Electron magnetic resonance study of radiation-induced radicals in DNA

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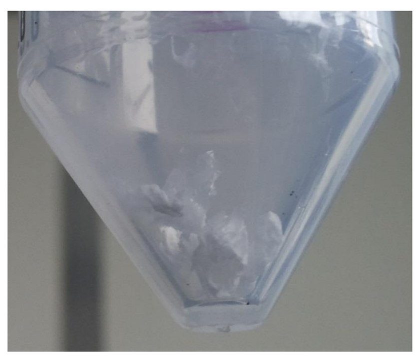
Introduction

It is widely known that free-radical-mediated damage to biomolecules brings dire consequences to living organisms. In the context of high energy radiation effects on DNA, neutral sugar radicals are very important because of their links to strand breaks – the main actors in radiation induced mutation and carcinogenesis. Considerable progress has been made in understanding the radical composition of irradiated DNA by studying it directly or by examining model systems [1]. Most of the identification relied on comparisons of isotropic HF interactions to DFT calculations, so chemical structures of radicals are still somewhat ambiguous. It is not unreasonable to assume that some of these ambiguities would be solved if anisotropic data was acquired by employing more advanced EPR techniques, like multifrequency EPR spectroscopy or hyperfine selective EPR techniques (ENDOR, e.g.).

