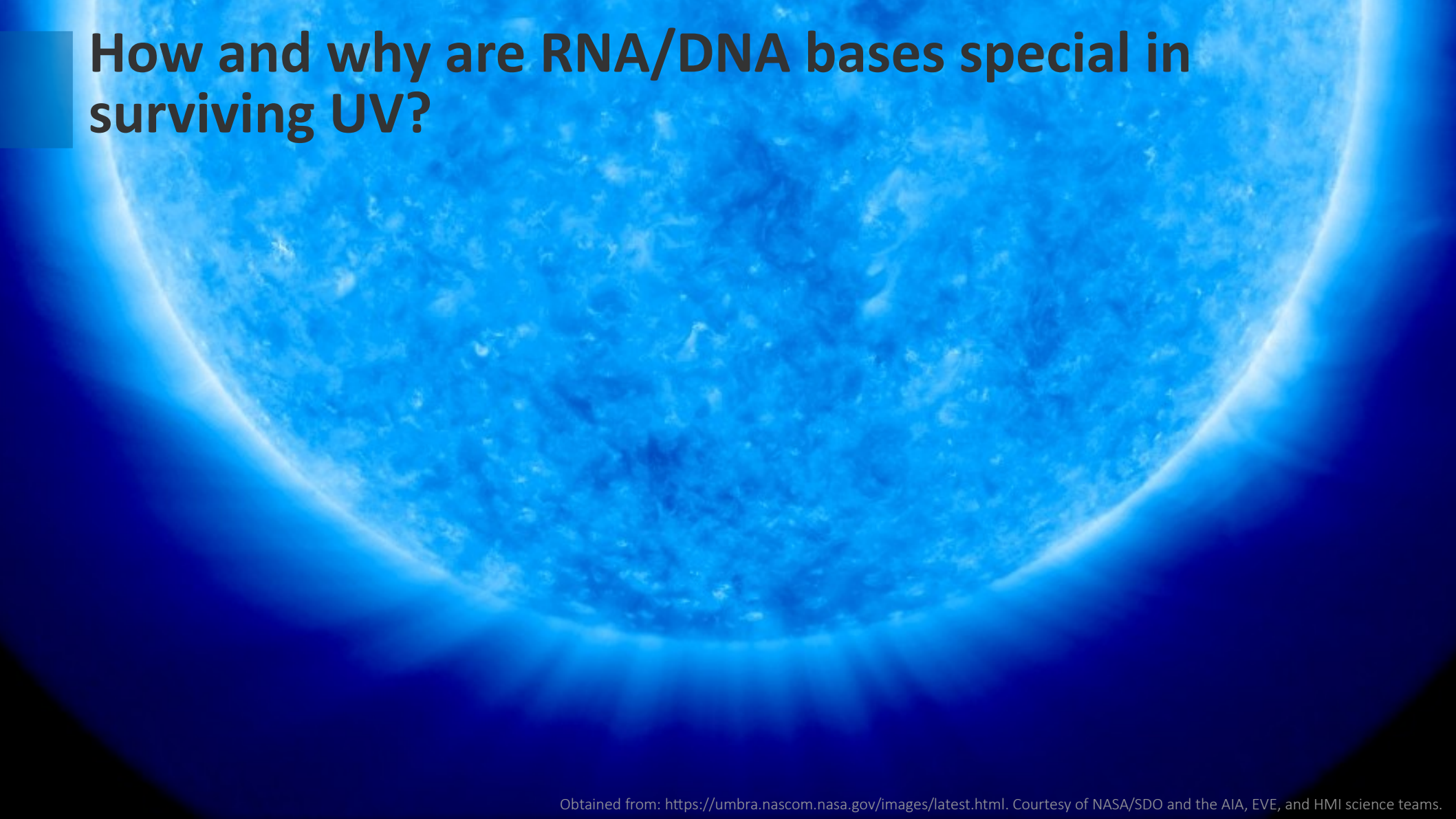
# How and why are RNA/DNA bases special in surviving UV?



Obtained from: https://umbra.nascom.nasa.gov/images/latest.html. Courtesy of NASA/SDO and the AIA, EVE, and HMI science teams.

# On RNA/DNA structure

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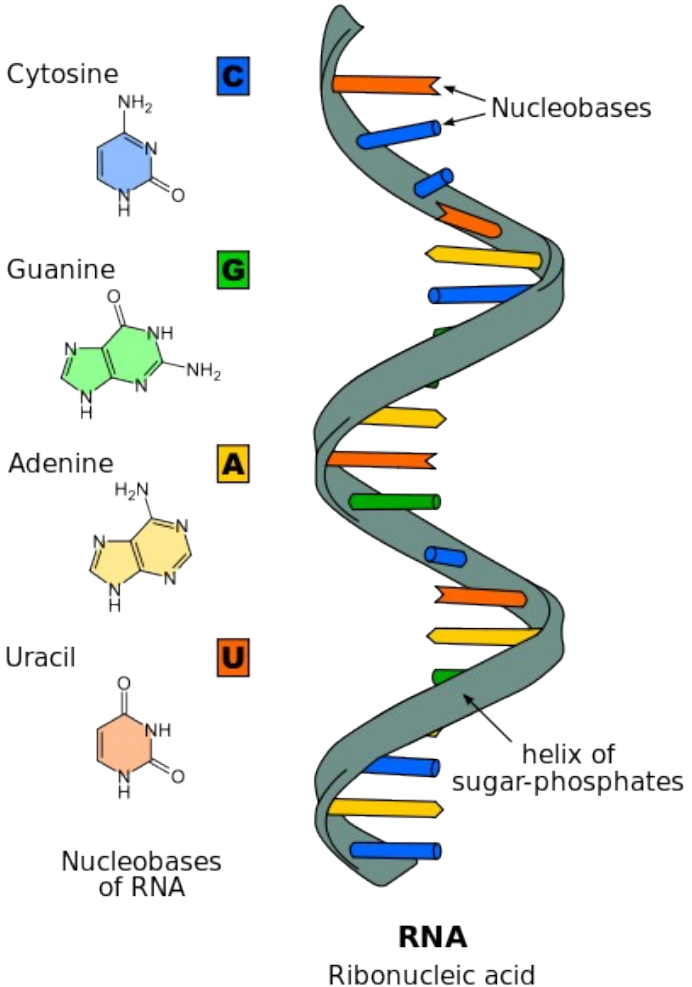

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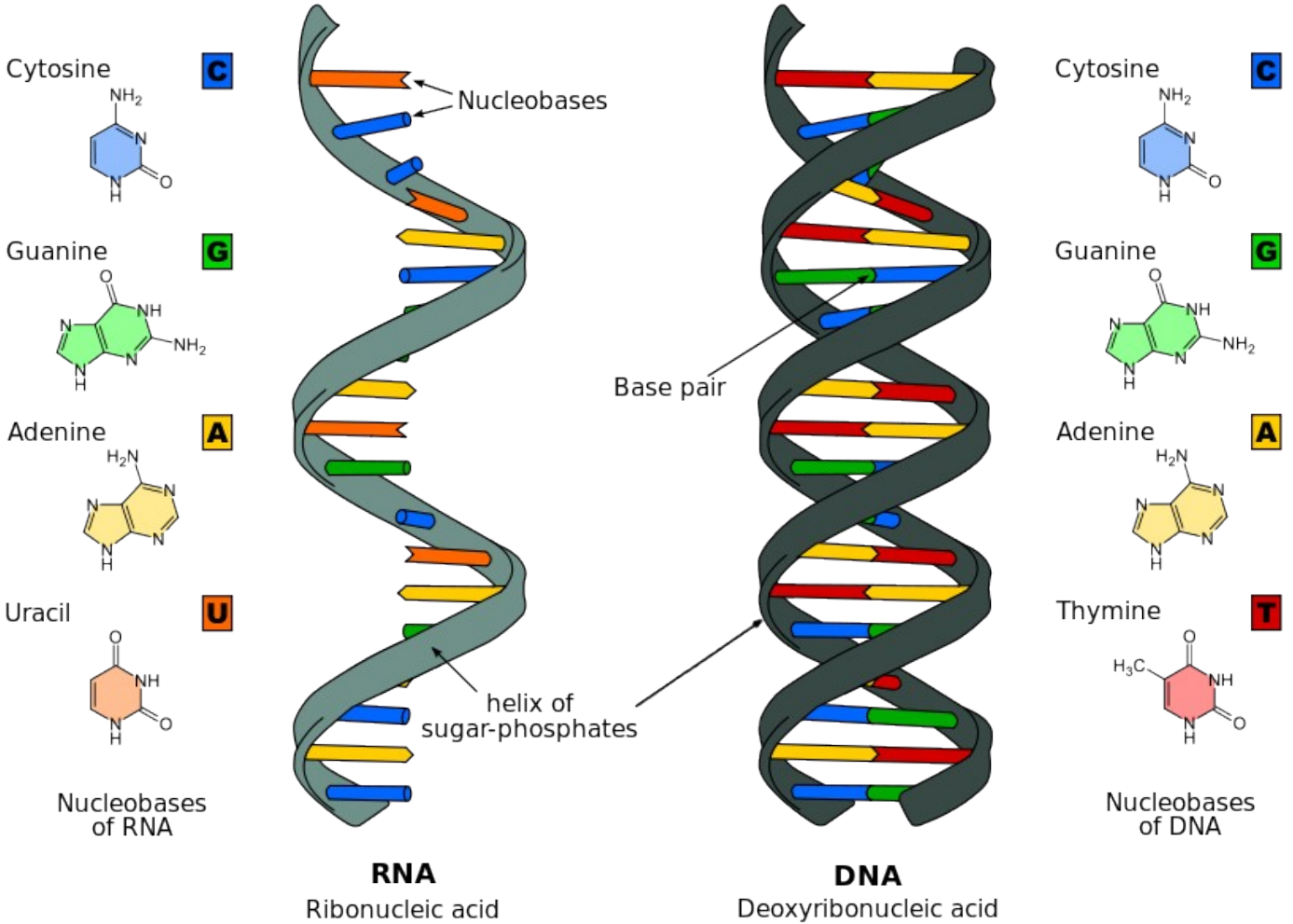

