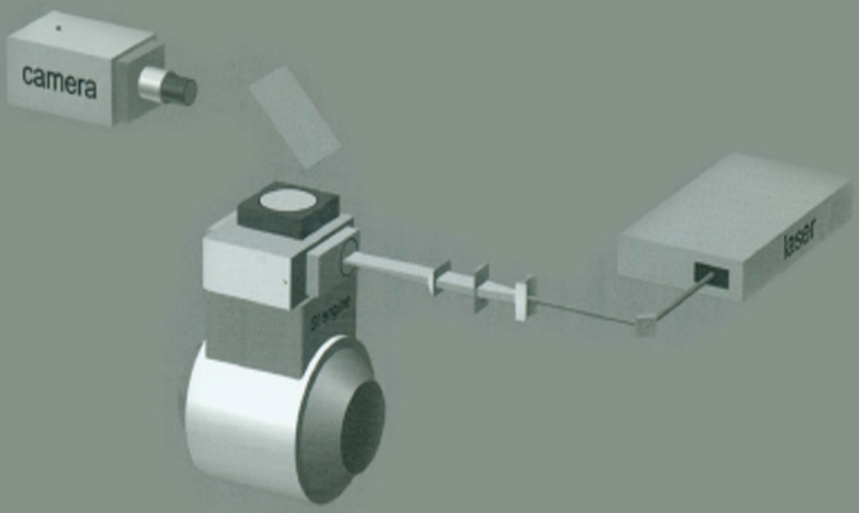
# APPLIED COMBUSTION DIAGNOSTICS




Edited by KATHARINA KOHSE-HÖINGHAUS and JAY B. JEFFRIES

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# APPLIED COMBUSTION DIAGNOSTICS

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# APPLIED COMBUSTION DIAGNOSTICS

Edited by
Katharina Kohse-Höinghaus
*Bielefeld University*
and
Jay B. Jeffries
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## COMBUSTION: AN INTERNATIONAL SERIES


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About the Cover:
The cover picture designed by Dr. Clemens Kaminski, Cambridge University, and Johan Hult, Lund Institute of Technology, schematically shows the principle of applying laser diagnostics for the study of combustion phenomena in an engine. Laser light from the right enters the combustion chamber through a transparent section in the cylinder wall. The scattered light from molecules and particulates in the chamber is collected through the top window and is imaged onto a camera. Such measurements can provide detailed information on parameters such as concentration fields and flow velocities as shown in the two dimensional image on the left.

To Eva and Klaus

and

To Sean, Ryan, and Robin

# About the Editors

Katharina Kohse-Höinghaus, Dr. rer. nat., has extensive experience in the use of laser diagnostics to unravel the chemistry important in combustion, chemical vapor deposition, and biological systems. As a Member of the Technical Staff at the German Aerospace Research Center, she conducted sabbatical research at Stanford University, and SRI International in the USA, and ONERA in France. She won a Heisenberg Fellowship in 1993, and in 1994, was appointed as full Professor of Chemistry at the University of Bielefeld, Germany. Prof. Kohse-Höinghaus is a colloquium chair for the 2002 International Combustion Symposium, a member of the editorial board of *Combustion and Flame*, and served as the Chair of the 1999 and vice Chair of the 1997 Gordon Research Conference on Laser Diagnostics in Combustion.

Jay B. Jeffries' Ph.D. career has focused on the development of laser-based diagnostics for practical applications, especially combustion, plasmas, and the atmosphere. In 2000, he joined the High Temperature Gasdynamics Laboratory, in the Mechanical Engineering Department at Stanford University, after 17 years in the Molecular Physics Laboratory at SRI International, and 3 years as a Research Assistant Professor at the University of Pittsburgh. He is a past chair of the Fundamental and Applied Spectroscopy Technical Group and the Optical Physics Division of the Optical Society of America. He serves as a Topical Editor for the *Journal of Applied Optics*. Dr. Jeffries was the Chair of the 2001 and vice Chair of the 1999 Gordon Research Conference on Laser Diagnostics in Combustion.

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# Preface

This book provides a pedagogical overview of the current state-of-the-art in the development of laser-based optical methods for the solution of fundamental and applied combustion problems. Laser-based diagnostics provide important tools to probe the harsh, high-temperature, and often high-pressure environment of modern combustion systems. These diagnostic measurements enable tests of fundamental understanding of combustion as well as enable empirical strategies to maximize the combustion efficiency and minimize the pollution of the combustion effluent from practical combustion devices.

This book gives a snapshot of the available diagnostic methods and their typical applications from the perspective of leading experts in the field. Teams of authors, sometimes from different groups, have written chapters with the intention to provide an educational approach to the subject, cutting-edge application examples from the research of their own and other groups, an acute literature survey, and well-balanced guidelines for current applications as well as indications of unsolved problems or of further perspectives.

The first part reviews the most widely used laser-based diagnostic techniques. Methods to detect trace concentrations of intermediate species in the chemical mechanism are reviewed in detail; laser-induced fluorescence, nonlinear optical methods, and cavity ringdown spectroscopy are highlighted. The current status of soot monitoring with laser-induced incandescence is presented with a focus on quantitative calibration. Temperature is an important combustion parameter, and fundamentals of accurate temperature measurements are discussed. Practical combustion is dominated by the interaction of chemistry and fluid mechanical transport; laser-based imaging techniques are an important tool to understand laminar and turbulent combusting flows. Chapters on flow-field diagnostics and multidimensional diagnostics attack the problems of spatially and temporally resolved combustion measurements.

The second part focuses on the current state-of-the-art application of these laser-based techniques to practical combustion problems. Chapters

on rich flame chemistry and on polycyclic aromatic hydrocarbons (PAH) and soot monitoring apply laser-based diagnostics to the important class of fuel-rich flames. This discussion naturally leads into chapters on two-phase fuel flows and fuel sprays in engines, followed by a detailed application of laser diagnostics to pollutant formation in engines. Catalytic combustion, fire suppression, combustion control, and gas turbine diagnostics round out Part II.

The final part discusses unsolved combustion problems and how laser-based measurements have the potential to provide the understanding needed to find solutions for these problems. We discuss the needs for diagnostic measurements to attack currently unsolved problems in detailed chemical modeling, gas–surface catalytic combustion, active combustion control, and commercial gas turbines. The book concludes with three chapters discussing the impact of toxic combustion effluent emissions on the atmosphere and two promising diagnostics schemes to provide the needed tools for in-situ monitoring of trace toxic species in the atmosphere; finally, a perspective on anticipated developments and emerging techniques is given.

Each chapter is written as a stand-alone contribution, providing an educational, concise and timely review of the present status of techniques, applications and perspectives. Cross-referencing to other chapters is provided throughout to allow for additional in-depth information related to individual chapters. The book may thus be used in different ways: by reading from start to end as a detailed course in combustion diagnostics, by reading individual chapters as a source of reference, or by browsing through different sections as a source of ideas. We intend to provide the active combustion research scientist with an understanding of the quality and content of the measurements from a variety of laser-based techniques. The book also provides supplemental reading to graduate courses in combustion and experimental methods in mechanical engineering. The laser-diagnostics specialist can learn the strengths and weaknesses of the various laser-based techniques, and the serious student can quickly get an up-to-date status of laser-based combustion measurements.

As we developed the program for the 1999 Gordon Research Conference on Laser Diagnostics in Combustion, we recognized the incredible progress in the application of laser-based measurement tools to combustion problems. During the summer of 2000, Professor Norman Chigier suggested that Katharina Kohse-Höinghaus might author or edit a diagnostics book. His subsequent encouragement of our book ideas led us to begin to enroll the author teams during the International Symposium on Combustion in Edinburgh.

We must acknowledge a great many people who have made this book possible. First, we thank the forty-six contributing authors whose names appear in the contents; not only did these experts provide the text of the book, but they met our very aggressive publication time schedule. In addi-

tion, another fifty-three reviewers donated their time to provide timely, provocative, and constructive criticism for the individual chapters.

KKH wishes to acknowledge the stimulating work environment in Bielefeld and the support, suggestions and often late-night discussions with her collaborators and students. Especially, the scientific interaction with Dr. Burak Atakan, Dr. Andreas Brockhinke, and Dr. Heidi Böhm has been extremely rewarding. The involvement of KKH in the active field of research highlighted in this book would not have been possible without the financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, which is gratefully acknowledged. Her special thanks are also due to her husband, Klaus Peter Kohse, and her daughter Eva, who both have been remarkably patient with regard to the disruptions this project has caused in their family life.

JBJ acknowledges the encouragement, scientific discussion, and support of Professor Ronald K. Hanson at Stanford; Ron provides an environment that fosters fundamental science and applied problem solving, and JBJ is delighted to work with him and the extremely capable students in his group. He also thanks long-time colleagues David Crosley and Gregory Smith at SRI for drawing him into this exciting field and their numerous engaging discussions over the past eighteen years. JBJ acknowledges financial support from the Air Force Office of Scientific Research, NASA-Ames University Consortium, and the Office of Naval Research. Finally, JBJ thanks his spouse, Robin Jeffries for all of his family time that she donated to this book project.

We thank Robert Bedford, Catherine Caputo, and their employer Taylor & Francis and Richard Cook at Keyword for supporting this endeavor. Book publishing was a new venture for us, and they have worked hard to make it a smooth and easy task.

Warm and especial thanks go to Regine Schröder, secretary to KKH at the Lehrstuhl für Physikalische Chemie I, Universität Bielefeld. Regine has kept us on track and on time throughout all phases of this project. She has tirelessly entreated timely response from all the contributing authors and reviewers, and she has kept track of all the details. This book has thus profited greatly from her able assistance.

We hope that you, the readers, find that this book improves your understanding of the use of laser-based diagnostics applied to combustion processes, systems, and problems; we hope the information presented here will be a valuable aid in your classes, laboratories, and in the solution of specific problems.

December 2001

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# 1

# Introduction

Katharina Kohse-Höinghaus and
Jay B. Jeffries

## 1.1 MOTIVATION

Combustion is the world's major source of energy; thus, it is of paramount importance to improve combustion efficiency to effectively use natural resources and minimize combustion-generated pollution to reduce the impact on air quality. Combustion and optical diagnostics have been intertwined since Swan's observation in 1857 of the green bands from $C_2$ emission in a candle flame. Flames became a good source for optical emission spectroscopy and this early literature is well reviewed in Gaydon's 1957 book [1].

The fundamental understanding needed for improved combustion devices and processes requires collaboration of scientists representing many fields of expertise. A minimal model of a practical combustion device requires chemistry, fluid mechanics, and heat transfer. Well-designed experiments are needed for the validation of numerical combustion models. Laser-based diagnostic techniques currently offer direct interrogation of the combustion process. Such diagnostic measurements provide a rigid test of our understanding of combustion, and stimulate our ideas on how to apply this knowledge to the control and optimization of combustion systems. Physicists, chemists, and engineers in many groups worldwide collaborate to develop and validate these laser methods and to interpret the results from measurements in systems ranging from fundamental combustion studies to practical combustion devices.

Combustion systems constitute a harsh, high-temperature environment, which often features impressively complex chemistry and a time-varying turbulent flow field. In addition, practical combustion often takes place at elevated pressures and in two-phase flows. Experimental determination of the most basic information requires significant effort: temperature, concentrations of major species and reactive intermediates, flow velocities, and

potential temporal and spatial fluctuations of these quantities must be measured, often simultaneously. Limited optical access, window deterioration, constraints in measurement time, vibrations, and other considerations may pose secondary problems when coupling a laser technique, or a laser-based instrument for measurements in a practical environment.

It is evident that not one single laser technique or measurement approach will provide all the necessary quantities to characterize a complex practical combustor. Many different laser-based techniques and methods have been developed to meet these demands, including Raman and Rayleigh scattering, nonlinear Raman spectroscopy, laser-induced fluorescence, multiphoton and pump-probe approaches, four-wave mixing and holographic grating techniques, as well as advanced laser absorption schemes. The design, application, and interpretation of laser-based measurements to characterize a combustion system require a thorough fundamental knowledge of laser physics, spectroscopy, and combustion chemistry. The fundamental principles of laser-based combustion diagnostics are treated by Alan Eckbreth [2]; this excellent book provides the background fundamentals for the techniques used for spatially resolved combustion diagnostics.

In the thirty years since the first application of laser techniques to combustion studies, the field of combustion diagnostics has matured significantly. Not only have basic techniques been tested and applied, but new concepts have been devised and more sophisticated equipment and evaluation tools are available enabling more ambitious questions to be addressed. Where the mere detection of important reactive intermediate species was an achievement several years ago, today accurate quantitative measurement of their concentrations is feasible. Where certain quantities could barely be measured under clean laboratory conditions, techniques have been conceived which allow measurement in the presence of particles and surfaces and under realistic operation conditions. Where only a single quantity could be obtained at a specific location in a pointwise measurement, one-, two-, and three-dimensional approaches are now available. Where a single temperature or concentration value could be measured at a given time, multispecies and multiquantity concepts, often combining several laser techniques, have been demonstrated. New lasers make new avenues and approaches feasible with faster pulses, higher repetition rates, better beam qualities, extended wavelength regimes and higher tunability, these properties being paralleled by similar advances in light detectors and electronics. With these exciting possibilities, the field of combustion diagnostics remains active in fundamental research, meeting the increasingly ambitious needs of combustion science and the related environmental considerations. Many techniques have meanwhile transformed into routine tools, and at least half of the experimental studies presented at the last Combustion Symposia arrived at their conclusions with data from laser measurements. The current state-of-the art of the application of laser-based measurements

to combustion problems is presented here from the diagnostics point of view. This book aims to arm the reader with the information to select from the arsenal of laser-based diagnostics the right solution for their combustion problem.

## 1.2 BACKGROUND

The multidisciplinary nature of laser-based combustion diagnostics creates a large and diverse introductory literature. The basic physics underlying linear and nonlinear diagnostic techniques used for spatially resolved gas-phase measurements is reviewed by Eckbreth [2], and this book assumes the reader is familiar with this background. For a more complete discussion of laser physics, the text by Siegman [3] is recommended. Demtröder [4] provides an overview of laser spectroscopy. The fundamental reference on molecular spectroscopy is the series by Herzberg [5–8] and there are numerous modern references [e.g., 9 and 10]. The design of laser-based diagnostics requires data on the optical properties of materials and optical design; the classic textbook on optics by Born and Wolf [11] and the Optical Society of America Handbook [12] are recommended. General design considerations for laser diagnostics for combustion research, including the choice of laser sources, the selection of optical components, wavelength-selective devices such as filters or monochromators, and detection devices are also covered by Eckbreth [2].

Techniques such as laser-induced fluorescence (LIF), coherent anti-Stokes Raman scattering (CARS), Raman, and Mie scattering are widely used combustion diagnostics. The underlying physics, typical experimental arrangements, merits, and disadvantages can be found in Ref. 2, and thus these topics are not individually treated in special chapters here. Here we discuss the application of these diagnostic techniques to applied combustion problems.

## 1.3 ORGANIZATION

The book is divided into three parts, *Techniques*, *Applications*, and *Perspectives*. The first part, *Techniques* (Chapters 2–9) focuses on methods suitable for the measurement of combustion properties, including minor species concentrations (Chapter 2), temperature (Chapter 6), and flow-field characteristics (Chapter 7). In addition, the novel possibilities that picosecond laser pulses (Chapter 5) and multidimensional approaches in space and time (Chapter 8) offer for the investigation of combustion phenomena are discussed. Finally, reviews are presented for some techniques that were emerging at the time the Eckbreth book was written, including coherent techniques devoted to measurements of intermediate species in Chapter 3, cavity ringdown (CRD) spectroscopy in Chapter 4, and laser-

induced incandescence (LII) in Chapter 9. The chapter sequence of this first section is arranged to proceed from the measurement of intermediates (Chapters 2–5) to that of temperature (Chapter 6), flow-field parameters (Chapters 7 and 8), and particle-related properties (Chapter 9).

During the past two decades a significant amount of fundamental information has been published on seemingly unrelated issues such as collision processes, polarization properties, spectral line shapes and spectral interferences, laser photolysis, laser absorption, beam steering, and beam profile deterioration. This fundamental data combined with the basic diagnostic principles developed in Eckbreth's book [2] provide the opportunity for sophisticated quantitative measurement strategies discussed in this first part. It thus encompasses a broad variety of tools that find use in probing detailed chemistry, pollution formation and combustion performance from laboratory flames to practical devices. The reader's attention is drawn to the extensive compilation of literature references and detection strategies for minor species in the appendix to Chapter 2.

