Ribose Photochemistry in Space: Non-adiabatic Reaction Pathways

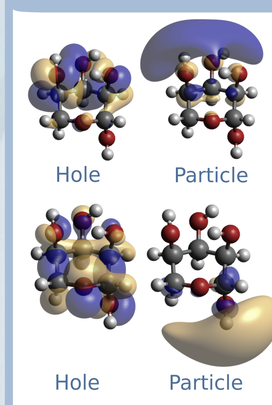
Katarína Vosovičová[1,2], Jiří Janoš[2], Petr Slavíček[2], Thanja Lamberts[1]

[1] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

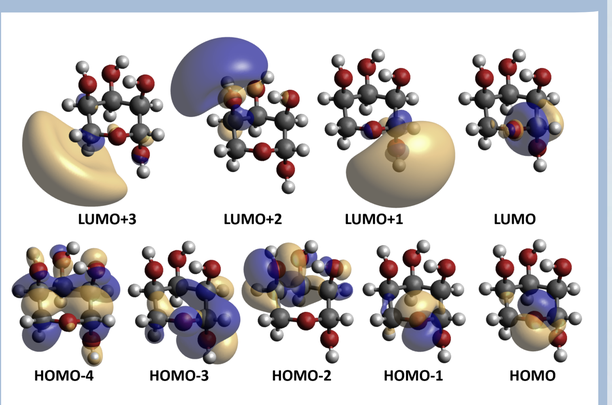
[2] Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 16628 Prague, Czech Republic

The discovery of numerous biomolecules, including ribose, on asteroid Bennu[1] and erythrulose in the interstellar medium[2] has highlighted the importance of understanding the photochemical stability of prebiotic molecules in extraterrestrial environments. We investigate the excited-state dynamics of the gas-phase cyclic form, β-D-ribopyranose, using non-adiabatic molecular dynamics (NAMD) simulations to elucidate its relaxation mechanisms following photoexcitation. By comparing different theoretical approaches and analyzing the topology of the relevant potential energy surfaces (PESs), we aim to identify the dominant reaction pathways, determine the relaxation time, evaluate the photostability of β-D-ribopyranose, and assess the robustness of the employed excited-state methodologies.

Orbitals involved in excitations



Natural Transition Orbitals (LR-TDDFT)



Complete Active Space (CASSCF)
CAS(10,9)

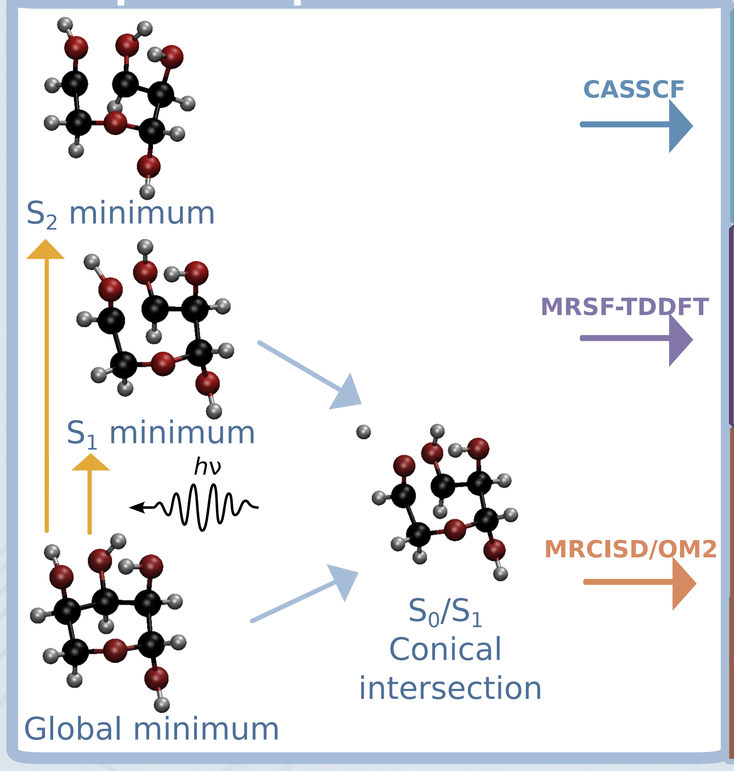
Agreement in character: from bonding σ to diffuse Rydberg orbitals