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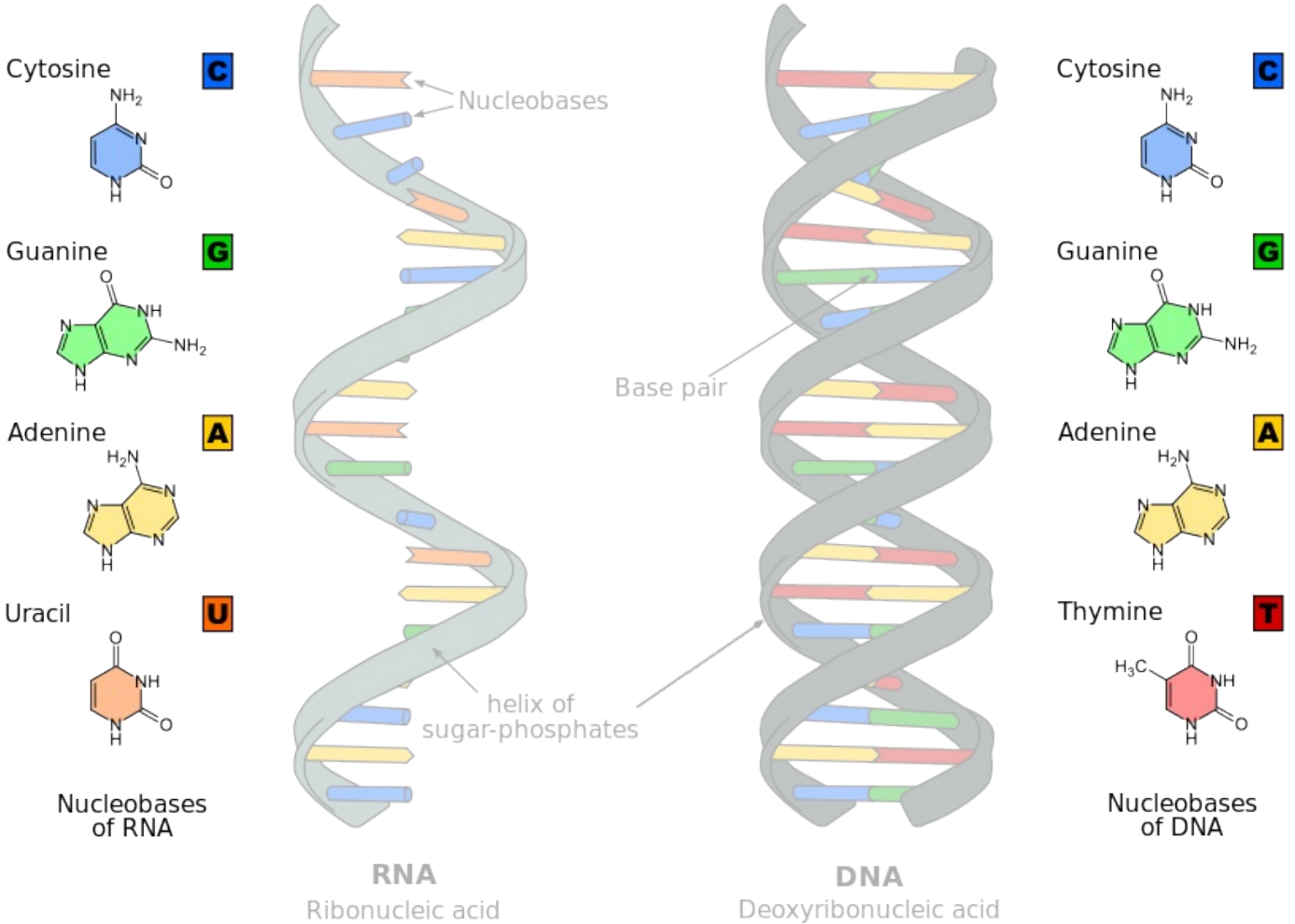

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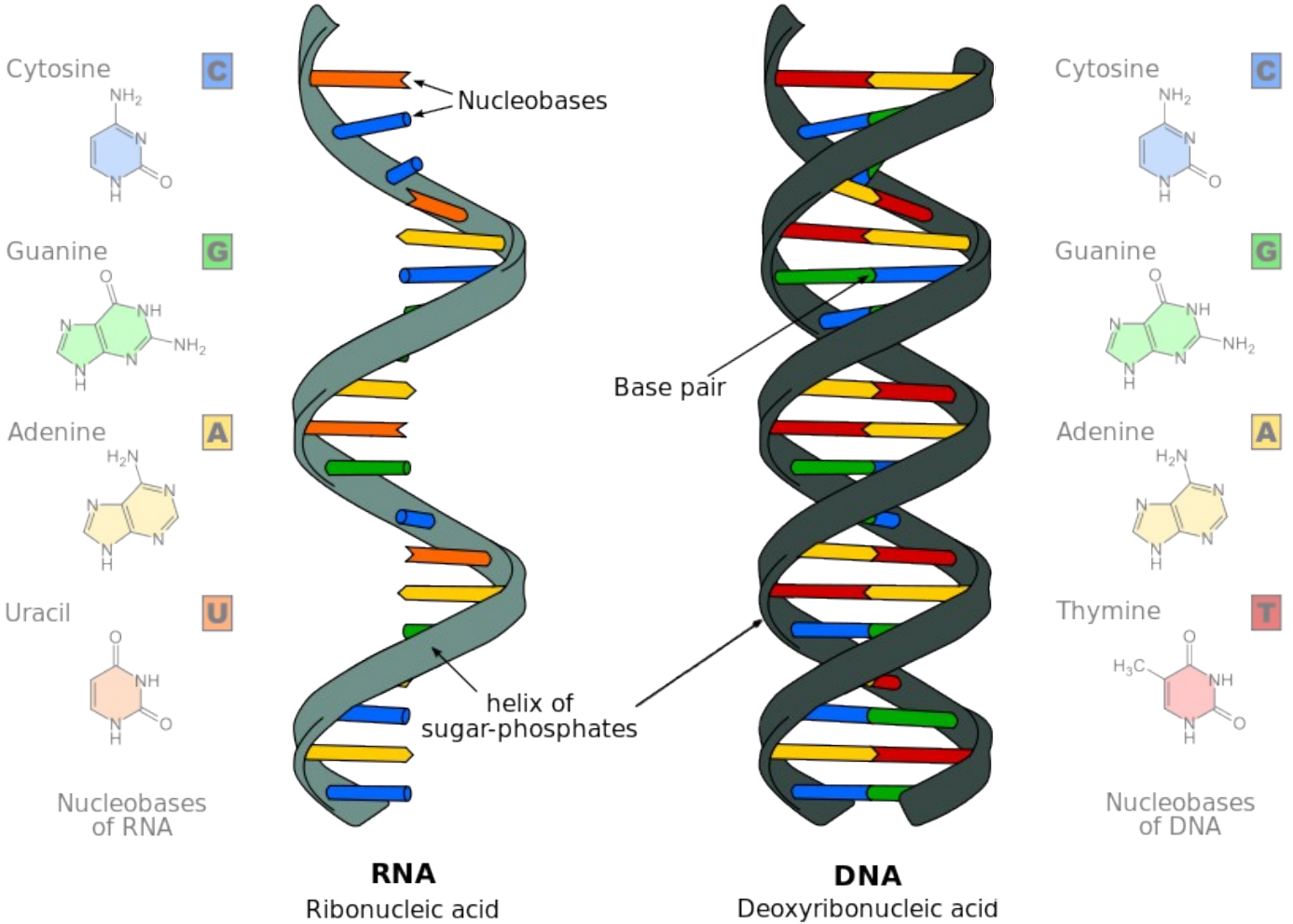

