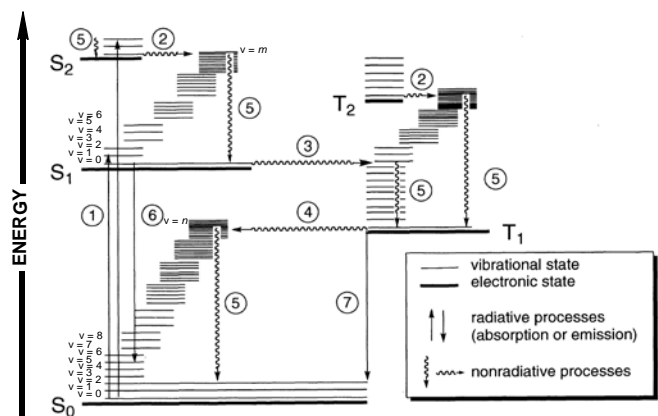


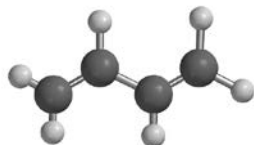


# A State Energy Diagram and Photophysical Processes

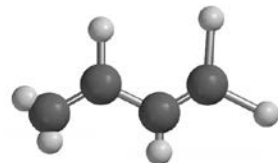


vibrationally excited

less



more

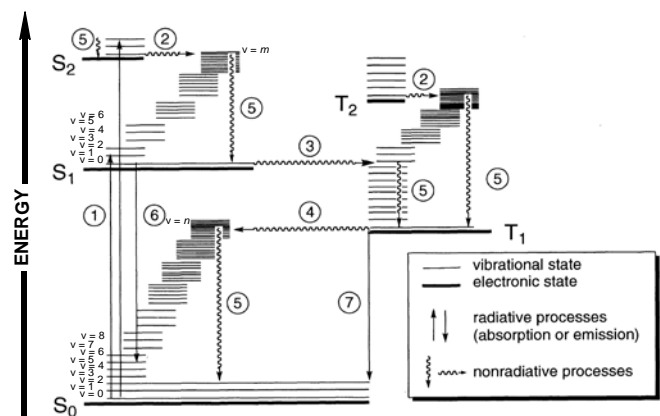


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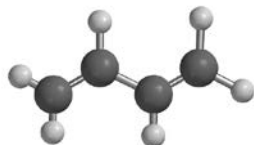