Excitation and ionisation energies

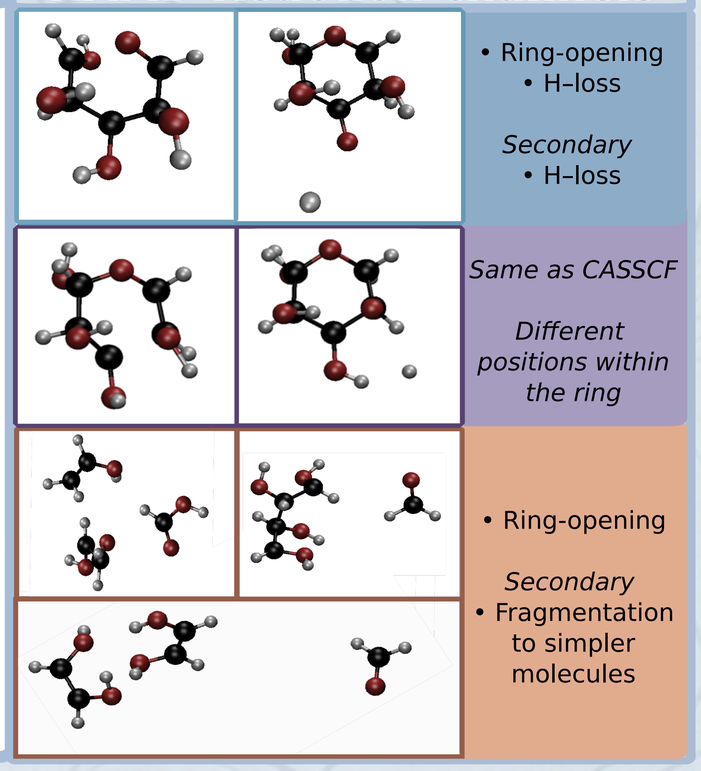
Electronic state	ΔE (eV)
S_1	6.91–7.35
S_2	7.25–7.80
IE	9.07

- Good agreement among the methods for VUV excitation energies, with EOM-CCSD as the reference.
- Ionization is unlikely.

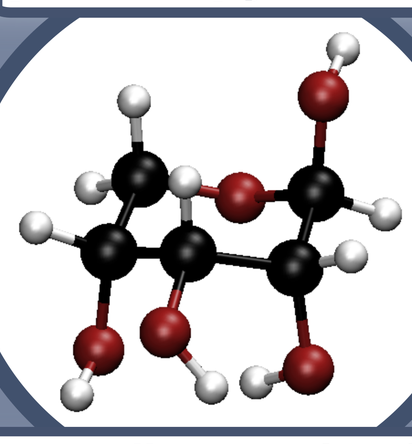
Important points on the PES



NAMD Reaction channels



β-D-ribopyranose

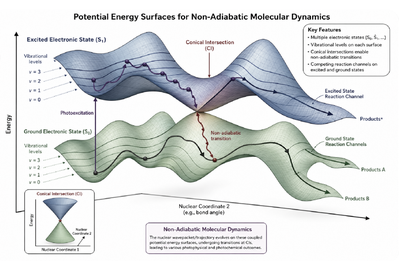


Target ribose molecule
Structural form with the lowest electronic and Gibbs free energy

Excited β-D-ribopyranose relaxes quickly, can dissociate, but can also reform, contributing to its partial photostability under astrochemical conditions.

A) NVT equilibration → Sampling
- 300 K, 10 a.u.
- GLE thermostat, *Orca*
- 100 trajectories

B) Simulations in excited states
- NAMD
- S_1 and S_2
- surface hopping: LZSH and FSSH
- 5 and 10 a.u.
- 3 levels of theory
- *Molpro, OpenQP, MNDO*