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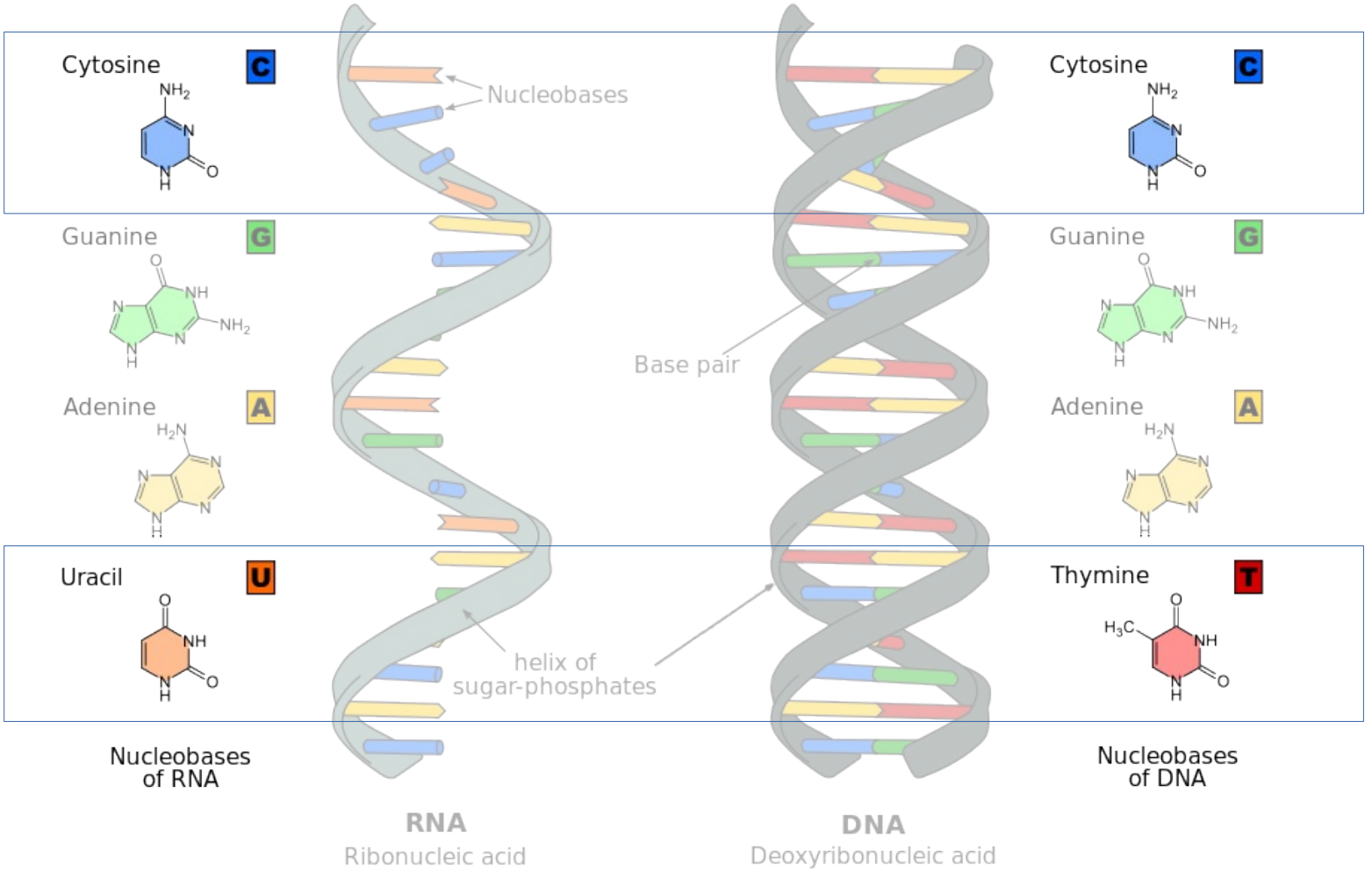

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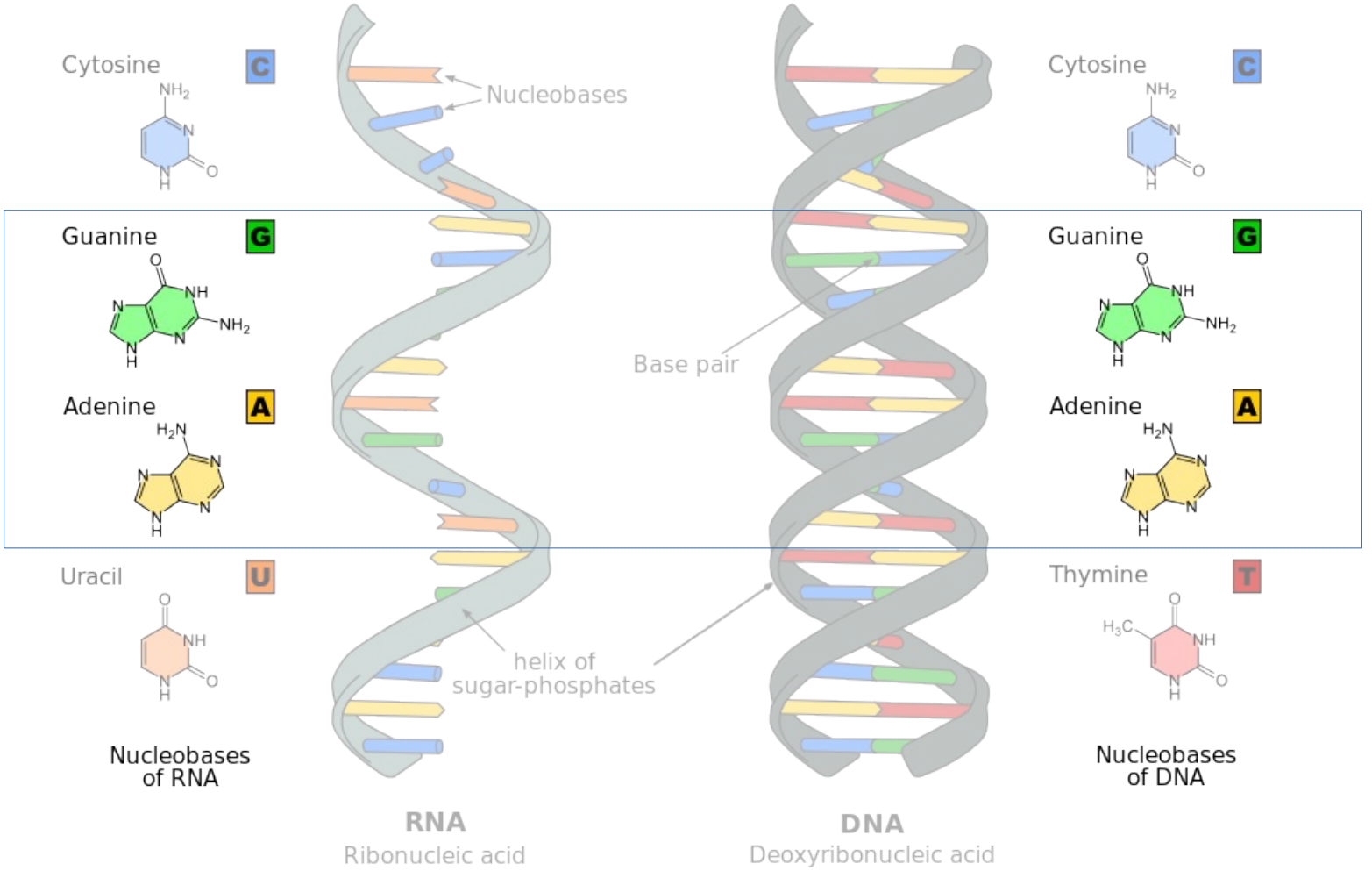
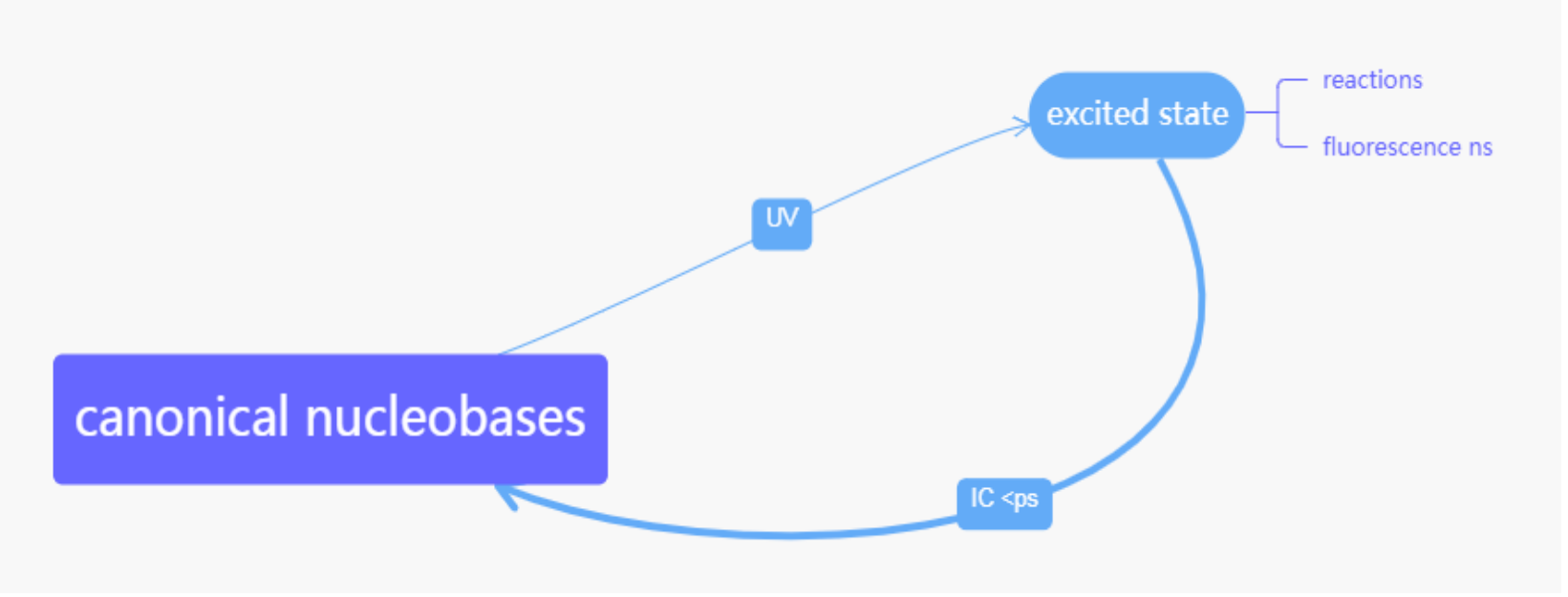