# A State Energy Diagram and Photophysical Processes

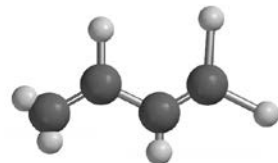


vibrationally excited

less



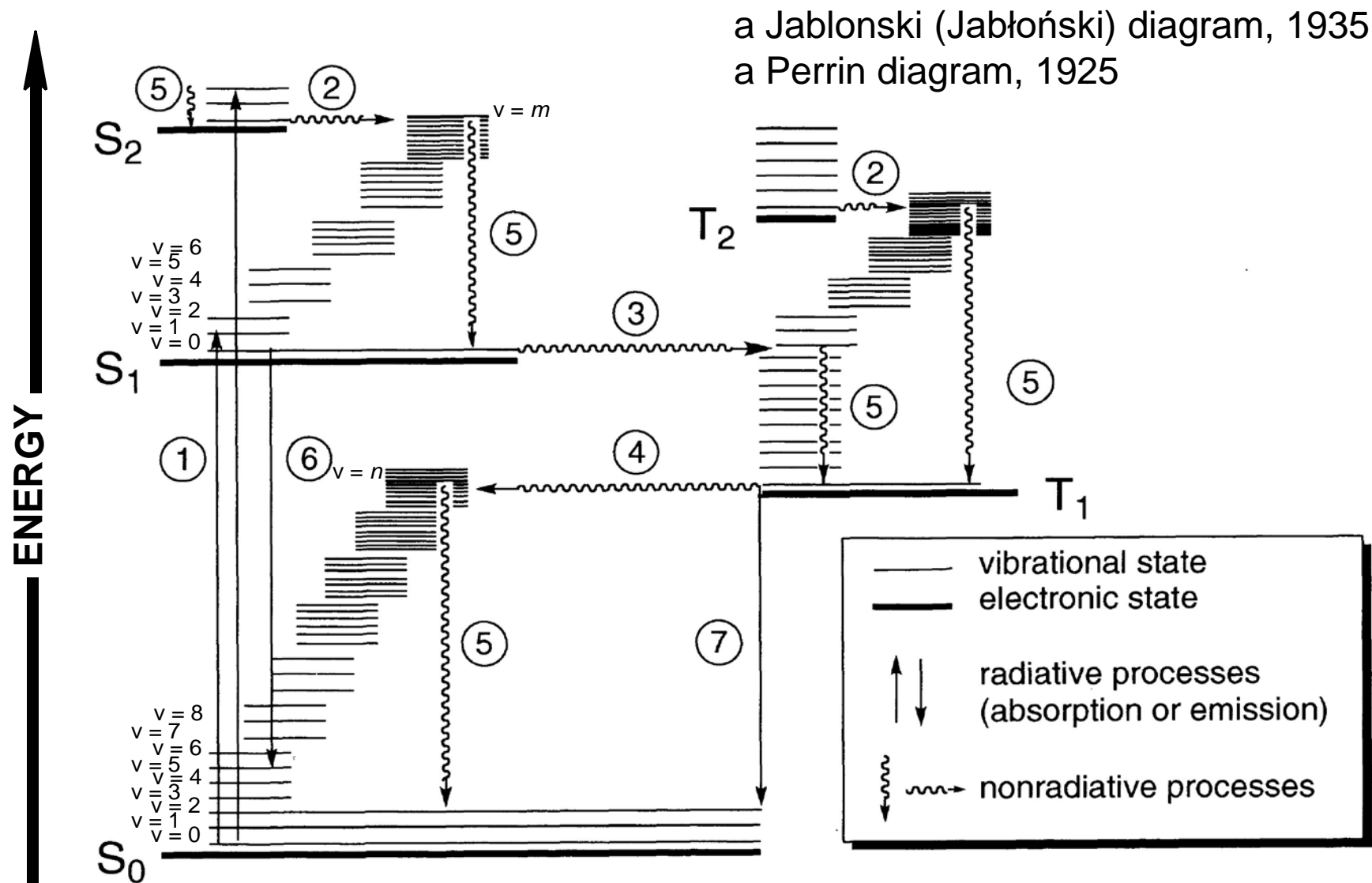
more



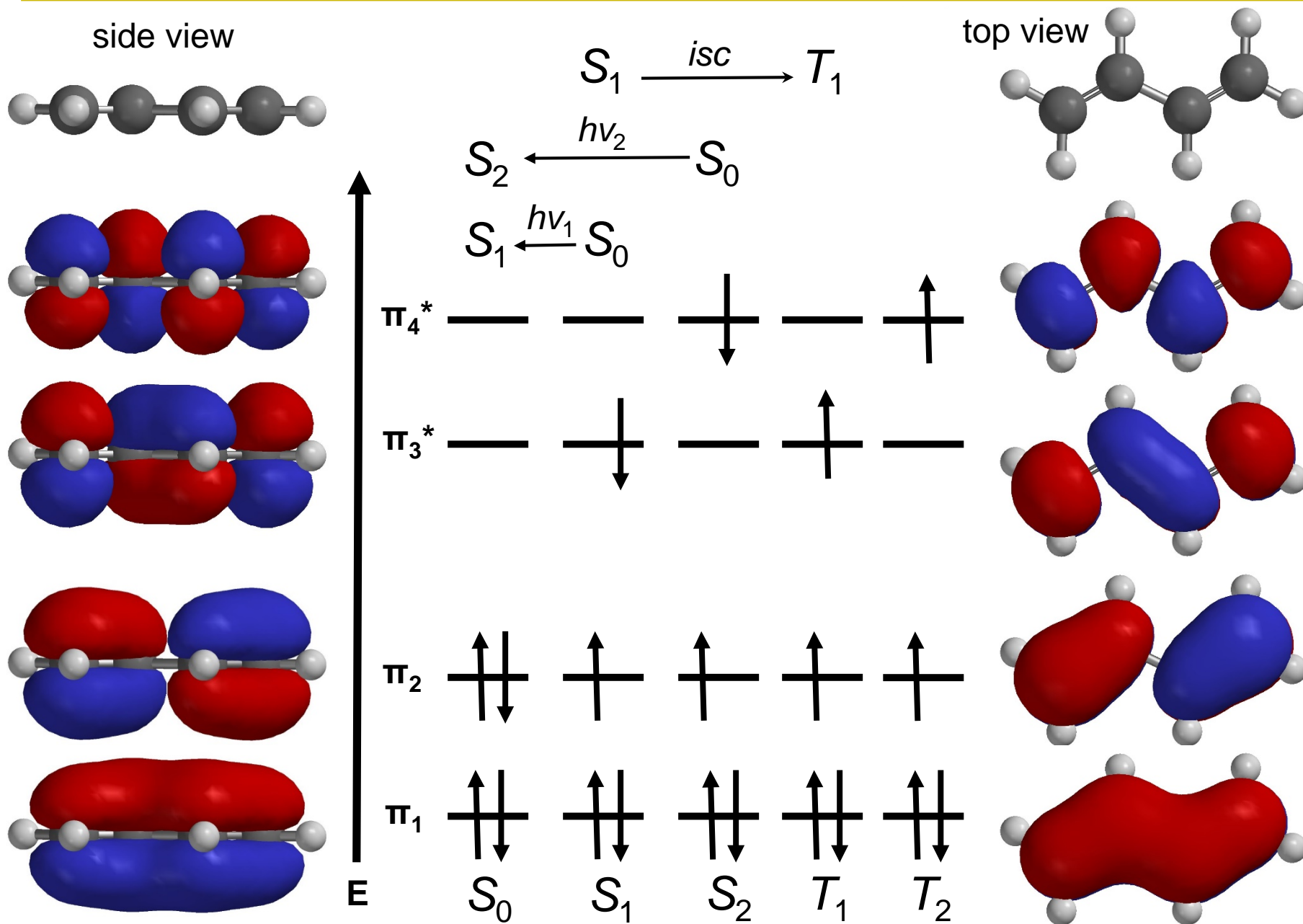
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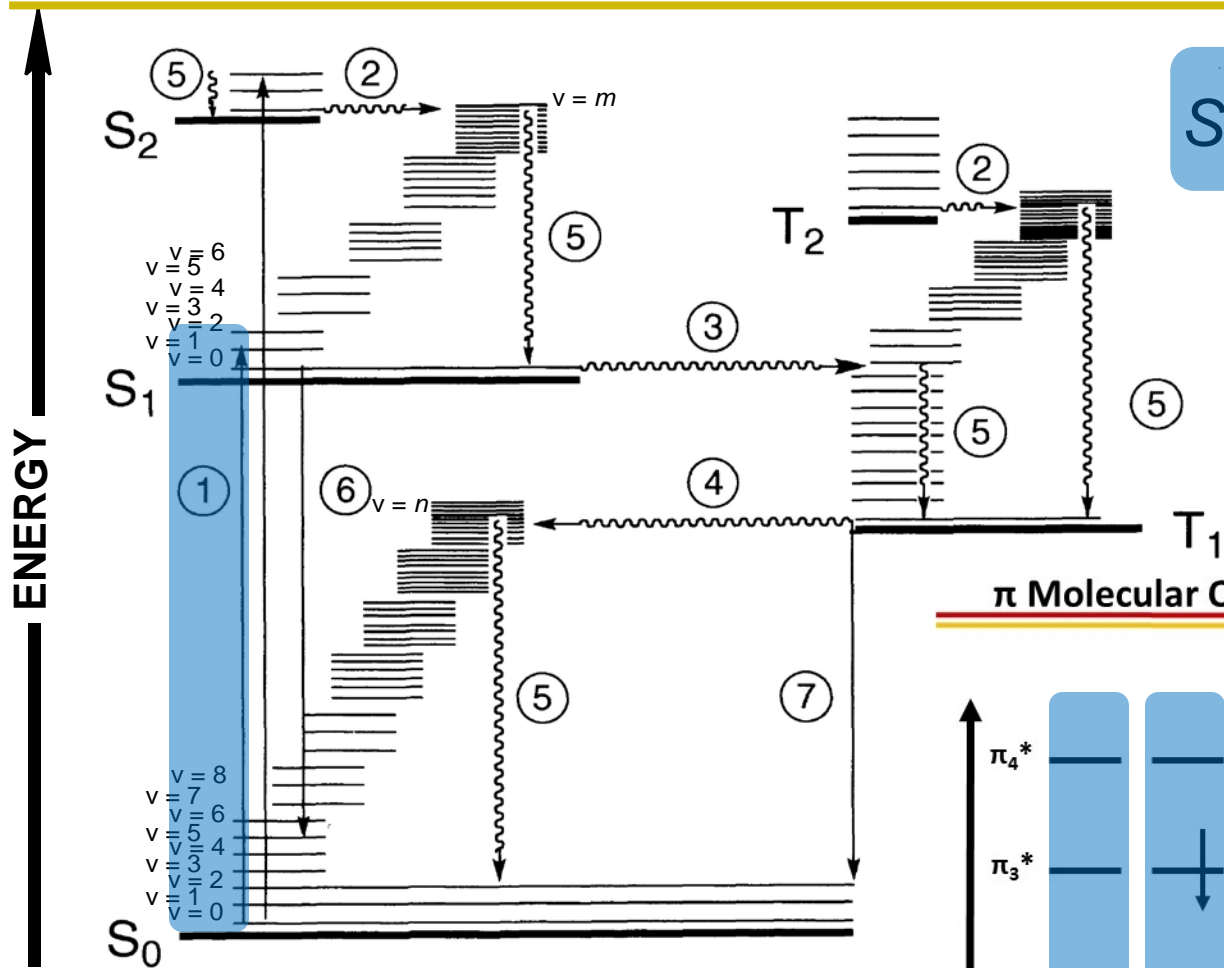
# A State Energy Diagram



