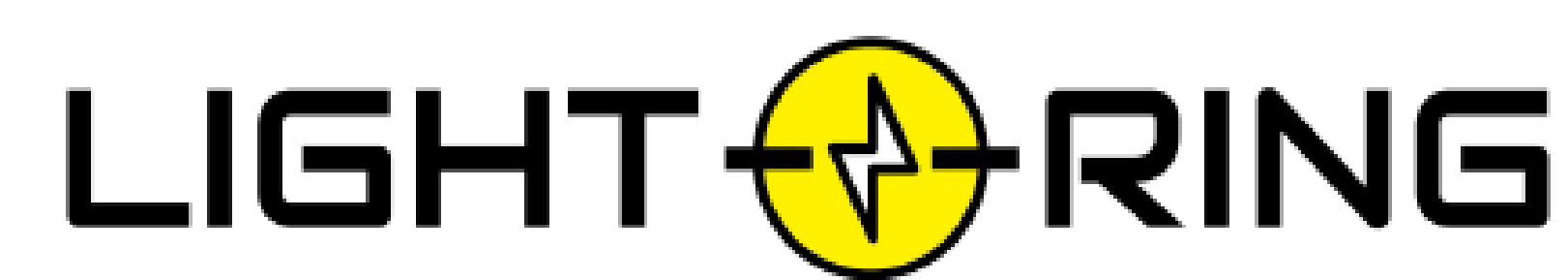


A quantum chemical insight into radicals forming upon gamma irradiation in crystals of 2-thiothymine



Gabrijel Zubčić, Valerije Vrčec, Viktor Pilepić, Davor Šakić and Erim Bešić

University of Zagreb, Faculty of Pharmacy and Biochemistry, Ante Kovačića 1, 10000 Zagreb

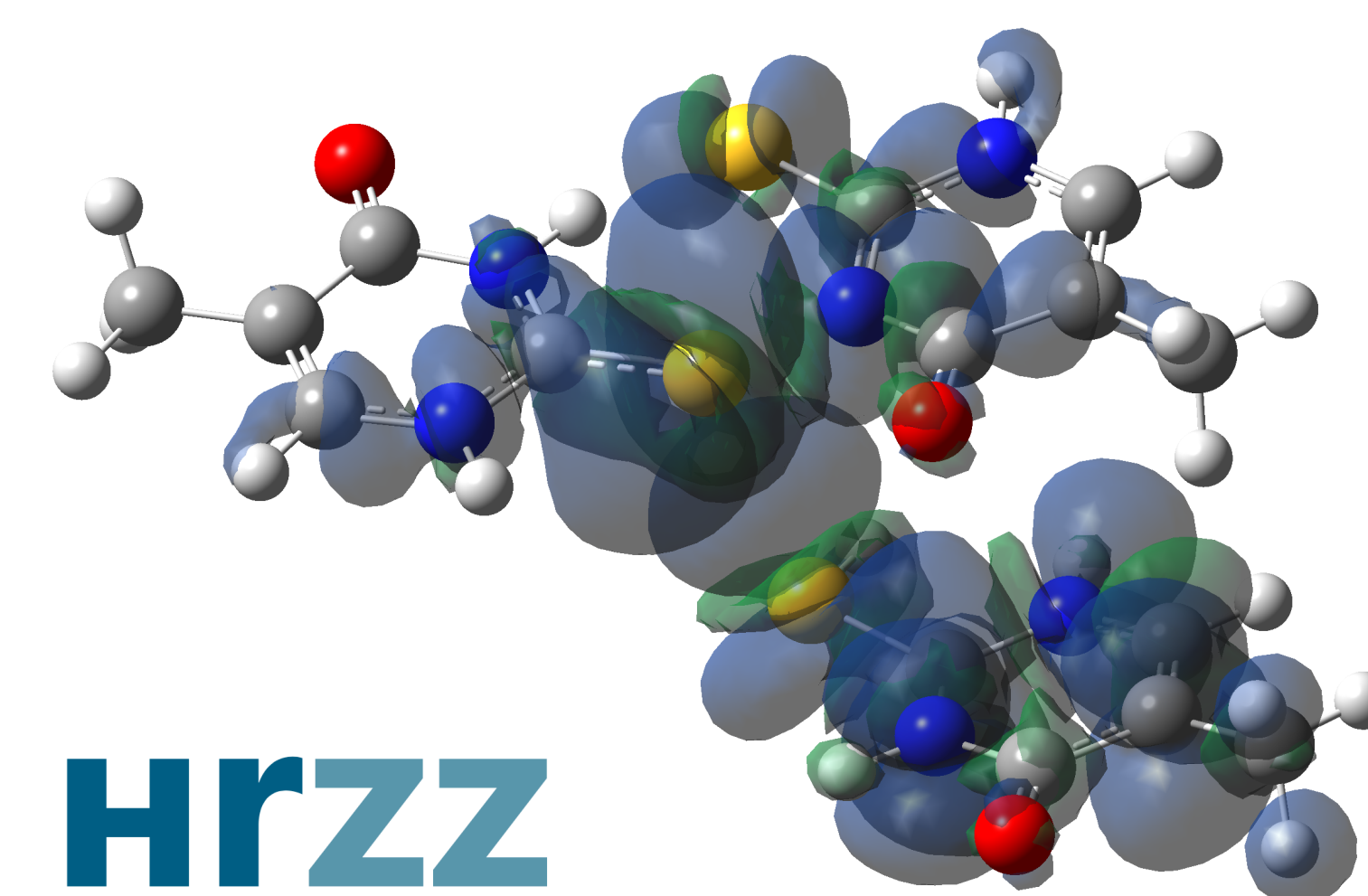
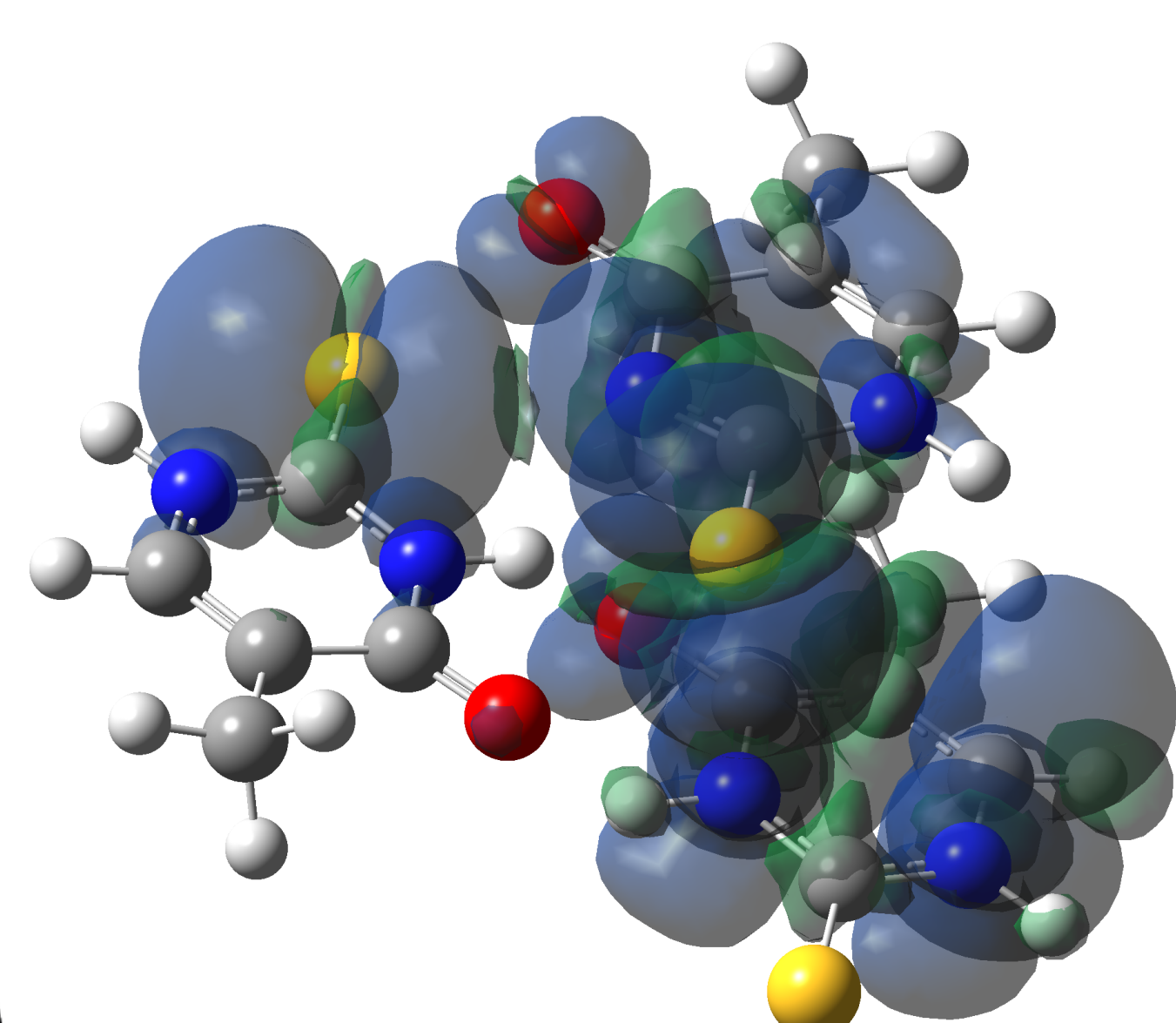
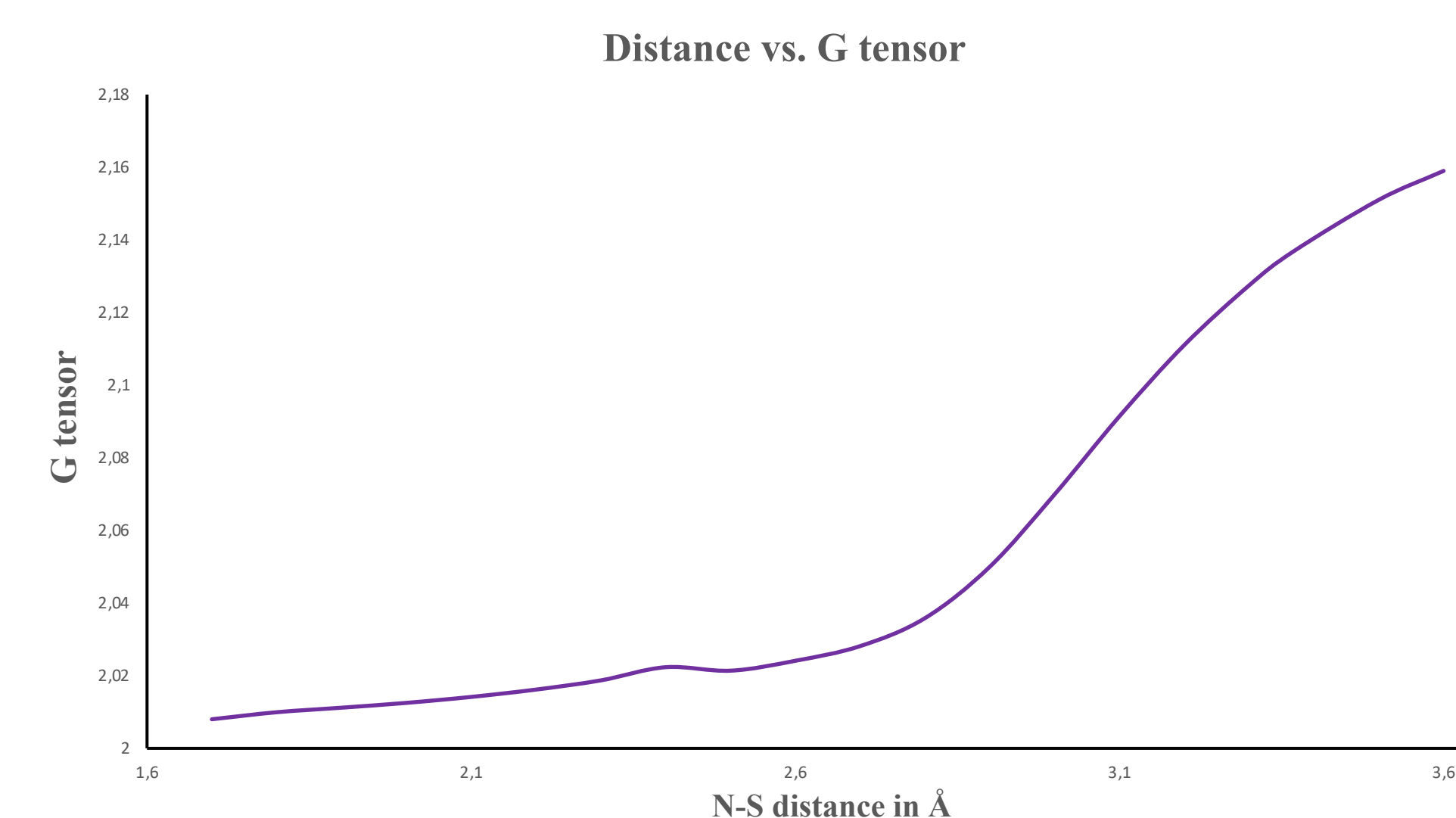