# 4-billion-year old chemical selection

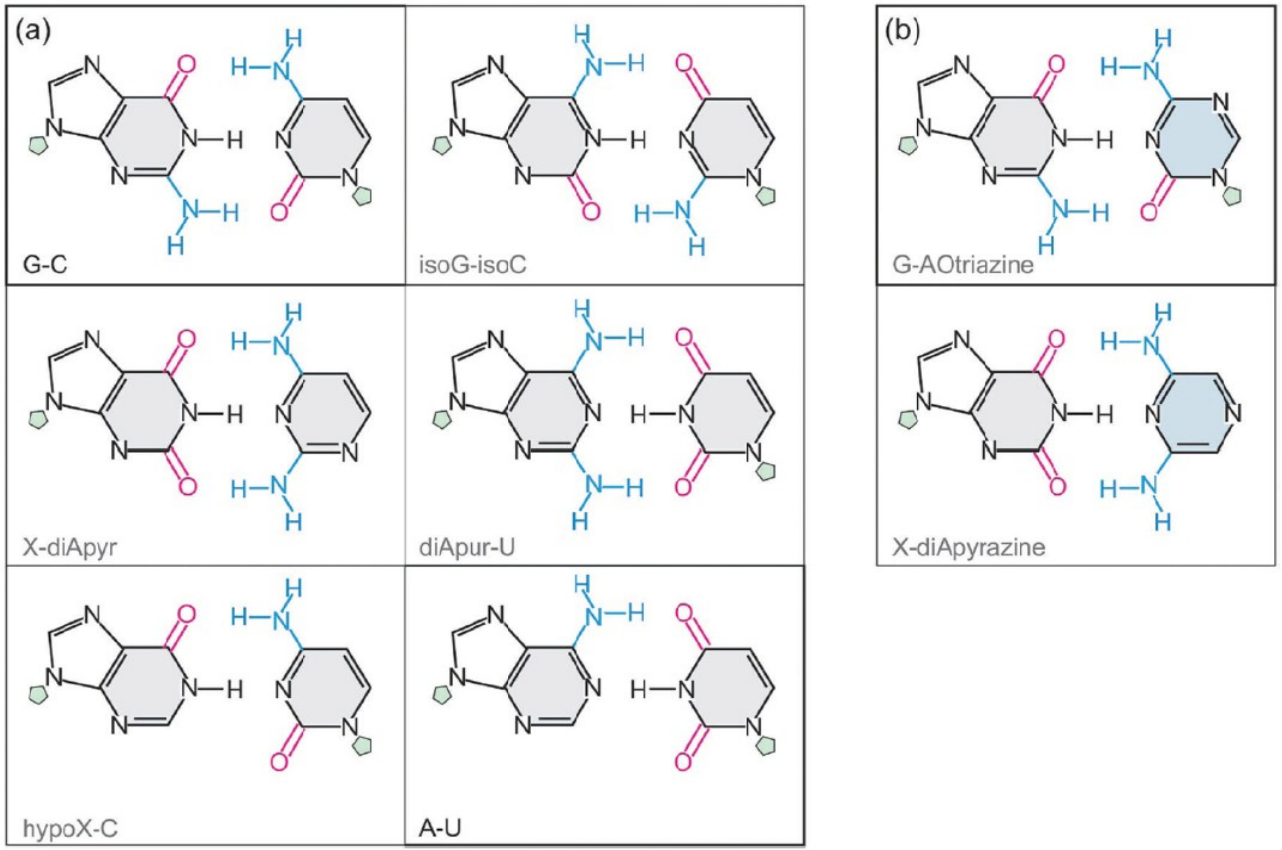
Among Rapid Decay Pathways:

Internal Conversion

- decay in a few picoseconds or less
- Orders of magnitude faster than many of the other heterocyclic compounds



# Exquisite dependence on molecular structure




~~Fig.~~ 1 Examples of alternative base pairs. diA = diamino, AO = amino-oxo, X = xanthine, pur = purine, pyr = pyrimidine.

From S. Boldissar and M.S. de Vries, How nature covers its bases, Phys.Chem.Chem.Phys.,2018, 20, 9702

# The Potential Energy Landscape

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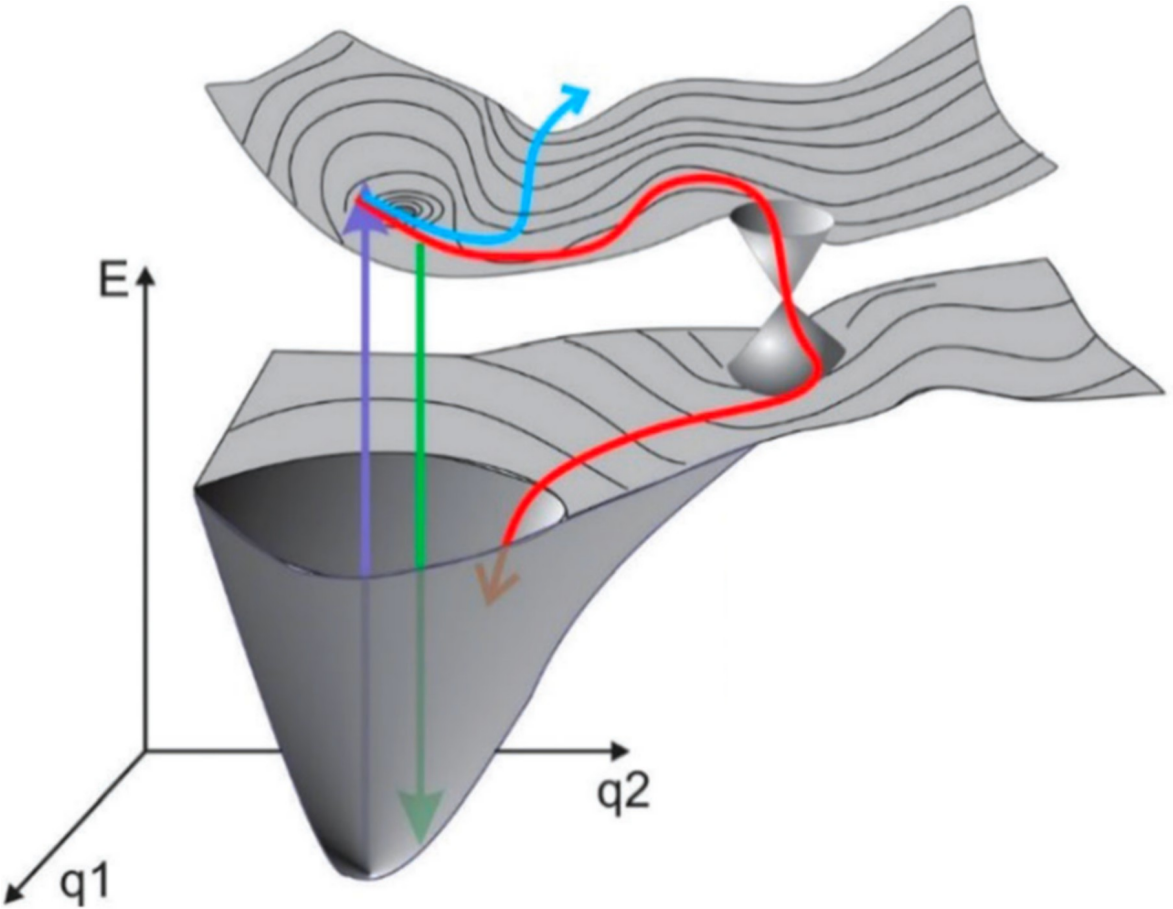


From S. Boldissar and M.S. de Vries, How nature covers its bases, Phys.Chem.Chem.Phys.,2018, 20, 9704

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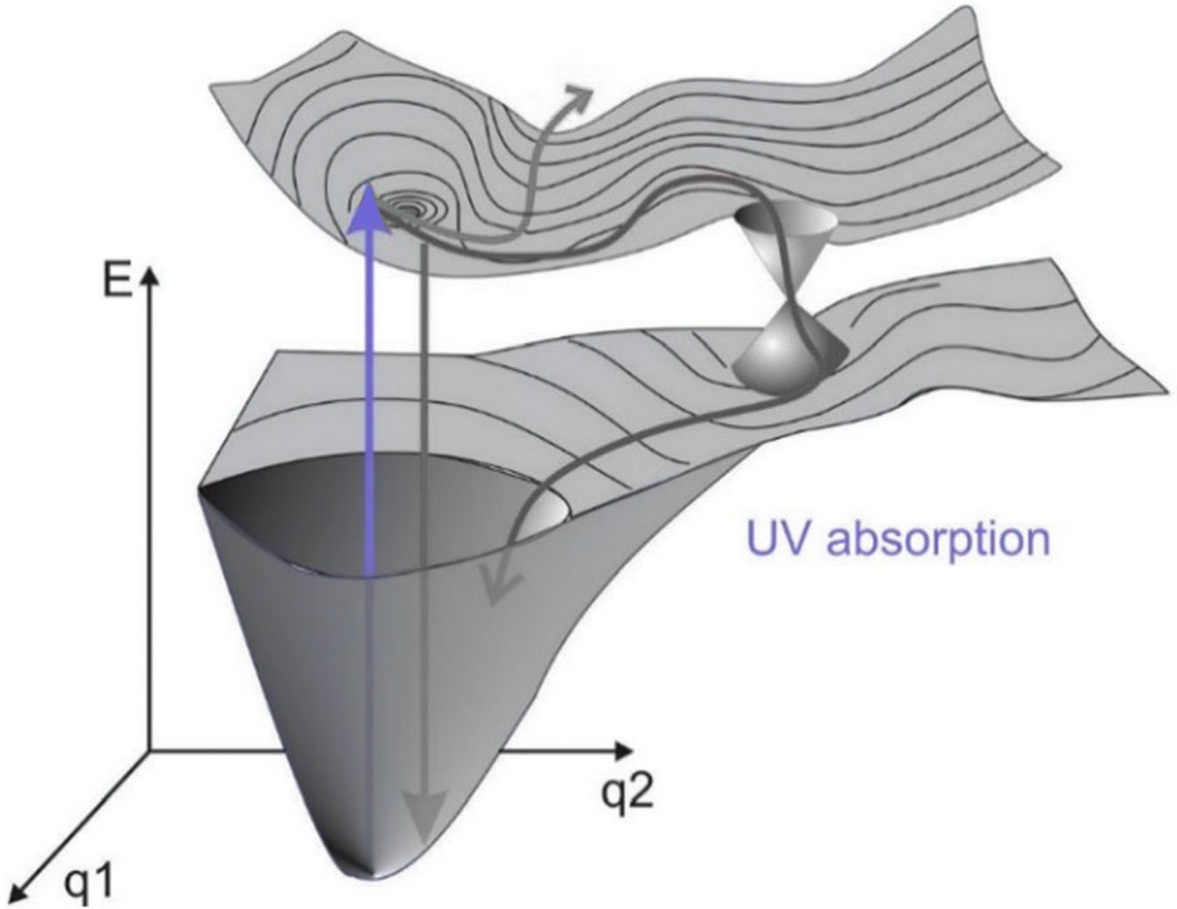


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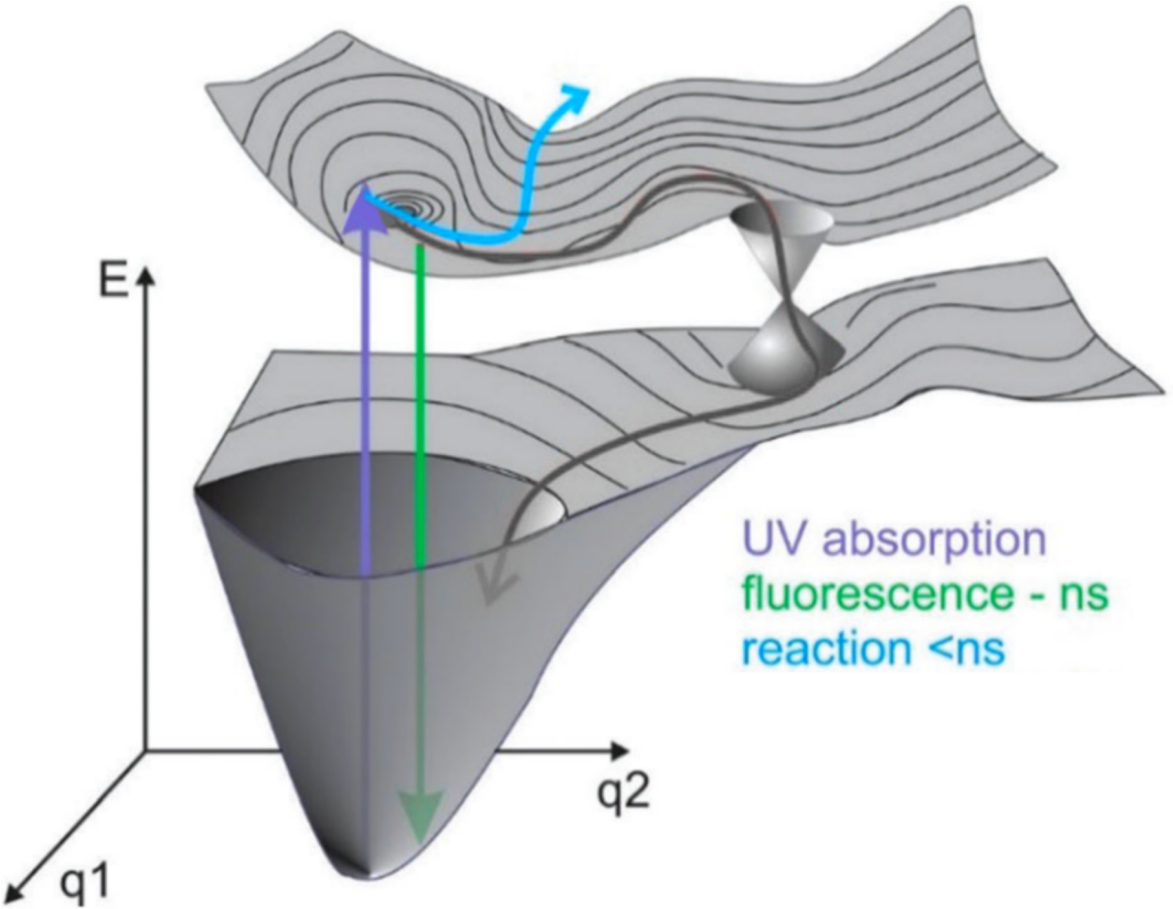