# $\pi$ Molecular Orbitals (MOs) of 1,3-Butadiene



# ① Electronic Absorption

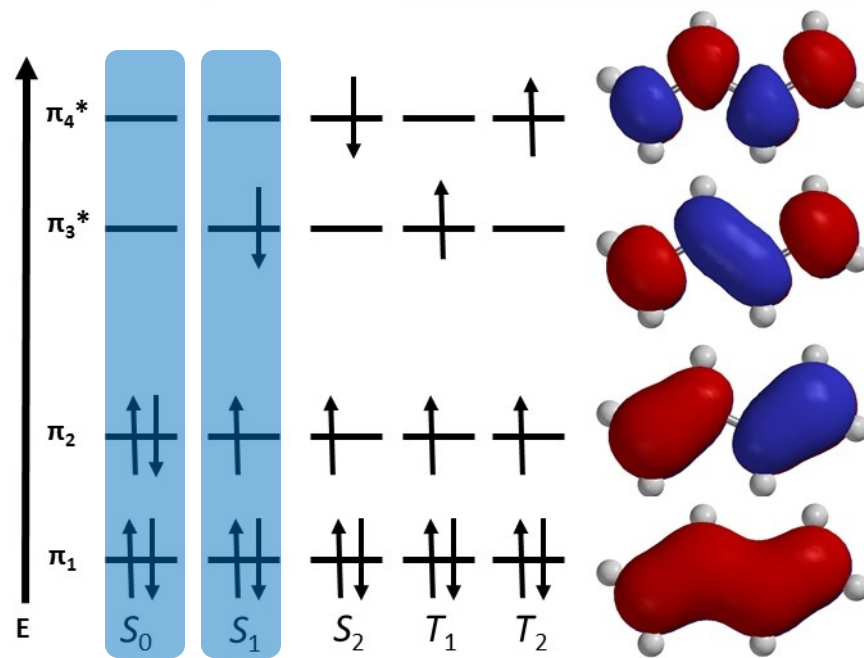


$$S_1 (v = 1) \leftarrow S_0 (v = 0) + h\nu_1$$

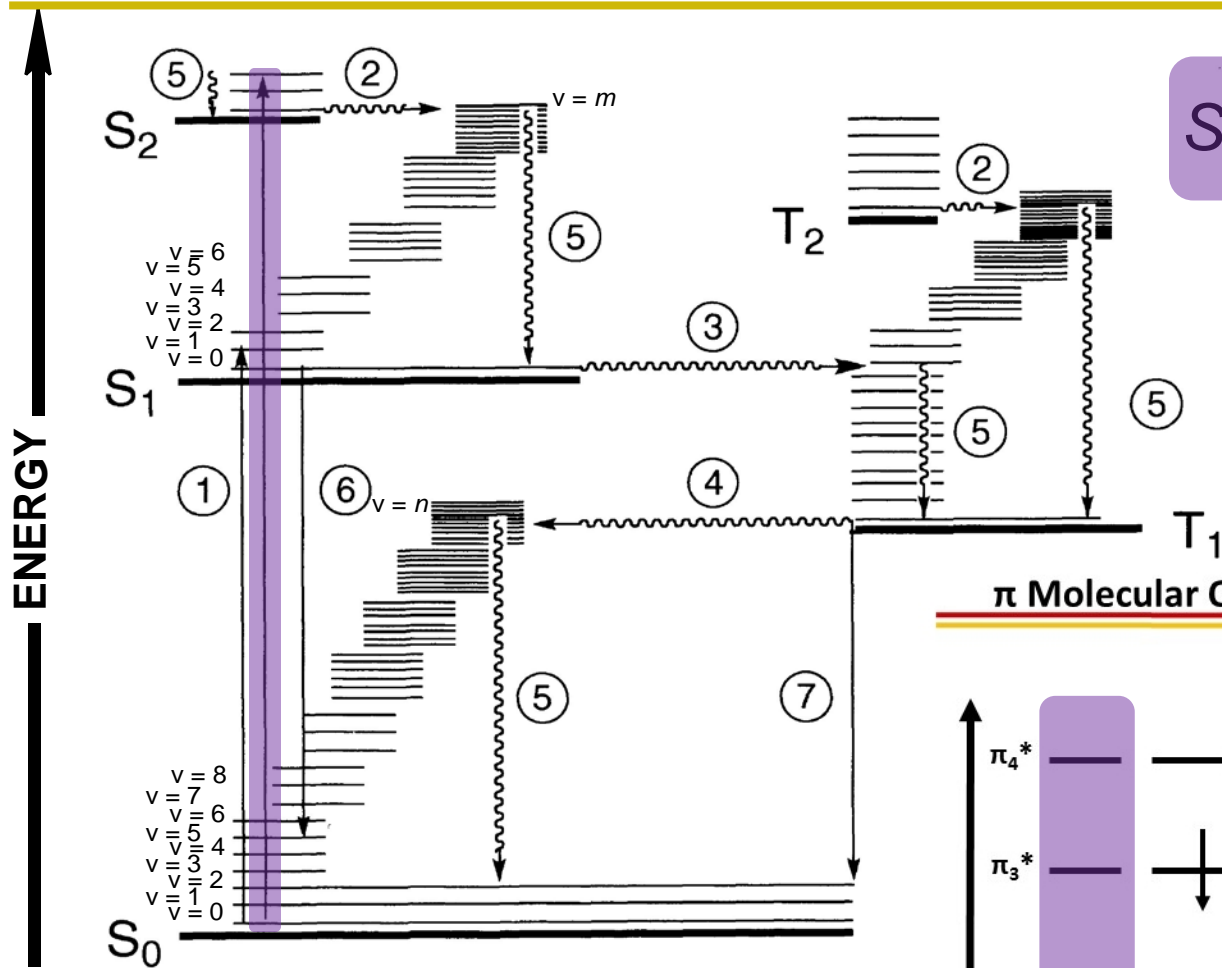
time scale:  $10^{-15}$  s

a radiative transition:  
electromagnetic radiation  
is involved

## $\pi$ Molecular Orbitals (MOs) of 1,3-Butadiene



# ① Electronic Absorption ( $h\nu_2 > h\nu_1$ )

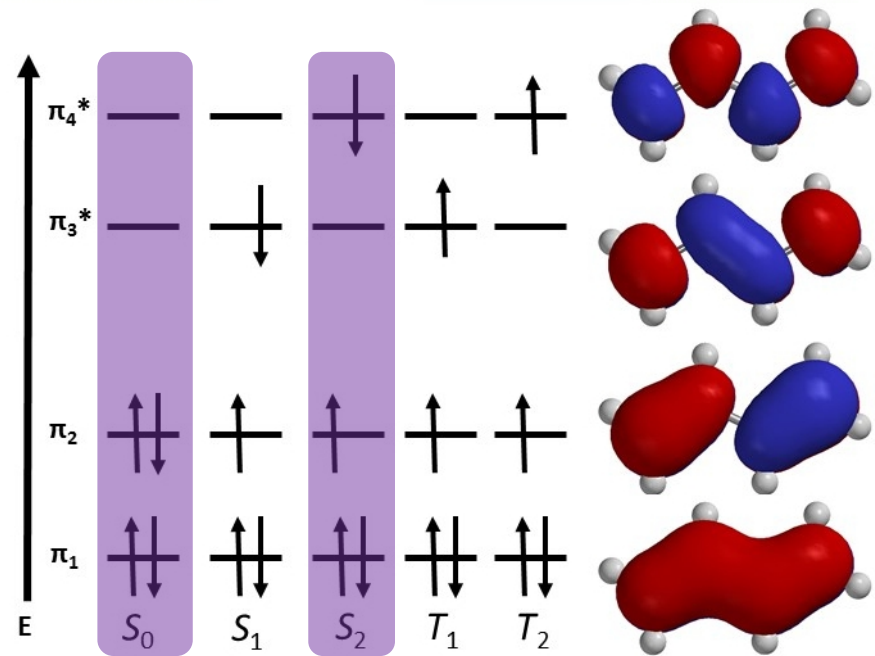


$$S_2 (v = 2) \leftarrow S_0 (v = 0) + h\nu_2$$

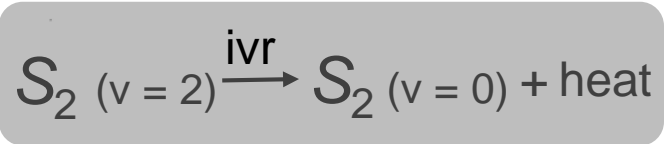
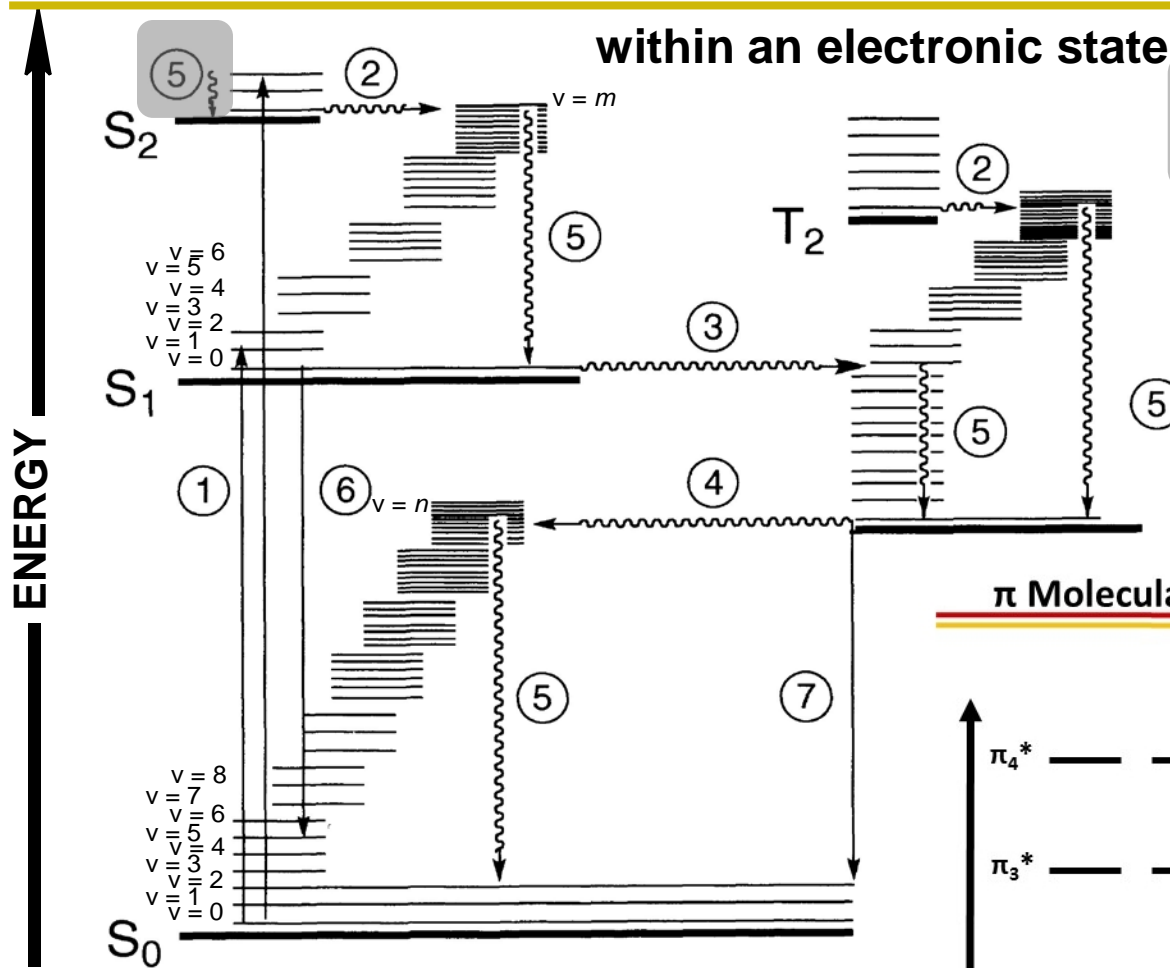
time scale:  $10^{-15}$  s

a radiative transition:  
electromagnetic radiation  
is involved

## $\pi$ Molecular Orbitals (MOs) of 1,3-Butadiene



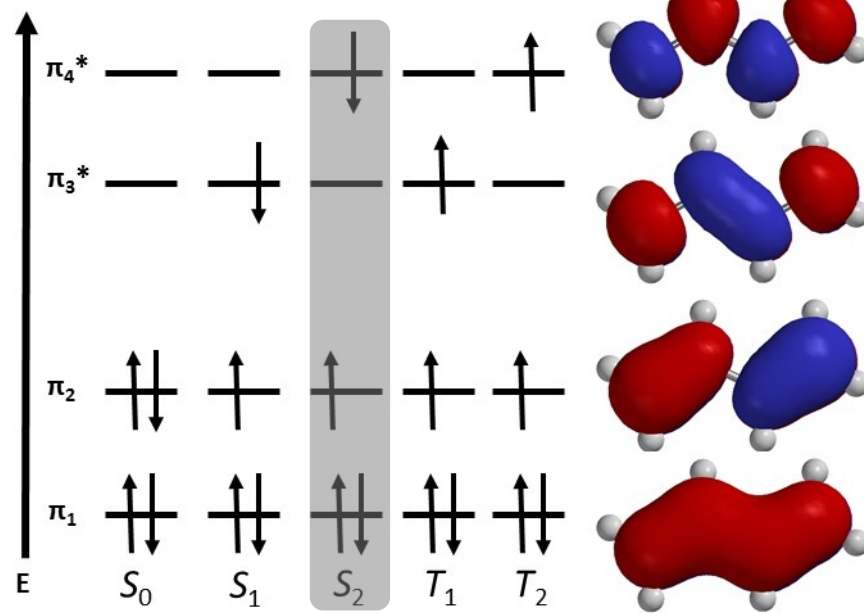
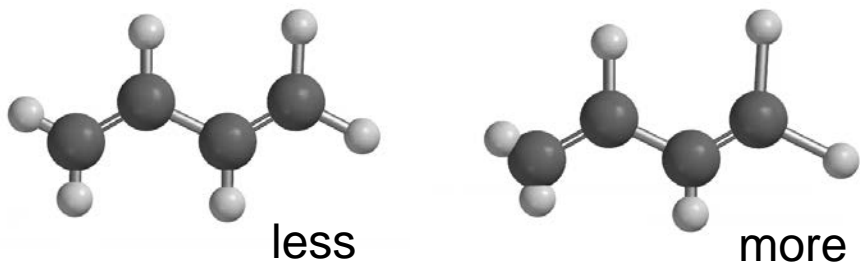
# ⑤ Intramolecular Vibrational Relaxation