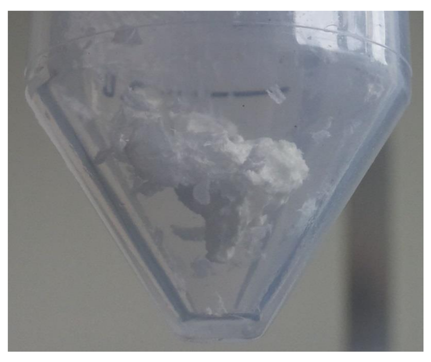
Sample preparation

Lyophilized from D_2O solution at RT

Salmon testes ds-DNA

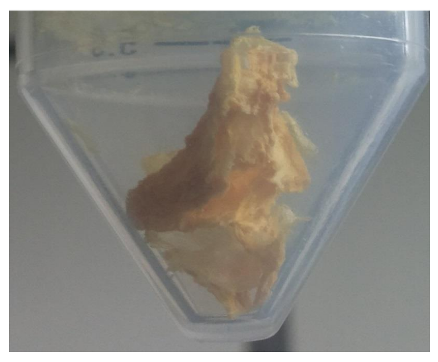


+ $K_3Fe^{3+}(CN)_6$



e⁻ scavenger

+ $K_4Fe^{2+}(CN)_6$



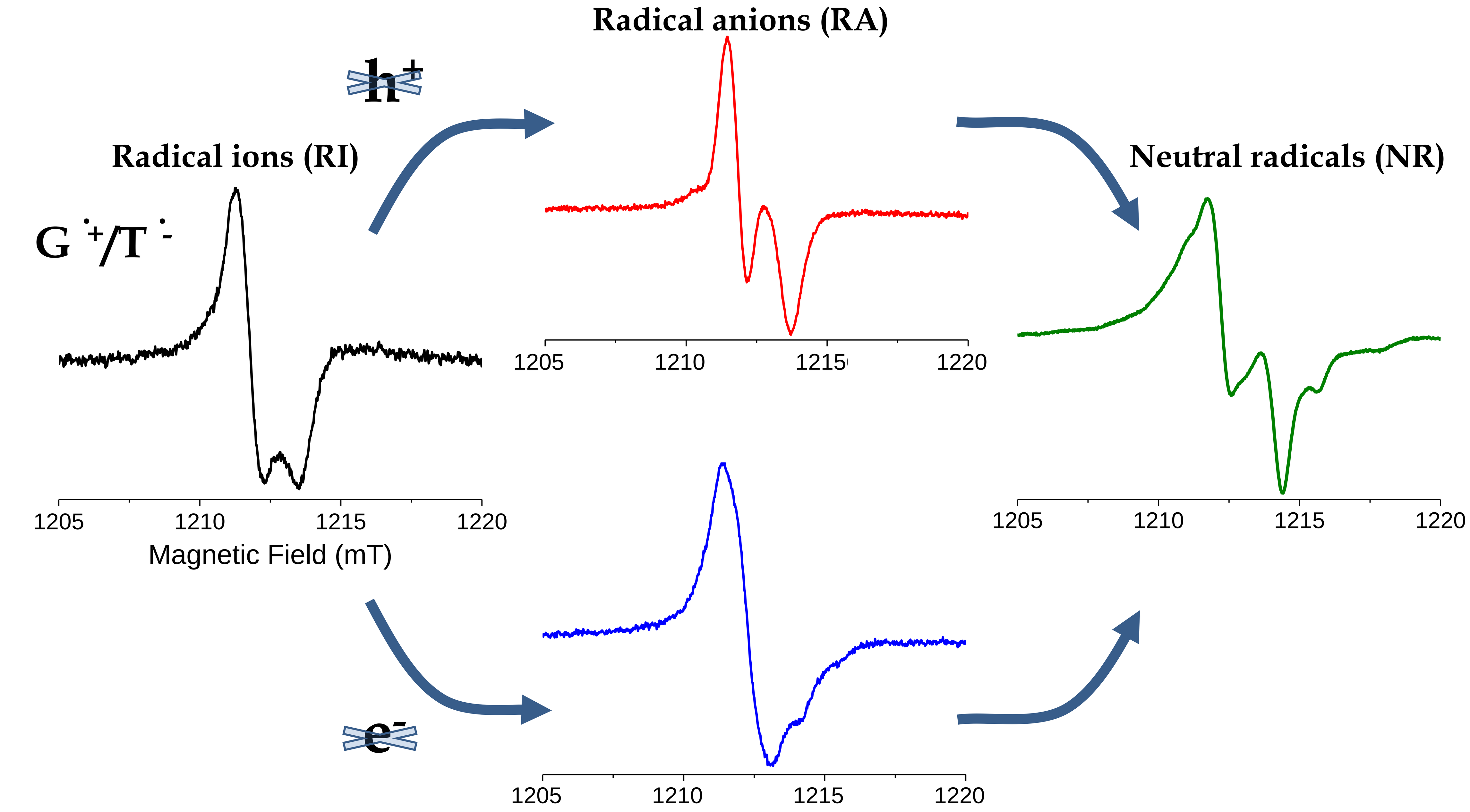
h⁺ scavenger

+ $K_3Fe^{3+}(CN)_6$ + $K_4Fe^{2+}(CN)_6$