From S. Boldissar and M.S. de Vries, How nature covers its bases, Phys.Chem.Chem.Phys.,2018, 20, 9704

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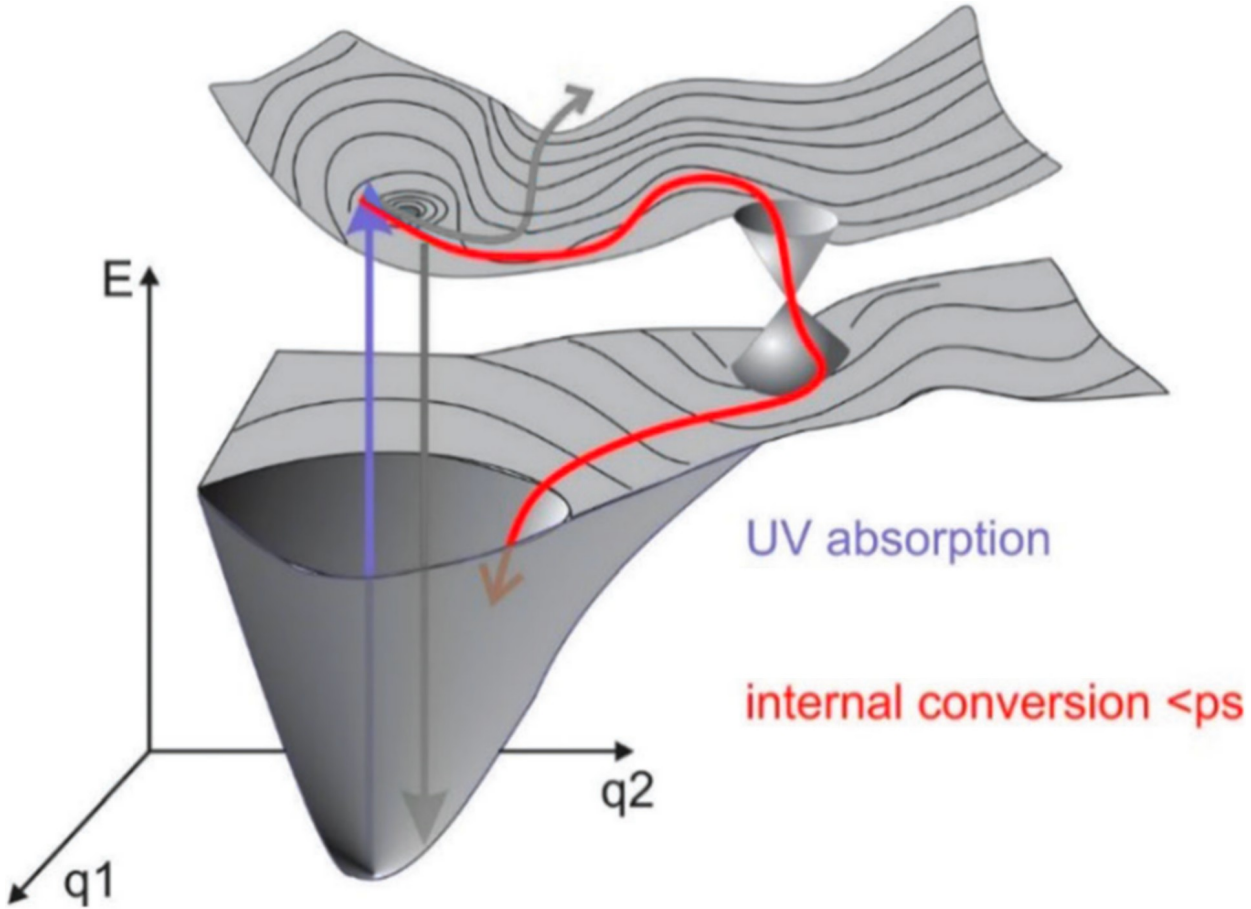


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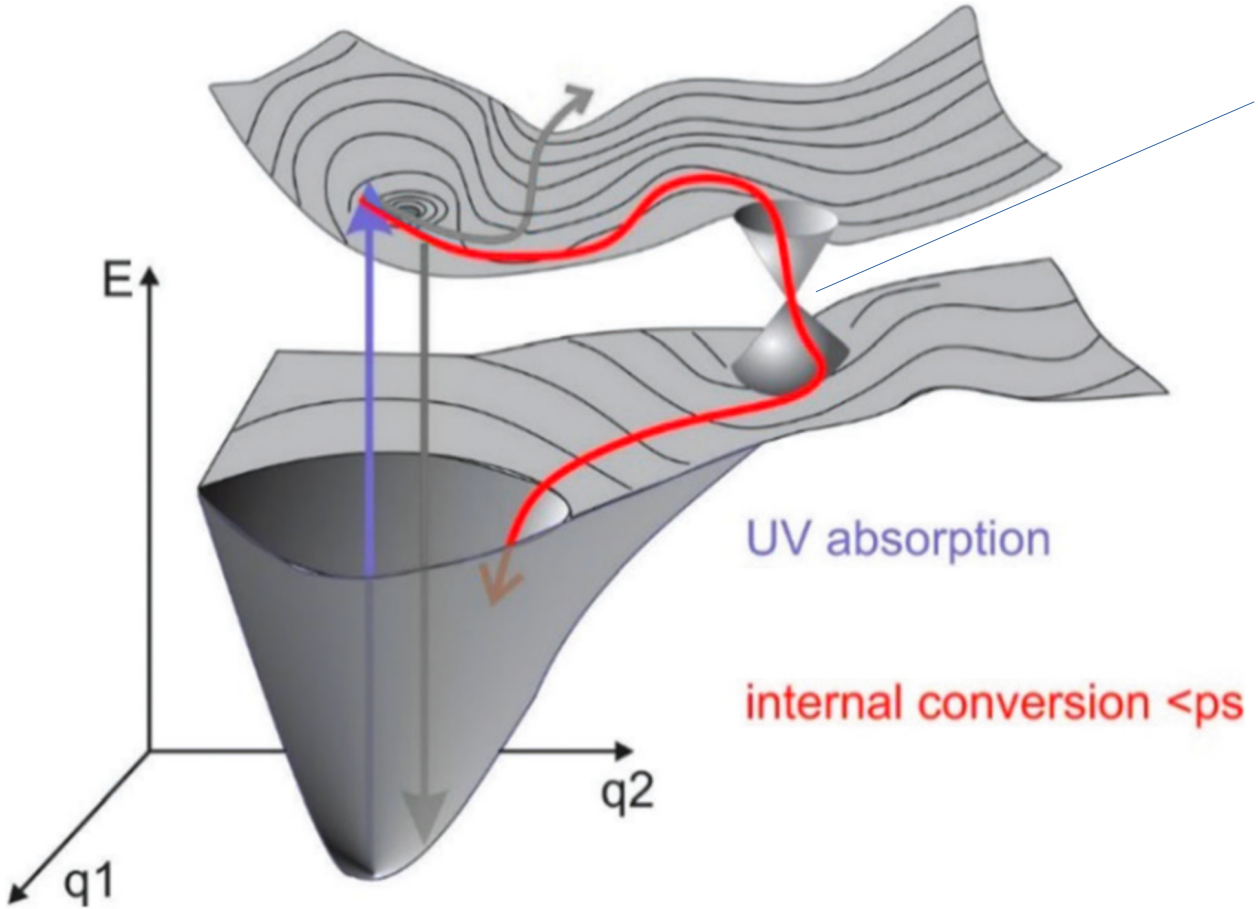