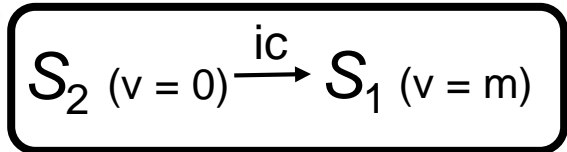
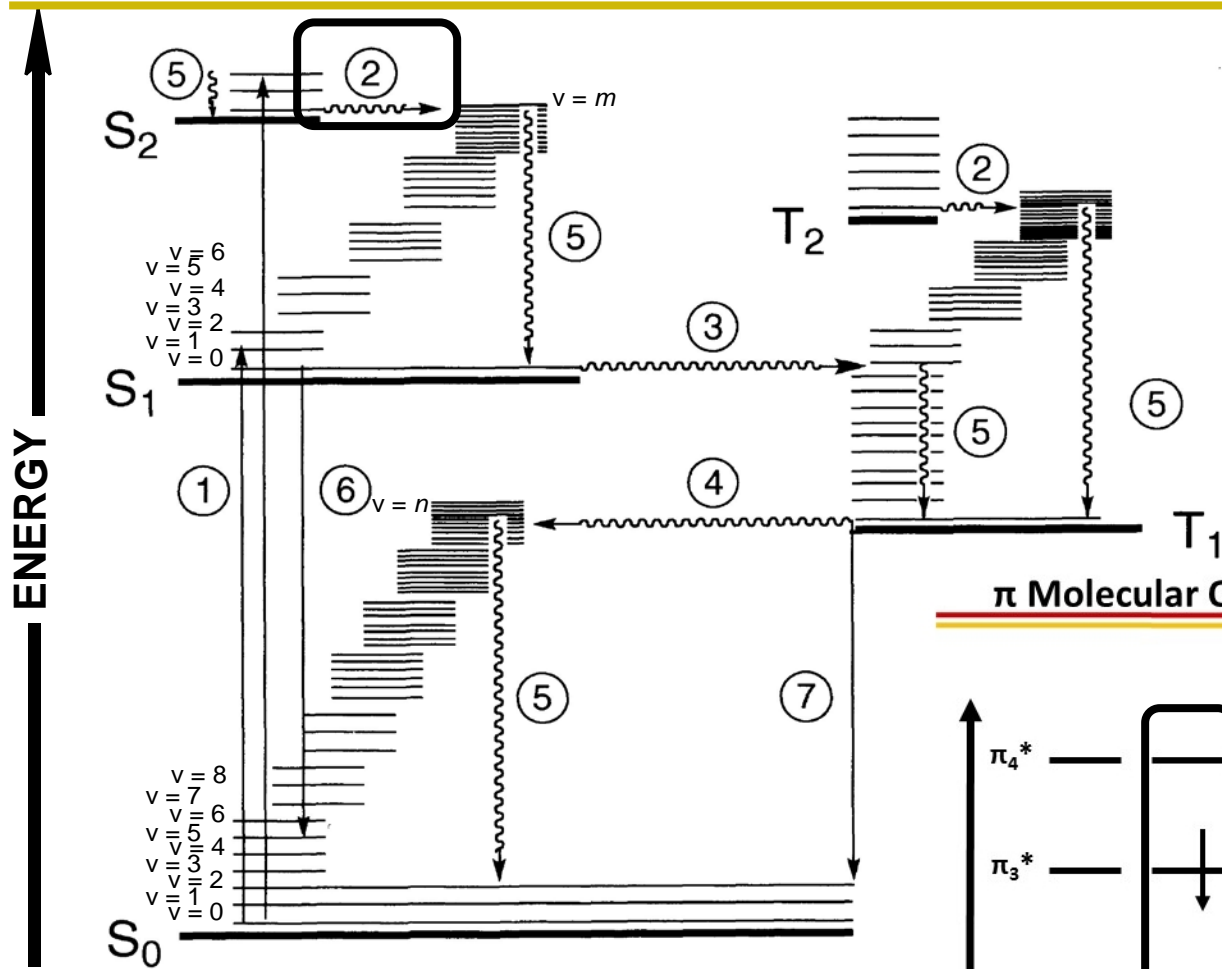
time scale:  $10^{-13} - 10^{-12}$  s

a nonradiative transition:  
no electromagnetic radiation  
is involved; heat is released

## $\pi$ Molecular Orbitals (MOs) of 1,3-Butadiene



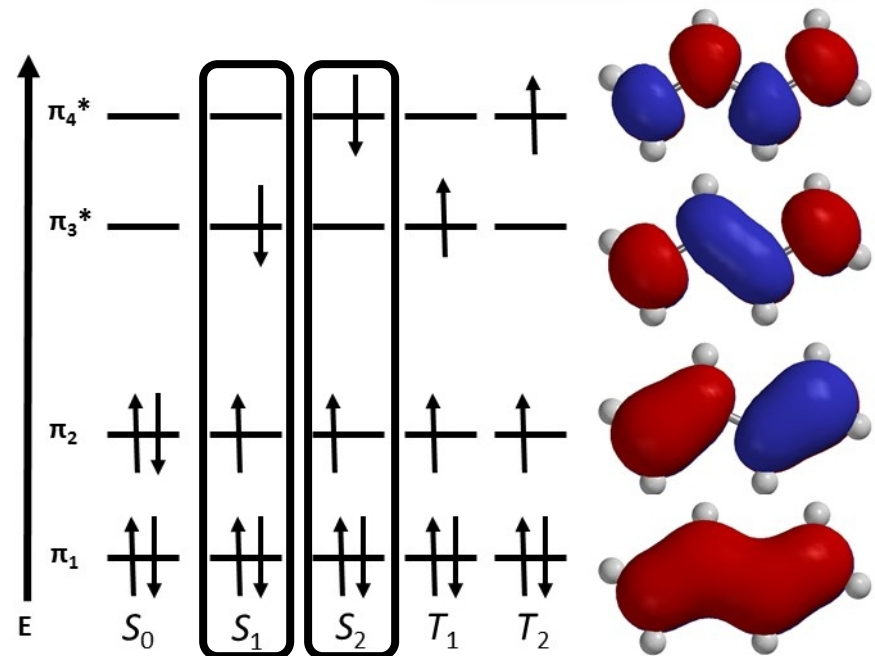
# ② Internal Conversion, an Isoenergetic Process



time scale:  $10^{-12} - 10^{-6}$  s

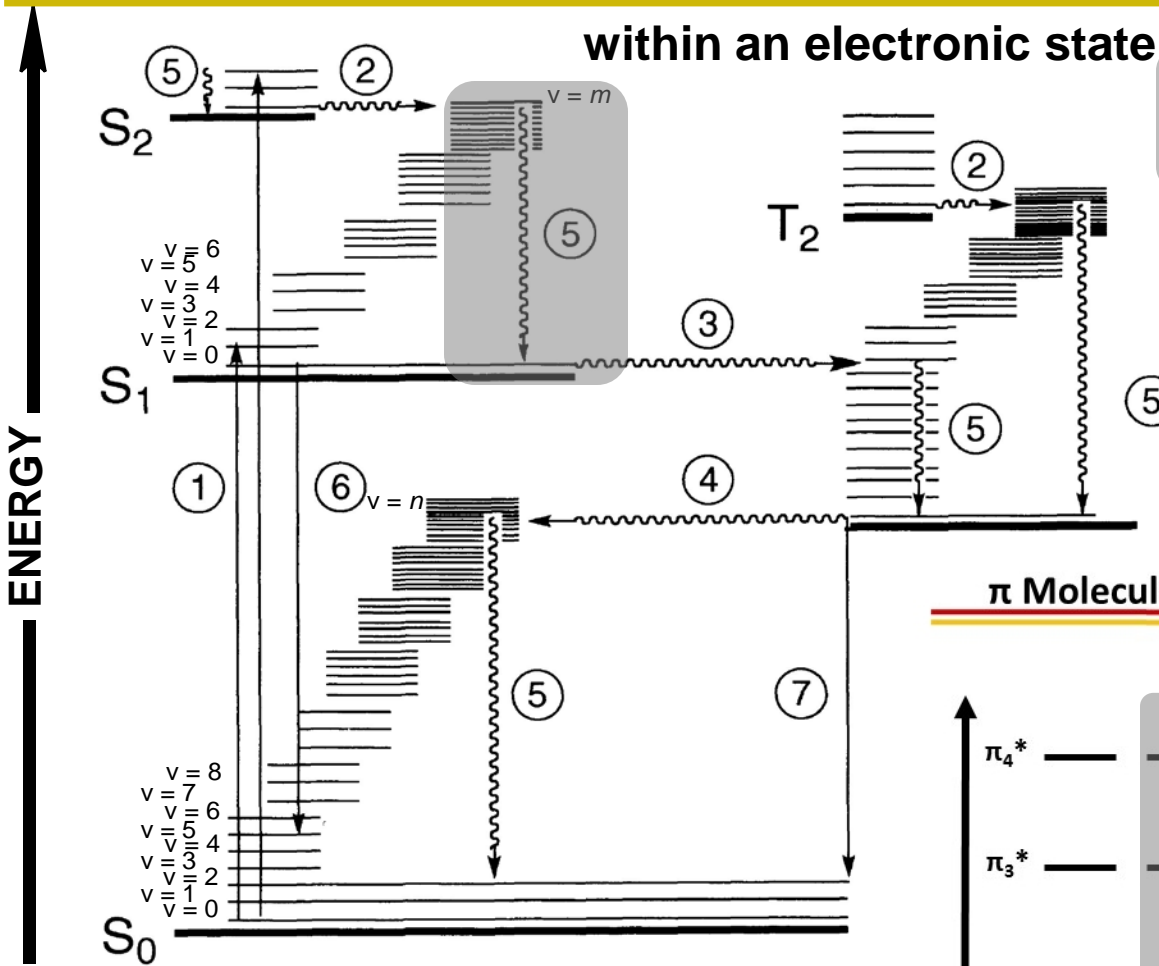
a nonradiative transition:  
no electromagnetic radiation  
is involved