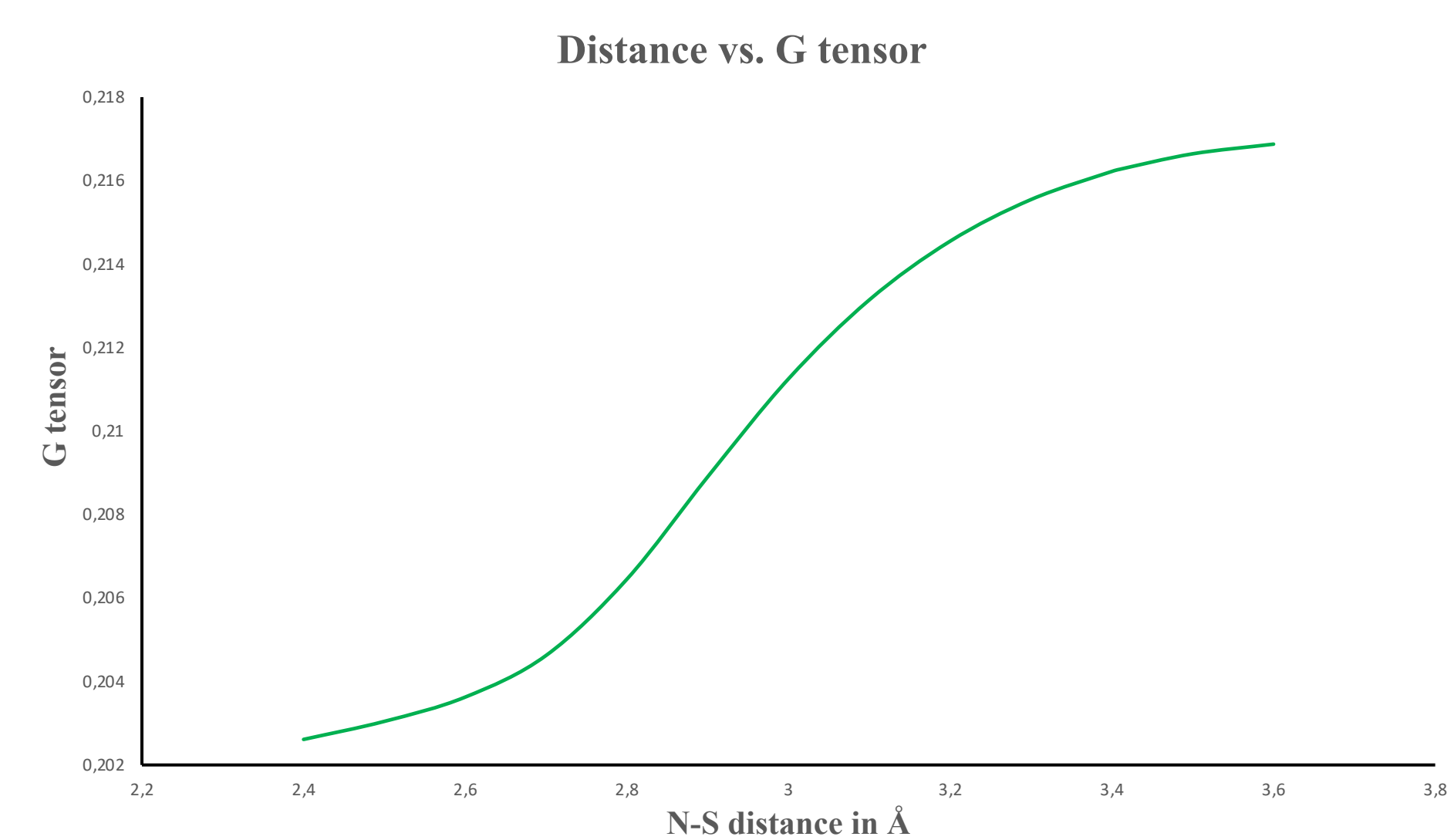
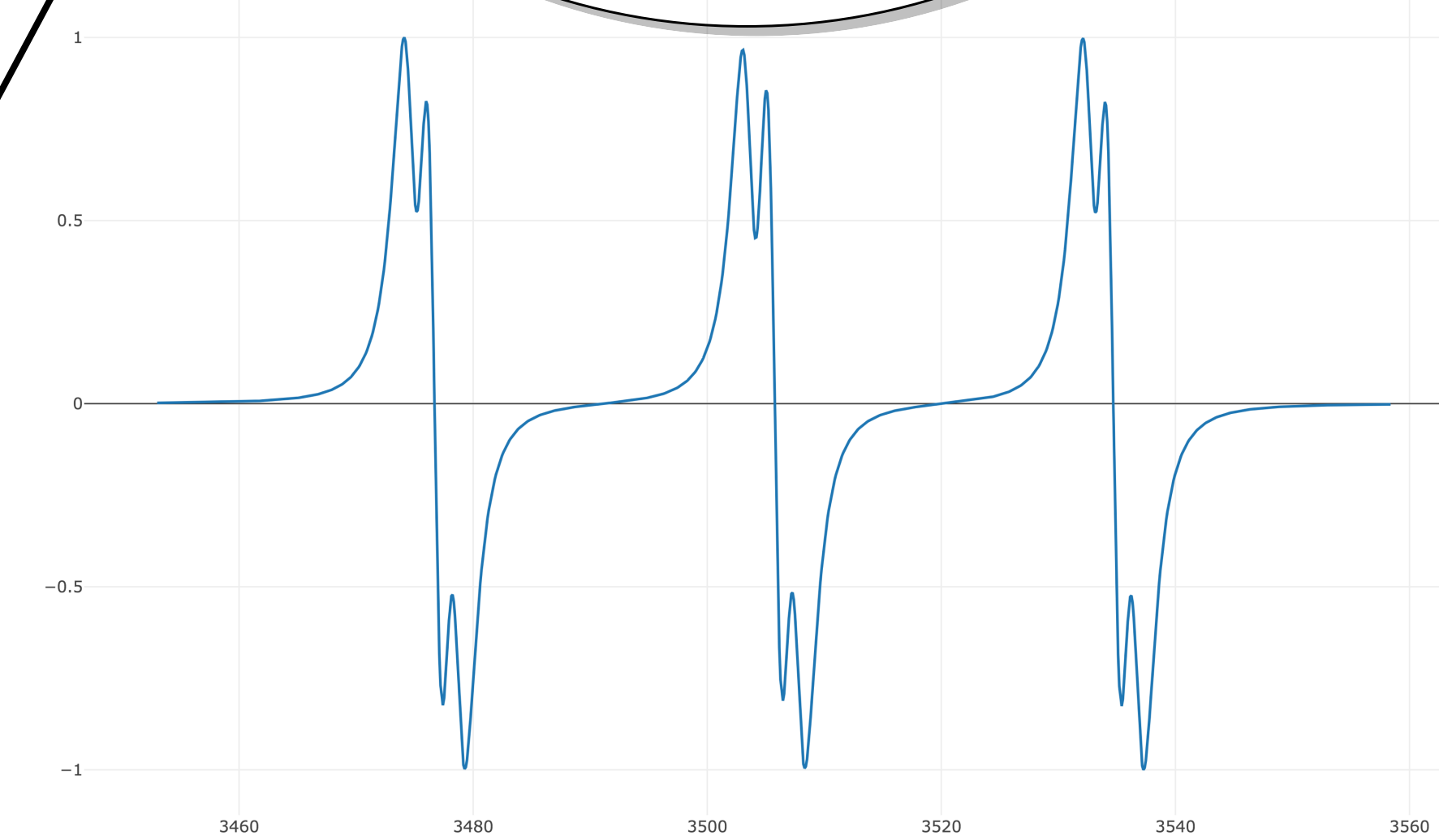
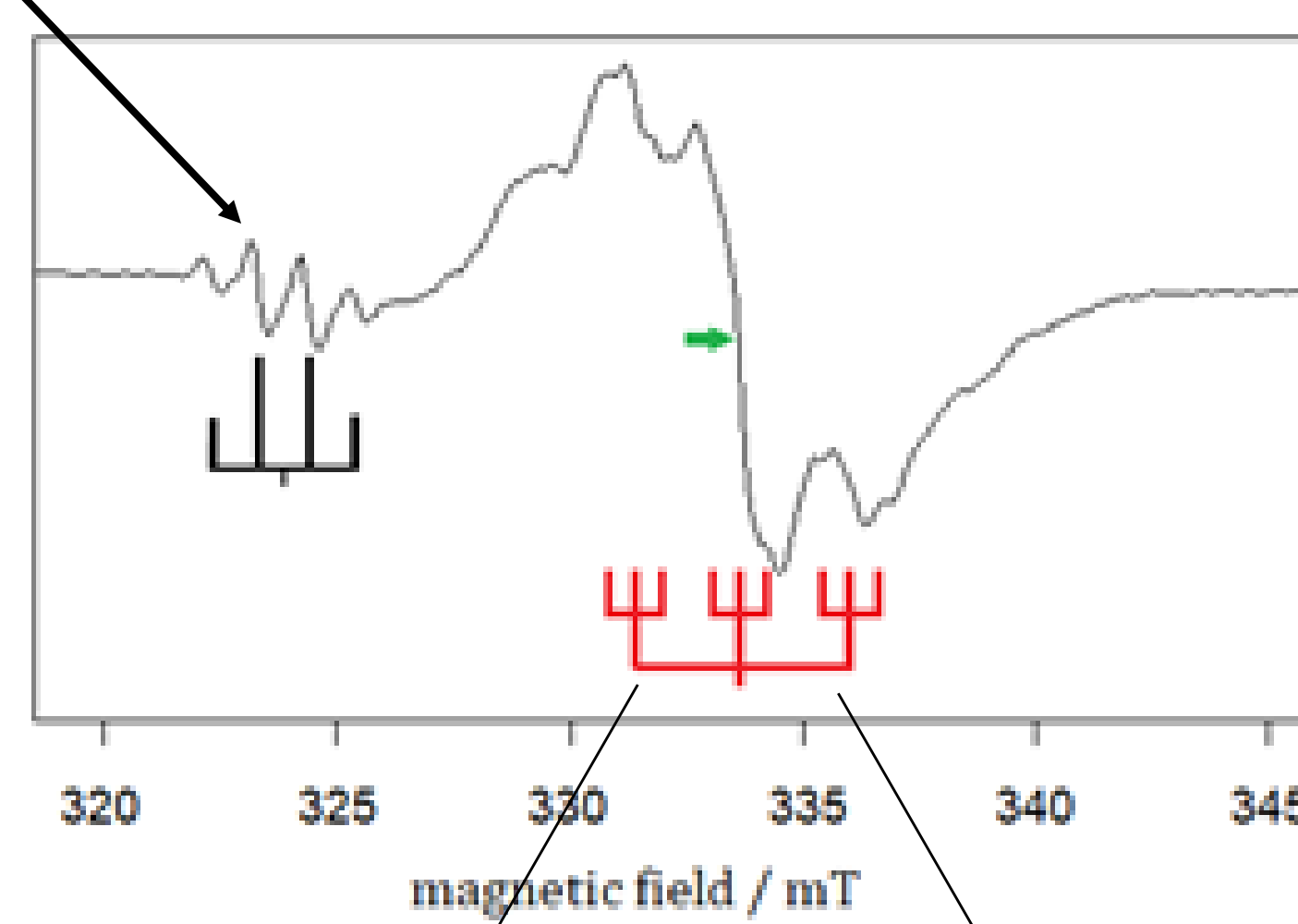
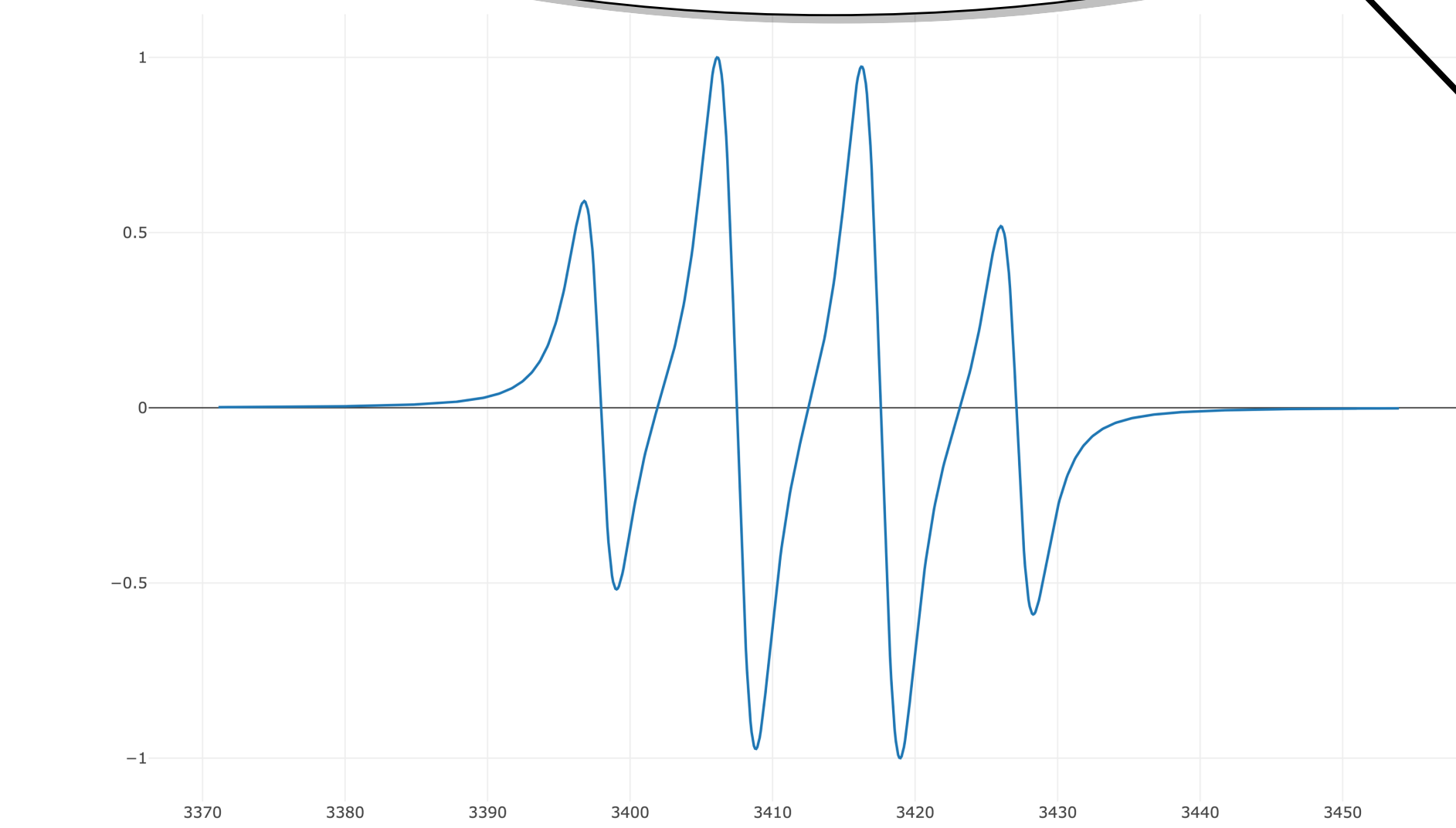
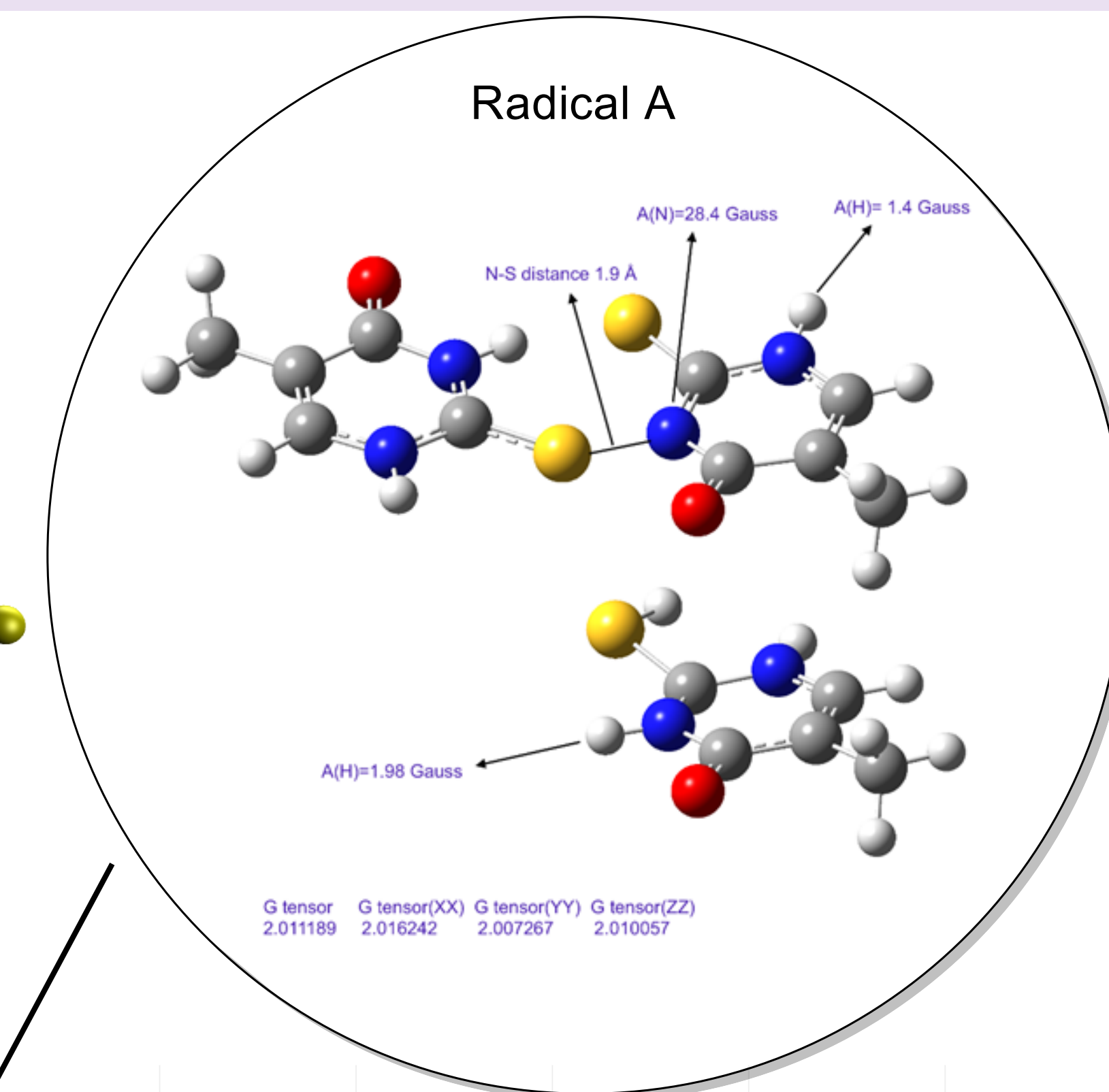
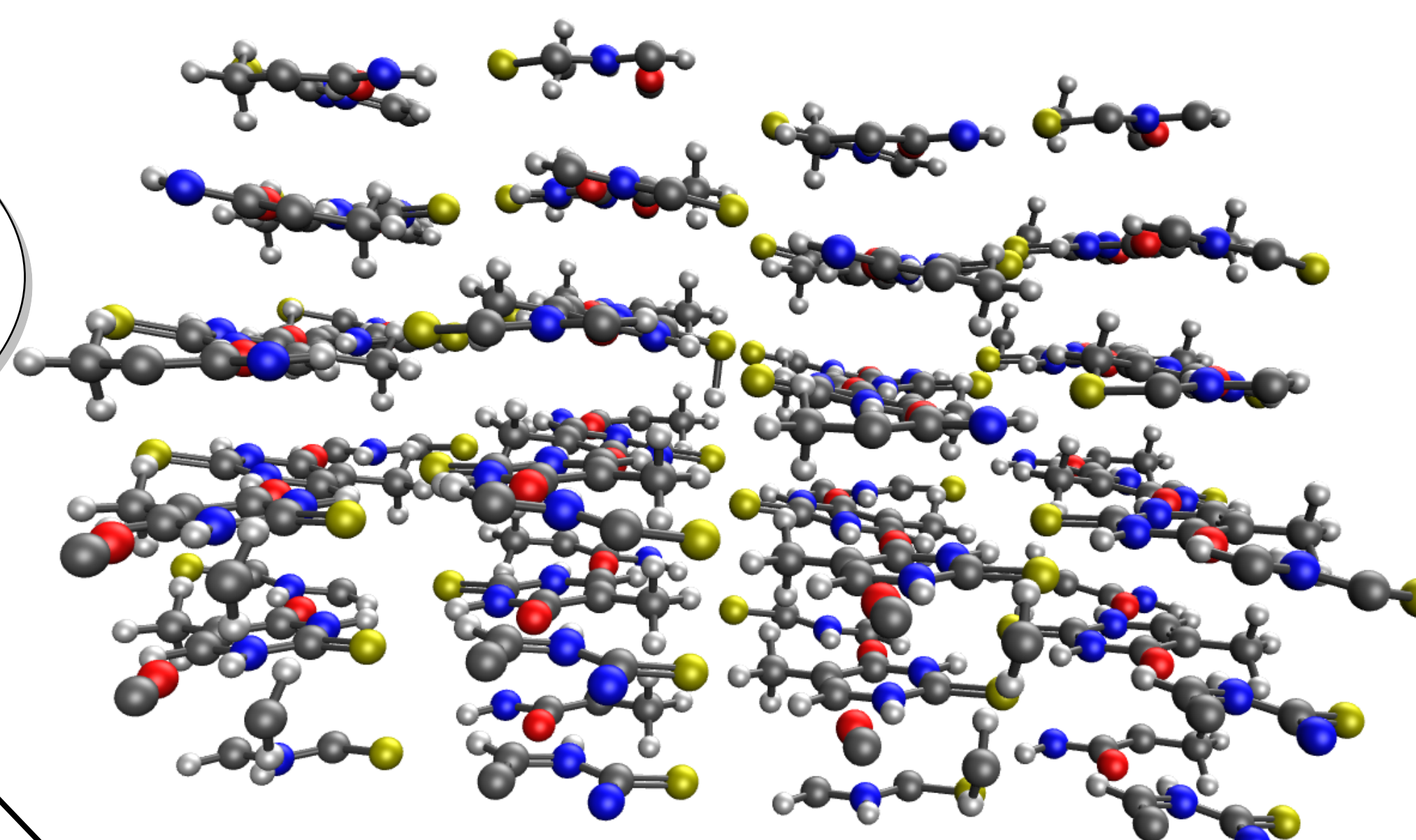
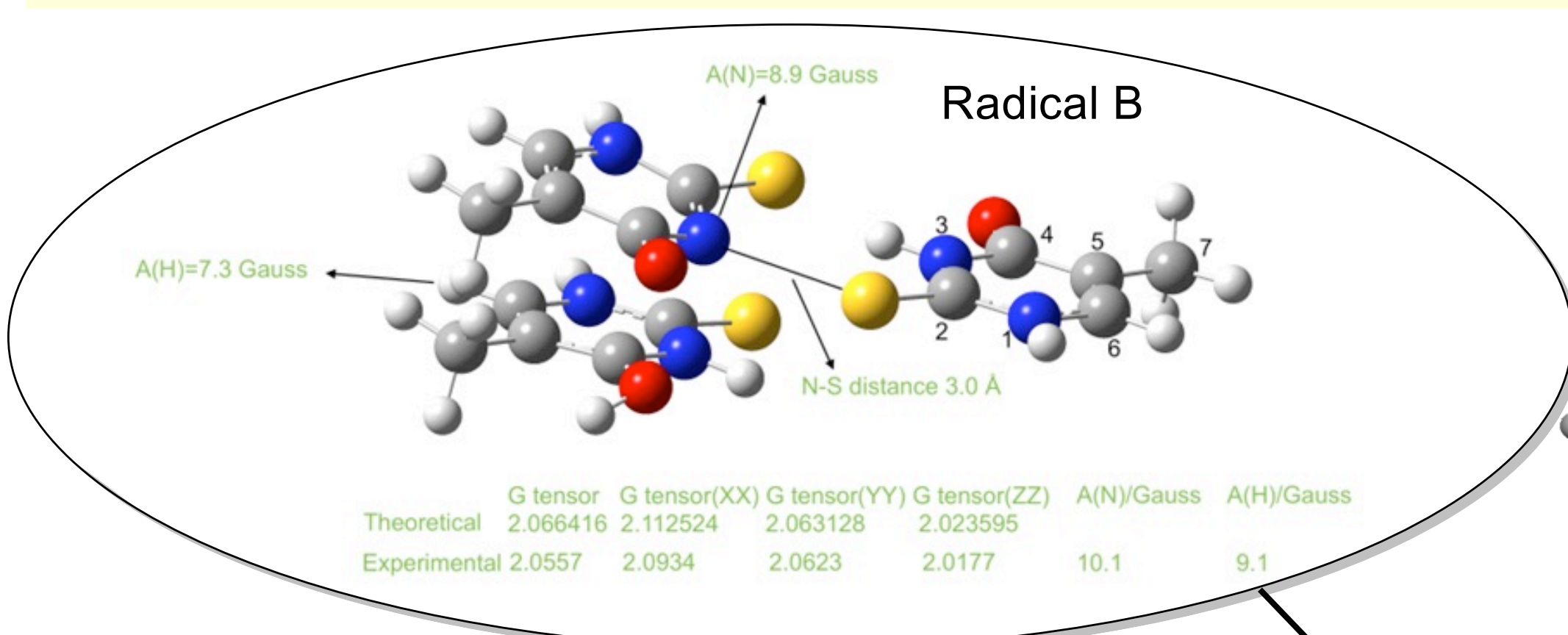


Introduction

- In single crystals of nucleic acids and their constituents, as well as in single crystals of 2-thiocytosine¹, 6-thioguanine² and 2-thiouracil³, γ -irradiated at low temperature (77 K), only radicals of the π -type have been observed.
- Irradiated thioanalogue of thymine, 2-thiothymine (5-methyl-2-thiouracil), reveals different properties from regular bases and other thio-nucleobases.
- Only in the single crystals of 2-thiothymine, ionizing radiation induces two types of radicals at low temperatures, with quite unusual of H atom from N₃ nitrogen, generating a σ -radical⁴.
- This σ -radical was the first observed radical of σ -electron configuration in all nucleic-acid bases or their thioanalogs in ordered structure.
- The proposed structure of the radical (B) present in the system is the π -type radical, generated by loss of an H atom from N₃ nitrogen⁵.

Methods

- GaussView, IQmol
- Gaussian 16 opt+freq @B3LYP/6-31G(d)
- EPR calculations: B3LYP functional with mixed basis set; EPR-III for C, H, O atoms, def2-QZVP for S-atom, and 6-31G(d) for N-atom and NMR keyword in the route section.
- Geometry optimization within the crystal lattice were performed with unrestricted periodic constrained DFT (CDFT) calculations with PBO functional, GTH pseudopotentials, Grimme's D3 dispersion correction and DZVP-SR-MOLOPT-GTH basis set
- Klaster Supek @SRCE
- Klaster Padobran @SRCE
- Klaster sw.pharma.hr, Farmlnova @FBF



Hypothesis