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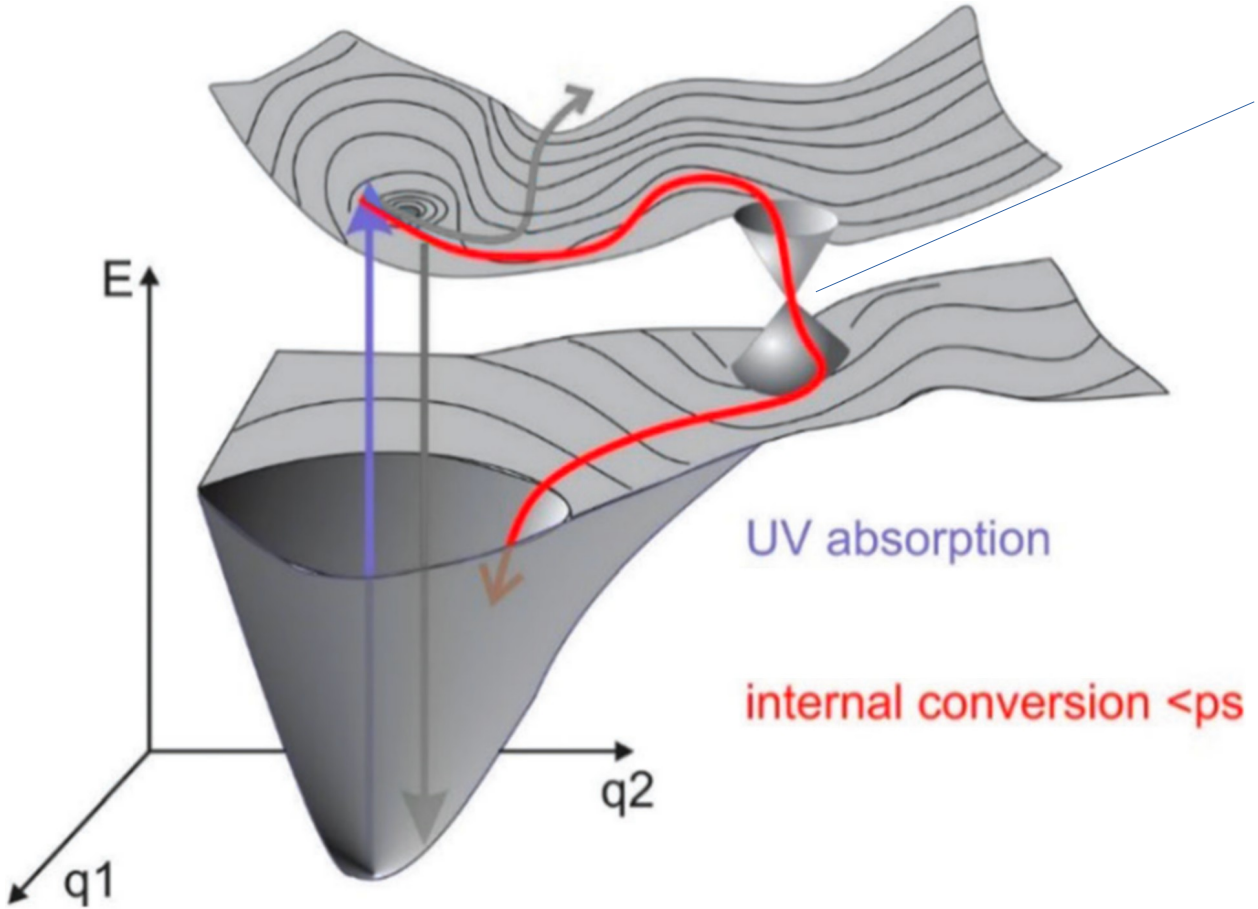


Conical intersection

Born-Oppenheimer-Approximation

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibrational}}$$

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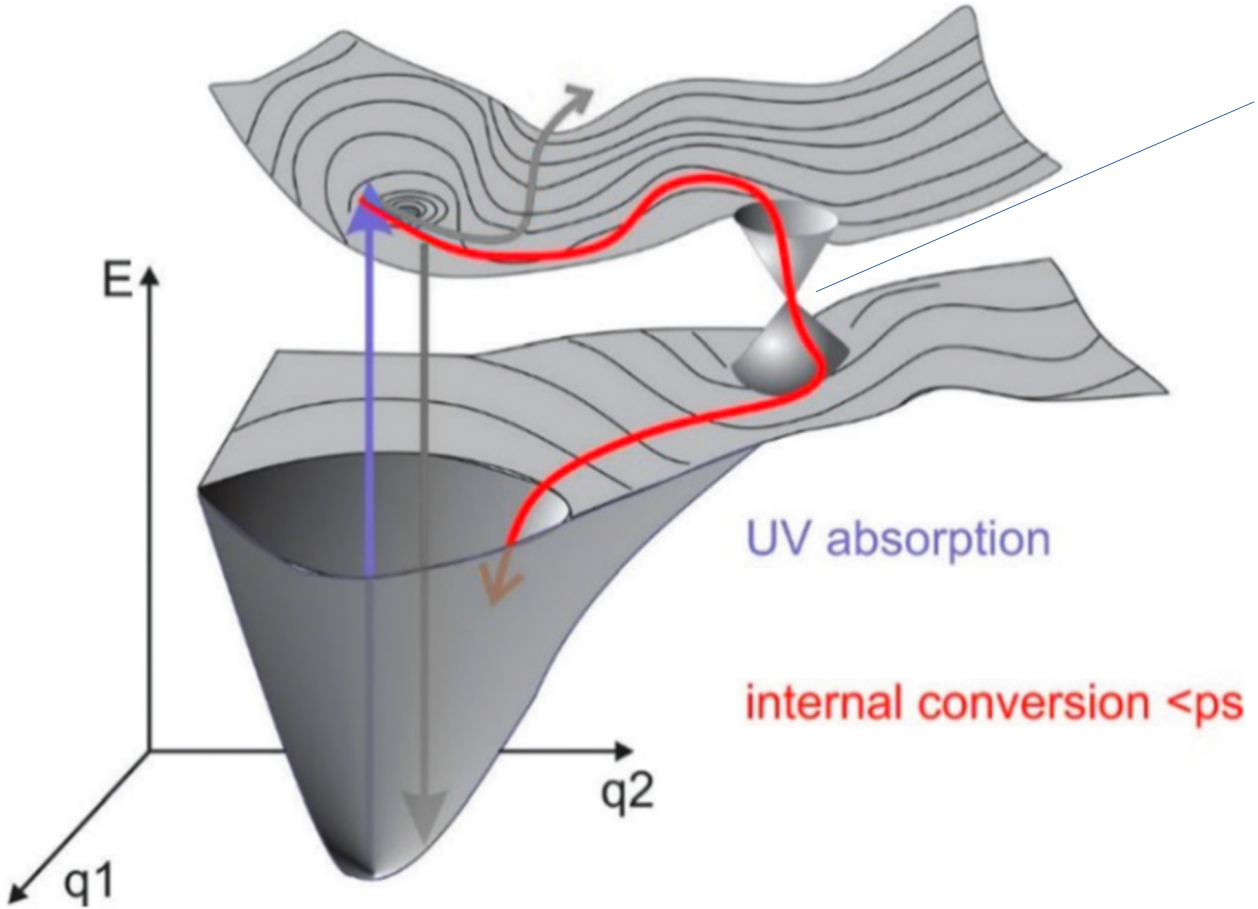