$\pi$  Molecular Orbitals (MOs) of 1,3-Butadiene





# ⑤ Intramolecular Vibrational Relaxation

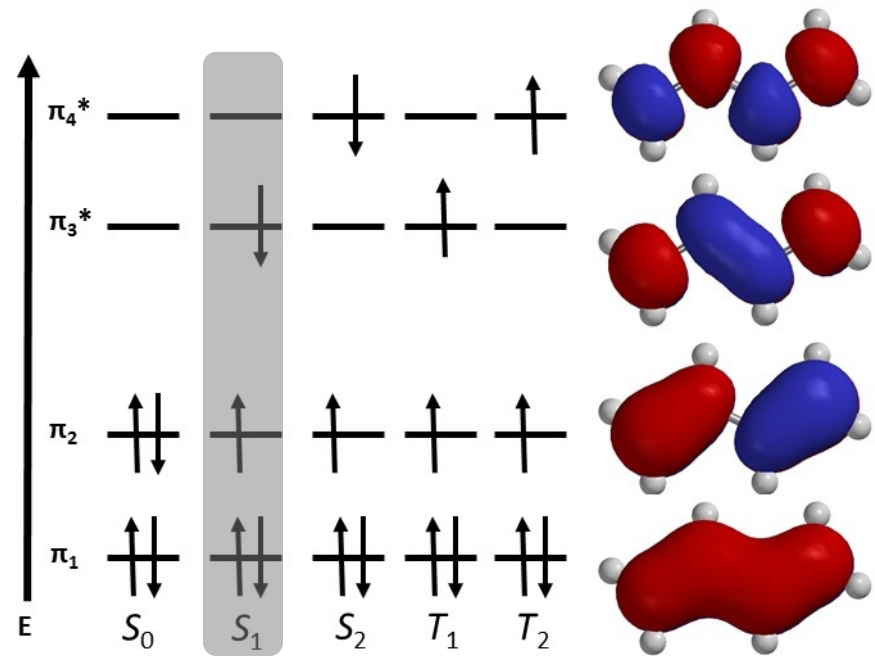


$$S_1 (v = m) \xrightarrow{\text{ivr}} S_1 (v = 0) + \text{heat}$$

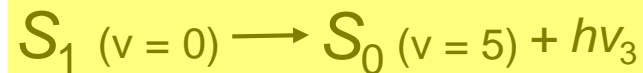
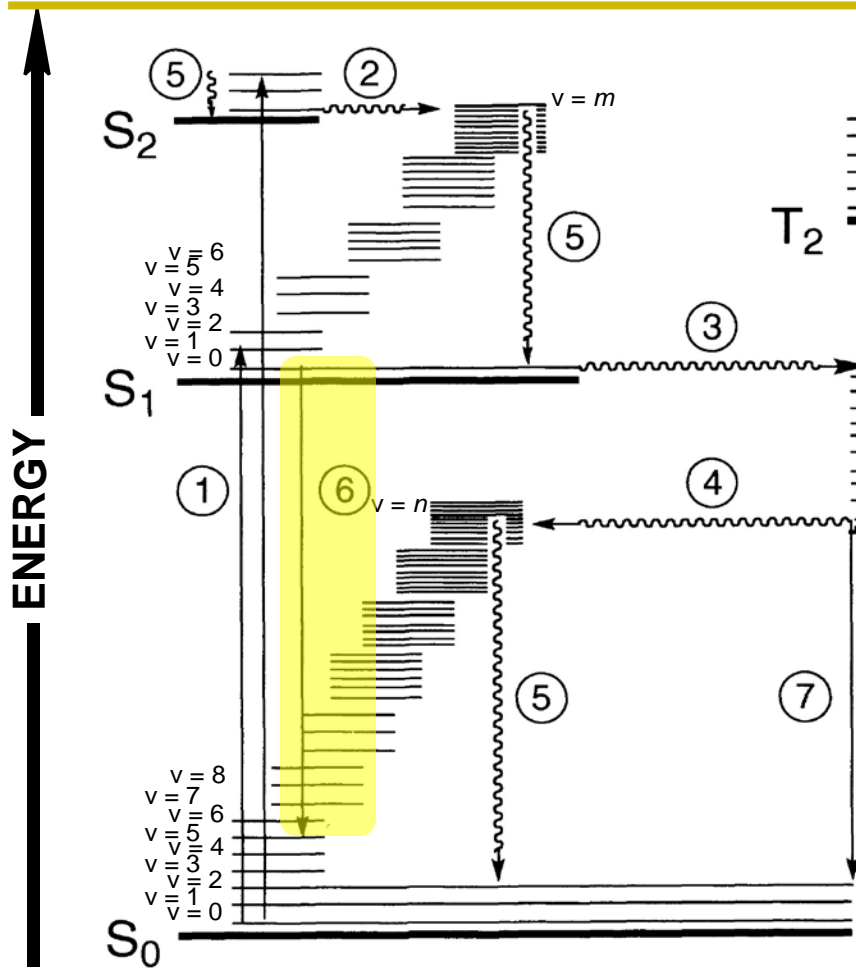
time scale:  $10^{-13} - 10^{-12}$  s

a nonradiative transition:  
no electromagnetic radiation  
is involved; heat is released

$\pi$  Molecular Orbitals (MOs) of 1,3-Butadiene



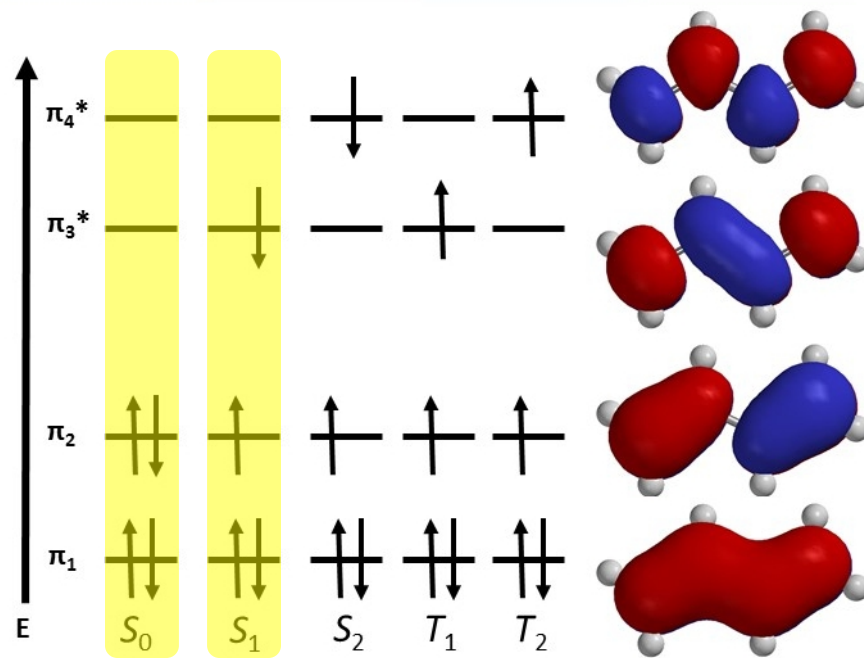
# ⑥ Fluorescence



time scale:  $10^{-9} - 10^{-7}$  s

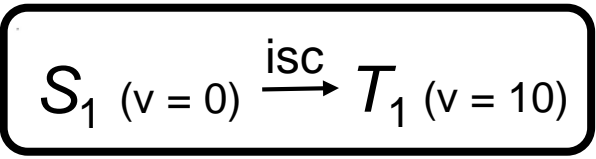
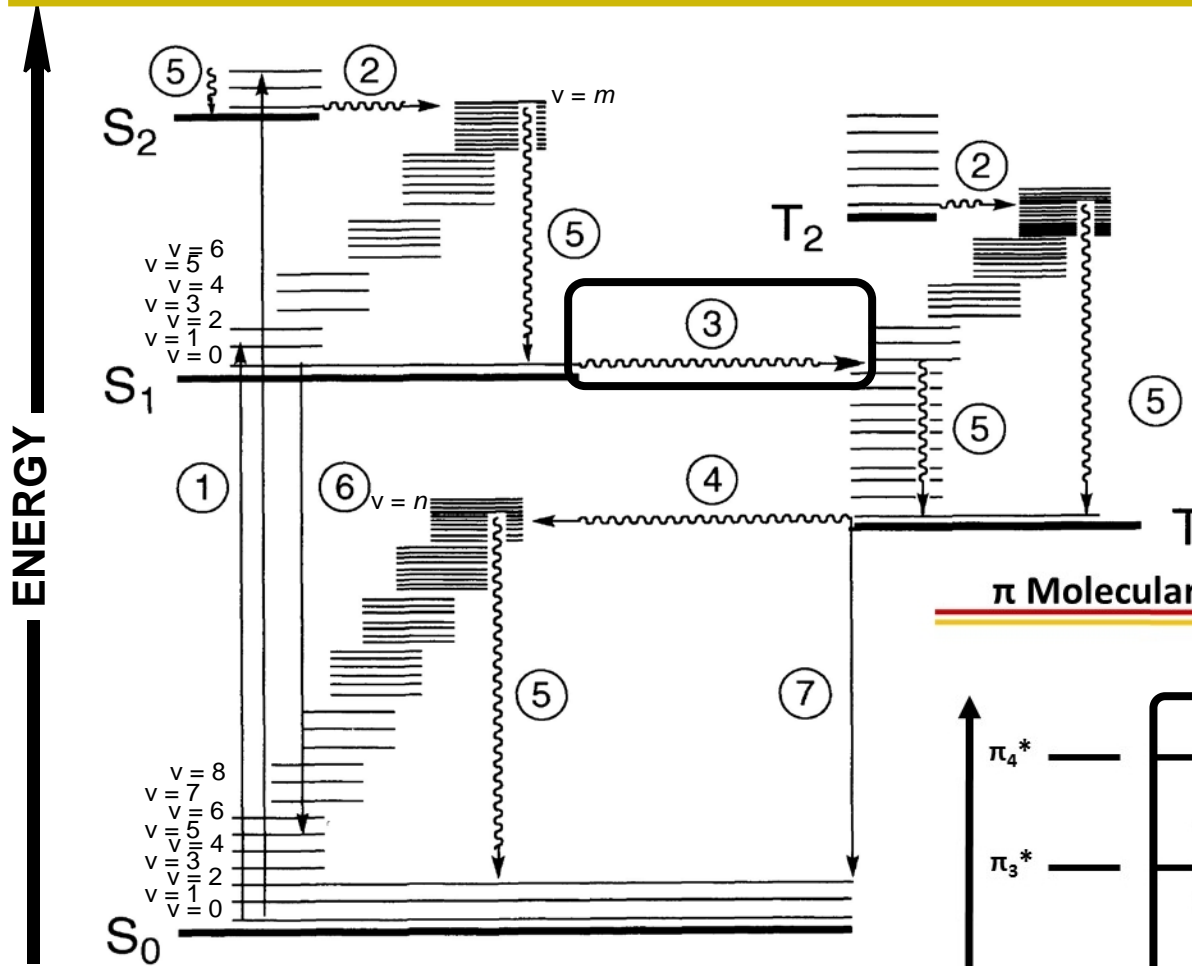
a radiative transition:  
electromagnetic radiation  
is involved

## $\pi$ Molecular Orbitals (MOs) of 1,3-Butadiene



**Kasha's rule:** polyatomic molecules generally luminesce only from the lowest energy electronically excited state of a given multiplicity.

