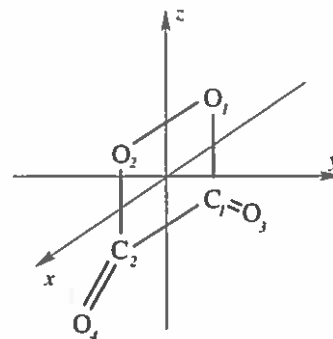


The dissociation will be modelled by starting the atoms at locations deduced from simple bond length estimates and then moving all the atoms with $x > 0$ a distance $\Delta$ along the $x$-axis and all atoms with $x < 0$ a distance $-\Delta$ along the $x$-axis, with $\Delta = 0.0\,nm, 0.2\,nm, \ldots, 2.0\,nm$. In total, 11 different $EHT$ calculations were made. In the diagram at right, the numbers represent the positions in the $x, z$-plane of the atoms where state calculations were performed. The initial $O_1 - O_2$, $O_1 - C_1$ and $C_1 - O_3$ bond lengths were 1.09 $nm$.

2222222222    LLLLLLLLLLLL

4444444444    3333333333

6666666666    5555555555
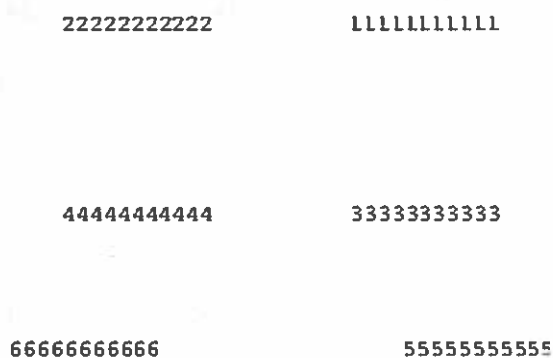
The *real* dissociation path deviates from this calculated path because the calculated path does not locate the true minimum energy configuration of the ground state of the

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system. It is qualitatively correct, however, and that is all that is required to identify the qualitative result that one of the $CO_2$ molecules ends up in an electronically excited state.

## Molecular Symmetry

There are four symmetry transformations that leave the molecule invariant. Let

$E$ denote the identity transformation

$C_2$ denote the rotation by angle $\pi$ about the $z$-axis

$\sigma$ denote the reflection in the $z, y$-plane

$\sigma'$ denote the reflection in the $z, x$-plane

All these transformations leave the molecule invariant. The set of transformations $\{E, C_2 \, \sigma, \sigma'\}$ forms a group. The Schönflies symbol for this group is $C_{2v}$ and the character table is

| $C_{2v}$ | $E$ | $C_2$ | $\sigma$ | $\sigma'$ |
|----------|-----|-------|----------|-----------|
| $A_1$ | 1 | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | $-1$ | $-1$ |
| $B_1$ | 1 | $-1$ | 1 | $-1$ |
| $B_2$ | 1 | $-1$ | $-1$ | 1 |

This symmetry describes the molecule at all $\Delta$. That is, the dissociation path was chosen to not alter the symmetry of the molecule.

## The orbitals deduced from EHT

There are 6 atoms in the molecule. Each atom will contribute four Slater type orbitals,

$$2S, 2P_x, 2P_y, 2P_z$$

So there are 24 orbitals. There are 32 valence electrons, so the *aufbau* principle says that the 16 lowest energy orbitals will be filled in the electronic ground state.

The *EHT ansatz* is that the orbitals and energies are determined by solving something like

$$\hat{H}\psi = E\,\hat{S}\,\psi$$

with $\hat{H}$ and $\hat{S}$ symmetric, 24×24 matrices. The eigenvalues of this system are the same as the eigenvalues of the matrix $\hat{S}^{-1}\hat{H}$. But $\hat{S}^{-1}\hat{H}$ is not symmetric so the eigenvectors discovered this way are not orthogonal. This can be worked around in various ways, but – since the *symmetry* of the orbitals is important – we can simply start by constructing a symmetry adapted basis set.