The second part of the book, *Applications* (Chapters 10–18) focuses on specific uses of laser-based diagnostics in combustion research. Even though much combustion diagnostics research during the last decade has been devoted to improvement of established techniques or initial demonstration of the potential of novel approaches, many research groups have begun to investigate increasingly complex combustion problems with an array of diagnostics techniques. Accordingly, new measurement strategies employ a suite of diagnostic methods to explore these applied systems to provide design guidelines, validate numerical models, and estimate performance parameters such as pollutant emissions. Typical combinations of diagnostic techniques for specific combustion problems are thus outlined in this second part, the sequence of chapters coarsely reflecting the increasing complexity of the combustion problems. Note that appropriate diagnostic strategies include nonlaser methods and probe techniques to complement the laser-based measurements.

Understanding turbulence, the formation of polycyclic aromatic species and soot, and spray combustion represent some of the most pressing questions of practical relevance that may, eventually, not be regarded as separable problems. These combustion questions require innovative diagnostic schemes and combinations to test newly evolving theories and models.

In spite of the many valuable approaches and measurement schemes that have already been explored, the field is still confronted by the need for the simultaneous quantitative in-situ measurement of all relevant scalar and vector quantities in a turbulent flame, which should also reveal the pertinent three-dimensional structures and their development in time. To assist the fundamental understanding of the underlying processes, numerical models increasingly ask for quantities that are not easily observable, including local heat release or reaction fluxes.

Part II begins with a chapter on fuel-rich combustion (Chapter 10) that illuminates the complex chemistry in these flames. Similarly, chemical aspects are treated in Chapter 11, on fire suppression. While most of the detailed chemistry in these chapters concerns gas-phase reactions, later chapters consider two-phase combustion systems. Chapter 12 starts with diagnostics in catalytic combustion where heterogeneous chemistry is directly probed on the surface under realistic pressure conditions. This chapter is followed by polycyclic aromatic hydrocarbons (PAH) and soot diagnostics in Chapter 13; here, methods, including LII, are applied, which were reviewed in the first part. After the description of chemically complex applications, the focus switches to more applied systems, first treating diagnostics in turbulent flames (Chapter 14) as a prerequisite for measurements in realistic devices, and then concentrating on diagnostics in spray combustion of importance in gas turbine and engine research (Chapters 15–17). Part II ends with a chapter on diagnostics suitable for combustion control sensors (Chapter 18); such devices must provide data rapidly enough to enable timely control decisions for closed-loop operation and real-time optimization of advanced combustion devices. Although these examples of pertinent combustion problems may not be exhaustive, they provide the reader with valuable guidelines about which combinations of techniques may be suitable under conditions including turbulence, swirl, dense, evaporating and combusting sprays, high pressure, and particle load.

Although diagnostics in combustion systems have come a long way, unsolved questions remain. Tasks of high complexity awaiting further advancements in diagnostics include the quantitative characterization of sooting flames, two-phase combustion, and incineration. Furthermore, combustion science is increasingly seen to branch into adjacent fields. Combustion reactors are used to produce nanoscale materials, addressing completely different chemical reaction sequences that may need to be investigated for an optimization of these processes. Combustion-generated pollutants have an impact on climatic issues and on detailed atmospheric reaction balances, and diagnostics requirements might thus not end at the tailpipe. Similarly, public health considerations may require specification not only of the size distribution but also of the chemical nature of the surface of combustion-generated carbonaceous particles.

The third part of the book, *Perspectives* (Chapters 19–26) concentrates on some of these unsolved questions and on directions for future research. This is intended to articulate more clearly the needs for tomorrow's combustion investigations that may profit from advanced diagnostics, and to identify new avenues for application of similar techniques and instrumentation in related fields. Again, the sequence is ordered roughly with increasing complexity of (or decreasing knowledge of) the system to be analyzed. As a characteristic feature, some of these brief statements are written from the modeler's perspective, explaining their wish list for model design and vali-

dation. In this spirit, Chapter 19 starts with the needs for diagnostics that would improve detailed chemical models, concentrating on gas-phase chemistry. Heterogeneous systems are addressed when discussing catalytic combustion in Chapter 20. The following chapters identify the diagnostic needs for active combustion control (Chapter 21) and for gas turbine combustor model validation (Chapter 22). The last chapters in this part focus on prospective diagnostic applications in combustion material synthesis (Chapter 23), on toxic emission control (Chapter 24), on monitoring combustion effluents (Chapter 25), and on advanced sensor techniques for measuring combustion-related atmospheric pollution (Chapter 26). With that, the reader's attention is not only drawn to the combustion device itself, but to the ambitious questions that diagnostics related to combustion might be able to solve on a more global perspective. Naturally, these chapters highlight some of the potential ascribed to methods that have been discussed in the previous parts of the book.

Finally, in Chapter 27 titled "Continuing Developments," we highlight diagnostic schemes and strategies that potentially will join the arsenal of tools for laser-based combustion diagnostics.

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# Techniques

Sed demonstratio longe optima est experientia.
(By far the best proof is the experiment.)

Francis Bacon
*Novum organum sive vera de interpretatione naturae*, London, 1620

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# 2

# Detection of Minor Species with Laser Techniques

Kermit C. Smyth and David R. Crosley

## 2.1 INTRODUCTION

Combustion can be thought of as a self-sustaining reactive flow, in which chemical energy is converted into heat. Thermochemistry, fluid dynamics, mass and heat transport, and chemical kinetics all play significant roles in combustion processes. System efficiency, be it in a steady-state flame, or a transitory process such as an explosion or internal combustion engine, is usually the prime issue in combustion. Efficiency is generally governed by the first three topics; detailed knowledge of the reaction kinetics of minor species is usually not needed for efficiency considerations.

However, the chemistry of those minor species, present at concentrations ranging from 1% down to the parts per billion level, plays key roles in other combustion problems. The major questions concern pollutant formation ($NO_x$, $SO_x$, soot, toxic organic compounds), flame ignition, and inhibition of flames. Because of increasingly stringent environmental regulations, understanding the chemistry of pollutant formation is a major topic in combustion research. This chapter focuses on the measurement in flames of those minor species important in these processes. Much of our discussion will center on the technique of laser-induced fluorescence (LIF), which has become the predominant method used for minor species measurements in flames. This owes to the ease of the measurement technique, the existence of a pertinent data base for interpretation, and the possibility of two-dimensional imaging. We will briefly mention other approaches, some of which are covered in other chapters of this book. Of the minor species, the OH, NO, and CH radicals are by far the most frequently investigated, due to their importance in flames and well-established measurement strategies, and we will give them the most attention.

Furthermore, we will discuss measurements made only in simple flow fields, that is, laminar flames of various types. In such flames, chemical pathways can be investigated in detail, since mixing and other transport processes are much simpler than in a turbulent flow field. Measurements of the radical species form demanding tests of predictive chemical mechanisms needed to understand the chemistry in more complex flows, where mechanisms cannot be isolated for study. What is needed are quantitative profiles of individual species, preferably absolute, and accurate temperature measurements. Nonetheless, minor species measurements in turbulent combustors can serve as qualitative checks on both chemistry and mixing phenomena. That is, our philosophy is to develop an understanding of the chemistry under the simplest, most controllable conditions tested via measurement of minor species, and then later insert that improved understanding of chemistry into computational codes describing more complex systems.

Unlike stable combustion gases, free radicals do not survive a sampling line leading to, e.g., a gas chromatograph or Fourier transform infrared spectrometer. Thus it is important that the methods for detecting radicals are noninvasive, that is, they require no sampling head inserted into the flame. (A molecular beam mass spectrometer can detect numerous radicals but also perturbs the flame at the point of measurement.) The text portion of this chapter will first list noninvasive, laser-based techniques for minor species measurements, referring often to other chapters; and then we shall undertake a more detailed description of LIF. Both relative and absolute concentration profile measurements will be discussed. We also include a section on selected papers comparing detailed model predictions with minor species measurements. The heart of this chapter is the table listing 60 minor species relevant to flame chemistry investigations, included as an appendix. Excitation and detection schemes, the type of flame in which the measurement is made, and pertinent references are included. A few minor species of importance in combustion have been studied only in flow tubes, reactors, and photolysis experiments, and these are included. In the text we comment on other species crucial to particular problems, such as polyaromatic hydrocarbons or metals, that we have not included in the table.

## 2.2 LASER-BASED MEASUREMENT TECHNIQUES FOR MINOR SPECIES

### 2.2.1 Laser-Induced Fluorescence

In laser-induced fluorescence a laser is tuned to a wavelength matching that of some absorption line of the atom or molecule of interest. That species is then elevated to an electronically excited state, from which it fluoresces, and this fluorescent emission is then detected. Tuning the laser traces out the absorption spectrum, providing secure identification. Temperature can also

be measured by determining the distribution of the molecules over their rotational and/or vibrational levels. LIF can be used for pointwise measurements, which are the most useful for understanding flame chemistry. However, LIF is also very convenient for two-dimensional planar images of the minor species distribution throughout a flame.

LIF is the most successful technique used in flame studies of minor species concentrations. The method has gained maturity in the field of combustion research. Early studies were dominated by proof-of-concept and demonstration experiments. By 1992, at the Twenty-Fourth Combustion Symposium, LIF was used in 13% of all papers (oral plus poster) reporting any kind of experimental result. Notably, in each case LIF was utilized for a combustion study, and no new diagnostics papers appeared. By 1998, at the Twenty-Seventh Symposium, 20% of all published experimental papers involved LIF applications.

LIF is generally easy to implement, especially for the popular species OH, CH, and NO, where a significant database for spectroscopy, quenching, and energy transfer already exists. However, there are many complications which must be considered to obtain accurate, quantitative results. Many of these concern the energy transfer among individual rotational, vibrational, and electronic levels during the measurement. These will be discussed briefly in the following section and covered in more detail in Chapter 5.

There have been several reviews of LIF techniques and measurements. Historical progress can be followed in two books on general laser diagnostics in combustion [1,2]. Two articles published in *Progress in Energy and Combustion Science* are especially noteworthy. The first [3] is a comprehensive treatise (over 700 references) on many experiments concerned with the detection of minor species in flames. Several techniques are discussed, although the emphasis is on LIF. The second [4] concerns LIF only, and describes the mathematical formalism of LIF and of collisions that complicate the signal; much detail about experiments and instrumentation is given. The use of tunable excimer lasers for both LIF and Raman measurements in flames is the topic of another comprehensive review [5]. These excellent papers contain more detail about the detection of minor species than space allows here, and this chapter is meant in large part to provide an introduction to the method in the text and build upon those articles in the table.

A few minor species, particularly O, H, N, and CO, cannot be accessed in a flame by the absorption of a single laser photon, because vacuum ultraviolet light must be used to reach their first excited electronic states. In these cases successful detection is achieved by tuning the laser to a wavelength where the species absorbs two photons at the same time. Two-photon LIF presents additional challenges in quantification, which will be discussed below.

Two-dimensional imaging by LIF has become very popular, especially for mapping flame zones by OH LIF in complex systems. Most such experiments utilize a KrF laser at 248 nm; they may suffer from lack of quantitation but in many cases that is not an important issue. We refer the reader to Ref. 5 and to Chapters 7 and 8, which discuss imaging by LIF and other methods, for further details.

### 2.2.2 Resonantly Enhanced Multiphoton Ionization (REMPI)

The REMPI technique is a multiphoton process. The first step is accessing an excited state by absorption of one or more photons. An additional laser photon ionizes the molecule directly from the excited state. The process is described in the table by numbers $n + m$, where $n$ is the number of photons in the first step and $m$ the number in the second, for example, $2 + 1$ REMPI at 333.5 nm has been used to detect the important $CH_3$ radical in flames [6]. The signal is detected by the electrons ejected from the molecule, which are collected by an anode inserted into the flame.

REMPI can exhibit exceptional sensitivity and can be configured to give essentially point measurements. In general, REMPI and the other techniques noted in this section have similar sensitivities for those species amenable to more than one approach. It is also very well suited to the measurement of species which can be excited but do not fluoresce. For example, $CH_3$ has an excited state which can be accessed by a laser photon at 217 nm, but it predissociates so rapidly that fluorescence does not occur. However, the methyl radical can be ionized in a multiphoton process using a different electronically excited state, as noted above [6]. REMPI has also been applied to a variety of species and has found important applications for detecting hydrocarbon radicals in sampled gases. These are not included in the table; for examples see Refs. 7 and 8 and Chapter 22. Also not included are the wealth of REMPI results on species containing second and third row elements reported by Hudgens and coworkers in, for example, Ref. 9.

On the other hand, REMPI is not truly a noninvasive technique, that is, unlike LIF and the techniques listed below, it requires an anode in the flame itself. In order to make reliable relative concentration measurements in flames, the sensitivity of the probe as a function of flame position must be determined. Examples have been presented for both diffusion [10] and premixed [11] flames.

### 2.2.3 Degenerate Four-Wave Mixing (DFWM)

The DFWM approach utilizes three laser beams. It is a nonlinear process like coherent anti-Stokes Raman spectroscopy (CARS) but, like LIF, operates on real transitions. It combines some attributes of both processes: it produces a fourth coherent beam that can be spatially filtered to eliminate

background (unlike LIF where the fluorescence is emitted throughout the entire $4\pi$ steradians sphere); like CARS, it depends on $\chi^{(3)}$, the nonlinear susceptibility of the molecule and can be used in a broadband mode; like LIF, it can be used to produce images. As with REMPI, DFWM is of particular consequence in measuring species that have excited states but do not fluoresce, such as the methyl radical at 217 nm [12]. However, DFWM is a more complex optical process to implement, and its spatial resolution can be limited, so despite its attributes it has not been used widely for flame structure measurements.

DFWM, as well as CARS and LITGS (laser-induced thermal grating spectroscopy) will be covered in detail in Chapter 3. We do list DFWM measurements in the table, but shall not discuss it further here.

### 2.2.4 Cavity Ringdown (CRD) Spectroscopy

CRD is the newest laser technique to be applied to study minor species important in combustion chemistry. In this approach, a pulsed laser is tuned to some absorption transition of the molecule of interest; a small fraction of the beam is inserted into an optical cavity made by two mirrors, between which the flame is situated. When the flame is off, the photons reflect back and forth throughout the cavity, diminished in each round trip by the (small) transmission of the mirrors and any scattering in the gases inside the cavity. This produces an exponentially decaying signal, which is observed with a photomultiplier or photodiode located behind one of the mirrors. When the flame is on, and the minor species of interest is present, absorption of the tuned laser light by that species adds to the loss per pass, resulting in a faster decay and thus a measurement of the total absorption.

Like REMPI and DFWM, CRD requires only that the molecule absorb laser light, so that nonfluorescing molecules are accessible. This direct absorption method provides absolute concentrations with no calibration if the relevant absorption coefficient is known. However, the effective path length needs to be known accurately. If the absorbing species is not evenly distributed along the cavity path, the actual distribution must be taken into account for quantitative measurements. Even a carefully controlled flat laboratory flame, such as that on a McKenna type sintered disk burner used in many studies of flame chemistry, can exhibit curvature. As a consequence, the resulting species profile can be broadened. One way of dealing with this problem is to image LIF from the CRD laser, directly giving the effective absorption path length [13].

The CRD technique will be described in detail in Chapter 4; again, we list measurements in the table but do not discuss it further here.

### 2.2.5 Tunable Diode Laser (TDL) Absorption

Tunable diode lasers operate in the infrared or far red regions of the spectrum. They can be used to detect species present at moderate concentrations, such as CO and NO, with great success. Applications have been in shock tubes and flames, and for process control where rapid feedback is needed. With multipass absorption and frequency modulation techniques, TDL spectroscopy can be quite sensitive; it and its uses are covered in Chapter 18.