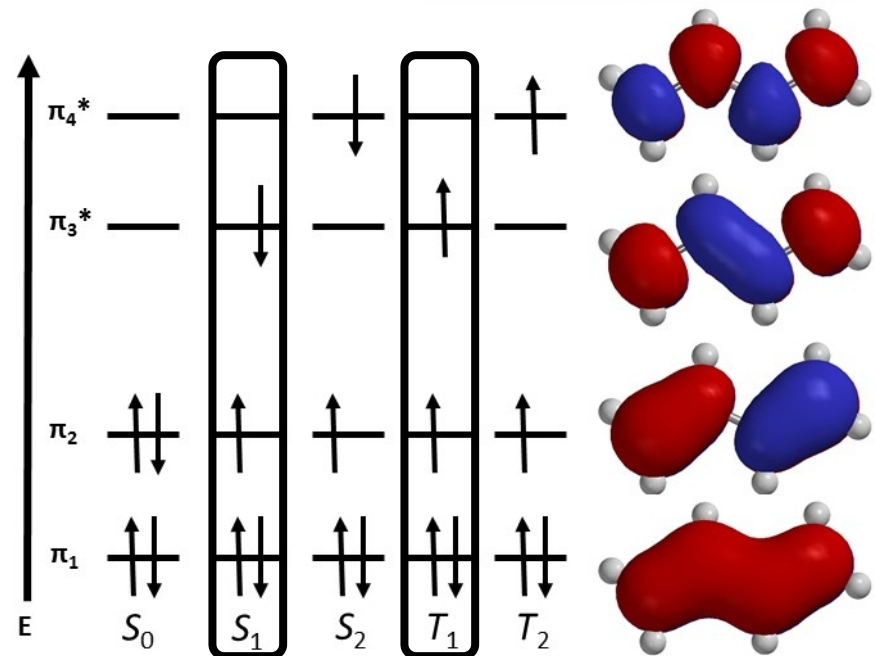
# ③ Intersystem Crossing, an Isoenergetic Process



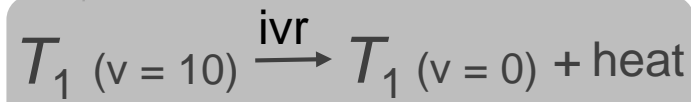
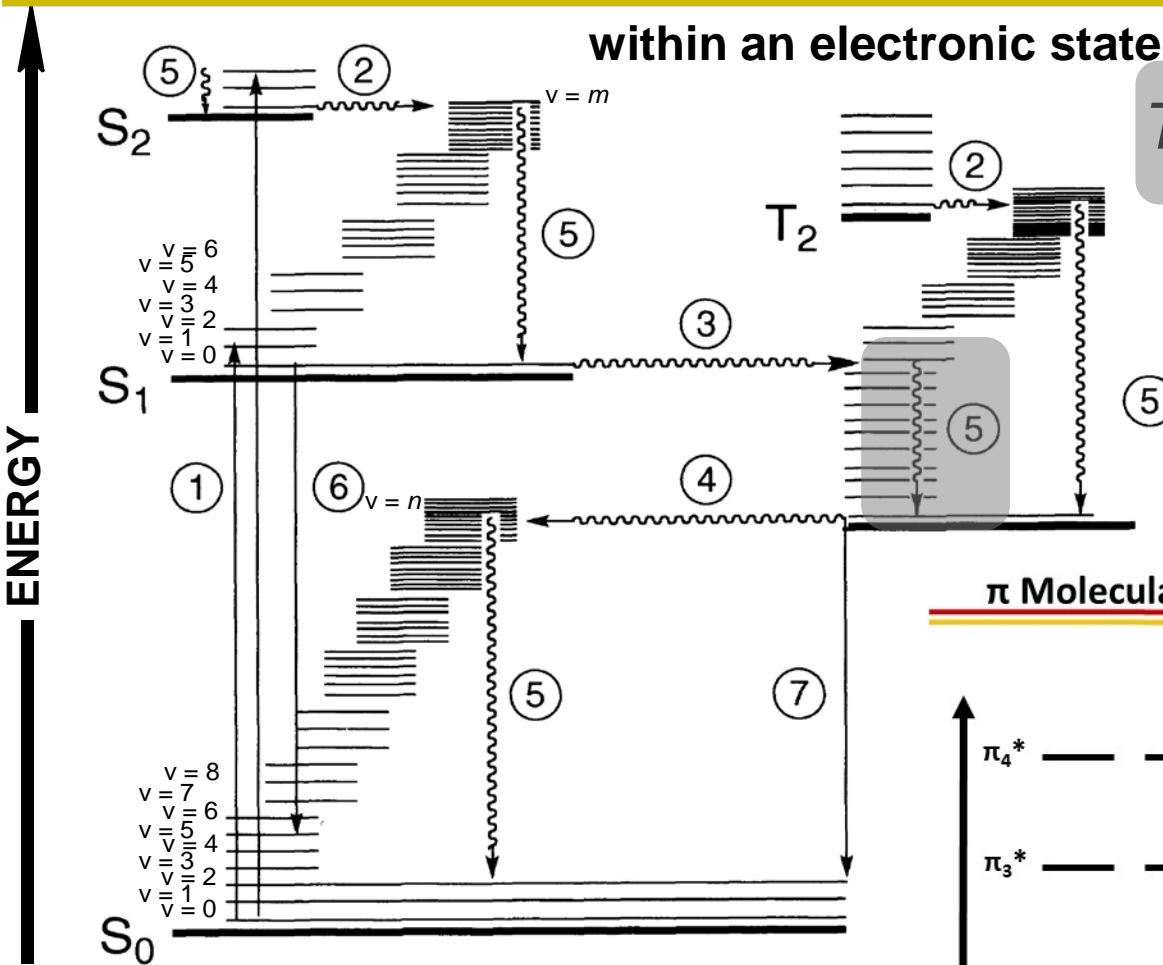
time scale:  $10^{-12} - 10^{-6}$  s

a nonradiative transition:  
no electromagnetic radiation  
is involved

$\pi$  Molecular Orbitals (MOs) of 1,3-Butadiene



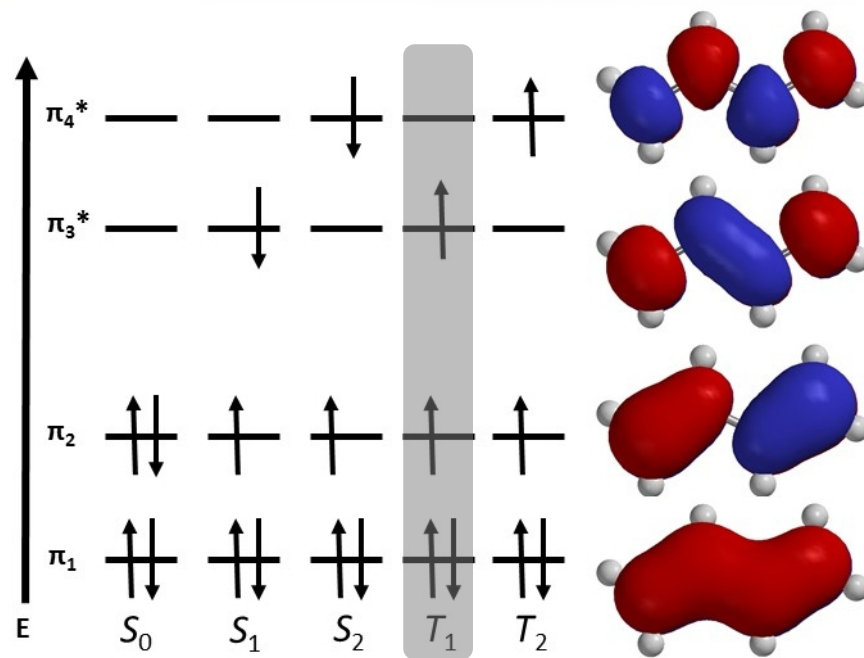
# ⑤ Intramolecular Vibrational Relaxation