Non-adiabatic molecular dynamics

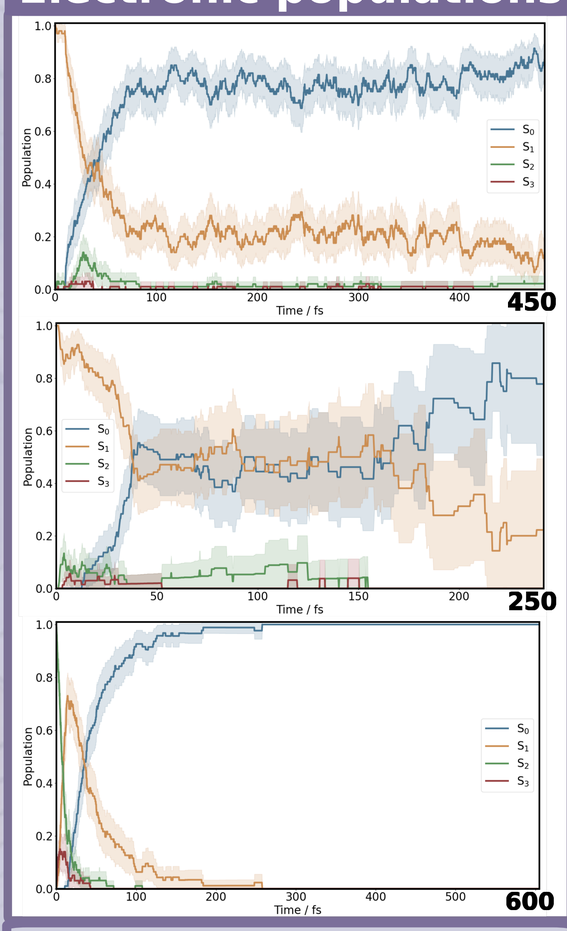
Level of theory

CASSCF
multi-reference

MRSF-TDDFT
TD density functional theory

MRCISD/OM2
semi-empirical

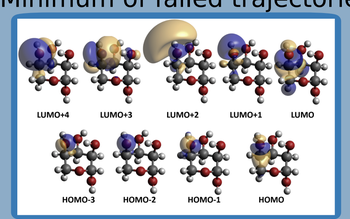
Electronic populations



Ultrafast relaxation to the ground state

Outcome

- No feasible active space
- Big kinetic energy drift (max >1000 eV)
- Minimum of failed trajectories



- Sensitivity of reaction channels and stability of simulations towards parameters, functional:

ring-opening → H–loss

- Good energy conservation (max 1–2 eV)
- Most of the trajectories failed

- Diverse reaction channels

→ simple molecules (CH_2O)

- Longer simulation times
- Good energy conservation (max 2–3 eV)
- Minimum of failed trajectories

Statistics

	CASSCF		MRCISD		MRSF		MRSF(2)
	S_1	S_2	S_1	S_2	S_1	S_2	S_1
Average number of steps	3978	2593	6902	7744	426	370	193
Average simulation time	962.0	626.9	834.7	936.5	102.8	85.5	23.2
Failed trajectories	0	0	3	3	45	56	91
Average energy drift	466.1	21.9	0.4	0.5	0.6	0.9	0.6
Relaxation time	64.6	295.8	43.3	52.6	187.2	102.1	53.3
Reaction channels							
Ring opening	43	66	91	91	56	45	17
O–H dissociation	54	11	0	0	14	7	42
Return	16	27	39	25	35	16	2

Summary of trajectory statistics. Time and energy metrics are reported in femtoseconds (fs) and electronvolts (eV), respectively. Reaction fractions are shown as percentages (%). The relaxation time is defined as the time at which 70% of the trajectories remaining at a given time have reached the ground state. Failed trajectories are defined as trajectories that ended prematurely before reaching 48 fs simulation length.

Conclusion & outlook

We find that β-D-ribopyranose relaxes from its excited state within 300 fs in all cases, with no evidence of long-lived excited states. VUV excitation predominantly induces ultrafast ring-opening or O–H bond dissociation, followed by competing pathways involving bond dissociation into multiple fragments and, in approximately 1/3 of cases, ring re-closure. Across the different computational methods, our results indicate efficient UV energy dissipation and partial photostability of gas-phase ribose under astrochemical conditions. In future work, we will extend this methodology to orbital-optimized density functional theory approaches, enabling us to go beyond the limitations of TDDFT.

1. Furukawa, Y.; Sunami, S.; Takano, Y.; Koga, T.; Hirakawa, Y.; Oba, Y.; Naraoka, H.; Saigusa, D.; Yoshikawa T.; Tanaka, S.; et al. Bio-essential sugars in samples from asteroid Bennu. *Nature Geoscience* **2026**, *19*, 19–24.
2. Jiménez-Serra, I.; García de la Concepción, J.; Cuppen, H.M.; et al. Detection of a four-carbon sugar in interstellar space. *Nature Astronomy* **2026**.