TDL absorption has also been applied to species that appear in minor amounts in flames, such as OH, $C_2H_2$, and several fluorine-containing radicals. The table also includes measurements on species of combustion interest, such as $HO_2$ and $C_2H_3$, but not yet demonstrated in flame environments. For applications to minor species detection in flames, TDL absorption suffers from two problems. First, like CRD and the techniques described below, it is a line-of-sight method and as such can provide useful profile information only in well-characterized one-dimensional and two-dimensional flames. Second, unless the pressure is low enough, considerable line broadening of the rotational/vibrational transitions occurs. The wings of broadened lines of major species can obscure the small absorptions due to minor species. For example, $H_2O$ lines can mask OH stretches, and hydrocarbons can mask CH stretches. For this reason, we would not expect TDL absorption to be of widespread value for minor species measurements in atmospheric pressure flames. For flames at lower pressure (many studies are made in the 25–40 Torr region) TDL absorption has proven to be valuable [14].

### 2.2.6 Other Methods

There are several other methods that have been used for the measurement of minor species in flames or other reactive flow systems. They have not found widespread use in the combustion community, largely due to difficulty in implementation or lack of quantitative, spatially precise information. We list these methods together with relevant references, but shall not discuss them further.

Photoacoustic spectroscopy [15] relies on the heating produced locally in the flame as the molecule of interest absorbs laser light. This heating (even a few K) produces a shock wave that can be detected with a microphone (and often heard audibly). However, the shock originates along the laser beam and, despite sensitivity comparable to LIF, spatial definition is poor.

Intracavity absorption has been described and compared with CRD for HCO and $^1CH_2$ [16]. In this method, the flame burns inside the laser cavity itself. Per pass losses owing to absorption by the species of interest as the laser is tuned decrease the laser gain and can be easily observed in the laser

output. As with CRD, effective path lengths must be known for quantitative measurements.

Amplified spontaneous emission (ASE), as with two-photon LIF, begins with two photon excitation to a highly elevated electronic state of the species of interest (in particular H, N, O, and CO). In LIF, the excited species fluoresces into one or more lower lying excited states. In ASE [17], the upper state is pumped strongly enough to produce a population inversion between it and other excited states to which it can emit light. Stimulated emission then occurs; it propagates along the laser beam and can be distinguished from the simultaneously occurring fluorescence by its strength in the beam direction. In a study of ASE in O atoms in $H_2/O_2$ flames [18], the ASE was found to be $10^4$ times as strong as the LIF. However, ASE has poor spatial resolution because the gain occurs all along the laser path. In addition, studies have shown that for H atoms [19] and O atoms [20] accurate concentration profiles are not obtained with ASE.

## 2.3 LASER-INDUCED FLUORESCENCE

Most LIF measurements are made using a pulsed laser; the increased intensity during the short (typically 3–10 ns long) laser pulse usually discriminates well against background chemiluminescent emission from flame radicals. For a pulsed laser, the fluorescence signal $S_F$ measured in an LIF experiment in a single laser pulse is given (in mV across a known impedance, for example, in a boxcar integrator) by:

$$S_F = BI_L\Gamma\tau_L N f_B \Phi F_{\text{fl}}(\Omega/4\pi)\epsilon\eta V \tag{2.1}$$

Here, $B$ is the Einstein absorption coefficient divided by the speed of light, given in $m^2/J \cdot cm$; $I_L$ the laser spectral power density per unit area, divided by the laser bandwidth, $J/m^2s \cdot cm^{-1}$; $\Gamma$ a linewidth integral reflecting the overlap between laser and absorption line bandwidths; $\tau_L$ the laser pulse length; $N$ the number of molecules ($cm^{-3}$) in the ground electronic state and the desired result of the experiment; $f_B$, often termed the Boltzmann fraction, the portion of those molecules in the particular electronic–vibrational–rotational level(s) being excited by the laser; $\Phi$ the fluorescent quantum yield from the excited state, that is, the number of photons emitted per molecule excited and a key quantity affected by collisions and dissociation as discussed later; and $F_{\text{fl}}$ the fraction of fluorescence collected within the detector bandwidth. The remaining terms are $\Omega$, the solid angle of fluorescence collected by the detector, $\epsilon$ and $\eta$ the transmission and photoelectron efficiencies of the detector system, and $V$ the interaction volume observed. It should be noted that this equation holds only in the linear limit, that is, when $BI_L\tau_L$ is small enough that only a small fraction of the population in the absorbing ground state level is excited. Operation under "saturated"

conditions, when a significant fraction of that population is excited, will be discussed briefly later.

This last set of terms, $(\Omega/4\pi)\epsilon\eta V$, is crucial to determining absolute measurements via LIF when direct absorption measurements are not possible; this quantity must then be obtained using some type of calibration scheme as discussed further below. Many measurements made in flames are relative profiles of concentration as a function of height above a flat burner, radius and height in an axisymmetric flame like a Bunsen burner, or distance between fuel and air inlets in a diffusion flame such as on a Wolfhard–Parker burner. Precise relative measurements show an $S_F$ depending only on the spatially varying terms $\Gamma$, $N$, $f_B$, and $\Phi$; the precision in determining $N$ from $S_F$ is only as good as the precision in the variation of the other three quantities.

A particular minor species is usually identified by its characteristic "excitation" scan, that is, the fluorescence resulting as the laser wavelength is scanned through the molecule's absorption spectrum. Such an excitation scan is illustrated in Fig. 2.1 for the $B^2\Sigma^- - X^2\Pi$ transition of CH. Each line corresponds to one (or more, if overlap occurs) rotational level of the

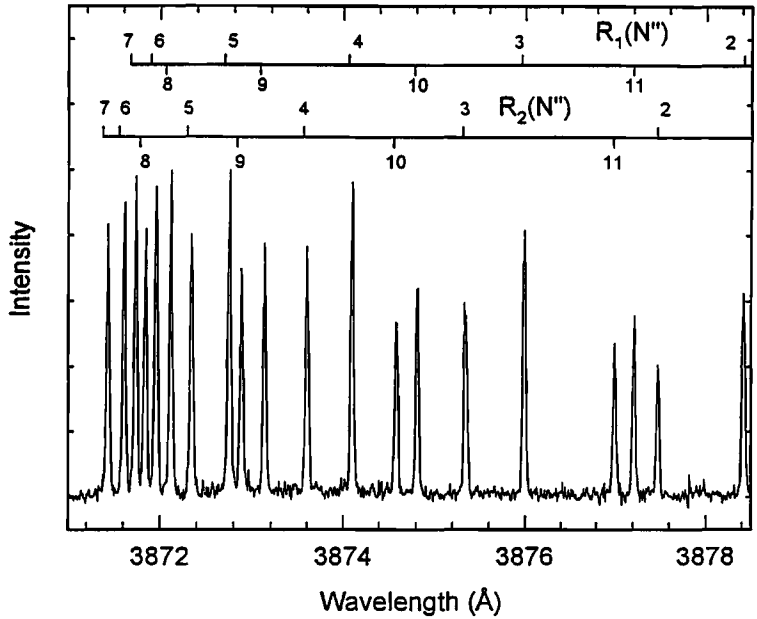


**Fig. 2.1** Excitation scan through the $R$ branch of the (0,0) excitation band of the $B^2\Sigma^- - X^2\Pi$ band system of the CH radical, in an 8 Torr $CH_4/O_2$ flame; a 10 ns integration gate was used. [37] (Courtesy of the Optical Society of America.)

ground electronic state. When the rotational energy distribution is thermal (always the case in flames because chemical removal is slower than rotational energy transfer), the relative intensity of each line can be related to the population of each level (i.e., $f_B$) via Eq. 2.1, and hence yield the temperature at the local point of measurement. An accurate and spatially precise temperature determination is crucial for obtaining meaningful comparisons with model predictions, as discussed later. In low-pressure flames, where good spatial resolution can be achieved, precision of ±30 K has been reasonably claimed. The analysis of Eq. 2.1 must account for the rotational level dependence of $B$, $\Phi$, and $F_{fl}$, which is most noticeable in hydrides, i.e., OH, CH, and NH. The effect on these quantities is a manifestation of the large rotational energy spacing in these molecules.

For polyatomic molecules, spectroscopic complexity increases. Figure 2.2 shows excitation scans for NCO, present in abundant quantity in a $CH_4/N_2O$ flame. This is a linear triatomic species, with spectroscopic data reasonably well understood; however, the much larger number of vibrational levels makes the spectrum quite complex. Moreover, in a polyatomic molecule the population at flame temperature is spread over a large number of rotational and vibrational levels, making $f_B$ much smaller than in the case of a diatomic, thus leading to lower signal intensity for the same concentration.

Although the table shows a large number of minor flame species that can be measured using LIF, there are three molecules that are by far the most popular: OH, CH, and NO. This fact derives from their relative ease of measurement, the existence of large databases of spectroscopic ($B$, $f_B$, and $F_{fl}$) and collisional ($\Phi$, $F_{fl}$) information, and their importance in many flame measurements. We will emphasize discussion of LIF measurements of these species; see the appendix references to measurements using a wide variety of additional approaches.

### 2.3.1 Spectroscopy

Many years of experimental and theoretical work have gone into determining spectroscopic parameters for OH, CH, and NO. Recent studies of both kinds have been undertaken on these three species at SRI International, with the results collected in a program entitled LIFBASE [21,22]. This program calculates absorption and emission transition probabilities, and can simulate spectra for both thermal and nonthermal rotational/vibrational distributions in the absorbing or emitting state. (A few other molecules—$N_2^+$, CN, CF, and SiH—are also given in LIFBASE but the underlying experimental data are not as well determined as for OH, CH, and NO.) For a comprehensive set of spectroscopic coefficients and band systems of diatomic molecules, see Huber and Herzberg [23].

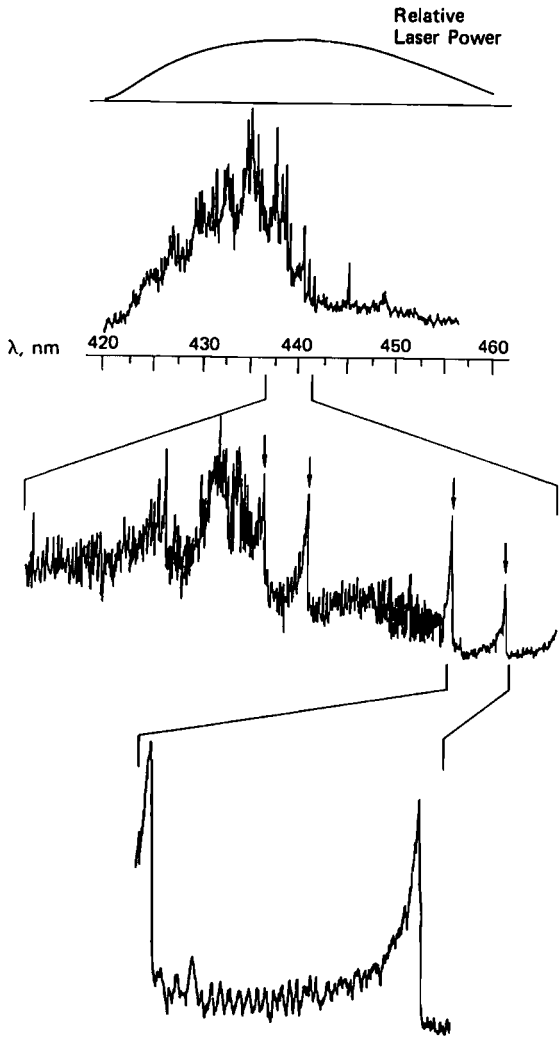


**Fig. 2.2** Excitation scans for the $A^2\Sigma^+$–$X^2\Pi_i$ electronic transition of the linear NCO radical in the reaction zone of a $CH_4/N_2O$ flame at atmospheric pressure. The rotational structure is similar to that of a diatomic but the vibrational structure is much more complicated. *Top*: total spectrum over the range of a single laser dye. *Middle*: 4 nm portion showing the region of the 000 ← 000 vibrational band. *Bottom*: region 0.45 nm in extent showing the rotationally resolved $^{O}P_{12}$ branch, with a head near $J \sim 70$. (Courtesy of The Combustion Institute.)

### 2.3.2 Collisions

The influence of collisions is the most troublesome aspect of making accurate profile measurements (absolute or relative) of minor species using LIF. Figure 2.3 illustrates the situation using as an example excitation of the $v' = 1, v'' = 0$ vibrational band of the OH molecule's $A^2\Sigma^+$–$X^2\Pi_i$ electronic band system. The initially excited $v' = 1$ level fluoresces to both $v'' = 0$ and 1 (not shown in the figure). However, it also undergoes collisions. Rotational energy transfer (RET) distributes the population from the initially excited rotational level ($J'$) among other $J'$ levels of $v' = 1$, and these can have different radiative and collisional characteristics. Vibrational energy transfer (VET) moves population downward into $v' = 0$, resulting in a possible nonthermal $J'$ population in that level (this occurs in OH [24]). However, fluorescence observed in the (0,0) band, as illustrated in the figure,

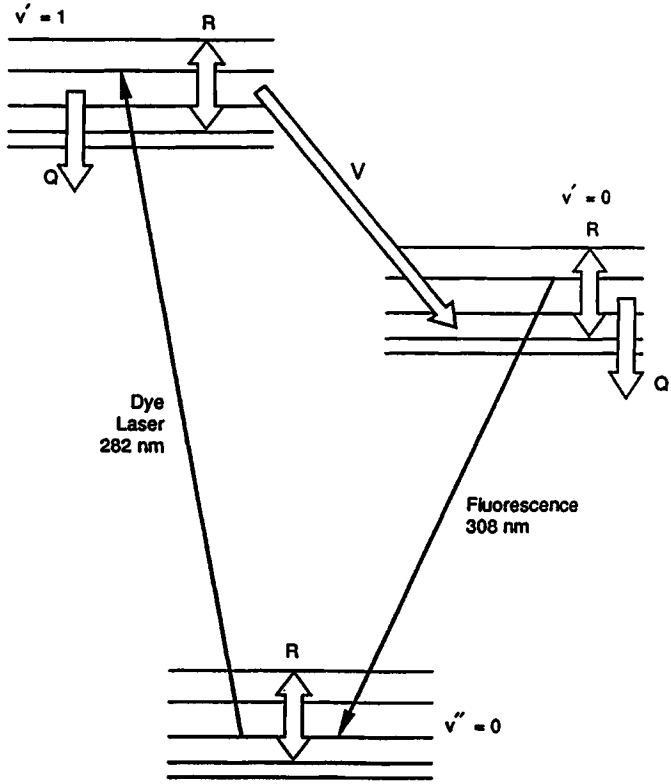


**Fig. 2.3** Schematic diagram of collisional effects important in flame diagnostics when exciting $v' = 1$ in the upper state and observing the (0,0) band in fluorescence to the ground state. For definition of symbols, refer to the text. (Courtesy of the American Geophysical Union.)

avoids scatter from laser light, and can be advantageous; moreover, excitation to $v' = 1$ via the weaker (1,0) band can help avoid problems of optical thickness in the flame. RET affects the $J'$ population distribution in $v' = 0$, causing complications similar to those in $v' = 1$. Quenching (Q) removes the electronically excited OH molecule altogether, transferring population to $v''$ levels within the $X^2\Pi_i$ ground electronic state that emit no light during the experiment. Moreover, a molecule can undergo predissociation (P) if the excited state lies higher than the dissociation limit and there exists a state that can couple excited and predissociating states (P is not illustrated in the figure). Both the Q and P processes are also $J$ and $v$ dependent in general. In some cases, when the excited electronic state is not the lowest lying one, electronic energy transfer can populate a lower level which also emits, but of course with a different $F_{\text{fl}}$. This is the case, for example, in CH where excitation of the $B^2\Sigma^-$ state (Fig. 2.1) results in some energy transfer to, and emission from, the $A^2\Delta$ electronically excited state. Finally, all of these processes are temperature dependent.

This daunting complexity suggests at first that quantitative measurement of minor species in flames is a very difficult task. However, the picture is usually somewhat simpler than shown in Fig. 2.3. If the $v' = 0$ level of the lowest electronic state is excited, VET and electronic transfer need not be considered. There is often enough information to estimate the influence of rotational redistribution. For OH, CH, and NO enough is known about collisional effects under flame or flamelike conditions to obtain good relative profiles, which if desired can often be calibrated to absolute values at some point. Kohse-Höinghaus [3] presents an excellent and comprehensive discussion of the state of the art in 1994. Since then, there are only a few pertinent publications to be mentioned here.