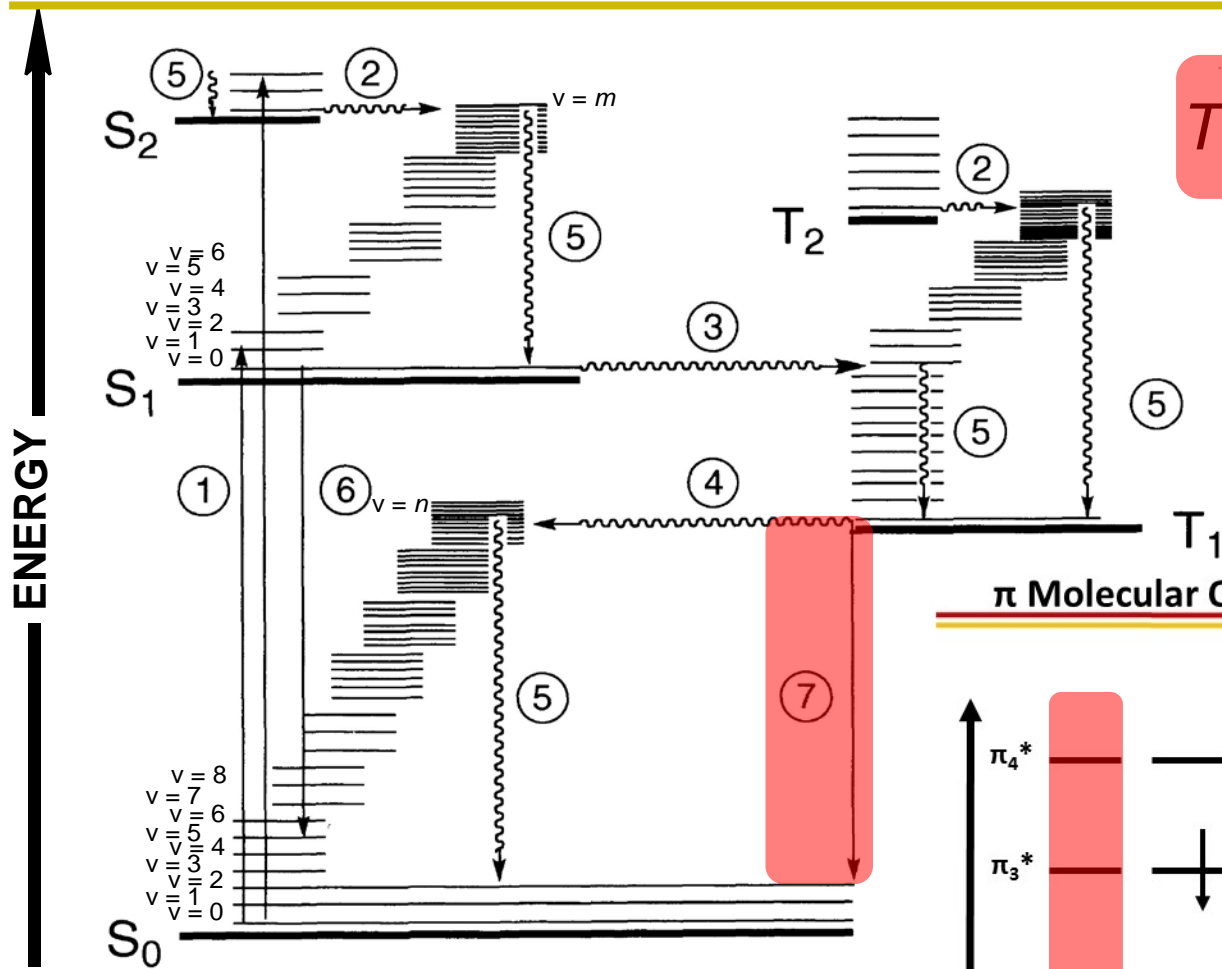
time scale:  $10^{-13} - 10^{-12}$  s

a nonradiative transition:  
no electromagnetic radiation  
is involved; heat is released

## $\pi$ Molecular Orbitals (MOs) of 1,3-Butadiene



# 7 Phosphorescence

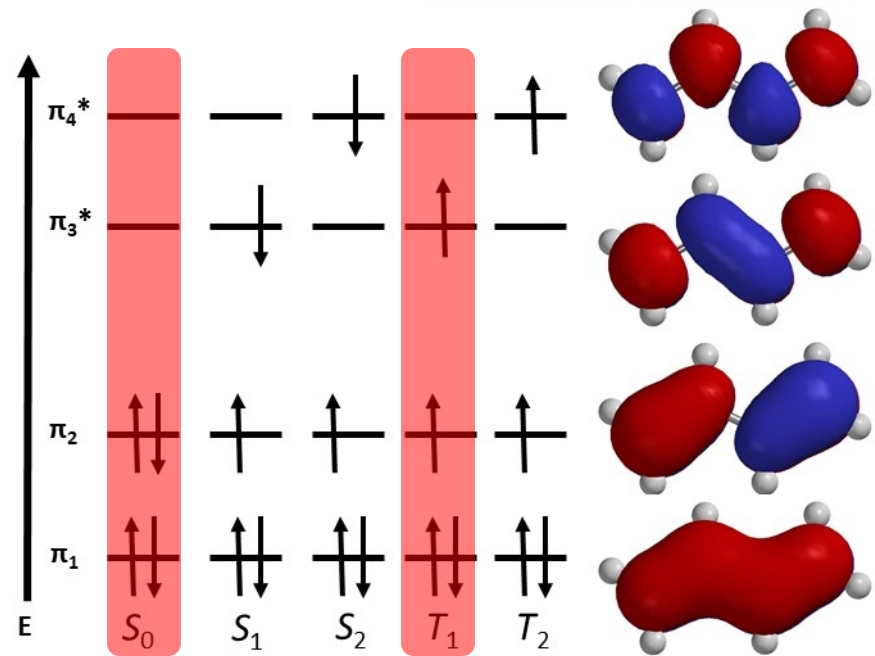


$$T_1 (v=0) \longrightarrow S_0 (v=2) + hv_4$$

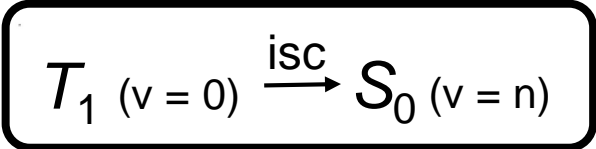
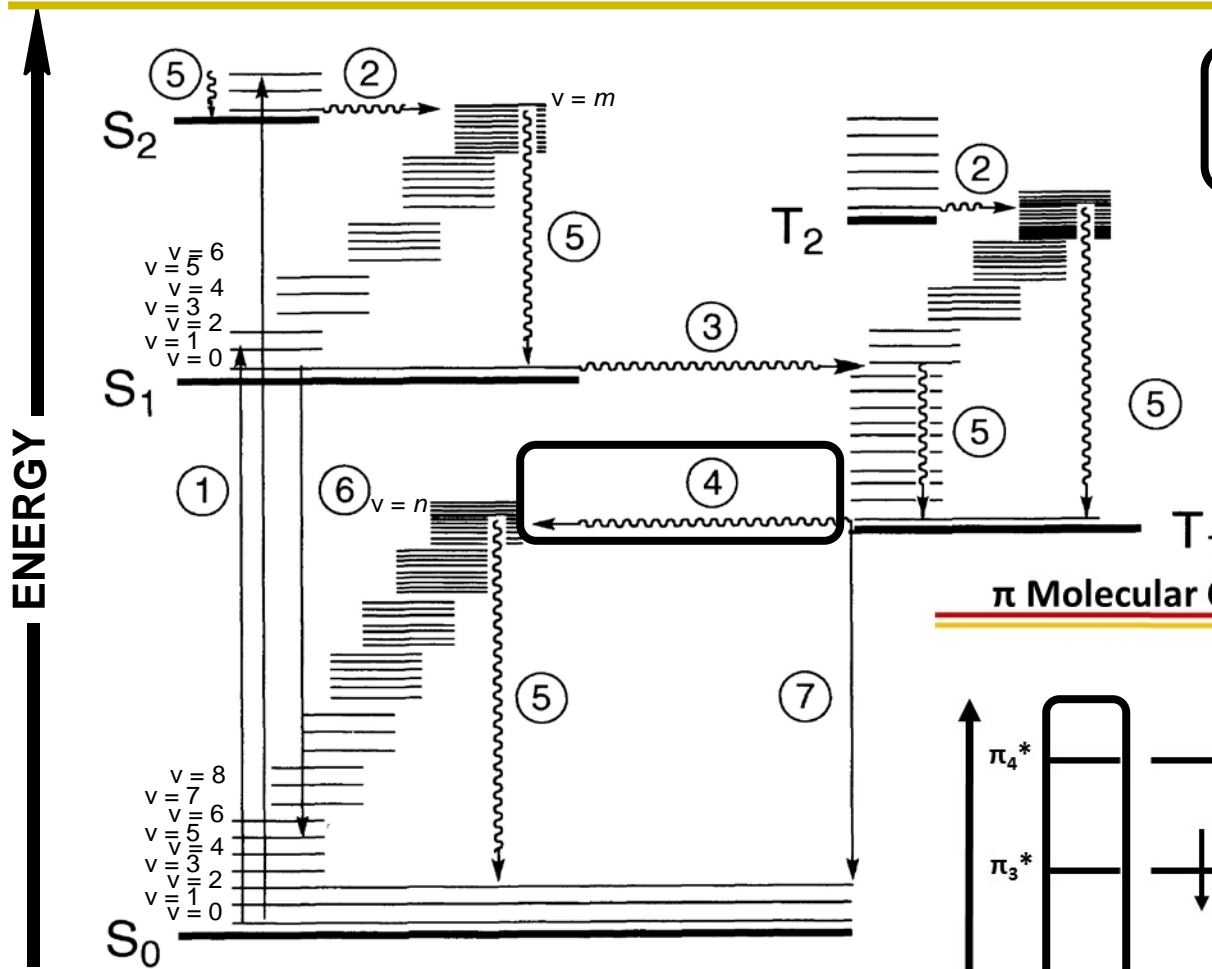
time scale:  $10^{-6} - 10^{-3}$  s

a radiative transition:  
electromagnetic radiation  
is involved

## $\pi$ Molecular Orbitals (MOs) of 1,3-Butadiene



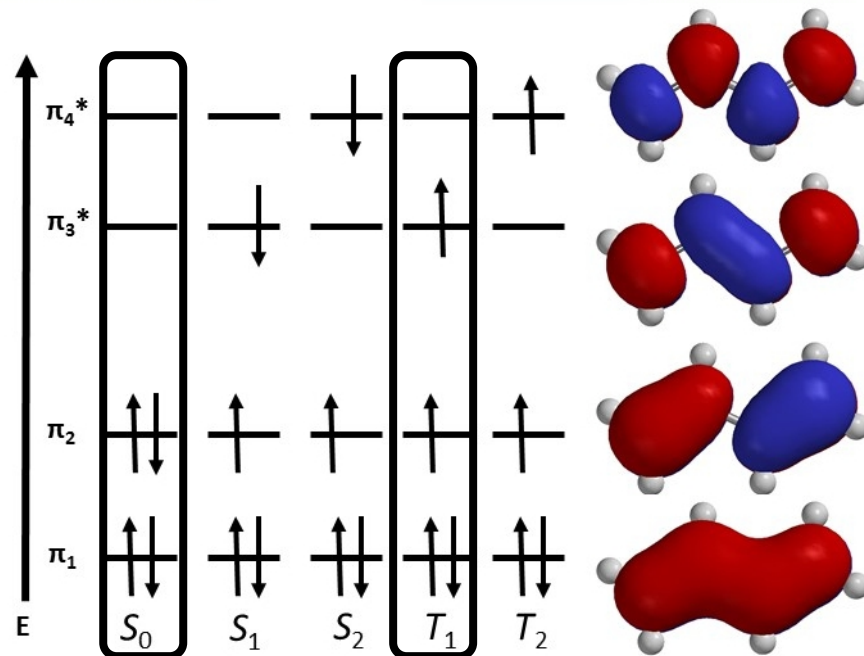
# ④ Intersystem Crossing, an Isoenergetic Process