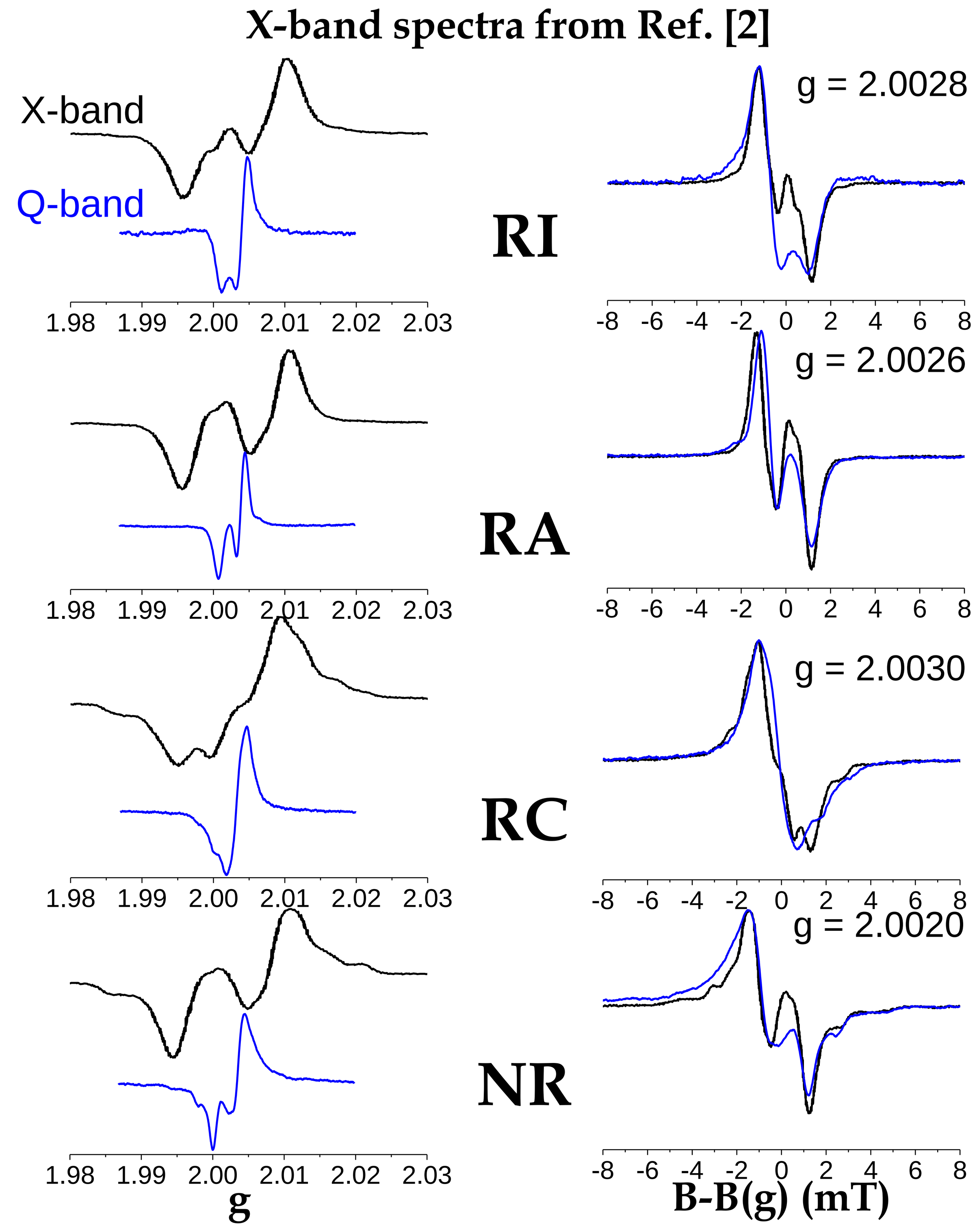
Irradiated at 80 K

Q-band EPR spectrum at 50 K

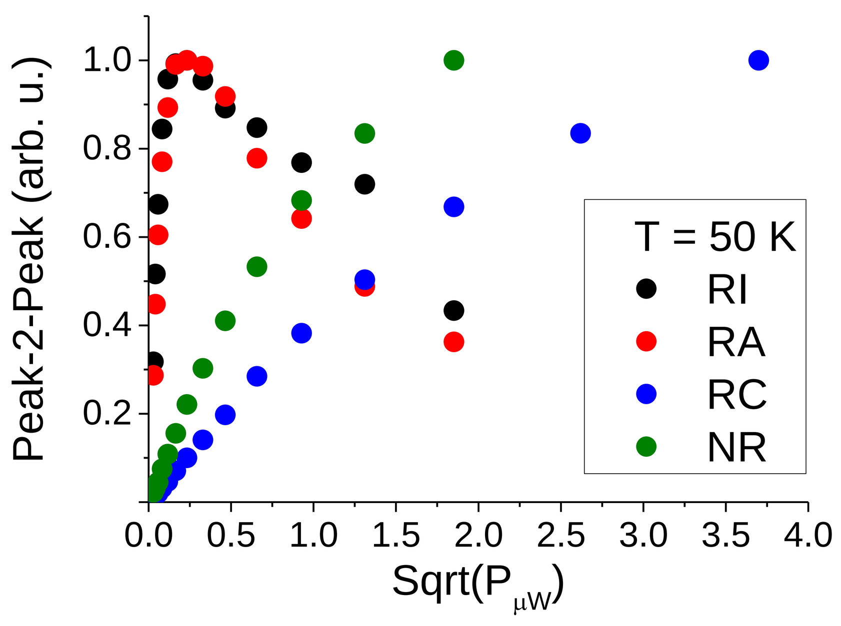
After irradiation the EPR spectrum of DNA is known to be dominated by base radicals: e^-/h^+ scavengers have to be employed to suppress their formation.

