

# Contents

<b>1</b>	<b>Introduction to Cavity Enhanced Absorption Spectroscopy . . . . .</b>	<b>1</b>
	Daniele Romanini, Irène Ventrillard, Guillaume Méjean, Jérôme Morville, and Erik Kerstel	
1.1	Introduction . . . . .	1
1.1.1	A Short History of Cavity Enhanced Methods . . . . .	3
1.1.2	A Review of Reviews on CEAS Developments and Applications . . . . .	13
1.2	The High Finesse Optical Resonator . . . . .	15
1.2.1	Intensity Transmitted by a Cavity: A Simplified One-Dimensional Model . . . . .	15
1.2.2	The Real World of Transverse Modes . . . . .	23
1.3	Detection Limit, Noise, Fringes, and More . . . . .	26
1.4	Coupling of Light into a High Finesse Optical Cavity . . . . .	30
1.4.1	Single Mode Injection: From the Ideal Monochromatic Laser to the Realistic Noisy Laser . . . . .	30
1.4.2	Multi-mode Injection (Longitudinal and Transverse): Incoherent Pulsed Lasers . . . . .	38
1.4.3	Multi-mode Injection (Longitudinal): Coherent Pulsed Lasers, or Frequency Combs . . . . .	42
1.5	Conclusion . . . . .	51
	References . . . . .	51
<b>2</b>	<b>Detection and Characterization of Reactive Chemical Intermediates Using Cavity Ringdown Spectroscopy . . . . .</b>	<b>61</b>
	Neal Kline and Terry A. Miller	
2.1	Introduction . . . . .	61
2.2	The Chemistry and Spectroscopy of Peroxy Radicals . . . . .	63
2.3	CRDS Spectrometers and Results . . . . .	65
2.3.1	Room Temperature, Moderate Resolution CRDS of Ethyl Peroxy . . . . .	66
2.3.2	Jet-Cooled, High Resolution CRDS of Ethyl Peroxy . . . . .	71

2.3.3	Dual Wavelength Spectroscopy . . . . .	76
2.3.4	Self-Reaction Kinetics . . . . .	81
2.4	Dynamics . . . . .	85
2.5	Conclusion . . . . .	89
	References . . . . .	89
<b>3</b>	<b>Quantum Cascade Laser Based Chemical Sensing Using Optically Resonant Cavities . . . . .</b>	<b>93</b>
	S. Welzel, R. Engeln, and J. Röppke	
3.1	Introduction to Molecular Absorption Spectroscopy . . . . .	94
3.2	Mid-Infrared Light Sources . . . . .	98
3.2.1	Overview About Conventional Sources . . . . .	98
3.2.2	Quantum Cascade Lasers (QCLs) . . . . .	101
3.3	Theoretical Considerations . . . . .	106
3.3.1	Cavity Ring-Down Spectroscopy (CRDS) . . . . .	106
3.3.2	Cavity Enhanced Absorption Spectroscopy (CEAS/ICOS) . . . . .	107
3.3.3	Cavity Mode Structure . . . . .	108
3.3.4	Sensitivity Considerations . . . . .	109
3.4	QCL Based Excitation of Optical Cavities . . . . .	111
3.4.1	CRDS Using p-QCLs . . . . .	111
3.4.2	CEAS Using cw-QCLs . . . . .	116
3.4.3	Optical Feedback to QCLs . . . . .	122
3.4.4	Absorption Spectroscopy Using EC-QCLs . . . . .	124
3.5	Applied Mid-Infrared Chemical Sensing Using Optical Cavities . . . . .	125
3.5.1	Brief Historical Background . . . . .	125
3.5.2	Trace Gas Sensing . . . . .	126
3.5.3	Reactive Gas Mixtures . . . . .	130
3.5.4	Overview of Cavity Enhanced mid-IR Spectrometers: System Performance . . . . .	133
3.6	Conclusions and Perspectives . . . . .	136
	References . . . . .	137
<b>4</b>	<b>Saturated-Absorption Cavity Ring-Down (SCAR) for High-Sensitivity and High-Resolution Molecular Spectroscopy in the Mid IR . . . . .</b>	<b>143</b>
	P. Cancio, I. Galli, S. Bartalini, G. Giusfredi, D. Mazzotti, and P. De Natale	
4.1	Sensitivity and Resolution Limits of Linear Cavity Ring-Down Molecular Spectroscopy with CW Laser Sources in the Mid IR . . . . .	143
4.2	SCAR Technique . . . . .	147
4.2.1	Inhomogeneously Broadened Transitions . . . . .	149
4.2.2	Homogeneously Broadened Transitions . . . . .	151
4.3	Mid-IR CW Laser Sources for SCAR Spectroscopy . . . . .	152
4.3.1	Non-linear Frequency Down Converted Coherent Sources . . . . .	152
4.3.2	Quantum Cascade Lasers . . . . .	153
4.4	Sub-Doppler SCAR Molecular Spectroscopy . . . . .	155

