



Universiteit
Leiden
The Netherlands

T-CYCLE EPR Development at 275 GHz for the study of reaction kinetics & intermediates

Panarelli, E.G.

Citation

Panarelli, E. G. (2018, December 10). *T-CYCLE EPR Development at 275 GHz for the study of reaction kinetics & intermediates*. *Casimir PhD Series*. Retrieved from <https://hdl.handle.net/1887/68233>

Version: Not Applicable (or Unknown)

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/68233>

Note: To cite this publication please use the final published version (if applicable).

Cover Page



Universiteit Leiden



The handle <http://hdl.handle.net/1887/68233> holds various files of this Leiden University dissertation.

Author: Panarelli, E.G.

Title: T-CYCLE EPR Development at 275 GHz for the study of reaction kinetics & intermediates

Issue Date: 2018-12-10

T-CYCLE EPR

Development at 275 GHz for the study
of reaction kinetics & intermediates.

Proefschrift

ter verkrijging van
de graad van Doctor aan de Universiteit Leiden,
op gezag van Rector Magnificus prof.mr. C.J.J.M. Stolker,
volgens besluit van het College voor Promoties
te verdedigen op maandag 10 december 2018
klokke 16.15 uur

door

Enzo Gabriele Panarelli

geboren te Cuneo (Italië)
in 1989

Promotor: Prof. dr. E. J. J. Groenen

Co-promotor: Dr. P. Gast

Promotiecommissie: Prof. dr. W. J. Buma (Universiteit van Amsterdam)

Prof. dr. E. Giamello (Università di Torino, Turijn, Italië)

Prof. dr. H. J. Steinhoff (Universität Osnabrück, Osnabrück, Duitsland)

Prof. dr. E. R. Eliel

Prof. dr. M. A. G. J. Orrit

Casimir PhD series, Delft-Leiden 2018-43

ISBN 978-90-85933731

An electronic version of this thesis can be found at <https://openaccess.leidenuniv.nl>

Drawing on the cover: © 2018 Michelle Martinengo

Contents

1	Introduction	1
1.1	Motivation and scope	2
1.2	Chemical kinetics	2
1.3	Rapid Freeze-Quench	6
1.4	Laser-induced Temperature-jumps	9
1.5	Electron Paramagnetic Resonance	10
1.5.1	The electron Zeeman effect and the g -factor	11
1.5.2	Electron spin – nuclear spin interaction: the hyperfine coupling	13
1.5.3	High-spin systems	16
1.5.4	Slow-to-fast motion and rigid limit in EPR spectra	20
1.5.5	Home-built 275 GHz EPR spectrometer	22
2	Effective coupling of RFQ to High-Frequency EPR	27
2.1	Introduction	28
2.2	Experimental	31
2.2.1	Materials	31
2.2.2	Sample preparation	31
2.2.3	EPR measurements	37
2.2.4	Internal calibration	37
2.2.5	Methodology	38
2.3	Results	39
2.4	Discussion and conclusions	41
3	T-Cycle EPR for the investigation of chemical dynamics	49
3.1	Introduction	50
3.2	Temperature-Cycle EPR	52

3.3	Experimental	54
3.3.1	Materials	54
3.3.2	Setup	56
3.3.3	Internal standard	57
3.4	Temperature-Cycle EPR demonstrated on a model reaction	58
3.4.1	The TEMPOL-ascorbic acid reaction as a model system	58
3.4.2	First demonstration of Temperature-Cycle EPR	61
3.4.3	Flexibility of Temperature-Cycle EPR	62
3.5	Discussion and conclusions	64
3.6	Appendix	66
4	Exploring Temperature-Cycle EPR in the sub-second time domain	75
4.1	Introduction	76
4.2	Experimental	76
4.2.1	Materials and setup	76
4.2.2	The TEMPOL-dithionite reaction	79
4.2.3	Sub-zero mixing	79
4.3	Results	81
4.3.1	Temperature-Cycle EPR on a sub-second time scale	81
4.3.2	Quantitative analysis of the sub-second kinetics	82
4.4	Discussion	90
4.4.1	Modeling of the temperature decay following a laser pulse	91
4.5	Conclusions	95
5	Venturing on the reoxidation of T1D SLAC with T-Cycle EPR	99
5.1	Introduction	100
5.2	Experimental	102
5.2.1	Materials and setup	102
5.3	Results	106
5.3.1	T1D SLAC sample mixed at room temperature	106
5.3.2	Application of sub-second Temperature-Cycle EPR on the cryo-mixed T1D SLAC sample	107
5.4	Discussion and conclusions	109
	Bibliography	115
	Summary	123

CONTENTS

Samenvatting	127
Curriculum Vitae	131
Acknowledgments	133