#### *2.3.2.1 Quenching of OH, CH, and NO*

Paul and coworkers at Sandia have made quenching measurements in shock tubes, measuring time decays for NO and OH in various mixtures of gases so as to determine bimolecular quenching cross-sections at high temperatures. OH quenching is reported [25], and the results are summarized graphically [26]. Also listed are the parameters of a fit to a model [27]. This model concept is an electron transfer (harpoon) mechanism, important at large internuclear separation and operative at high temperature. If no other physical mechanism took part in quenching, there would be little temperature dependence, in agreement with shock tube measurements [25]. However, OH forms a collision complex which lives sufficiently long to contribute to quenching at lower temperatures [28], owing to attractive force interactions between OH and its collision partners. The full model [27] takes this into account by anchoring the fit to quenching measurements near 300 K, measured in flow tubes.

Quenching for NO has been measured over the entire temperature range from 200 to 2500 K, in flow cells, flames, and shock tubes, as discussed in Ref. 3, which gives pertinent prior references, and in Ref. 29. NO behaves like OH for all colliders studied except $N_2$ and CO, that is, with attractive force interactions resulting in collision cross-sections decreasing monotonically with increasing temperature to a constant value. For $N_2$, a very inefficient collider at room temperature, quenching increases sharply with temperature, and, though still a small cross-section, could be significant due to the amount of $N_2$ present in many flames.

CH quenching appears to be dominated in general by repulsive force collisions, so that cross-sections increase with increasing temperature [30] . The exceptions are the polar colliders $NH_3$ and $H_2O$; unfortunately the cross-section for quenching of CH by $H_2O$ has not been measured above 415 K. Such measurements would be most valuable.

A study of quenching of $v' = 0$ in the lowest electronically excited states for these three important radicals is presented in [31]. Measurements as a function of height above the burner were performed in a low-pressure flame using direct time decay of fluorescence. Quenching cross-sections as a function of temperature for major species colliders were selected from literature values (in some cases disagreements exist), and simple parametrizations given. A two-parameter form sufficed for the cases of OH and NO where attractive forces govern, whereas modified Arrhenius forms were necessary for some NO and CH cross-sections. A computer model of the flame chemistry, using a measured temperature profile as input, predicted cross-sections for comparison with experiment. The results were quite good for NO and OH. For the case of CH, the profile appeared reasonable, although the absolute value is uncertain, owing to the lack of knowledge of the efficiency of $H_2O$ as a CH quencher at high temperature.

The results in Ref. 31 are encouraging. If one can reasonably estimate the temperature and major species concentrations at the point of measurement, quenching of NO and OH should be predictable within ±30%. In both cases, $H_2O$ is a major quencher. A measurement of the temperature alone (e.g., by Rayleigh scattering) can often be used to estimate the major species in many flames. For CH, the same would be true if quenching by $H_2O$ at higher temperatures were known.

A method of avoiding quenching can be used if the pressure is low enough ($<\sim$ 50 Torr) that the fluorescence can be time resolved. A detection gate is opened promptly after the laser pulse ceases and is left on only for a short time, perhaps 10% of the total decay. During this time, the excited molecules are little affected by quenching (or other potential energy transfer processes). This prompt/short gate method was first applied to OH [32]. Other approaches exploiting processes competing with quenching are discussed below. If a picosecond laser excitation pulse is used (see Chapter 5),

direct time decay measurements can be made at atmospheric pressure, giving the total quenching rate, as also discussed in Chapter 5.

#### 2.3.2.2 *Rotational and Vibrational Energy Transfer in Temperature Measurements*

At Bielefeld a few studies have been made after the publication of Ref. 3. RET and quenching were investigated at high temperatures [33], resulting in a rate equation model (termed LASKIN) including VET, RET, and Q [34] sufficient for including collisional effects in quantitative temperature measurements for OH. Of special importance is the attention given to initial excitation of $v' = 1$ in the $A^2\Sigma^+$ electronic state. It can be necessary to excite OH into this level, rather than $v' = 0$, to avoid optical depth problems in both the absorption and emitting transitions. Much of the work at Bielefeld since that time has centered on energy transfer studies in flames at atmospheric pressure using picosecond laser excitation and fast decay time measurements; these experiments are described in detail in Chapter 5. Results on OH VET in a shock tube at high temperatures have also been presented [35].

We choose for illustration one example of the influence of rotational energy on temperature measurements. (Temperature measurements in general are discussed in Chapter 6.) CH can be used as a flame thermometer, exciting into either the $A^2\Delta$ or $B^2\Sigma^-$ states. Because of RET, VET, energy transfer among these two states, and predissociation at high rotational levels in the $B$ state, complications can occur. An earlier study [36] showed discrepancies of as much as 20% in temperatures measured using the two band systems. A recent investigation [37] attributes this to rotational-level-dependent transition probabilities, and RET into and out of predissociating levels. Once these are accounted for, temperatures measured using both band systems are in good agreement.

### 2.3.3 Multiphoton LIF

For some flame species, the first electronically excited state lies far in the vacuum ultraviolet, at a wavelength where it is hard (or impossible) to produce laser radiation or where it cannot penetrate laboratory air or flame gases. Notable minor flame species that fall into this category are H, C, N, O, and CO. These can be accessed by the absorption of two (or, in the case of H, also with three) photons simultaneously, proceeding through a virtual state. The absorption is of course weaker than in the case of resonant absorption but can produce easily measurable signals in flames. While multiphoton LIF can give signal profiles, they are often difficult to analyze quantitatively. This can owe to problems in defining the (nonlinear) interaction volume in the flame, but also because the high laser intensities needed for two-photon excitation can dissociate other flame species, producing unwanted chemistry

(including sometimes forming the very species one is trying to probe). For example, $H_2O$ and $CO_2$ photolysis can occur at the wavelengths used for exciting H and CO, respectively. Multiphoton LIF can provide accurate information on the positions and shapes of species profiles, so long as measurements are made as a function of laser fluence to identify possible interferences and photochemical perturbations. In general, these problems are minimized for: (a) fewer photons required in the excitation step (with the advent of beta-barium-borate frequency doubling crystals, more than two are never required); (b) longer excitation wavelengths; and (c) leaner stoichiometries at the measurement position.

### 2.3.4 Saturated LIF

For a simple two-level system, the balance between upper and ground state populations (assuming for simplicity equal degeneracies in each state) can be given by

$$N_u/N_g = BI_L/(A + BI_L + Q + P + P_I I_L) \tag{2.2}$$

with $A$ the Einstein emission coefficient, $I_L$, $BI_L$ as before, $Q$ and $P$ the quenching and predissociation rates, $P_I$ a photoionization rate coefficient; all quantities are in units of $s^{-1}$. $BI_L$ in the denominator denotes stimulated emission from $u$ to $g$. This equation holds only when the laser pulse is on, that is, $I_L \neq 0$.

Due to the complexity of the various quenching and energy transfer processes described above, a number of approaches have been proposed whereby a given term in the denominator is made sufficiently larger than $Q$ to yield a quenching-independent measurement. However, Eq. 2.2 shows that an unavoidable cost is signficant reduction in signal strength, and these schemes have not found widespread application for quantitative measurements.

An early strategy attempting to overcome the complications of collisions was to operate at very high laser power, so that $BI_L \gg A + Q + P + P_I I_L$ with a fluorescence signal still proportional to $AN_u$. To make this approach quantitative, one must know the degree of saturation, deal with the fact that collisions do occur, and understand the volume of laser interaction in this highly nonlinear situation. Detailed discussion is given in Ref. 4. Measurements using NO in a variety of flames (referenced in the appendix) are good examples when saturated fluorescence proves very useful.

A related technique, when photoionization cross-sections are suitably large, is increasing the laser intensity $I_L$ to a point where $P_I I_L$ dominates the denominator. If the photoionization cross-section is well known, this can be used for quantitative measurements [38] but the method has not found widespread application. Yet another approach, utilizing a transition where $P$ is large, is described immediately below.

### 2.3.5 Predissociative LIF

If one excites a state that predissociates fast enough, $P$ can dominate the terms in the denominator of Eq. 2.2 so that knowledge of quenching (or any other kind of collisions) is also not needed. This approach has most often been applied to the $v' = 3$ state of the OH radical, which predissociates in a few picoseconds (a typical lifetime for a quenched OH radical in $v' = 0$ at 1 atm is about 1.8 ns, as calculated from the quenching rate coefficients in Ref. 31). Moreover, excitation of $v' = 3$ is accessible using a tunable KrF laser operating near 248 nm. Such a laser can be made powerful enough to create images of OH despite the low oscillator strength in the (3,0) transition. This approach has proven very popular for locating OH in complex flows, but has not been used for determination of OH concentrations and chemical structure in laminar flows.

Again, there are problems in making this method quantitative, even for relative measurements. Although collisions are few, they populate lower lying vibrational levels of OH that have much higher quantum yields, so that about half the light emitted after exciting $v' = 3$ is dominated by complex collisions. This was recognized in the first paper on KrF excitation [39] and quantified later [40]. The key to successful measurements is detecting only the transitions that originate from $v' = 3$, but this decreases the signal strength. In many cases reported in the literature, all fluorescence was detected, resulting in signals whose correct interpretations must include complex collision processes. Moreover, the high laser intensities depopulate the ground state levels, blurring the meaning of the Boltzmann fraction [41]. These and other issues (including excitation of other species such as $O_2$) are discussed in the comprehensive review of excimer laser applications to combustion [5].

### 2.3.6 Absolute Concentration Measurements with LIF

Species profiles range from raw signal intensities through relative profiles to calibrated absolute concentration measurements. The quality of the transformation from raw signals to reported concentrations determines the value of profile results. In many cases, precise relative concentration profiles form excellent tests of models of flame chemistry. By precise, we mean accounting for the variation in $f_B$, $\Gamma$, $F_{fl}$, and collisional effects throughout the flame.

In other cases, however, it is desirable to have absolute concentration measurements of minor species. An important example is quantitative measurements of the CH radical in hydrocarbon flames (particularly methane or natural gas) where the prompt Fenimore mechanism can be a major source of NO. The key reaction in this mechanism is $CH + N_2 \rightarrow N + HCN$ (it has been recently proposed [42] that the products are not these but $NCN + H$). Thus the ability to predict NO concentrations in natural gas flames, a crucial

issue for industry, is predicated on the ability to predict the absolute concentration of CH.

For short-lived free radicals or atoms such as OH, CH, H, and O, absolute measurements pose a problem because there is no way of introducing known amounts of these radicals in flames. For stable species such as CO and NO, the flames can be seeded with known amounts of these compounds, but even then chemical reactions can alter the flame concentration compared with that in the flows. For example, introducing large amounts of NO into a flame can alter the flame chemistry; moreover, the presence of CH radicals causes NO in even small quantities to be reburned in hot later stages of the flame [43]. Thus the delivered, calibrated amount can differ from the concentration measured downstream.

For absolute measurements of free radicals, a variety of techniques is available. These include direct absorption, independent determination of the quantity $(\Omega/4\pi)\epsilon\eta V$ in Eq. 2.1, the use of partial equilibrium assumptions, and comparison to a known quantity of radicals either by calculation or by measurement in a separate system.

OH can be calibrated in two ways. The first is direct absorption, the second is calculation. OH is often present even in low-pressure flames in sufficient amount that direct absorption measurements can be made. These are best done in the burnt gases of premixed flames where the OH concentration is greatest and varies little in space. The accuracy of this mode of calibration reflects the accuracy in determination of the absorption path length. The same technique may be used in atmospheric pressure flames, although care must be taken to ensure that the flame is optically thin, or else a curve of growth analysis must carried out. Second, OH is found in burnt gases in full or partial equilibrium among O, H, and $H_2O$ in premixed flames (but not in hydrocarbon diffusion flames [44]). If the temperature is known at the point of measurement (e.g., by an OH excitation scan), one should be able to reliably calculate the concentration of OH. A measurement in the burnt gases can then serve as a calibration for the entire concentration profile.

CH forms an interesting problem. This radical is not present in high enough quantity in low-pressure flames for direct absorption measurements (although it can be detected by CRD). The approach to absolute LIF measurements of CH is described in Ref. 45; both the $A$–$X$ and $B$–$X$ systems were used. Referring to Eq. 2.1, $B$ was known from spectroscopic studies, $I_L$ was measured (and kept at very low pulse energies, in the few $\mu$J/pulse range, to ensure linear excitation with no saturation). $f_B$ was calculated using temperature measurements by excitation scans in the CH spectrum at the point of measurement; $\Gamma$ was calculated from a convolution of the laser and CH Doppler bandwidths, the latter changing with temperature; and $\tau_L$ was directly measured. $\Phi$ was directly determined by the time decay of the fluorescence, which was some tens of nanoseconds in this 40 Torr flame. $F_{fl}$ was determined by fluorescence scans.

This leaves the term $(\Omega/4\pi)\epsilon\eta V$ to be determined. This was measured as a collective single quantity using both Rayleigh scattering in $N_2$ and Raman scattering in $H_2$. (The use of Rayleigh scattering was first described in Ref. 46.) The same term enters into these scattering signals as into the LIF, so all that is needed further is knowledge of the scattering cross-sections and number density of the scatterers. Thus four independent determinations were made: the two electronic systems and the two scattering approaches. The result showed that the GRIMech chemical mechanism [47], which was known to have difficulties in predicting prompt NO in methane/air flames, was suffering from an inability to correctly predict absolute CH concentrations. New measurements of the $CH + O_2$ reaction in a shock tube [48,49] showed where the correction was needed. Currently this mechanism does an excellent job of predicting CH in lean and stoichiometric flames (although not so well in rich ones); see Chapter 19 of this book.

Because of the importance of the CH absolute measurement, an independent experiment using CRD spectroscopy was later performed on the same flame [13]. After proper consideration of the nonhomogeneous path length, the LIF and CRD measurements were found to be in excellent agreement.

This same approach of Rayleigh scattering has been applied to determine absolute concentrations of electronically excited, emitting CH and OH molecules [50,51]. These are formed by chemiluminescent reactions directly producing the radicals in their excited states. In many practical flames LIF is not available and chemiluminescence is the only approach that can be used. This emission does not yield the important reactive ground state radical concentrations, but if enough is known about the chemiluminescent reactions themselves, it can be used reliably as a diagnostic for flame structure; see also Chapter 21 for more information on chemiluminescence sensors for combustion control.

Another approach to absolute measurements is formation of known amounts of the radical in a calibration cell. An important example is absolute measurements of O and H performed in the early 1980s (references are given in the appendix, and the work is summarized in Ref. 3). In this case, measurements were made in a flame; a flow cell containing known amounts of the atoms replaced the flame without changing the optical setup, and the measurements were repeated.

A similar philosophy using photodissociative formation of radicals has been applied to the HCO radical, which is important in flame propagation and may serve as a marker of heat release [52]. To determine the absolute concentration of HCO [53], acetaldehyde ($CH_3CHO$) was photolyzed by an excimer laser at 308 nm and LIF measured via the $B$–$X$ system with a tunable laser near 258 nm. The $CH_3CHO$ cross-section at 308 nm is known (and was also directly measured); the quantum yield for HCO formation is well established at 93% at this wavelength. The differences in $\Gamma$, $f_B$, and $\Phi$ between flame and cell are accounted for. The quantity $(\Omega/4\pi)\epsilon\eta V$

is the same in both experiments. It has been suggested [54] that this same photodissociation could also be used for determining absolute concentrations of the very important $CH_3$ radical.

In the case of O and H atoms, partial equilibrium arguments have also been used to establish their maximum concentrations, based on measurements of OH, stable species, and the temperature. Examples include H atoms in premixed and diffusion flames [44, 55] and O atoms in turbulent diffusion flames [56].

## 2.4 COMPARISON WITH MODELS OF COMBUSTION CHEMISTRY

As noted in the introduction, the purpose of this chapter is a discussion of laser measurements of trace species to understand combustion chemistry. Properly chosen and quantitatively measured, these radicals can form very stringent tests of the flame chemistry. Accuracies and uncertainties in flame chemistry models, and comparisons with experiment, are discussed in Chapter 19.

Some important conclusions are drawn from that chapter and from prior experience in model–measurement comparisons. References 57–61 are good examples of such comparisons, although this list is not comprehensive. As throughout this chapter, we consider laminar flames and LIF measurements as the subjects of such comparisons. First, it is important to measure the temperature field accurately. Various types of temperature measurements are discussed in Chapter 6. When LIF temperatures are measured for a given radical at the same place in the flame as the concentration, accurate spatial precision is achieved. OH, CH, and a small fraction of added NO can be used for this purpose, although care must be taken in interpreting the data [36]. Full excitation scans as in Fig. 2.1 provide the most complete data set, and can result in temperatures precise to $\sim \pm 30$ K, sufficient to compare to chemical model predictions.