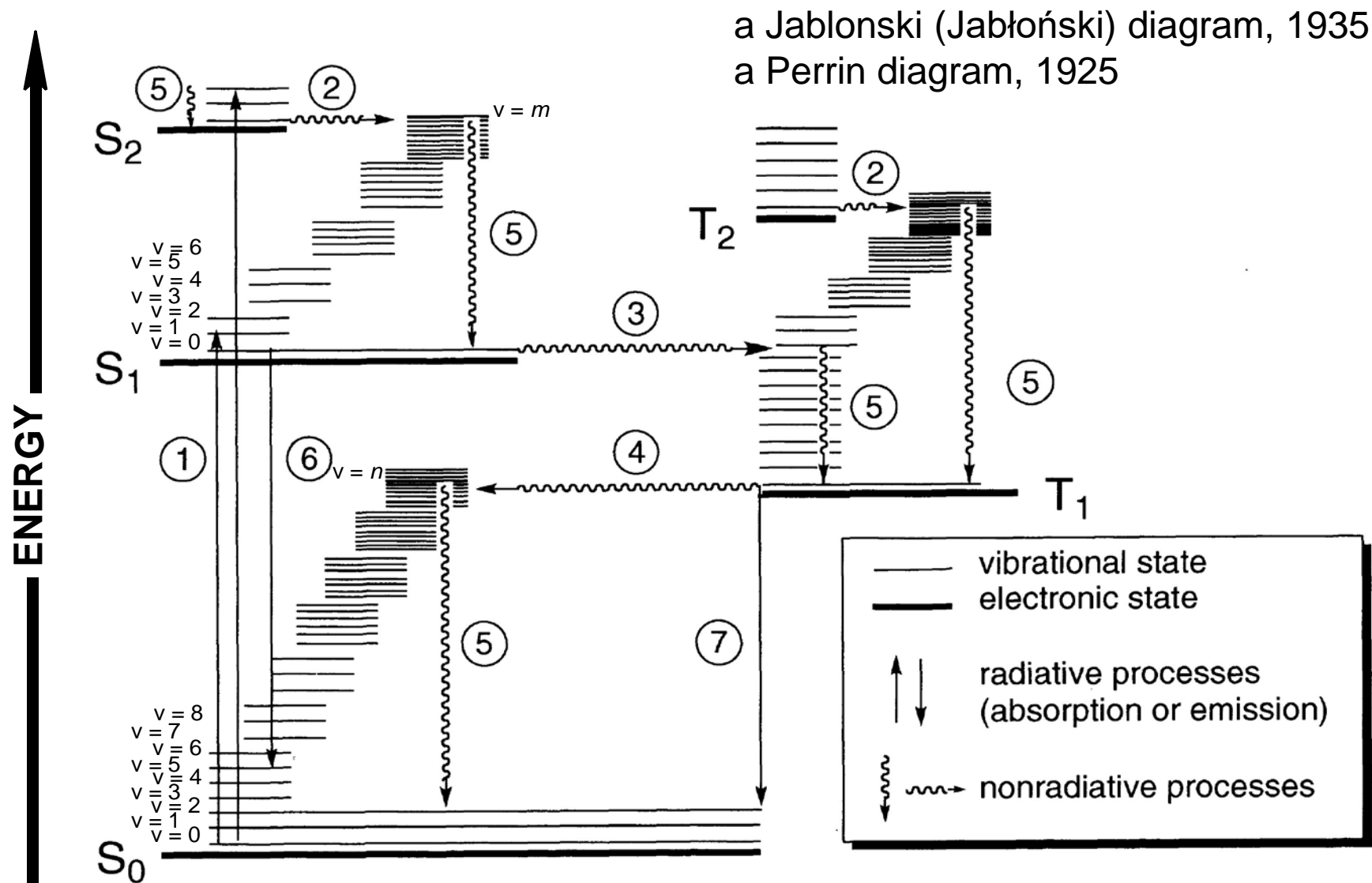
time scale:  $10^{-12} - 10^{-6}$  s

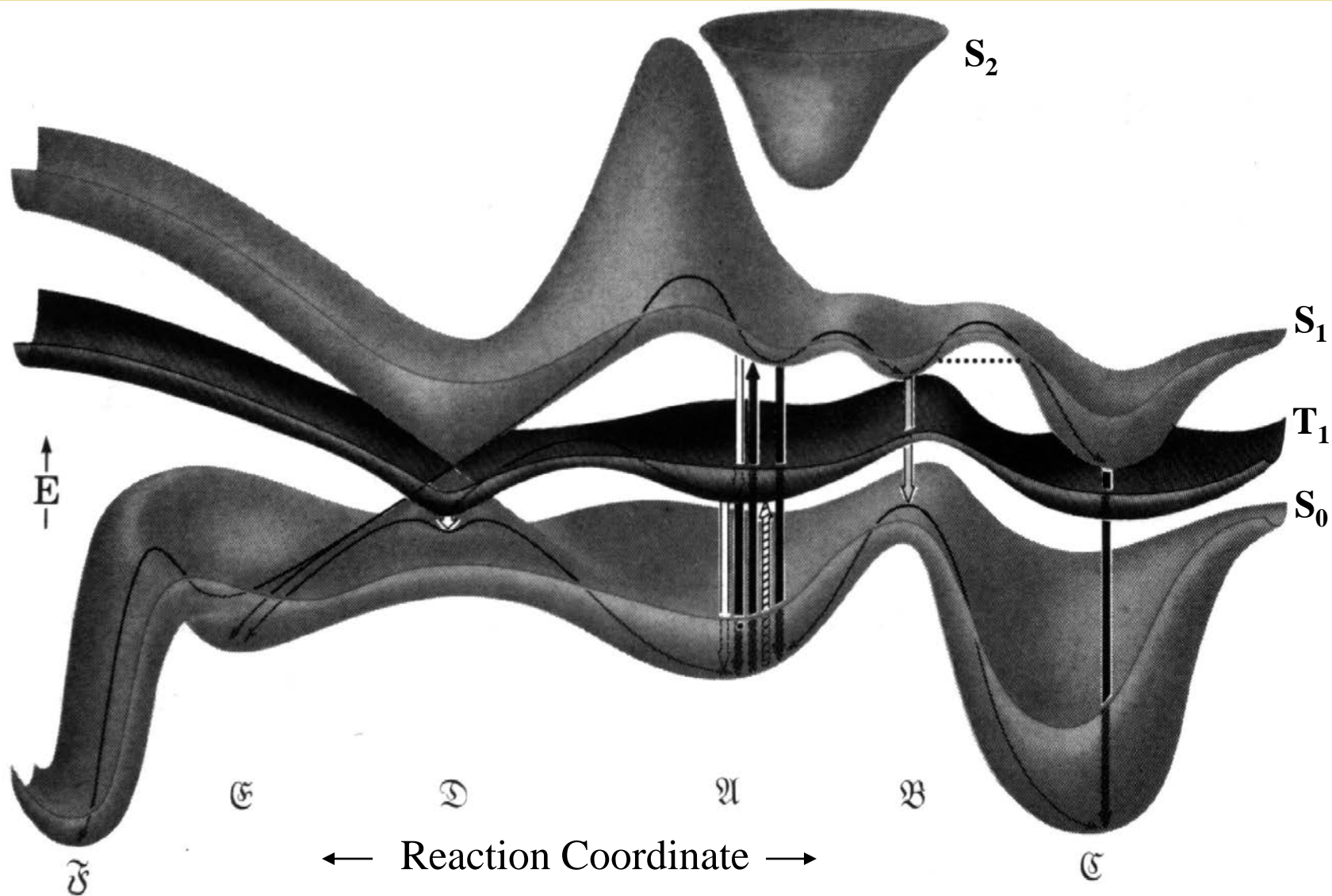
a nonradiative transition:  
no electromagnetic radiation  
is involved

## $\pi$ Molecular Orbitals (MOs) of 1,3-Butadiene



# A State Energy Diagram









# A State Energy Diagram and Photophysical Processes

**Ed Hilinski**

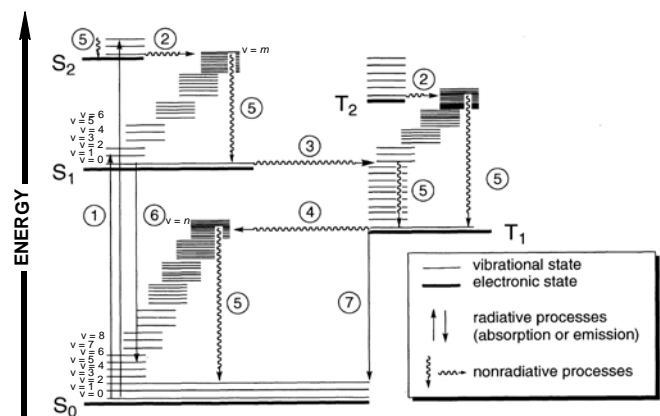
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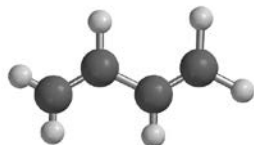
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[www.chem.fsu.edu/hilinski](http://www.chem.fsu.edu/hilinski)



vibrationally excited

less



more