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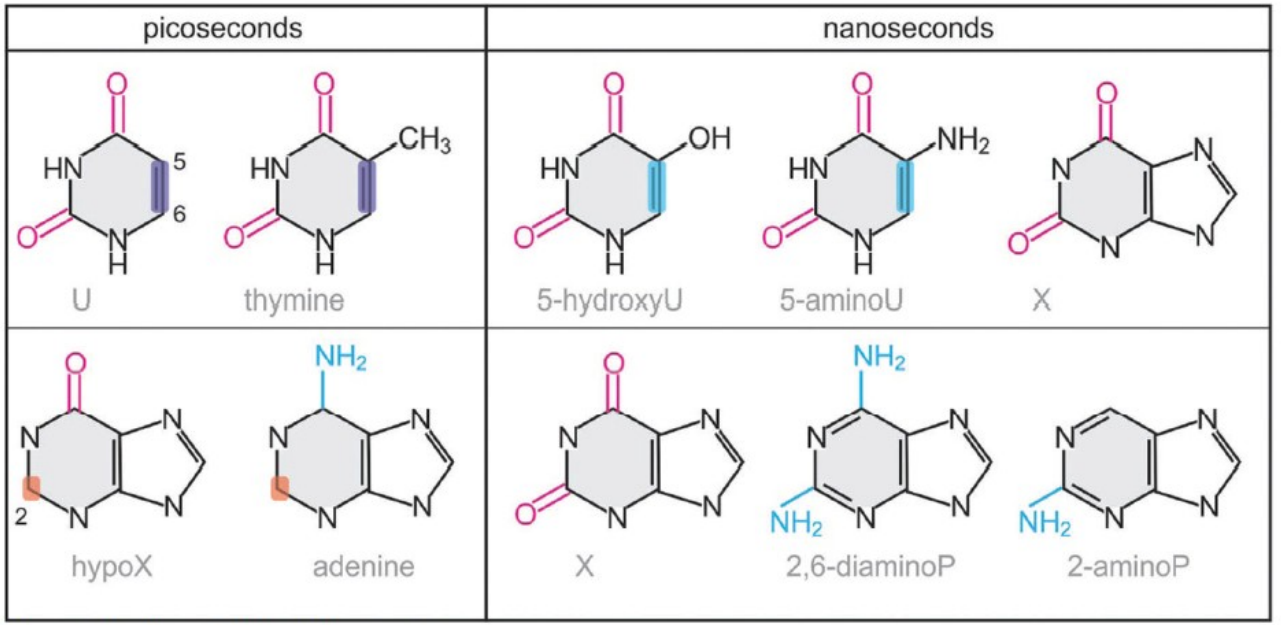
From S. Boldissar and M.S. de Vries, How nature covers its bases, Phys.Chem.Chem.Phys.,2018, 20, 9704

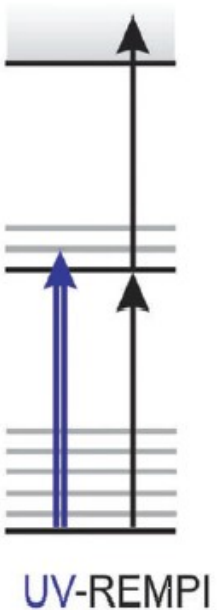
# How excited state lifetime depends on structure




U = uracil, X = xanthine, P = purine.

From S. Boldissar and M.S. de Vries, How nature covers its bases, Phys.Chem.Chem.Phys.,2018, 20, 9704

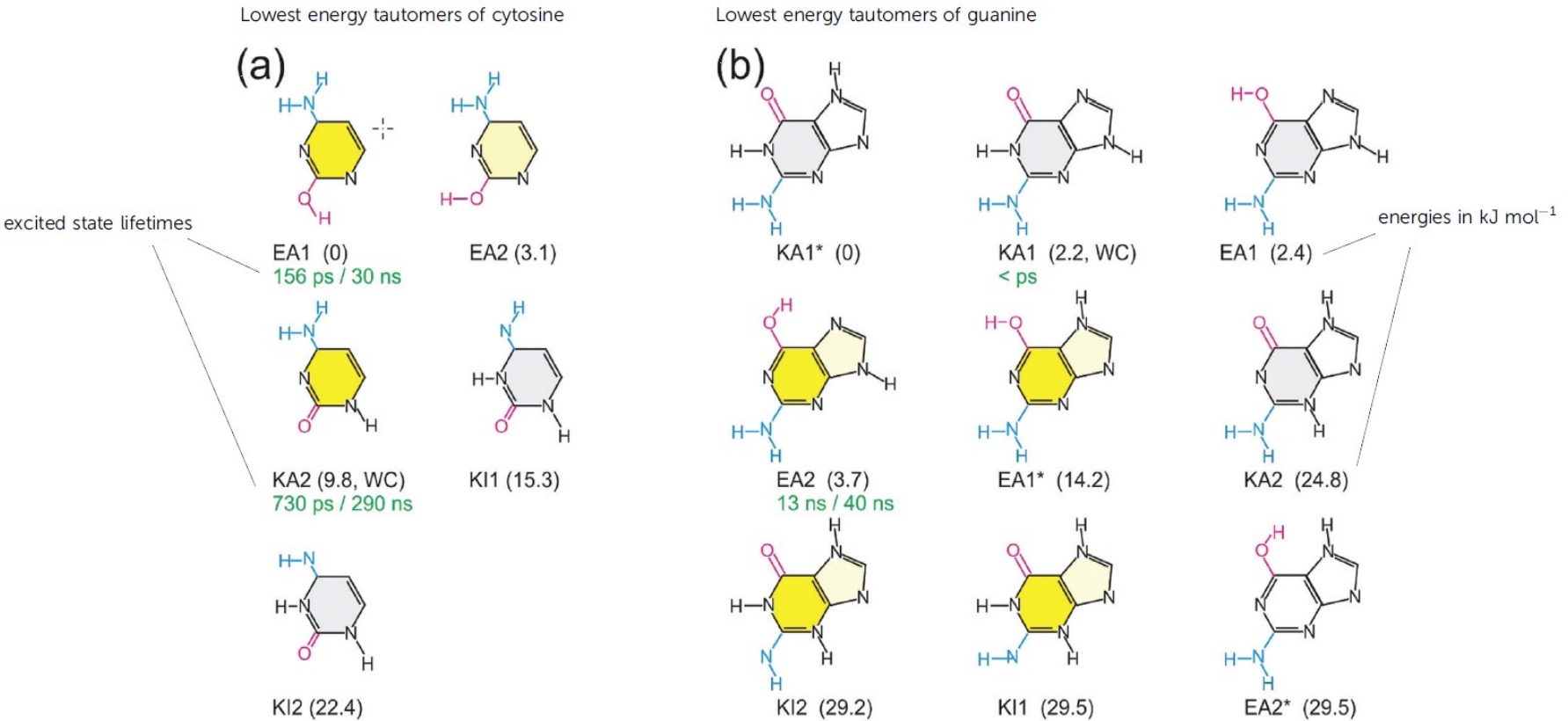
# REMPI




- Action spectroscopy
- Detecting excitation by ionizing the excited state
- With typical ns laser pulses, ps or fs excited states can therefore be obscured.

From S. Boldissar and M.S. de Vries, How nature covers its bases, Phys.Chem.Chem.Phys.,2018, 20, 9706

# Guanine tautomers - absence of data as evidence




From S. Boldissar and M.S. de Vries, How nature covers its bases, Phys.Chem.Chem.Phys.,2018, 20, 9706

# Yet to our unsatisfaction

- Non-zero quantum yields for dark states
- Increasing complexity, such as base pairing, solvent interactions, and macromolecular structure eg. stacking in helix, modifies the dynamics.
- Nucleosides could possibly be synthesized directly without nucleobases as intermediate steps.
- rapid internal conversion to the ground state: a necessary but not sufficient condition

# Summary

- **Rapid internal conversion** as a ‘safe’ way to dissipate energy
- [High quantum yields = **short timescales**] to limit more harmful alternatives
- De-excitation behaviour in nucleobases dictated by Potential Energy Landscape
  - Starting point
  - Barriers
  - Intersections
- **Small changes** in molecular geometry can result in **crucial changes** in photochemistry
- Ideal UV protection depends on **additional properties**, which results in exceptions
- Nucleobases are the chromophores in nucleosides, but properties in DNA/RNA may still vary

# References


- File:latest_aia_171.gif
  https://sdo.gsfc.nasa.gov/gallery/copyright/
  Courtesy of NASA/SDO and the AIA, EVE, and HMI science teams.
  Obtained from:
  https://umbra.nascom.nasa.gov/images/latest.html.
- File:Difference DNA RNA-DE.svg: Sponk / *translation: Sponk / CC BY-SA
  https://creativecommons.org/licenses/by-sa/3.0
  Obtained from:
  https://upload.wikimedia.org/wikipedia/commons/3/37/Difference_DNA_RNA-EN.svg
- Fig.1, 2, 3, 4, 6 from S. Boldissar and M.S. de Vries, How nature covers its bases, Phys.Chem.Chem.Phys.,2018, 20, 9701-9716

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- https://en.wikipedia.org/wiki/Vibronic_coupling

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- https://en.wikipedia.org/wiki/Indirect_DNA_damage
- https://en.wikipedia.org/wiki/Purine
- https://en.wikipedia.org/wiki/Pyrimidine
- https://en.wikipedia.org/wiki/Conical_intersection