4.5	Ultra High-Sensitivity SCAR Molecular Spectroscopy: Application to Detection of Very Rare Species . . . . .	157
	References . . . . .	160
<b>5</b>	<b>Cavity Enhanced Absorption Spectroscopy with Optical Feedback</b>	<b>163</b>
	Jérôme Morville, Daniele Romanini, and Erik Kerstel	
5.1	Introduction . . . . .	163
5.2	An Intuitive Picture of the Technique . . . . .	164
5.3	Theoretical Foundations of OF-CEAS . . . . .	170
5.3.1	Optical Feedback: Model Equations . . . . .	170
5.3.2	The Locked Frequency Behavior and the Resulting Cavity Transmission Pattern . . . . .	174
5.3.3	Optical Feedback Phase and the Cavity Transmission Beating Patterns . . . . .	176
5.3.4	The OF-CEAS Operating Conditions . . . . .	178
5.3.5	Locked-Laser Linewidth and Optical Feedback Phase Tolerance . . . . .	179
5.3.6	The High Frequency Scanning Speed of OF-CEAS . . . . .	180
5.4	Implementation . . . . .	183
5.4.1	Different Laser Sources for OF-CEAS . . . . .	183
5.4.2	OF-CEAS Schemes . . . . .	185
5.5	Absorption Scale Calibration by a Single Ring-Down . . . . .	189
5.6	Typical Performance of OF-CEAS . . . . .	194
5.7	Precursory Works on OF-Locking of a Semiconductor Laser to an Optical Cavity . . . . .	199
5.7.1	Laser Stabilization . . . . .	199
5.7.2	Optical-Feedback Cavity Ring-Down Spectroscopy . . . . .	200
5.8	Applications . . . . .	202
5.8.1	Trace Gas Detection . . . . .	202
5.8.2	Isotope Ratio Analyses . . . . .	204
5.8.3	Aerosol Studies . . . . .	205
5.8.4	Other Applications . . . . .	205
5.9	Conclusions . . . . .	205
	References . . . . .	207
<b>6</b>	<b>NICE-OHMS—Frequency Modulation Cavity-Enhanced Spectroscopy—Principles and Performance . . . . .</b>	<b>211</b>
	Ove Axner, Patrick Ehlers, Aleksandra Foltynowicz, Isak Silander, and Junyang Wang	
6.1	Introduction . . . . .	211
6.2	Theory—NICE-OHMS Analytical Signals . . . . .	213
6.2.1	Frequency Modulation Spectroscopy . . . . .	213
6.2.2	Doppler-Broadened NICE-OHMS . . . . .	214
6.2.3	Sub-Doppler NICE-OHMS . . . . .	225
6.3	Experimental Implementation . . . . .	230
6.3.1	Generic Setup . . . . .	230