## Orbital Symmetries

There are 6 atoms in the molecule. Here is how the 24 Slater type orbitals are transformed by the transformations $E, C_2, \sigma$ and $\sigma'$ of $C_{2v}$:

| $E$ | $C_2$ | $\sigma$ | $\sigma'$ |
| --- | --- | --- | --- |
| $2S_{O_1}$ | $2S_{O_2}$ | $2S_{O_2}$ | $2S_{O_1}$ |
| $2S_{O_2}$ | $2S_{O_1}$ | $2S_{O_1}$ | $2S_{O_2}$ |
| $2S_{O_3}$ | $2S_{O_4}$ | $2S_{O_4}$ | $2S_{O_3}$ |
| $2S_{O_4}$ | $2S_{O_3}$ | $2S_{O_3}$ | $2S_{O_4}$ |
| $2S_{C_1}$ | $2S_{C_2}$ | $2S_{C_2}$ | $2S_{C_1}$ |
| $2S_{C_2}$ | $2S_{C_1}$ | $2S_{C_1}$ | $2S_{C_2}$ |
| $2P_{x,O_1}$ | $-2P_{x,O_2}$ | $-2P_{x,O_2}$ | $2P_{x,O_1}$ |
| $2P_{x,O_2}$ | $-2P_{x,O_1}$ | $-2P_{x,O_1}$ | $2P_{x,O_2}$ |
| $2P_{x,O_3}$ | $-2P_{x,O_4}$ | $-2P_{x,O_4}$ | $2P_{x,O_3}$ |
| $2P_{x,O_4}$ | $-2P_{x,O_3}$ | $-2P_{x,O_3}$ | $2P_{x,O_4}$ |
| $2P_{x,C_1}$ | $-2P_{x,C_2}$ | $-2P_{x,C_2}$ | $2P_{x,C_1}$ |
| $2P_{x,C_2}$ | $-2P_{x,C_1}$ | $-2P_{x,C_1}$ | $2P_{x,C_2}$ |
| $2P_{y,O_1}$ | $-2P_{y,O_2}$ | $2P_{y,O_2}$ | $-2P_{y,O_1}$ |
| $2P_{y,O_2}$ | $-2P_{y,O_1}$ | $2P_{y,O_1}$ | $-2P_{y,O_2}$ |
| $2P_{y,O_3}$ | $-2P_{y,O_4}$ | $2P_{y,O_4}$ | $-2P_{y,O_3}$ |
| $2P_{y,O_4}$ | $-2P_{y,O_3}$ | $2P_{y,O_3}$ | $-2P_{y,O_4}$ |
| $2P_{y,C_1}$ | $-2P_{y,C_2}$ | $2P_{y,C_2}$ | $-2P_{y,C_1}$ |
| $2P_{y,C_2}$ | $-2P_{y,C_1}$ | $2P_{y,C_1}$ | $-2P_{y,C_2}$ |
| $2P_{z,O_1}$ | $2P_{z,O_2}$ | $2P_{z,O_2}$ | $2P_{z,O_1}$ |
| $2P_{z,O_2}$ | $2P_{z,O_1}$ | $2P_{z,O_1}$ | $2P_{z,O_2}$ |
| $2P_{z,O_3}$ | $2P_{z,O_4}$ | $2P_{z,O_4}$ | $2P_{z,O_3}$ |
| $2P_{z,O_4}$ | $2P_{z,O_3}$ | $2P_{z,O_3}$ | $2P_{z,O_4}$ |
| $2P_{z,C_1}$ | $2P_{z,C_2}$ | $2P_{z,C_2}$ | $2P_{z,C_1}$ |
| $2P_{z,C_2}$ | $2P_{z,C_1}$ | $2P_{z,C_1}$ | $2P_{z,C_2}$ |

Projecting the original orbitals into a symmetry adapted basis set gives 9 orbitals with $a_1$ symmetry, 3 orbitals with $a_2$ symmetry, 3 orbitals with $b_1$ symmetry, and 9 orbitals with $b_2$ symmetry:

| irreducible representation | $\psi$ |
|:---:|:---:|
| $a_1$ | $2S_{O_1} + 2S_{O_2}$ |
| $a_1$ | $2S_{O_3} + 2S_{O_4}$ |
| $a_1$ | $2S_{C_1} + 2S_{C_2}$ |
| $a_1$ | $2P_{x,O_1} - 2P_{x,O_2}$ |
| $a_1$ | $2P_{x,O_3} - 2P_{x,O_4}$ |
| $a_1$ | $2P_{x,C_1} - 2P_{x,C_2}$ |
| $a_1$ | $2P_{z,O_1} + 2P_{z,O_2}$ |
| $a_1$ | $2P_{z,O_3} + 2P_{z,O_4}$ |
| $a_1$ | $2P_{z,C_1} + 2P_{z,C_2}$ |
| $a_2$ | $2P_{y,O_1} - 2P_{y,O_2}$ |
| $a_2$ | $2P_{y,O_3} - 2P_{y,O_4}$ |
| $a_2$ | $2P_{y,C_1} - 2P_{y,C_2}$ |
| $b_1$ | $2P_{y,O_1} + 2P_{y,O_2}$ |
| $b_1$ | $2P_{y,O_3} + 2P_{y,O_4}$ |
| $b_1$ | $2P_{y,C_1} + 2P_{y,C_2}$ |
| $b_2$ | $2S_{O_1} - 2S_{O_2}$ |
| $b_2$ | $2S_{O_3} - 2S_{O_4}$ |
| $b_2$ | $2S_{C_1} - 2S_{C_2}$ |
| $b_2$ | $2P_{x,O_1} + 2P_{x,O_2}$ |
| $b_2$ | $2P_{x,O_3} + 2P_{x,O_4}$ |
| $b_2$ | $2P_{x,C_1} + 2P_{x,C_2}$ |
| $b_2$ | $2P_{z,O_1} - 2P_{z,O_2}$ |
| $b_2$ | $2P_{z,O_3} - 2P_{z,O_4}$ |
| $b_2$ | $2P_{z,C_1} - 2P_{z,C_2}$ |

It is easy to construct an orthonormal basis set from these states. In this basis set, $\hat{H}$ and $\hat{S}$ will be block diagonal, the blocks associated with the irreducible representations.

Looking at this list of symmetry adapted orbitals, it is clear that the $a_1$ symmetry orbitals are *bonding* orbitals between the two $CO_2$ parts of the molecule, the $a_2$ symmetry orbitals are *anti-bonding* orbitals within each of the $CO_2$ parts, the $b_1$ symmetry orbitals are the *bonding* orbitals corresponding to the $a_2$ orbitals, and the $b_2$ symmetry orbitals are the *anti-bonding* orbitals corresponding to the $a_1$ orbitals.

## Orbital Energies

For each of the 11 configurations, the *overlap* integrals were calculated for all 276 pairs of orbitals and the *EHT* $\hat{H}$ and $\hat{S}$ were constructed.

Evaluating the $\hat{H}$ and $\hat{S}$ in the symmetry adapted basis set identifies the four blocks corresponding to the different irreducible representations. The eigenvalues associated with each block were determined by calculating the eigenvalues of the corresponding $\hat{S}^{-1}\hat{H}$ blocks.

The three energies associated with the $a_2$ irreducible representations are -28.541 $eV$, -13.618 $eV$, and -13.618 $eV$ for *all* configurations (consistent with the view that these are *anti-bonding* orbitals in the separate $CO_2$ molecules) and the three energies associated with the $b_1$ irreducible representations are -20.377 $eV$, -11.26 $eV$, and -11.26 $eV$ for *all* configurations (consistent with the view that these are *bonding* orbitals in the separate $CO_2$ molecules).

The following four tables give the orbital energies associated with the four irreducible representations as a function of the distortion parameter $\Delta$.

$a_1$ orbital energies ($eV$) as a function of $\Delta$ (column #1)