A smaller subset of lines may be used as well. One simplified method is the use of two rotational lines coming from levels of different energy; a separation of around $kT$ is needed for sufficient accuracy. This has been applied to three pairs of two closely spaced lines in OH [62], for example, $Q_2(11)$ and $R_2(8)$ differ in energy by about 1980 K (1376 $cm^{-1}$). An even simpler method is choosing a single rotational level of NO seeded into the flame; this level must have an $f_B$ that is nearly temperature independent or can be iteratively corrected. The signal then gives the NO density, which can be directly related to the temperature by the ideal gas law for a constant pressure condition, assuming no NO dilution or chemical reaction occurs. One-line and two-line NO temperatures have been compared with full OH R-branch excitation scans [63]. It was found that one-line temperatures were in error by as much as 25% (unless dilution and reaction corrections can be made reliably with a model). The two-line NO temperatures agreed well with the OH scans.

A second important conclusion from Chapter 19 is that some trace species often do not tell much about the flame chemistry. At higher temperatures in the flame, H, O, OH, and $H_2O$ are in a quasi-equilibrium, so OH measurements do not provide much insight into chemistry; they really just inform the experimenter that the flame is actually burning. On the other hand, an OH profile needs to be made; any disagreement with predictions reveals real problems with the model (likely transport or fluid dynamic considerations) or the measurement itself. By contrast, CH and HCO provide good tests of chemistry in hydrocarbon flames. For a given flame, the trace species to be measured (besides OH) should be chosen from a combination of sensitivity/uncertainty analysis as described in Chapter 19. Absolute concentrations can be a much more powerful test of the model than only the widths and positions of relative profiles.

Third, agreement should be considered quantitatively, not by a visual inspection of the profiles. Uncertainties in both model predictions and experiment should be taken into account when making a comparison between model and measurement. We again refer to Chapter 19 for an excellent illustration using CH.

## 2.5 OTHER MINOR SPECIES

This discussion has centered on OH, CH, and NO, the most popular species for which LIF or other laser-based measurements are made. A total of 57 other species are given in the appendix. For the sake of length, many other molecules are not included; they are mentioned here.

We have omitted polyaromatic hydrocarbons, whose measurement is addressed in Chapter 13. Many other larger molecules which are products of incomplete combustion and can be made to fluoresce (e.g., benzene, acetaldehyde) are not given. At flame temperatures, the partition function for such species is very large and the signals small because the population is distributed over many levels. We do not include metals, most of which can fluoresce, or their compounds such as HgCl or VO which have appropriate electronic states for LIF detection. For such species we refer the reader to standard compilations, in particular for atoms [64] and for diatomics [23]. A few fluorine-containing fire suppressant molecules are included in the appendix owing to the increasing importance of such studies (see Chapter 11).

## 2.6 REFERENCES

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## 2.7 APPENDIX: LITERATURE REVIEW OF FLAME MEASUREMENTS OF MINOR CONSTITUENTS

The following table is intended to be a guide to the best papers for the measurement of minor species concentrations in flames using laser-based diagnostics. It contains information on 60 species with 302 references, and was completed on May 24, 2001. Special emphasis is placed on in-situ measurements (as opposed to sample-and-detect approaches), in particular on reports of profile measurements obtained under laminar combustion conditions. In general, laser-induced fluorescence is the preferred method when possible, especially when combined with absorption measurements or other calibration schemes to yield quantitative profile data. For this reason LIF papers are listed first, followed by citations to other approaches.

*Please note*: First observations of a species and first applications of a given technique are not cited when more comprehensive and thorough investigations have subsequently been reported. For the most often studied molecules—OH, CH, and NO—only a few of the many hundreds of LIF papers are included. In contrast, essentially all of the papers are cited for species where few measurements are known. Selected work on spectroscopy and imaging strategies is also listed.

### 2.7.1 Guide to Abbreviations

| | |
|---|---|
| * | Wavelengths (nanometers) are given in air, and energies (wavenumbers) are given in vacuum |
| ABS | Absorption (see also CRD and TDL) |
| ASE | Amplified Spontaneous Emission |
| CARS | Coherent Anti-Stokes Raman Scattering |
| CRD | Cavity Ringdown |
| 2C-LIGS | Two-Color Laser-Induced Grating Spectroscopy |
| 2C-RFWM | Two-Color Resonant Four-Wave Mixing |
| DFWM | Degenerate Four-Wave Mixing |
| EM | Emission |
| ICLAS | Intracavity Laser Absorption Spectroscopy |
| LIF | Laser-Induced Fluorescence |
| MP-LIF | Multiphoton Laser-Induced Fluorescence |
| OA | Optoacoustic |
| PAD | Photoacoustic Deflection |
| PD | Photodissociation |
| PTD | Photothermal Deflection |
| POL | Polarization |
| REMPI | Resonance-Enhanced Multiphoton Ionization |
| TDL | Tunable Diode Laser |

| Species | Method | Excitation: Transition | Excitation: Wavelength (nm)* | Detection: Transition | Detection: Wavelength (nm) | Flame: Premixed [P] Diffusion [D] | Reference: Profile [P] Detection [D] Image [I] Spectroscopy [S] |
|---|---|---|---|---|---|---|---|
| *(A) Species Containing H, C, and O* | | | | | | | |
| H atom | MP-LIF | $3p^2P, 2s^2S–1s^2S$ | $2 \times 243 + 656$ | $3p^2P–2s^2S$ | 656 | $H_2$/air [D] | Gol & And 1985 [P,I] |
| | | | | | | $H_2$, $CH_4$, $C_2H_2$–$O_2$–Ar [P] | Gol 1988 [P] |
| | | | | | | $H_2$–$O_2$ [P] | Gol 1989a [P] |
| | | | | | | $H_2$–$O_2$–$N_2$, $C_2H_2$–$O_2$–Ar [P] | Gol et al. 1990 [P] |
| | | | | | | $CH_4$, $C_2H_4$, $C_2H_6$–$O_2$–Ar [P] | Ber et al. 1993 [P] |
| | | $4p^2P, 2s^2S–1s^2S$ | $2 \times 243 + 486$ | $4p^2P–2s^2S$ | 486 | $H_2$–$O_2$–Ar [P] | Gol & Lau 1990 [P] |
| | | $3s^2S, 3d^2D–1s^2S$ | $2 \times 205.1$ | $3s^2S, 3d^2D–2p^2P$ | 656.3 | $H_2$–$O_2$–Ar [P] | Luc et al. 1983a [P] |
| | | | | | | $H_2$–$O_2$[P] | Gol 1986 [P] |
| | | | | | | $H_2$–$O_2$–$N_2$ [P] | Sal & Lau 1986, 1987 [P] |
| | | | | | | $C_2H_4$–$O_2$-Ar [P] | Sal & Lau 1988 [P] |
| | | | | | | $H_2$–$O_2$–Ar [P] | Bit et al. 1988 [P] |
| | | | | | | $H_2$, $CH_4$, $C_2H_2$–$O_2$–Ar [P] | Gol 1988 [P] |
| | | | | | | $C_3H_8$–air [P] | Wes et al. 1994 [P] |
| | | | | | | $H_2$–$O_2$ [P] | Agr et al. 1995 [D] |
| | | | | | | $CH_4$–$N_2$–$O_2$,Ar [P] | Gas et al. 1997 [P] |
| | | $4p^2P–1s^2S$ | $3 \times 291.7$ | $4p^2P–2s^2S$ | 486.1 | $C_2H_2$–$O_2$ [P] | Ald et al. 1984a [D] |
| | | | | | | $H_2$, $CH_4$, $C_2H_2$–$O_2$–Ar [P] | Gol 1988 [P] |
| | | | | | | $H_2 + N_2$/air [D] | Bro et al. 2001 [P] |
| | | $4p^2P, 2s^2S–1s^2S$ | $2 \times 243 + 486$ | $4p^2P–2s^2S$ | 486.1 | $CH_4$–$O_2$–$NO_2$–$N_2$ [P] | Wil & Fle 1995 [P] |
| | MP-LIF, ASE | $3s^2S–1s^2S$ | $2 \times 205$ | $3s^2S–2p^2P$ | 656 | $H_2$–$O_2$ [P] | Gol 1989b [P] |
| | 2 + 1 REMPI | $2s^2S–1s^2S$ | $2 \times 243$ | Electrons | | $H_2$–$O_2$ [P] | Gol 1984 [P] |
| | | | | | | $CH_4$/air [D] | Smy & Tjo 1990a [P] |
| | | | | | | $CH_4$, $C_2H_4$, $C_2H_6$–$O_2$–Ar [P] | Ber et al. 1993 [P] |
| | 3 + 1 REMPI | $2p^2P–1s^2S$ | $3 \times 364.7$ | Electrons | | $H_2$–$O_2$–Ar [P] | Tjo & Coo 1983 [P] |
| | 2C-LIGS | $3p^2P, 2s^2S–1s^2S$ | $2 \times 243 + 656$ | $3p^2P–2s^2S$ | 656 | $H_2$–$O_2$ [P] | Gra et al. 1993 [P] |
| | DFWM, LIF | $3p^2P, 2s^2S–1s^2S$ | $2 \times 243$ | Scattered beam | | $H_2$–$O_2$–$N_2$ [P] | Gra & Tre 1993 [P] |
| C atom | MP-LIF | $3p^3P–2p^2\,^3P$ | $2 \times 280$ | $3p^3P–3s^2P$ | 910 | $C_2H_4$–$O_2$–$N_2$ [P] | Wes et al. 1991a [P] |
| | 2 + 1 REMPI | $3p^3D–2p^2\,^3P$ | $2 \times 287$ | Electrons | | $CH_4$, $C_2H_4$–air [P] | Tjo & Smy 1988 [D] |
| | ASE | $3p^3P–2p^2\,^3P$ | $2 \times 280$ | $3p^3P–3s^3P$ | 910 | $C_2H_2$–$O_2$ [P] | Ald et al. 1989a [P] |

| Species | Method | Excitation | | Detection | | Flame<br>Premixed [P]<br>Diffusion [D] | Reference<br>Profile [P]<br>Detection [D]<br>Image [I]<br>Spectroscopy [S] |
|---|---|---|---|---|---|---|---|
| | | Transition | Wavelength (nm)[a] | Transition | Wavelength (nm) | | |
| O atom | MP-LIF | $3p^3P$-$2p^3P$ | 2 × 226 | $3p^3P$-$3s^3S$ | 845 | $C_2H_2$–$O_2$ [P] | Ald et al. 1984b [P] |
| | | | | | | $CH_4$–$N_2O$–$N_2$ [P] | Miz & DeW 1984 [P] |
| | | | | | | $H_2$–$O_2$ [P] | Gol 1987 [P] |
| | | | | | | $H_2$, $CH_4$, $C_2H_2$–$O_2$ [P] | Mei et al. 1988 [P] |
| | | | | | | $H_2$–$N_2O$ [P] | Wes & Ald 1990b [P] |
| | | | | | | $CH_4$, $C_2H_4$, $C_2H_6$–$O_2$–Ar [P] | Ber et al. 1993 [P] |
| | | | | | | $CH_4$–air [P] | van et al. 1993 [I] |
| | | | | | | $CH_4$–$O_2$–Ar [P] | Fei et al. 1994 [P] |
| | | | | | | $C_3H_8$–air [P] | Wes et al. 1994 [P] |
| | | | | | 845, 777 | $CH_4$–$N_2$–$O_2$,Ar [P] | Gas et al. 1997 [D] |
| | | | | $3p^5P$-$3s^5S$ | 777 | $H_2$–air [D] | Gol & And 1985 [P,I] |
| | | | | | | $CH_4$–$O_2$ [P] | Dye & Cro 1989 [S] |
| | | | | | | $H_2$–$O_2$ [P] | Wys et al. 1989 [D] |
| | MP-LIF, ASE | $3p^3P$-$2p^3P$ | 2 × 226 | $3p^3P$-$3s^3S$ | 845 | $H_2$–$O_2$ [P] | Ald et al. 1989b [P] |
| | | | | | | $H_2$–$O_2$ [P] | Agr & Ald 1994 [D] |
| | 2 + 1 REMPI | $3p^3P$-$2p^3P$ | 2 × 226 | Electrons | | $H_2$–$O_2$ [P] | Gol 1984 [P] |
| | | | | | | $CH_4$/air [D] | Smy & Tjo 1990a [P] |
| | | | | | | $CH_4$, $C_2H_4$, $C_2H_6$–$O_2$–Ar [P] | Ber et al. 1993 [P] |
| | | | | | | $CH_4$–$O_2$–Ar [P] | Fei et al. 1994 [P] |
| | Raman | $^3P_2$-$^3P_{2,0}$ | 158, 227 $cm^{-1}$ | Scattered light | | $H_2$–$O_2$ [P] | Das & Bec 1981 [D] |
| | CARS | $\omega_1$-$\omega_2$ | 158, 227 $cm^{-1}$ | $\omega_3$ beam | | $H_2$–$O_2$ [P] | Tee & Bec 1981 [D] |
| | ICLAS | $2p^1D$-$2p^3P$ | 630, 636 | Absorption | | $H_2$–air [P] | Che & Kov 1994 [D] |
| | ASE, gain | $3p^3P$-$2p^3P$ | 2 × 226 | $3p^3P$-$3s^3S$ | 845 | $H_2$–$O_2$ [P] | Bro & Jef 1995 [D] |
| | DFWM | $3p^3P$-$2p^3P$ | 2 × 226 | Scattered beam | | $H_2$–air [P] | Krü et al. 2000 [P] |
| $C_2$ | LIF | $d^3\Pi_g$-$a^3\Pi_u$ | 514.5 | $d^3\Pi_g$-$a^3\Pi_u$ | 516.5 | $C_2H_6$–$O_2$ [P] | Vea & Hen 1972 [D] |
| | | | 516.5 | | 563.5 | $C_2H_2$–$O_2$ [P] | Bec et al. 1974 [D] |
| | | | 514.5 | | 516.5 | $CH_4$–$O_2$ [P] | Jon & Mac 1976 [D] |
| | | | 509–517 | | 555–565 | $C_2H_2$–$O_2$ [P] | Bar & McD 1977 [D] |
| | | | 514.5 | | 563.5 | $CH_4$–$N_2O$–$N_2$ [P] | Van et al. 1983 [P] |
| | | | 473.7 | | 513 | $CH_4$, ...–$O_2$–$N_2$ + NO [P] | Wil & Pas 1997 [P] |
| | | $e^3\Pi_g$-$a^3\Pi_u$ | 248 | $e^3\Pi_g$-$a^3\Pi_u$ | 250–400 | $C_3H_6$–$O_2$ [P] | Bro et al. 1998 [D] |
| | | $D^1\Sigma_u^+$-$B'^1\Sigma_g^+$ | 248 | $D^1\Sigma_u^+$-$X^1\Sigma_g^+$ | 232 | $C_3H_6$–$O_2$ [P] | Bro et al. 1998 [D] |