- With gamma irradiation of single crystal of 2-thiothymine at 100 K homolytic cleavage of N₃-H bond occurs.
- Upon cleavage intralayer hydrogen atom transfer (HAT) transpires.

Conclusion

- Gamma irradiation homolytically cleaves N₃-H bond with two radicals forming at 100 K.
- One is in σ electronic state and the other is in π electronic state.
- Some spin on the N₃ radical is delocalized on the neighbouring sulphur atom.
- An interaction between N₃ radical and sulphur atom is established.
- This interaction has a crucial influence on the electronic state of the radical formed.
- For radical B, G tensor is right at the inflection point on the curve (pronounced anisotropic character of the g tensor and π electronic state).
- For radical A, G tensor is at a point on the curve where first derivation with respect to the distance is almost zero (σ electronic state).

MC²hem
a . o . .
t . . m .
h . . . p



- References
- J. N. Herak, K. Sanković, D. Krilov, J. Hüttermann, K. Sankovic, J. Huttermann, *Radiation Research* **1999**, 151, 319.
 - K. Sankovic, D. Krilov, J. N. Herak, *Radiation Research* **1991**, 128, 119.
 - J. P. Jørgensen, E. Sagstuen, *Radiat Res* **1981**, 88, 29.
 - E. Bešić, K. Sanković, V. Gomzi, J. N. Herak, *Phys. Chem. Chem. Phys.* **2001**, 3, 2723.
 - E. Bešić, *Journal of Molecular Structure* **2009**, 917, 71.