| | | | | | | | | |
|------|----------|---------|----------|----------|----------|----------|----------|---------|
| 0.0 | -38.2657 | -15.4148 | -14.5817 | -14.2963 | -13.1989 | -12.84 | -12.8358 | 12.1444 | 66.7007 |
| 0.2 | -37.7946 | -15.8602 | -14.4931 | -14.2021 | -13.3426 | -12.9655 | -12.9585 | 5.04851 | 51.0382 |
| 0.4 | -37.277 | -16.616 | -14.394 | -14.112 | -13.458 | -13.081 | -13.071 | -1.80249 | 44.5087 |
| 0.6 | -36.732 | -17.859 | -14.2962 | -14.02 | -13.549 | -13.185 | -13.17 | -6.79335 | 41.7094 |
| 0.8 | -36.177 | -19.629 | -14.20 | -13.955 | -13.62 | -13.276 | -13.257 | -9.74617 | 40.4587 |
| 1.0 | -35.632 | -21.586 | -14.12 | -13.8907 | -13.674 | -13.353 | -13.329 | -11.2878 | 39.8998 |
| 1.2 | -35.116 | -23.352 | -14.054 | -13.8361 | -13.713 | -13.417 | -13.390 | -12.1026 | 39.6607 |
| 1.4 | -34.64 | -24.787 | -13.99 | -13.7905 | -13.738 | -13.470 | -13.439 | -12.5713 | 39.5633 |
| 1.6 | -34.23 | -25.89 | -13.9478 | -13.753 | -13.752 | -13.512 | -13.479 | -12.8647 | 39.5194 |
| 1.8 | -33.88 | -26.720 | -13.9081 | -13.757 | -13.72 | -13.544 | -13.510 | -13.0606 | 39.4874 |
| 2.0 | -33.613 | -27.320 | -13.8751 | -13.756 | -13.698 | -13.568 | -13.535 | -13.1979 | 39.4507 |

$a_2$ orbital energies ($eV$) as a function of $\Delta$ (column #1)

| | | | |
|------|--------|--------|--------|
| 0.0 | -11.26 | -11.26 | -11.26 |
| 0.2 | -11.26 | -11.26 | -11.26 |
| 0.4 | -11.26 | -11.26 | -11.26 |
| 0.6 | -11.26 | -11.26 | -11.26 |
| 0.8 | -11.26 | -11.26 | -11.26 |
| 1.0 | -11.26 | -11.26 | -11.26 |
| 1.2 | -11.26 | -11.26 | -11.26 |
| 1.4 | -11.26 | -11.26 | -11.26 |
| 1.6 | -11.26 | -11.26 | -11.26 |
| 1.8 | -11.26 | -11.26 | -11.26 |
| 2.0 | -11.26 | -11.26 | -11.26 |

$b_1$ orbital energies ($eV$) as a function of $\Delta$ (column #1)

| | | | |
|------|---------|--------|--------|
| 0.0 | -20.337 | -11.26 | -11.26 |
| 0.2 | -20.337 | -11.26 | -11.26 |
| 0.4 | -20.337 | -11.26 | -11.26 |
| 0.6 | -20.337 | -11.26 | -11.26 |
| 0.8 | -20.337 | -11.26 | -11.26 |
| 1.0 | -20.337 | -11.26 | -11.26 |
| 1.2 | -20.337 | -11.26 | -11.26 |
| 1.4 | -20.337 | -11.26 | -11.26 |
| 1.6 | -20.337 | -11.26 | -11.26 |
| 1.8 | -20.337 | -11.26 | -11.26 |
| 2.0 | -20.337 | -11.26 | -11.26 |

$b_2$ orbital energies ($eV$) as a function of $\Delta$ (column #1)

| | | | | | | | | |
|------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 0.0 | -34.9595 | -17.1363 | -14.04 | -13.9652 | -13.5398 | -13.2506 | -13.2454 | -10.7231 | -6.18174 |
| 0.2 | -34.1797 | -18.7006 | -14.0039 | -13.8995 | -13.6168 | -13.3201 | -13.2906 | -11.0314 | -9.16851 |
| 0.4 | -33.4122 | -20.5434 | -13.97 | -13.8435 | -13.6771 | -13.3821 | -13.3274 | -11.7662 | -10.0706 |
| 0.6 | -32.6792 | -22.2645 | -13.9385 | -13.7967 | -13.7212 | -13.4329 | -13.361 | -12.3916 | -10.2631 |
| 0.8 | -31.9995 | -23.6959 | -13.9093 | -13.7582 | -13.75 | -13.4739 | -13.3916 | -12.7755 | -10.3273 |
| 1. | -31.3864 | -24.8323 | -13.8825 | -13.7654 | -13.727 | -13.5066 | -13.4194 | -13.016 | -10.3568 |
| 1.2 | -30.848 | -25.7177 | -13.8579 | -13.7696 | -13.7021 | -13.5325 | -13.4446 | -13.1751 | -10.3727 |
| 1.4 | -30.3864 | -26.4016 | -13.8357 | -13.7651 | -13.6824 | -13.5528 | -13.4672 | -13.2855 | -10.382 |
| 1.6 | -29.9995 | -26.9272 | -13.8158 | -13.7544 | -13.667 | -13.5685 | -13.4876 | -13.3648 | -10.3879 |
| 1.8 | -29.6817 | -27.3298 | -13.7981 | -13.7401 | -13.6551 | -13.5807 | -13.5058 | -13.4234 | -10.3917 |
| 2.0 | -29.4252 | -27.637 | -13.7824 | -13.7241 | -13.6459 | -13.59 | -13.5221 | -13.4675 | -10.3944 |

