Cavity Ring-Down Spectroscopy

Cavity Ring-Down Spectroscopy: Techniques and Applications Edited by Giel Berden and Richard Engeln

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Techniques and Applications

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Preface

Direct absorption spectroscopy is probably the most widespread analytical technique used to study atoms and molecules in the gas and condensed phases. It provides an absolute value for the frequency dependent absorption coefficient, which is the product of the frequency-dependent absorption cross-section and the number density. In a direct absorption experiment, the intensity of the light transmitted through a sample is measured. The attenuation of the light follows the Beer–Lambert law so that the intensity decays exponentially as a function of absorption coefficient and path length through the sample. The sensitivity of direct absorption techniques is often limited by intensity fluctuations of the light source. At best, a relative intensity change of the order of 0.001 can be measured. Many schemes have been developed to increase the sensitivity, such as multi-pass geometries to increase the absorption path lengths and modulation techniques to minimise the effects of noise in the measurement system. Alternatively, indirect absorption techniques that are based upon the measurement of an effect induced by the absorption of light, rather than the absorption of light itself, can be used. Although these indirect techniques are many orders of magnitude more sensitive than direct absorption, the drawback is that these techniques are not self-calibrating; that is, they do not provide the absorption coefficient on an absolute scale.

Cavity ring-down spectroscopy (CRDS) is a direct absorption technique with a significantly higher sensitivity than conventional absorption spectroscopy. It is based on the measurement of the rate of absorption, rather than the magnitude of absorption, of light circulating in an optical cavity. Let us consider a simple CRDS experiment. A short laser pulse is coupled into an optical cavity consisting of two highly reflective mirrors. The laser pulse is reflected back and forth inside the cavity, the so-called 'ring-down cavity'. Every time the pulse is reflected by one of the mirrors, a small fraction of the light is transmitted through that mirror. A fast detector measures the intensity of the transmitted light as a function of time, and the result will be an exponentially decaying intensity. The decay time is called the cavity ring-down time, and is inversely proportional to all losses inside the cavity. Thus, by measuring the decay time – instead of the total intensity – after the cavity, the rate of absorption is determined, directly providing the losses on an absolute scale. In an empty cavity, the losses are only determined by the reflectivity of the cavity mirrors. Inserting an absorbing sample inside the cavity leads to a larger cavity loss, and therefore to a shorter ring-down time.

The sensitivity enhancement of the CRDS technique arises from two effects. The effective absorption path length, which depends on the reflectivity of the cavity mirrors, can be very long (up to several kilometres) while the sample volume can be kept rather small. Additionally, since the absorption is determined from the time behaviour of the signal, the sensitivity is independent of intensity fluctuations of the light source. CRDS techniques have been applied to species in the gas, liquid and solid phases. It is especially powerful for measurements of either strong absorptions of species present in trace amounts or measurements of weak absorptions of abundant species. In the gas phase, for example, CRDS has been used to detect atoms, molecules, and ions in many environments, such as open air, static gas cells, supersonic expansions, flames, and discharges.

An attractive property of cavity ring-down spectroscopy is its simplicity. It is rather easy to set up an experiment in which an improvement in the sensitivity compared with a conventional single-pass absorption experiment of 3–4 orders of magnitude is readily obtained. With more effort, such as a careful selection of components and knowledge of the theory of optical cavities, a further improvement of 3–4 orders of magnitude in sensitivity can be obtained.

Although the concepts of CRDS had already been available in the literature for several decades, it was not until 1988 that the first cavity ring-down absorption measurements were reported by O'Keefe and Deacon. Since then, the field of CRDS has evolved spectacularly, and not only in improving the sensitivity! Several schemes have been developed in order to be able to use almost every kind of light source for CRDS, from deep ultraviolet to far infrared, from narrow bandwidth lasers to ultra-broadband lamps, from continuous wave lasers to femtosecond pulsed lasers. Several variants of CRDS exist: robust, simple and cheap, offering a decent sensitivity on the one hand, and delicate, complicated and expensive, offering spectacular sensitivity on the other. The best choice depends on the application and the budget.

Up to now, about a thousand papers have been published on cavity ring-down spectroscopy and its applications. More and more papers appear with titles without the words 'cavity ring-down', indicating that CRDS has now become a standard spectroscopic tool. Several companies have developed commercial cavity ring-down spectrometers for specific applications, which is also indicative that the CRDS schemes have matured. Nevertheless, the CRDS field is still expanding. As the field became broader, the published review papers became more specialised, limiting the topic of the review to certain CRDS techniques or to specific applications. Until the publication of this book, a single source providing an overview of the cavity ring-down field did not exist, thus making a start in the field difficult for those researchers who are not familiar with the subject and who are thinking of applying CRDS in their research activities.