**Flame Measurements of Minor Species** *Continued*

| Species | Method | Excitation: Transition | Excitation: Wavelength (nm)* | Detection: Transition | Detection: Wavelength (nm) | Flame: Premixed [P] Diffusion [D] | Reference: Profile [P] Detection [D] Image [I] Spectroscopy [S] |
|---|---|---|---|---|---|---|---|
| | ICLAS | $d^3\Pi_g$–$a^3\Pi_u$ | 617.3 | Absorption | | $C_2H_2$–$O_2$ [P] | Har & Wei 1981 [P] |
| | CARS | $\omega_1$–$\omega_2$ | 1610–1620 $cm^{-1}$ | $\omega_3$ beam | | $C_2H_2$–$O_2$ [P] | Att et al. 1983 [D] |
| | DFWM | $d^3\Pi_g$–$a^3\Pi_u$ | 516.5 | Scattered beam | | $C_2H_2$–$O_2$ [P] | Nyh et al. 1994 [D] |
| | | | 516.6 | | | $C_2H_2$–$O_2$ [P] | Kam et al. 1997 [D] |
| | POL | $d^3\Pi_g$–$a^3\Pi_u$ | 516.5 | Polarization change | | $C_2H_2$–$O_2$ [P] | Nyh et al. 1995a [P] |
| | PD | Photodissociation | 282 | $d^3\Pi_g$–$a^3\Pi_u$ | 516.5 | $C_2H_2$–$O_2$ [P] | Ald et al. 1982 [P] |
| | | | 266, 355, 532 | | 473 | $C_2H_4$–$O_2$–$N_2$ [P] | Ben & Ald 1990 [P] |
| | | | 266, 292 | | 560 | $C_2H_2$–$O_2$–Ar [P] | Gol & Kea 1990 [P] |
| CH | LIF, ABS | $A\,^2\Delta$–$X\,^2\Pi_r$ | 427 | $A\,^2\Delta$–$X\,^2\Pi_r$ | 431 | $C_2H_2$–$O_2$ [P] | Bon & Shi 1979 [D] |
| | | $B\,^2\Sigma^-$–$X\,^2\Pi_r$ | 390 | $B\,^2\Sigma^-$–$X\,^2\Pi_r$ | ? | $CH_4$, $CH_2O$–$NO_2$–$O_2$ [P] | Bra et al. 1991 [P] |
| | LIF | $A\,^2\Delta$–$X\,^2\Pi_r$ | 425 | $A\,^2\Delta$–$X\,^2\Pi_r$ | 423–432 | $CH_4$–$O_2$ [P] | Cat et al. 1984 [D] |
| | | | 431–435 | | 427–428 | $C_2H_2$–$O_2$ [P] | Koh et al. 1984 [P] |
| | | | 427.4 | | 431.0 | $CH_4$/air [D] | Nor & Smy 1991 [P] |
| | | | 431 | | 486 | $CH_4$, $C_2H_4$, $C_2H_6$–$O_2$–Ar [P] | Ber et al. 1993 [P] |
| | | | 435.4 | | 431 | $CH_4$–$O_2$–$N_2$ [P] | Ber et al. 2000 [P] |
| | | $A\,^2\Delta$, $B\,^2\Sigma^-$–$X\,^2\Pi_r$ | 434.4, 387.2 | $A\,^2\Delta$, $B\,^2\Sigma^-$–$X\,^2\Pi_r$ | 432, 392 | $C_3H_8$–air [P] | Luq & Cro 1996 [P] |
| | | $B\,^2\Sigma^-$–$X\,^2\Pi_r$ | 390 | $B\,^2\Sigma^-$–$X\,^2\Pi_r$ | 390 | $CH_4$–$O_2$–Ar + $N_2O$, NO, . . . [P] | Wil & Fle 1994b [P] |
| | | | 387 | | 431 | $C_3H_8$–air [P] | Pau & Dec 1994 [I] |
| | | | 365 | | 405 | $CH_4$–$O_2$–$NO_2$–$N_2$ [P] | Wil & Fle 1995 [P] |
| | | | 389.5 | | > 420 | $CH_4$–air–$N_2$ [P] | Ngu & Pau 1996 [I] |
| | | | 387.4 | | 320–460 | $CH_4$–$O_2$ + NO [P] | Juc et al. 1998 [P] |
| | | | 364 | | 404 | $CH_4$–$O_2$,air [P] | Luq et al. 2000 [D] |
| | | $C\,^2\Sigma^+$–$X\,^2\Pi_r$ | 316.1 | $C\,^2\Sigma^+$–$X\,^2\Pi_r$ | 314.4 | $CH_4$–$O_2$–air [P] | Cho & Dea 1985 [D] |
| | | | 314–317 | $A\,^2\Delta$–$X\,^2\Pi_r$ | 431 | $CH_4$–$O_2$ [P] | Jef et al. 1986 [D] |
| | | | 310–314 | $C\,^2\Sigma^+$–$X\,^2\Pi_r$ | 314.5 | $CH_4$, $C_2H_4$–air [P] | Tjo & Smy 1988 [D] |
| | ABS | $A\,^2\Delta$–$X\,^2\Pi_r$ | 430.4–431.3 | Absorption | | $C_2H_2$–$O_2$ [P] | Jok et al. 1986 [P] |
| | REMPI | $D\,^2\Pi_i$–$X\,^2\Pi_r$ | 312.1 | Electrons | | $CH_4$, $C_2H_4$–air [P] | Tjo & Smy 1988 [D] |
| | DFWM | $A\,^2\Delta$–$X\,^2\Pi_r$ | 426.1–426.5 | Scattered beam | | $C_2H_2$–$O_2$ [P] | Wil et al. 1992 [P] |
| | 2C-RFWM | $B\,^2\Sigma^-$–$X\,^2\Pi_r$ | 387–394 | $A\,^2\Delta$–$X\,^2\Pi_r$ | 426 | $C_2H_2$–$O_2$ [P] | Hun et al. 1995 [D] |
| | CRD | $A\,^2\Delta$–$X\,^2\Pi_r$ | 430 | Absorption | | $CH_4$–air, $C_2H_2$–$O_2$ [P] | Eve et al. 1999 [P] |
| | | | 420–431 | | | $CH_4$–$O_2$–Ar [P] | Tho & Mcl 2000 [P] |
| | | $B\,^2\Sigma^-$–$X\,^2\Pi_r$ | 387 | | | $CH_4$–air [P] | Mer et al. 2001a [P] |

| Species | Method | Excitation | | Detection | | Flame<br>Premixed [P]<br>Diffusion [D] | Reference<br>Profile [P]<br>Detection [D]<br>Image [I]<br>Spectroscopy [S] |
|---|---|---|---|---|---|---|---|
| | | Transition | Wavelength (nm)* | Transition | Wavelength (nm) | | |
| | | | 388.3 | | | $CH_4$–$O_2$–$N_2$ [P] | Luq et al. 2001a [P] |
| | | $C\,^2\Sigma^+$–$X\,^2\Pi_r$ | 314.0–317.0 | | | $CH_4 + N_2/O_2 + N_2$ [D] | Mer et al. 1999a [P] |
| | | | 314.5 | | | $CH_4$–$O_2$–$N_2$ [P] | Der et al. 1999a [P] |
| | | | 314.5 | | | $CH_4$–$O_2$–$N_2 + N_2O$ [P] | Der et al. 1999b [P] |
| | | | 317 | | | $CH_4$–air [P] | Mer et al. 2001a [P] |
| | TDL | $A\,^2\Delta$–$X\,^2\Pi_r$ | 426 | Absorption | | $CH_4$/air, $C_2H_4$/air [D] | Pet & Oh 1999 [P] |
| | EM | | | $C, B, A$–$X\,^2\Pi_r$ | 300–500 | $C_2H_2$–$O_2$ [P] | Bas & Bro 1961 [S] |
| CO | MP-LIF | $B\,^1\Sigma^+$–$X\,^1\Sigma^+$ | 2 × 230 | $B\,^1\Sigma^+$–$A\,^1\Pi$ | 484 | $CH_4$–air [P] | Ald et al. 1984c [P] |
| | | | | | 451–725 | CO–air, $CH_4$–air [P] | Hau et al. 1986 [I] |
| | | | | | 451–725 | CO,$CH_4$–air [P], CO–air [D] | Sei et al. 1987 [I] |
| | | | | | 484 | $CH_4$–$O_2$–Ar [P] | Tjo & Smy 1989 [D,S] |
| | | | | | 451 | $C_3H_8$–air [P] | Wes et al. 1994 [P] |
| | | | | | 484 | $CH_4$/air [D] | Eve et al. 1996 [P,I] |
| | | | | | 475 | $CH_4$–$O_2$–$N_2$ [P] | Gas et al. 1999 [P] |
| | | $C\,^1\Sigma^+$–$X\,^1\Sigma^+$ | 2 × 217.66 | $C\,^1\Sigma^+$–$A\,^1\Pi$ | 350–550 | $CH_4$–air [P], $CH_4$/air [D] | Lin et al. 2000 [D] |
| | MP-LIF, ASE | $B\,^1\Sigma^+$–$X\,^1\Sigma^+$ | 2 × 230 | $B\,^1\Sigma^+$–$A\,^1\Pi$ | 480–725 | Cell | Wes et al. 1990 [S] |
| | LIF | (2,0) band | 4300 $cm^{-1}$ | (1,0) band | 2100 $cm^{-1}$ | CO–Ar–$H_2$ [P] | Kir & Han 2000 [I] |
| | 2 + 1 REMPI | $B\,^1\Sigma^+$–$X\,^1\Sigma^+$ | 2 × 230 | Electrons | | $CH_4$–$O_2$–Ar [P] | Tjo & Smy 1989 [D,S] |
| | | | | | | $CH_4$, $C_2H_4$, $C_2H_6$–$O_2$–Ar [P] | Ber et al. 1993 [P] |
| | 2 + 1 REMPI | $C\,^1\Sigma^+$–$X\,^1\Sigma^+$ | 2 × 217.5 | Electrons | | $CH_4$–$O_2$–Ar [P] | Tjo & Smy 1989 [D] |
| | 3 + 2, 3 REMPI | $A\,^1\Pi$–$X\,^1\Sigma^+$ | 3 × 430–470 | Electrons | | $CH_4$–$O_2$–Ar [P] | Tjo & Coo 1984 [P] |
| | TDL | (1,0) band | 2020–2213 $cm^{-1}$ | Absorption | | $CH_4$–air [P] | Sch & Han 1981 [P] |
| | | | 2128 $cm^{-1}$ | | | $CH_4$/air [D] | Mil et al. 1993 [P] |
| | | | 2028, 2034 $cm^{-1}$ | | | $CH_4$–air [P] | Ngu et al. 1993 [P] |
| | | | 2173–2169 $cm^{-1}$ | | | $C_2H_4$/air [D] | Ska & Mil 1995, 1996 [P] |
| | | | 2020–2100 $cm^{-1}$ | | | $CH_4$–$O_2$–Ar + $CF_3Br$, ... [P] | Dan et al. 1996 [P] |
| | | (2,0) band | 4344 $cm^{-1}$ | | | $C_2H_4$–air [P] | Wan et al. 2000 [D] |
| | | (3,0) band | 6412 $cm^{-1}$ | | | $CH_4$–air [P] | Ups et al. 1999 [D] |
| | CARS | $\omega_1$–$\omega_2$ | 2143 $cm^{-1}$ | $\omega_3$ beam | | $CH_4$–air [P] | Far et al. 1985 [P] |
| | | | 2143 $cm^{-1}$ | | | $C_3H_8$/air [D] | Mag et al. 1995 [P] |
| | POL | $B\,^1\Sigma^+$–$X\,^1\Sigma^+$ | 2 × 230 | Polarization change | | CO–$O_2$ [P] | Nyh et al. 1995b [D] |

**Flame Measurements of Minor Species** *Continued*

| Species | Method | Excitation: Transition | Excitation: Wavelength (nm)* | Detection: Transition | Detection: Wavelength (nm) | Flame: Premixed [P] Diffusion [D] | Reference: Profile [P] Detection [D] Image [I] Spectroscopy [S] |
|---|---|---|---|---|---|---|---|
| OH | LIF, ABS | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 282.9 | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 308 | $C_3H_8$–air [P] | Kai et al. 1986 [P] |
| | | | 306–309 | | 306–309 | $H_2$–$O_2$, $H_2$–$N_2O$ [P] | Koh et al. 1988 [P] |
| | | | 285.6 | | 314 | $CH_4$/air [D] | Smy et al. 1990 [P] |
| | | | 310 | | 310 | $C_2H_6$–$O_2$–$N_2$ [P] | Car et al. 1991 [P] |
| | | | 309.3 | | 307.1, 312.5 | $C_2H_6$–$O_2$–$N_2$ [P] | Car & Lau 1994 [P] |
| | LIF | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 310–312 | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 310–312 | $H_2$–$O_2$–Ar [P] | Luc et al. 1983b [P] |
| | | | 313.3 | | 319.5 | $C_2H_2$–$O_2$ [P] | Koh et al. 1984 [P] |
| | | | 281, 306, 612: Five excitation/detection strategies | | | $H_2$–$O_2$–Ar [P] | Lau & Gol 1989 [P] |
| | | | 282 | | 315 | $CH_4$–air [P] | Koh et al. 1990 [P] |
| | | | 278.8, 283.6 | | 305–385 | $CH_4$, $C_2H_4$/air [D] | Pur et al. 1992 [P] |
| | | | 248–310: Three excitation/detection strategies | | | — | Sei & Han 1993 [I] |
| | | | 287.9 | | 295–340 | $CH_4$–air [P] | Ngu et al. 1996 [P] |
| | | | 248.5 | | 295 | $CH_4$–air [P] | Ngu & Pau 2001 [D] |
| | | | 282.6–283.5 | | 295–395 | $H_2 + N_2$/air [D] | Bro et al. 2001 [P] |
| | LIF, DFWM | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 281.4, 306.4 | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 308.9 | $C_3H_8$–$O_2$ [P] | Krö et al. 1993 [D] |
| | ABS | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 308.6 | Absorption | | $NH_3$–$O_2$–$N_2$ [P] | Cho et al. 1982 [P] |
| | | | 306.9 | | | $CH_4$–air [P] | Cat 1982 [P] |
| | | | 307.4–313.7 | | | $H_2$–$O_2$ [P] | Gol 1984 [P] |
| | OA | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 308.0, 309.3 | Pressure wave | | $CH_4$–$O_2$–$N_2$ [P] | Ros et al. 1984 [P] |
| | PTD | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 309.0 | Beam deflection | | $C_3H_8$–air [P] | Kiz et al. 1984 [P] |
| | PTD, PAD | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 309.2 | Beam deflection | | $CH_4$–air/air [P] | Ros & Gup 1984 [P] |
| | CARS | $\omega_1$-$\omega_2$ | 3065 $cm^{-1}$ | $\omega_3$ beam | | $CH_4$–air [P] | Att et al. 1990 [P] |
| | CARS, DFWM | $\omega_1$-$\omega_2$, $A$-$X$ | 3065 $cm^{-1}$, 311.2 | Scattered beam | | $CH_4$–air [P] | Ber et al. 1992 [P] |
| | POL | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 306.4 | Polarization change | | $C_2H_2$–$O_2$,$C_3H_8$–air [P] | Nyh et al. 1993 [P] |
| | | | 306.4–309.3 | | | $CH_4$–air [P] | Suv et al. 1995 [D] |
| | | | 284.9 | | | $H_2$–$N_2O$ [P] | Löf & Ald 1996 [D] |
| | | | 308.6 | | | $H_2$–air [P] | Rei et al. 2000 [D] |
| | DFWM | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 309.7 | Scattered beam | | $C_3H_8$–air + $SO_2$ [P] | Mis et al. 1996 [P] |
| | | | 309.7 | | | $H_2$–air + $SO_2$ [P] | Rad et al. 1999 [P] |
| | | | 308.6, 309.2 | | | $H_2$–air [P] | Rei et al. 1999 [D] |
| | CRD | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 312.2 | Absorption | | $CH_4$–air [P] | Che et al. 1998 [P] |
| | CRD, LIF, ABS | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 302.4, 304.0 | Absorption, $A$-$X$ | | $H_2$, $CH_4$–air[P],$CH_4/N_2/O_2$[D] | Mer et al. 1999b [P] |
| | TDL | (2,0) band | 6420 $cm^{-1}$ | Absorption | | $CH_4$–air [P] | Ups et al. 1999 [D] |
| | | | 6421 $cm^{-1}$ | | | $CH_4$–air [P] | Aiz et al. 1999 [D] |
| | 2 + 1 REMPI | $D\,^2\Sigma^-$-$X\,^2\Pi_i$ | 2 × 243–247 | Electrons | | Photolysis | Col et al. 1991 [S] |