For each $\Delta$, the *aufbau* principle will identify the ground state of the system as the state in which the 16 lowest energy orbitals will be occupied by 32 electrons. Plotting the orbital energies as a function of $\Delta$ is confusing because there are so many (24) and because the orbital energies of different irreducible representations can (and do) cross each other. In the following table, the *symmetries* of the orbitals found at each $\Delta$ are listed in columns. The order of the listing is such that, as one rises in a column one encounters the oribitals in the order of increasing orbital energy.

| $\Delta$ | 0.0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.4 | 1.6 | 1.8 | 2.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ |
| | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ |
| | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ |
| | $b_2$ | $b_2$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ |
| | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ |
| | $b_1$ | $b_1$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ |
| | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ |
| | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_2$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ |
| | $a_2$ | $a_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ |
| | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $b_2$ | $b_2$ |
| | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $b_2$ | $b_2$ | $a_1$ | $a_1$ |
| | $a_1$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ |
| | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ |
| | $b_2$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ |
| | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ |
| | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $a_1$ | $b_2$ | $b_2$ |
| | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $a_1$ | $a_1$ | $b_2$ | $a_1$ | $a_1$ |
| | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ |
| | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ |
| | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ | $b_1$ |
| | $b_2$ | $b_2$ | $b_1$ | $b_1$ | $b_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ |
| | $b_1$ | $b_1$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ |
| | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ | $b_2$ |
| | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ | $a_1$ |

In this table, a horrizontal line has been drawn above the $16^{th}$ level. At each $\Delta$, the ground state configuration will consist of all the levels below this line filled and no levels above this line filled.

A rough image of the crossing of the levels as $\Delta$ is changed can be generated by passing lines through the symmetry symbols of the orbitals. The lowest energy orbital, for example, does not change with $\Delta$. But the highest occupied orbital ($a_2$ at $\Delta = 0.0$) moves out of the ground state configuration as $\Delta$ passes from $0.2 \rightarrow 0.4$! It is replaced as the highest energy occupied orbital by a $b_2$ symmetry orbital whose energy descends rapidly as $\Delta$ rises.

Thus, if we start in the ground state with $\Delta = 0$ and increase $\Delta$ *adiabatically*, the state will pass from a gound state configuration into an excited state configuration when $\Delta$ passes from $0.2 \rightarrow 0.4$.

If we suppose the de-excitation occurs when the molecule has a configuration $\approx \Delta = 2.0$, the energy that will be transferred to the dye will be the energy difference between the $a_2$ and $b_2$ orbitals in configuration $\Delta = 2.0$, $-11.26 \ eV + 13.4675 \ eV = 2.21 \ eV$. As a *red* photon has an energy $\approx 1.65 \ eV$, there is clearly enough energy to excite the dye!

## Some additional notes

In commercial software it is always easy to *optimize* the structure, i.e., move around on the Born-Oppenheimer surface to find the structure with a minimum energy. I did not cover in the class the *Feynmann-Hellman* theorem that shows that an essentially classical calculation can be used to determine the force on atoms in any given configuration (and hence it is easy move toward an energy minimum).

The orbital description doesn't tell *which* $CO_2$ molecule ends up in an excited state. But that is a classical question. Quantum mechanics recognizes the symmetry of the situation: It's possible to have a state in which the probability that either $CO_2$ molecule is excited is "50-50".

In fact, the description that "a $CO_2$ molecule is excited" is inaccurate, for it is based on the assumption that the orbital occupation remains constant in the dissociation process. This turns out not to be correct: The *ESR* spectroscopists were able to observe

that the dissociating complex went through a *biradical* configuration. Two separate one-electron jumps doesn't actually occur. Rather, the biradical is formed and it is the re-arrangement of the electrons in the biradical that provides the energy for the light emission.