This edited, multi-author, book provides an overview of the cavity ring-down field. We believe that most topics are covered, and that specialised contributing authors ensure that each topic is covered at the right level of expertise. However, it is not an attempt to review the literature! Since cavity ring-down spectroscopy is an ultra-sensitive direct absorption technique, the book is of interest to anyone who uses (or wants to use) direct absorption techniques in his/her research. Direct absorption techniques are especially prominent in research fields like physical, atmospheric, environmental and analytical chemistry, and, although perhaps less prominent, but still important, in combustion science, physics, medical diagnostics, biology, and process technology.

This book starts with a chapter describing the basic concepts of cavity ring-down spectroscopy. As the reader has already seen in this preface, the principle of CRDS can easily be understood by the intuitive picture of laser pulses bouncing back and forth in a cavity. This picture is, however, an over-simplification and can definitely not be used if continuous wave (CW) lasers are used. For many applications, CW lasers are important (think of the rather inexpensive diode lasers) and Chapter 2 shows how these lasers can be used in CRDS. Furthermore, other CRDS variants are described, such as phase shift CRDS. While both pulsed and CW lasers have to be wavelength tuned in order to record cavity ring-down absorption spectra, multiplexing CRDS techniques have been developed as well, which allow the use of broadband light sources (including arc lamps and white LEDs). Broadband CRDS techniques and applications are described in Chapter 3. As absorption bands in the condensed phase are relatively broad, broadband CRDS seems to be a natural choice for detecting molecules in liquids.

This and more general CRDS of liquid samples is the subject of Chapter 4. A fascinating application is the miniaturisation of the ring-down cavities so that they can be used as detectors in liquid chromatography. Ring-down cavities can also be made very long by using fibres, and this is the topic of Chapter 5. The ‘cavity mirrors’ can be integrated into the fibre design or, by connecting the two ends of the fibre together, a fibre loop can be created. The ring-down time is then a measure for the loss in the fibre that depends on strain, temperature, and pressure. Furthermore, picolitre liquid sample volumes are possible by introducing the liquid into the waveguide or by making use of the evanescent wave outside the fibre.

Spectroscopic studies of transient molecules, like radicals, ions and ionic complexes, can be performed in the laboratory using (pulsed) discharges in cells and molecular jets. Sensitive absorption techniques, such as CRDS, are indispensible for recording spectra of these species, and the application of CRDS in such hostile environments requires special techniques for synchronising the experiment and for keeping the cavity mirrors clean during the experiments. Chapter 6 describes such experiments, where complex molecular spectra of species relevant in astrophysics are recorded in the laboratory in order to compare them to spectra obtained from astronomical observations. Similarly, CRDS is used in the laboratory to measure molecular parameters of importance in understanding the photochemistry and reactions occurring in the atmosphere. This is discussed in Chapter 7, and this same chapter shows that CRD spectrometers have been designed that are robust enough to be used in field studies – for example, on an aircraft – for monitoring trace amounts of atmospheric species. Trace gas detection with ultrasensitive CRDS techniques is probably the most widespread application of CRDS, and is further highlighted in Chapter 8, where life sciences applications are described. Examples of clinical diagnostics, such as the detection of volatile disease markers in exhaled breath, and the special requirements of the CRDS techniques for these applications, are discussed.

The last two chapters discuss the applications of CRDS under extreme conditions, the detection of species in plasmas and flames. Chapter 9 focuses on silicon-containing plasmas for thin film deposition. Several applications of CRDS are discussed: the spatially resolved density measurements of SiH_x radicals, time-dependent measurements of the surface reaction probability of Si and SiH_3, and detection of low concentration species in thin films, such as dangling bonds in amorphous hydrogenated silicon. Finally, Chapter 10 discusses the application of CRDS in combustion studies. The goal is to determine the absolute concentration profiles of reactive species, mainly small radicals, in flames, in order to obtain a detailed understanding of the combustion chemistry in these flames. This chapter also describes the cavity alignment strategies for obtaining the highest spatial resolution.

This book does not intend to describe all CRDS applications. The selection of applications is made in such a way that most special precautions and techniques in the application of CRDS are covered. Therefore, we suggest that the reader does not omit reading the chapters that appear to be outside his/her research field, as those chapters may contain valuable and relevant CRDS insights as well.

Finally, we would like to thank those who helped to make this cavity ring-down book possible. First of all, the contributing authors, without whom this book would be rather empty. We realize that our request to describe specific topics was not always something you were waiting for! We also thank the staff at Wiley, especially Richard Davies, Sarahjayne Sierra, Sarah Hall and Rebecca Stubbs, who invited us to write a proposal for a cavity ring-down book. Our cavity ring-down 'adventures' started halfway through the 1990s in Gerard Meijer's group at the University of Nijmegen. Together with Gerard we explored the possibilities of the cavity ring-down technique and developed new variants. We thank him for the great time and for introducing us to the world of cavity ring-down spectroscopy!

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