| Species | Method | Excitation | | Detection | | Flame | Reference |
|---|---|---|---|---|---|---|---|
| | | Transition | Wavelength (nm)* | Transition | Wavelength (nm) | Premixed [P] Diffusion [D] | Profile [P] Detection [D] Image [I] Spectroscopy [S] |
| | EM | | | $A\,^2\Sigma^+ - X\,^2\Pi_i$ | 261-352 | $H_2$–$O_2$ [P] | Bas & Bro 1953 [S] |
| $C_3$ | LIF | $\tilde{A}\,^1\Pi_u - \tilde{X}\,^1\Sigma_g^+$ | 370–415 | $\tilde{A}\,^1\Pi_u - \tilde{X}\,^1\Sigma_g^+$ | 370–415 | $CH_4$–He plasma | Bal et al. 1994 [S] |
| | | | 405 | | 423 | $CH_4$–$H_2$–Ar plasma | Rai & Jef 1997 [P] |
| | TDL | $\nu_3$ band | 2040 $cm^{-1}$ | Absorption | | Photolysis | Mat et al. 1988 [S] |
| | DFWM, 2C-LIGS | $\tilde{A}\,^1\Pi_u - \tilde{X}\,^1\Sigma_g^+$ | 405 | Scattered beam | | Vaporized jet | But & Roh 1992 [D] |
| HCO | LIF | $\tilde{B}\,^2A' - \tilde{X}\,^2A'$ | 245 | $\tilde{B}\,^2A' - \tilde{X}\,^2A'$ | 276–284 | $CH_4$–$O_2$ [P] | Jef et al. 1990 [P] |
| | | | 258 | | 340–380 | $CH_4$–$O_2$–$N_2$ [P] | Dia et al. 1998 [P] |
| | | | 258.4 | | < 360 | $CH_4$–air–$N_2$ [P] | Naj et al. 1998 [I] |
| | | | 258.5 | | ? | $CH_4$–air [P] | Bom & Kap 1999 [I] |
| | | | 254 | | 280–400 | $CH_4$–air [P] | Naj et al. 2001 [I,P] |
| | 2 + 1 REMPI | $3p^2A'' - \tilde{X}\,^2A'$ | 2 × 397.4 | Electrons | | $CH_4$–$O_2$–Ar [P] | Ber et al. 1988 [P] |
| | | | | | | $CH_4$, $C_2H_4$–$O_2$–Ar [P] | Coo et al. 1988 [P] |
| | | | | | | $CH_4$, $C_2H_4$, $C_2H_6$–$O_2$–Ar [P] | Ber et al. 1993 [P] |
| | 1 + 1 REMPI | $3p^2\Pi - \tilde{X}\,^2A'$ | 208–222 | Electrons | | Photolysis | Son & Coo 1992 [S] |
| | | $\tilde{B}\,^2A' - \tilde{X}\,^2A'$ | 222–263 | | | Photolysis | Coo & Son 1992 [S] |
| | TDL | $\tilde{A}\,^2A'' - \tilde{X}\,^2A'$ | 758 | Absorption | | Flow reactor | Oh et al. 1993 [S] |
| | ICLAS | $\tilde{A}\,^2A'' - \tilde{X}\,^2A'$ | 615.5–615.8 | Absorption | | $CH_4$–air [P] | Che 1995 [D] |
| | | | 615.8 | | | $CH_4$–air [P] | Loz et al. 1997 [P] |
| | | | 615.8 | | | $CH_4$–$O_2$–$N_2$ [P] | Loz et al. 1998 [P] |
| | CRD | $\tilde{A}\,^2A'' - \tilde{X}\,^2A'$ | 615 | Absorption | | $CH_4$–$N_2$–$O_2$ [P] | Sch & Rak 1997 [D] |
| | | | 614.9 | | | $CH_4$–$O_2$–Ar [P] | McI 1999 [P] |
| $HO_2$ | TDL | $\nu_3$ band | 1117.5 $cm^{-1}$ | Absorption | | Photolysis | Thr & Tyn 1982 [D] |
| | | $2\nu_1$ band | 6625.8 $cm^{-1}$ | | | Photolysis | Joh et al. 1991 [S] |
| | | | | | | Flow reactor | Taa & Oh 1997 [S] |
| $^1CH_2$ | LIF | $\tilde{b}\,^1B_1 - \tilde{a}^1A_1$ | 538 | $\tilde{b}^1B_1 - \tilde{a}^1A_1$ | 450–650 | $CH_4$–$O_2$ [P] | Sap et al. 1990 [P] |
| | ICLAS | $\tilde{b}\,^1B_1 - \tilde{a}^1A_1$ | 612.4 | Absorption | | $CH_4$–$O_2$–$N_2$ [P] | Che et al. 1997 [P] |
| | | | 612.4 | | | $CH_4$–$O_2$–$N_2$ [P] | Loz et al. 1998 [P] |
| | | | 590–593, 640–645 | | | $CH_4$–$O_2$–$N_2$ [P] | Der et al. 1999c [P] |
| | CRD | $\tilde{b}\,^1B_1 - \tilde{a}^1A_1$ | 622 | Absorption | | $CH_4$–$O_2$–Ar [P] | McI 1998, 1999 [P] |
| $^3CH_2$ | 3 + 1 REMPI | 4 states–$\tilde{X}\,^3B_1$ | 385–430 | Electrons | | Flow reactor | Iri & Hud 1992 [S] |

**Flame Measurements of Minor Species** *Continued*

| Species | Method | Excitation: Transition | Excitation: Wavelength (nm)[a] | Detection: Transition | Detection: Wavelength (nm) | Flame: Premixed [P] Diffusion [D] | Reference: Profile [P] Detection [D] Image [I] Spectroscopy [S] |
|---|---|---|---|---|---|---|---|
| | 2 + 1 REMPI | $\tilde{H}(3p)$, $\tilde{I}(4p)$–$\tilde{X}\,^3B_1$ | 311.8, 269.4 | Electrons | | Flow reactor | Iri et al. 1992 [S] |
| $C_2H$ | LIF | $^2\Pi$–$\tilde{X}\,^2\Sigma^+$ | 250–312 | $^2\Pi$–$\tilde{X}\,^2\Sigma^+$ | 400–600 | Photolysis | Hsu et al. 1992, 1993 [S] |
| | ABS | $\tilde{A}\,^2\Pi$–$\tilde{X}\,^2\Sigma^+$ | 3000–4200 $cm^{-1}$ | Absorption | | Discharge | Car et al. 1982 [S] |
| | 2 + 1 REMPI | $3p\sigma^2\Pi(?)$–$\tilde{X}\,^2\Sigma^+$ | 2 × 272–283 | Electrons | | Photolysis | Coo & Goo 1991 [S] |
| | EM | | | $^2\Pi$–$\tilde{X}\,^2\Sigma^+$ | 250–300 | Discharge | Som et al. 1995 [S] |
| $C_2O$ | LIF | $\tilde{A}\,^3\Pi_i$–$\tilde{X}\,^3\Sigma^-$ | 588–689 | $\tilde{A}\,^3\Pi_i$–$\tilde{X}\,^3\Sigma^-$ | ? | Photolysis | Pit et al. 1981 [S] |
| | TDL | $\nu_1$ band | 1971 $cm^{-1}$ | Absorption | | Photolysis | Yam et al. 1986 [S] |
| $CH_3$ | 2 + 1 REMPI | $3p^2A_2''$–$\tilde{X}\,^2A_2''$ | 2 × 333.5 | Electrons | | $CH_4$/air [D] | Smy & Tay 1985 [P] |
| | | | | | | $CH_4$–$O_2$ [P] | Mei & Koh 1987 [P] |
| | | | | | | $CH_4$, $C_2H_4$–$O_2$–Ar [P] | Coo et al. 1988 [P] |
| | | | | | | $CH_4$–$O_2$ + NO [P] | Etz et al. 1992 [P] |
| | | | | | | $CH_4$, $C_2H_4$, $C_2H_6$–$O_2$–Ar [P] | Ber et al. 1993 [P] |
| | | | | | | Flow reactor | Hei et al. 1994 [S] |
| | ABS | $\tilde{B}\,^2A_1'$–$\tilde{X}\,^2A_2''$ | 216.5 | Absorption | | $CH_4$–$O_2$ [P] | Etz et al. 1993 [P] |
| | DFWM | $\tilde{B}\,^2A_1'$–$\tilde{X}\,^2A_2''$ | 217 | Scattered beam | | $CH_4$–air [P] | Sic et al. 1995 [P] |
| | | | | | | $CH_4$–air, $C_3H_8$–air [P] | Far et al. 1996 [P] |
| | PD | $\tilde{B}\,^2A_1'$–$\tilde{X}\,^2A_2''$ | 205 | CH $A\,^2\Delta$–$X\,^2\Pi_i$ | 427 | $CH_4$–air [P] | Des et al. 1996 [P] |
| | CRD | $\nu_3$ band | 3125 $cm^{-1}$ | Absorption | | $CH_4$–air [P] | Sch et al. 1997 [P] |
| $CH_2O$ | LIF | $\tilde{A}\,^1A_2$–$\tilde{X}\,^1A_1$ | 352.5 | $\tilde{A}\,^1A_2$–$\tilde{X}\,^1A_1$ | 395–550 | $CH_4$/air [D] | Har & Smy 1993 [P] |
| | | | 338.1 | | > 360 | Dimethyl ether-air [P] | Pau & Naj 1998 [I] |
| | | | 353.0 | | ? | $CH_4$–air [P] | Bom & Kap 1999 [I] |
| | | | 369.2–369.7 | | > 380 | $CH_4$–air [P] | Kle et al. 2000 [I] |
| | | | 353.2 | | > 375 | $CH_4$–air [P] | Böc et al. 2000 [I] |
| | | | 355 | | 425 | $C_2H_4$–$N_2$–Ar–air/air [P] | McE & Pfe 2000 [P] |
| | | | 339.2 | | 380–500 | $CH_4$–air [P] | Shi et al. 2001 [P] |
| | | | 353.1–353.6 | | 360–550 | $C_2H_4$, $C_7H_{16}$...–air [P] | Bur et al. 2000 [I] |
| | 3 + 1, 2 REMPI | $3p_y$, $3p_z$–$\tilde{X}\,^1A_1$ | 3 × 445–470 | Electrons | | Flow cell | Bom & Dou 1987 [S] |
| | TDL | $\nu_5$ band | 2868–2872 $cm^{-1}$ | Absorption | | Cell | Cli & Var 1990 [S] |
| | | | 2937 $cm^{-1}$ | | | Cell | Tol & Mil 1998 [D] |
| | CRD, LIF | $\tilde{A}\,^1A_2$–$\tilde{X}\,^1A_1$ | 368–373 | Absorption | | $CH_4$–$N_2$–$O_2$ [P] | Luq et al. 2001b [P] |

| Species | Method | Excitation | | Detection | | Flame | Reference |
|---|---|---|---|---|---|---|---|
| | | Transition | Wavelength (nm)[a] | Transition | Wavelength (nm) | Premixed [P] Diffusion [D] | Profile [P] Detection [D] Image [I] Spectroscopy [S] |
| HCCO | LIF | $\tilde{B}\,^2\Pi$–$\tilde{X}\,^2A''$ | 284.8–299.3 | $\tilde{B}\,^2\Pi$–$\tilde{X}\,^2A''$ | 375–425 | Photolysis | Bro et al. 1999 [S] |
| $C_2H_2$ | LIF, PD | $\tilde{A}\,^1A_u$–$\tilde{X}\,^1\Sigma_g^+$ | 215.9 | $C_2$ *d–a, C–A* | 330–650 | $C_2H_2$–$O_2$ [P] | Rai et al. 1989 [P] |
| | CARS | $\omega_1$–$\omega_2$ | 1935–1980 $cm^{-1}$ | $\omega_3$ beam | | $C_2H_4$/air [D] | Far et al. 1984 [D] |
| | | | | | | $CH_4$–$C_2H_2$–air [P] | Luc et al. 1986 [P] |
| | TDL | $\nu_4 + \nu_5$ band | 1273, 1298 $cm^{-1}$ | Absorption | | $C_2H_4$/air [D] | Tol & Mil 1994 [P] |
| $C_2H_3$ | TDL | $CH_2$ wag | 895 $cm^{-1}$ | Absorption | | Photolysis | Kan et al. 1990 [S] |
| | CRD | $\tilde{A}\,^2A''$–$\tilde{X}\,^2A'$ | 415–530 | Absorption | | Photolysis | Pib et al. 1999 [S] |
| $CH_3O$ | LIF | $\tilde{A}\,^2A_1$–$\tilde{X}\,^2E$ | 290–300 | $\tilde{A}\,^2A_1$–$\tilde{X}\,^2E$ | 330–420 | $CH_4$–$O_2$–$N_2$–$NO_2$ [P] | Wil & Fle 1994a [D,P] |
| | | | 297.6 | | 350–400 | $CH_4$–$O_2$–$N_2$–$NO_2$ [P] | Wil & Fle 1995 [P] |
| | | | 292.8 | | 320–400 | $CH_4$–air [P] | Naj et al. 2001 [I,P] |
| | REMPI | ?–$\tilde{X}\,^2E$ | 315–328 | Electrons | | Flow reactor | Lon et al. 1986 [D] |
| $CH_2OH$ | 2 + 1 REMPI | $\tilde{B}\,^2A'(3p)$–$\tilde{X}\,^2A''$ | 2 × 430–490 | Electrons | | Flow reactor | Dul & Hud 1986 [S] |
| | | | 2 × 450–470 | | | Photolysis | Bom et al. 1986 [S] |
| | | | 243–251, 2 × 460–505 | | | Flow reactor | Joh & Hud 1996 [S] |
| $C_2H_2O_2$ | LIF | $S_1$–$S_0$ | 428 | $S_1$–$S_0$ | 455.5, 477.7 | $C_2H_2$–air [P] | Tic et al. 1998 [I] |
| $C_3H_5$ allyl | 2 + 2 REMPI | $3s^2A_1$–$\tilde{X}\,^2A_2$ | 2 × 485–515 | Electrons | | Flow reactor | Hud & Dul 1985 [S] |
| | | | 2 × 488–513 | | | Photolysis | Sap & Wei 1987 [S] |
| | 1 + 1 REMPI | $\tilde{D}$, $\tilde{C}$, $\tilde{B}$–$\tilde{X}\,^2A_2$ | 238–250 | | | Flash pyrolysis | Blu et al. 1992 [S] |
| | TDL | $\nu_{11}$ band | 795–823 $cm^{-1}$ | Absorption | | Photolysis | Hir et al. 1992 [S] |
| $C_4H_7$ | 2 + 2 REMPI | $3s^2A_1$ Ryd–$\tilde{X}$ | 2 × 485–535 | Electrons | | Flow reactor | Hud & Dul 1985 [S] |
| $C_6H_5$ phenyl | CRD | $^2B_1$–$^2A_1$ | 504.8 | Absorption | | Photolysis | Yu & Lin 1994 [D] |
| $C_6H_6$ | Raman | $\nu_1$ band | 992 $cm^{-1}$ | Scattered light | | $CH_4 + C_6H_6$/air [D] | Get et al. 1992 [P] |
| | 1 + 1 REMPI | $S_1\,^1B_{2u}$–$S_0\,^1A_{1g}$ | 233–262 | Electrons | | Molecular beam | Ich et al. 1988 [S] |
| $C_7H_7$ benzyl | LIF | $1\,^2A_2$, $2\,^2B_2$–$1\,^2B_2$ | 432–459 | $1\,^2A_2$, $2\,^2B_2$–$1\,^2B_2$ | 464–538 | Flow reactor | Oka et al. 1982 [S] |
| | | | 425–460 | | 450–500 | Photolysis | Fuk & Obi 1990 [S] |
| | $n$ + 1 REMPI | ?–$\tilde{X}\,^2B_2''$ | 498–518 | Electrons | | Flow reactor | Hof & Hud 1985 [S] |
| tropyl | 2 + 1 REMPI | $np\pi$–$\tilde{X}\,^2E''$ | 2 × 415–590 | Electrons | | Flow reactor | Joh 1991 [S] |