6.3.2	Fiber-Laser-Based NICE-OHMS . . . . .	233
6.4	Performance . . . . .	236
6.4.1	Concentration, Pressure, and Power Dependence of the Analytical Signal . . . . .	236
6.4.2	Noise and Background Signals . . . . .	238
6.4.3	Detection Sensitivity . . . . .	244
6.5	Summary, Conclusions, and Future Outlook . . . . .	246
	References . . . . .	248
<b>7</b>	<b>Applications of NICE-OHMS to Molecular Spectroscopy . . . . .</b>	<b>253</b>
	Brian M. Siller and Benjamin J. McCall	
7.1	Introduction . . . . .	253
7.2	Laser Systems . . . . .	255
7.2.1	Near-Infrared . . . . .	255
7.2.2	Mid-Infrared . . . . .	259
7.3	Molecules . . . . .	261
7.3.1	Stable Neutral Molecules . . . . .	262
7.3.2	Radicals and Ions . . . . .	265
7.4	Future Prospects . . . . .	269
	References . . . . .	269
<b>8</b>	<b>Cavity-Enhanced Direct Frequency Comb Spectroscopy . . . . .</b>	<b>271</b>
	P. Masłowski, K.C. Cossel, A. Foltynowicz, and J. Ye	
8.1	Introduction . . . . .	271
8.2	Frequency Comb Sources . . . . .	274
8.2.1	Mode-Locked Lasers . . . . .	275
8.2.2	Indirect Sources . . . . .	277
8.2.3	Other Types of OFC Sources . . . . .	278
8.2.4	Typical Comb Sources . . . . .	279
8.3	Comb-Cavity Coupling . . . . .	282
8.3.1	Comb-Cavity Coupling—Tight Locking Scheme . . . . .	284
8.3.2	Comb-Cavity Coupling—Swept Coupling Scheme . . . . .	287
8.3.3	Effect of Comb-Cavity Resonance Mismatch on the Observed Line Shape . . . . .	289
8.4	Detection Methods . . . . .	290
8.4.1	Broadband Cavity Ringdown Spectroscopy . . . . .	293
8.4.2	VIPA Spectrometer . . . . .	295
8.4.3	Fourier-Transform Spectroscopy . . . . .	296
8.4.4	Sensitivity of CE-DFCS Detection Methods . . . . .	299
8.5	Applications . . . . .	300
8.5.1	Breath Analysis . . . . .	300
8.5.2	Trace Water in Arsine Vapor . . . . .	302
8.5.3	Trace Detection of Hydrogen Peroxide . . . . .	303
8.5.4	Comb-Mode Resolved Spectroscopy . . . . .	308
8.6	Summary . . . . .	312
	References . . . . .	312

<b>9</b>	<b>Whispering Gallery Mode Biomolecular Sensors</b> . . . . .	323
	Yuqiang Wu and Frank Vollmer	
9.1	Nano-Biotechnology: Sensors Interface the Molecular World . .	323
9.2	Whispering Gallery Mode Resonator Biosensors . . . . .	325
9.2.1	Whispering Gallery Mode . . . . .	325
9.2.2	Reactive Sensing Principle . . . . .	329
9.3	Detection of Bio-Samples . . . . .	334
9.3.1	Protein Detection . . . . .	334
9.3.2	Single Virus Detection . . . . .	337
9.3.3	Multiplexed Sensing Platform . . . . .	339
9.3.4	WGM Sensors with Plasmonic Enhancement . . . . .	340
9.4	Outlook . . . . .	342
9.5	Keywords and Notes . . . . .	343
	References . . . . .	345
<b>10</b>	<b>Cavity-Enhanced Spectroscopy on Silica Microsphere Resonators</b> .	351
	Jack A. Barnes, Gianluca Gagliardi, and Hans-Peter Loock	
10.1	Introduction: Microcavities in Chemical Sensing . . . . .	352
10.2	Theoretical Background . . . . .	353
10.2.1	Modes Inside a Dielectric Sphere . . . . .	353
10.2.2	Estimate of the Volume Fraction of the Evanescent Wave	355
10.2.3	Excitation and Detection of Cavity Modes . . . . .	357
10.2.4	Resonance Shifts in WGMs due to External Perturbations	359
10.2.5	Loss Mechanisms . . . . .	361
10.2.6	Determination of Optical Loss Using Cavity Ring-Down Methods . . . . .	362
10.3	Experimental Studies . . . . .	371
10.3.1	Introduction . . . . .	371
10.3.2	Properties and Spectra of Ethylene Diamine . . . . .	371
10.3.3	Experiment . . . . .	372
10.3.4	Photothermal Effect . . . . .	375
10.3.5	Determination of Ethylene Diamine Coverage and Absorption . . . . .	376
	References . . . . .	380
<b>11</b>	<b>Cavity Ringdown Spectroscopy for the Analysis of Small Liquid Volumes</b> . . . . .	385
	Claire Vallance and Cathy M. Rushworth	
11.1	Introduction . . . . .	385
11.2	Fundamentals of Cavity Ringdown and Cavity-Enhanced Absorption Spectroscopy . . . . .	387
11.2.1	General Principles of Cavity Ringdown Spectroscopy . .	387
11.2.2	General Principles of Cavity-Enhanced Absorption Spectroscopy . . . . .	388
11.2.3	Detection Limits in Cavity Ringdown and Cavity-Enhanced Absorption Measurements . . . . .	389