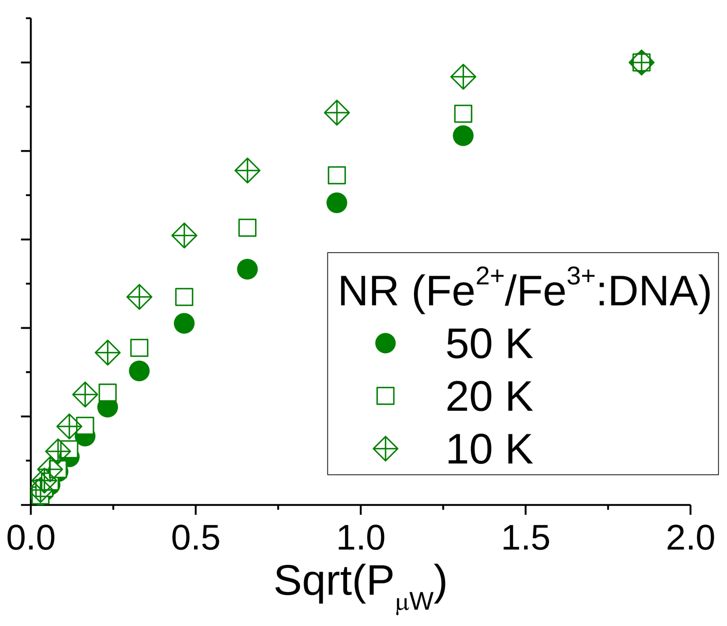


Comparison to X-band

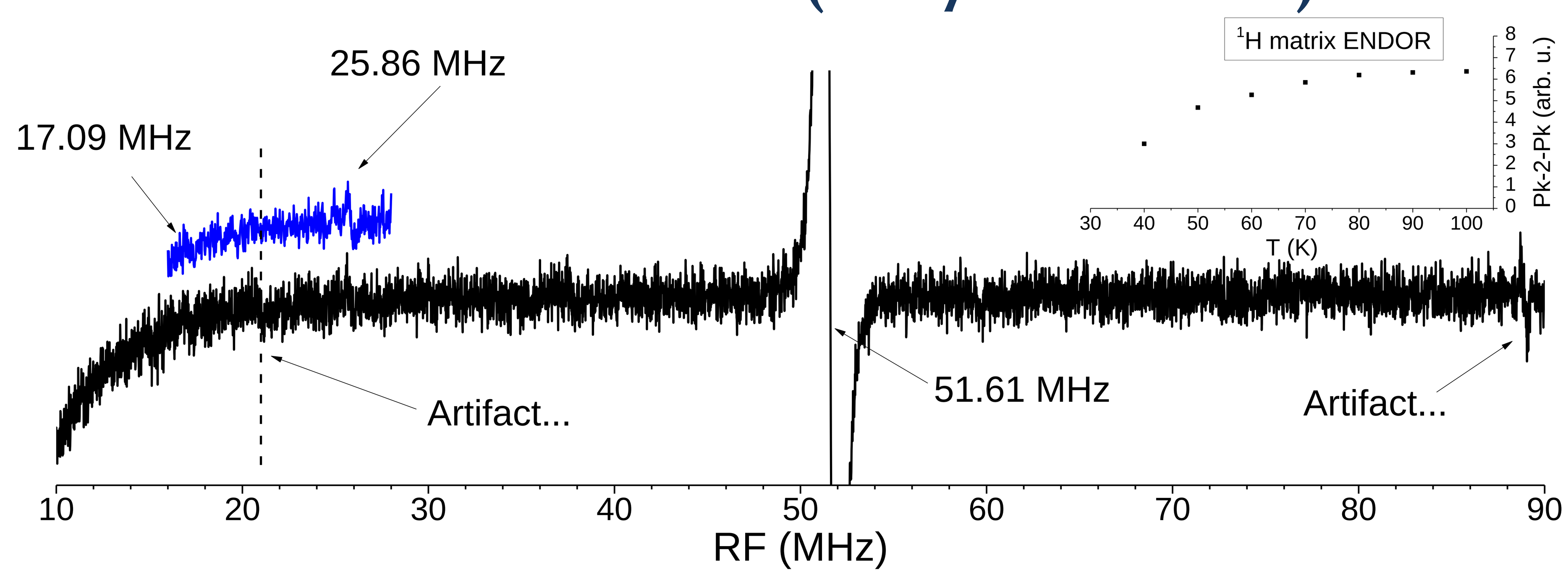


Power saturation of the EPR spectrum





ENDOR of NR (Fe^{2+}/Fe^{3+}:DNA)



Conclusions

- Good agreement with X-band, structure dominated by HF interactions
- Difficult reproducing good radical yields, so still optimizing lyophilization procedure
- Peculiar dependence of matrix ENDOR on T

References

1. Adhikary, A. et al. Applications of EPR in Radiation Research, Springer, 2014; pp 304-352.
2. Shukla, L. I. et al. Radiation Research (163) 2005; 591–602.

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