11.3	Applying Cavity-Enhanced Spectroscopies to the Liquid Phase . . . . .	390
11.3.1	Cavity Configurations for Liquid-Phase Analysis . . . . .	391
11.3.2	Broadband Cavity Ringdown Techniques . . . . .	395
11.4	Example Application: Microfluidic Sensors . . . . .	397
11.5	Example Application: Sensing of Trace Compounds in Water . . . . .	402
11.6	The Future . . . . .	405
	References . . . . .	406
<b>12</b>	<b>Fiber Loop Ringdown Sensors and Sensing . . . . .</b>	<b>411</b>
	Chuji Wang	
12.1	Introduction . . . . .	411
12.2	Fiber Loop Ringdown (FLRD) Basics . . . . .	412
12.2.1	Principle of FLRD . . . . .	412
12.2.2	FLRD—A Uniform Sensing Scheme . . . . .	414
12.2.3	Configuration of the FLRD Sensing Scheme . . . . .	414
12.2.4	FLRD Sensing Signal . . . . .	416
12.2.5	Optical Losses in a Fiber Loop and Detection Sensitivity of FLRD . . . . .	417
12.3	Fabrication of a FLRD Sensor Head . . . . .	420
12.3.1	Sensing Mechanisms . . . . .	421
12.3.2	Sensor Heads . . . . .	424
12.3.3	Sensing Parameters (Functions) . . . . .	431
12.4	Individual FLRD Sensors . . . . .	431
12.4.1	Chemical Sensors . . . . .	431
12.4.2	Physical Sensors . . . . .	436
12.4.3	Biomedical and Biological Sensors . . . . .	440
12.5	Applications of FLRD Sensors . . . . .	442
12.5.1	FLRD Instrumentation . . . . .	442
12.5.2	FLRD in Remote Sensing . . . . .	444
12.6	Future FLRD Sensor Network . . . . .	450
12.6.1	Parallel Configuration . . . . .	451
12.6.2	Serial Configuration . . . . .	452
12.6.3	Large-Scale FLRD Sensing Platform . . . . .	453
12.7	Conclusion . . . . .	454
	References . . . . .	455
<b>13</b>	<b>Fiber-Optic Resonators for Strain-Acoustic Sensing and Chemical Spectroscopy . . . . .</b>	<b>463</b>
	Saverio Avino, Antonio Giorgini, Paolo De Natale, Hans-Peter Loock, and Gianluca Gagliardi	
13.1	Introduction . . . . .	464
13.2	Strain Sensing . . . . .	464
13.2.1	Fiber Bragg Grating Fabry-Pérot Resonators . . . . .	464
13.2.2	Fiber-Loop Cavities . . . . .	468
13.2.3	$\pi$ -Phase Shifted Fiber Bragg Gratings . . . . .	469
13.3	Fiber Optic Sensors for Musical Recordings . . . . .	473

13.4	Evanescent-Wave Chemical Sensing . . . . .	476
13.4.1	Optical Fiber Loop Spectroscopy . . . . .	478
13.5	Conclusions . . . . .	481
	References . . . . .	482
<b>14</b>	<b>Broadband Cavity-Enhanced Absorption Spectroscopy with Incoherent Light . . . . .</b>	<b>485</b>
	A.A. Ruth, S. Dixneuf, and R. Raghunandan	
14.1	Introduction . . . . .	485
14.2	Broadband Cavity-Based Absorption Spectroscopy . . . . .	487
14.2.1	Classification of Experimental Broadband Approaches . . . . .	487
14.2.2	Time-Dependent Broadband Methods . . . . .	488
14.2.3	Intensity-Dependent Broadband Methods . . . . .	489
14.3	Experimental Aspects . . . . .	493
14.3.1	Light Source Considerations . . . . .	493
14.3.2	Cavity Considerations . . . . .	497
14.3.3	Detection Schemes . . . . .	505
14.4	Summary of Literature . . . . .	510
	References . . . . .	512
	<b>Index . . . . .</b>	<b>519</b>

Cavity-Enhanced Spectroscopy and Sensing

Gagliardi, G.; Loock, H.-P. (Eds.)

2014, XIX, 527 p. 206 illus., 97 illus. in color., Hardcover

ISBN: 978-3-642-40002-5