**Flame Measurements of Minor Species** *Continued*

| Species | Method | Excitation: Transition | Excitation: Wavelength (nm)* | Detection: Transition | Detection: Wavelength (nm) | Flame: Premixed [P] Diffusion [D] | Reference: Profile [P] Detection [D] Image [I] Spectroscopy [S] |
|---|---|---|---|---|---|---|---|
| *(B) Nitrogen-Containing Species* | | | | | | | |
| N atom | MP–LIF | $3p^4D–2p^3\,^4S$ | 2 × 211 | $3p^4D–3s^4P$ | 870 | $H_2–O_2–N_2 + NH_3, \ldots$ [P] | Law et al. 1990 [P] |
| | | | | | | $H_2–O_2–N_2 + NH_3, \ldots$ [P] | Bit et al. 1991 [P] |
| | | | | | | $NH_3–H_2–O_2$ [P] | Wes et al. 1991b [P] |
| | ASE | $3p^4D–2p^3\,^4S$ | 2 × 211 | $3p^4D–3s^4P$ | 870 | $NH_3–O_2$ [P] | Agr et al. 1990 [P] |
| CN | LIF, ABS | $B^2\Sigma^+–X^2\Sigma^+$ | 384.2 | $B^2\Sigma^+–X^2\Sigma^+$ | 388.3 | $C_2H_2–N_2O$ [P] | Bon & Shi 1979 [D] |
| | | | 386 | | ? | $CH_4$, $CH_2O–NO_2–O_2$ [P] | Bra et al. 1991 [P] |
| | | | 421.7, 386.4 | | 388 | $CH_4–NO–O_2$, $CH_4–N_2O$ [P] | Zab 1992 [P] |
| | LIF | $B^2\Sigma^+–X^2\Sigma^+$ | 388.5 | $B^2\Sigma^+–X^2\Sigma^+$ | 380–390 | $C_2H_4–O_2–Ar$ [P] | Mor 1982 [D] |
| | | | 454.5 | | 384–387 | $CH_4–N_2O–N_2$ [P] | Van et al. 1983 [P] |
| | | | 386.7 | | ? | $H_2–O_2–Ar + HCN$ [P] | Mil et al. 1984 [P] |
| | | | 309–315, 330–335 | | 388 | $CH_4–N_2O$ [P] | Jef et al. 1986 [D] |
| | | | 421.7 | | 388 | $CH_4–NO_2–O_2$ [P] | Zab 1991 [P] |
| | | | 388.5 | | 365–505 | $CH_4–O_2 + NO$ [P] | Etz et al. 1992 [P] |
| | | | 356.5 | | 389 | $CH_4$–air [P] | Hir & Tsu 1994 [I] |
| | | | 388.3 | | 420 | $CH_4–O_2–NO_2–N_2$ [P] | Wil & Fle 1995 [P] |
| | | | 388.1 | | 320–460 | $CH_4–O_2 + NO$ [P] | Juc et al. 1998 [P] |
| | DFWM | $B^2\Sigma^+–X^2\Sigma^+$ | 386.0–388.5 | Scattered beam | | $H_2–C_2H_2–O_2–N_2–NO$ [P] | Tsa et al. 1995 [D] |
| | CRD | $B^2\Sigma^+–X^2\Sigma^+$ | 388.3 | Absorption | | $CH_4–O_2–N_2$ [P] | Luq et al. 2001a [P] |
| | | | 384.8 | | | $CH_4–O_2 + NO$ [P] | Mer et al. 2001b [P] |
| NH | LIF, ABS | $A\,^3\Pi–X\,^3\Sigma^-$ | 335.4 | $A\,^3\Pi–X\,^3\Sigma^-$ | 337.3 | $CH_4–N_2O$ [P] | And et al. 1982a [P] |
| | | | 337 | | 337 | $CH_4–N_2O–Ar$ [P] | Sal et al. 1984 [P] |
| | | | 336 | | ? | $CH_4$, $CH_2O–NO_2–O_2$ [P] | Bra et al. 1991 [P] |
| | | | 302.6, 332.7 | | 336 | $CH_4–NO–O_2$, $CH_4–N_2O$ [P] | Zab 1992 [P] |
| | LIF | $A\,^3\Pi–X\,^3\Sigma^-$ | 338.8 | $A\,^3\Pi–X\,^3\Sigma^-$ | 337 | $CH_4–N_2O$ [P] | Cop et al. 1989 [P] |
| | | | 338.2 | | 338 | $CH_4–O_2–Ar + N_2O$, NO,.. [P] | Wil & Fle 1994b [P] |
| | | | 336 | | 336 | $C_2H_2$, $C_2H_4–O_2–N_2 + NO$ [P] | Wil & Pas 1997 [P] |
| | ABS | $A\,^3\Pi–X\,^3\Sigma^-$ | 332.7 | Absorption | | $NH_3–O_2–N_2$ [P] | Cho et al. 1982 [P] |
| | DFWM | $A\,^3\Pi–X\,^3\Sigma^-$ | 333.1 | Scattered beam | | $NH_3–O_2–N_2$ [P] | Rak et al. 1990 [P] |
| | POL | $A\,^3\Pi–X\,^3\Sigma^-$ | 333.2–333.6 | Polarization change | | $NH_3–O_2$ [P] | Dre et al. 1995 [D] |

| Species | Method | Excitation | | Detection | | Flame | Reference |
|---|---|---|---|---|---|---|---|
| | | Transition | Wavelength (nm)[a] | Transition | Wavelength (nm) | Premixed [P] Diffusion [D] | Profile [P] Detection [D] Image [I] Spectroscopy [S] |
| | | | 333.6–336.2 | | | $NH_3$–$O_2$ [P] | Suv et al. 1995 [D] |
| | 2C-RFWM | $A\,^3\Pi$–$X\,^3\Sigma^-$ | 333.5–337.7 | Scattered beam | | $NH_3$–$O_2$ [P] | Rad et al. 1997 [D] |
| | CRD | $A\,^3\Pi$–$X\,^3\Sigma^-$ | 333.8 | Absorption | | $CH_4$–$O_2$–$N_2$ + $N_2O$ [P] | Der et al. 1999b [P] |
| NO | LIF, ABS | $A\,^2\Sigma^+$–$X\,^2\Pi_i$ | 236.7 | $A\,^2\Sigma^+$–$X\,^2\Pi_i$ | 258 | $NH_3$–$O_2$–$N_2$, $CH_4$-air [P] | Cho et al. 1983 [P] |
| | LIF | $A\,^2\Sigma^+$–$X\,^2\Pi_i$ | 214.3 | $A\,^2\Sigma^+$–$X\,^2\Pi_i$ | 252.2 | $H_2$–$O_2$–Ar + NO [P] | Cat et al. 1988 [P] |
| | | | 225.8 | | 235–250 | $CH_4$–air [P] | Hea et al. 1992 [P] |
| | | | 225.5 | | 234–237 | $C_2H_6$–$O_2$–$N_2$ [P] | Rei et al. 1993 [P] |
| | | | 225.5 | | 234–237 | $C_2H_6$–$O_2$–$N_2$ [P] | Rei & Lau 1994 [D] |
| | | | 226.0 | | 285–400 | $CH_4$–$O_2$–$N_2$ [P] | Bat & Han 1995 [I] |
| | | | 225.5 | | 239 | $CH_4$/air [D] | Smy 1996 [P] |
| | | | 225.9 | | 230–300 | $CH_4$–air [P] | Ngu et al. 1996 [P] |
| | | | 225.6 | | Several λ's | $CH_4$–$O_2$–$N_2$,Ar [P] | Par et al. 1996 [D] |
| | | | 225.95–226.15 | | 240–270 | $CH_4$–$O_2$–$N_2$ [P] | DiR et al. 1996 [I] |
| | | | 225.6 | | 234–237 | $CH_4$–$O_2$–$N_2$,Ar [P] | Tho et al. 1997 [D] |
| | | | 226.0 | | 228–273 | $CH_4$–$O_2$–$N_2$ [P] | Mok et al. 1997 [D] |
| | | | 226.4 | | 248 | $CH_4$/air + NO, $NH_3$ [D] | Sic et al. 1998 [P] |
| | | | 225.4 | | 245 | $CH_4$–$O_2$–$N_2$ + $CH_3Cl$.... [P] | Des et al. 1998 [P] |
| | | | 247.9 | | 226–260 | $CH_4$-air,$C_7H_{16}$-air [P] | Sch et al. 1999 [I] |
| | | | 225.5 | | 234–237 | $C_2H_6$ + $N_2$/air [D] | Rav et al. 1999 [P] |
| | | | 226 | | 245 | $CH_4$–$O_2$–$N_2$ [P] | Gas et al. 1999 [P] |
| | | | 225.5 | | 234–237 | $CH_4$/air, $C_2H_6$/air [D] | Rav & Lau 2000 [P] |
| | | | 225.6 | | 230–400 | $C_3H_6$–air + NO [P] | Ata & Har 2000 [P] |
| | | $D\,^2\Sigma^+$–$X\,^2\Pi_i$ | 193.0–193.7 | $D\,^2\Sigma^+$–$X\,^2\Pi_i$ | 208.0 | $C_3H_8$–$O_2$ [P] | Wod et al. 1988 [D] |
| | 1 + 1 REMPI | $A\,^2\Sigma^+$–$X\,^2\Pi_i$ | 270–317 | Electrons | | $H_2$–air–$N_2O$ [P] | Mal & Smy 1982 [D] |
| | 2 + 2 REMPI | $A\,^2\Sigma^+$–$X\,^2\Pi_i$ | 2 × 452 | Electrons | | $CH_4$–air [P] | Roc et al. 1982 [P] |
| | TDL | $\nu_0$ band | 1850–1925 $cm^{-1}$ | Absorption | | $CH_4$–air + NO [P] | Fal et al. 1983 [D] |
| | | (3,0) band | 5400–5650 $cm^{-1}$ | | | Cell | Son & All 1997 [D] |
| | Raman | $\nu_0$ band | ~ 1875 $cm^{-1}$ | Scattered light | | $H_2$–$N_2O$ [P] | Van et al. 1986 [P] |
| | DFWM | $A\,^2\Sigma^+$–$X\,^2\Pi_i$ | 226 | Scattered beam | | $H_2/O_2$ + $N_2$ [D] | Van et al. 1992a [S,D] |
| | | | | | | $CH_4$–$O_2$–$N_2$ [P] | Far & Rak 1999 [S,D] |
| | POL | $A\,^2\Sigma^+$–$X\,^2\Pi_i$ | 226.5–227.1 | Polarization change | | $H_2$–$N_2O$ [P] | Löf et al. 1996 [D] |
| NF | ICLAS | $b^1\Sigma^+$–$X\,^3\Sigma^-$ | 528 | Absorption | | Photolysis | Pod et al. 1997 [D] |

**Flame Measurements of Minor Species** *Continued*

| Species | Method | Excitation | | Detection | | Flame | Reference |
|---|---|---|---|---|---|---|---|
| | | Transition | Wavelength (nm)[a] | Transition | Wavelength (nm) | Premixed [P] Diffusion [D] | Profile [P] Detection [D] Image [I] Spectroscopy [S] |
| NS | LIF | $C\,^2\Sigma^+$-$X\,^2\Pi_i$ | 230–232 | $C\,^2\Sigma^+$-$X\,^2\Pi_i$ | 237.1 | $CH_4$–$N_2O$ + $SF_6$, ... [P] | Jef & Cro 1986 [D] |
| $NH_2$ | LIF | $\tilde{A}\,^2A_1$-$\tilde{X}\,^2B_1$ | 571–662 | $\tilde{A}\,^2A_1$-$\tilde{X}\,^2B_1$ | 516–824 | $NH_3$–$N_2O$, $O_2$ [P] | Cop et al. 1984 [D] |
| | | | 647.1 | | 540–550 | $NH_3$, $H_2$, $CH_4$–$N_2O$–$N_2$ [P] | Won et al. 1987 [P] |
| | | | 600 | | ? | $CH_4$, $CH_2O$–$NO_2$–$O_2$ [P] | Bra et al. 1991 [P] |
| | | | 598 | | > 620 | $CH_4$–$O_2$–Ar + N-fuels [P] | Wil & Fle 1997 [P] |
| | ABS | $\tilde{A}\,^2A_1$-$\tilde{X}\,^2B_1$ | 602.7 | Absorption | | $NH_3$–$O_2$ [P] | Gre & Mil 1981 [P] |
| | | | 598 | | | $NH_3$–$O_2$–$N_2$ [P] | Cho et al. 1982 [P] |
| | OA | $\tilde{A}\,^2A_1$-$\tilde{X}\,^2B_1$ | 630 | Pressure wave | | $NH_3$–$O_2$ [P] | Smi et al. 1983 [D] |
| | CARS | $\omega_1$-$\omega_2$ | 3220 $cm^{-1}$ | $\omega_3$ beam | | Photolysis | Dre & Wol 1984 [D] |
| | ICLAS | $\tilde{A}\,^2A_1$-$\tilde{X}\,^2B_1$ | 597.3 | Absorption | | $CH_4$–$O_2$–$N_2$ + $N_2O$ [P] | Der et al. 1999b [P] |
| $N_2O$ | TDL | $3\nu_3$ band | 6535–6600 $cm^{-1}$ | Absorption | | Cell | Mih et al. 1998a [S] |
| | | Several bands | 4922–5108 $cm^{-1}$ | | | Cell | Mih et al. 1998b [S] |
| HCN | LIF | $\tilde{A}\,^1A''$-$\tilde{X}\,^1\Sigma^+$ | 193.1, 194.0 | $\tilde{A}\,^1A''$-$\tilde{X}\,^1\Sigma^+$ | 200–285 | Cell | Bar 1979 [S] |
| | CRD | $\tilde{X}^1\Sigma^+$ overtones | 434–572 | Absorption | | Cell | Rom & Leh 1993 [S] |
| HNO | LIF | $\tilde{A}\,^1A''$-$\tilde{X}\,^1A'$ | 570–640 | $\tilde{A}\,^1A''$-$\tilde{X}\,^1A'$ | > 640 | Pyrolysis | Dix & Nob 1979 [S] |
| | | | 617.8–619.0 | | > 620 | Pyrolysis | Dix & Nob 1980 [S] |
| | ICLAS | $\tilde{A}\,^1A''$-$\tilde{X}\,^1A'$ | 618, 642–644 | Absorption | | $CH_4$–$O_2$–$N_2$ + $N_2O$ [P] | Loz & Che 2000 [D] |
| | | | 618, 642–644 | | | $CH_4$–$O_2$–$N_2$ + NO [P] | Loz et al. 2001 [P] |
| NCO | LIF | $\tilde{A}\,^2\Sigma^+$-$\tilde{X}\,^2\Pi_i$ | 465.8 | $\tilde{A}\,^2\Sigma^+$-$\tilde{X}\,^2\Pi_i$ | 430–443 | $CH_4$–$N_2O$ [P] | And et al. 1982b [P] |
| | | | 435–512 | | 435–465 | $CH_4$–$N_2O$ [P] | Cop et al. 1984 [D] |
| | | | 466.4 | | 440 | $CH_4$–$O_2$–Ar + $N_2O$, NO, ... [P] | Wil & Fle 1994b [P] |
| | | | 439 | | 466 | $C_2H_2$–$O_2$–$N_2$ + NO [P] | Wil & Pas 1997 [P] |
| | | $\tilde{B}\,^2\Pi$-$\tilde{X}\,^2\Pi_i$ | 314.7–315.2 | $\tilde{B}\,^2\Pi$-$\tilde{X}\,^2\Pi_i$ | 365 | $CH_4$–$N_2O$ [P] | Jef et al. 1986 [D] |
| NCN | LIF | $A\,^3\Pi_u$-$X\,^3\Sigma_u^-$ | 315–320 | $A\,^3\Pi_u$-$X\,^3\Sigma_u^-$ | 330–440 | Discharge | Smi et al. 1989 [S] |
| $NO_2$ | LIF | ? | 450–470 | ? | > 510 | $CH_4$–$O_2$–$N_2$–$NO_2$ [P] | Bar & Kir 1978 [D] |
| | | ? | 453 | ? | 500–600 | $CH_4$–$O_2$–$N_2$–$NO_2$ [P] | Wil & Fle 1995 [P] |
| | OA | ? | 485–520, 575–620 | Pressure wave | | $CH_4$-air + $NO_2$ [P] | Ten et al. 1982 [D] |

| Species | Method | Excitation | | Detection | | Flame | Reference |
|---|---|---|---|---|---|---|---|
| | | Transition | Wavelength (nm)* | Transition | Wavelength (nm) | Premixed [P] Diffusion [D] | Profile [P] Detection [D] Image [I] Spectroscopy [S] |
| | PTD | ? | 490 | Beam deflection | | $CH_4$–air + $CH_3NH_2$ [P] | Ros et al. 1982 [D] |
| | DFWM | $\tilde{A}\,^2B_1$–$\tilde{X}\,^2A_1$ | 474.4 | Scattered beam | | $C_3H_8$-air + $NO_2$ [P] | Man et al. 1992, 1996 [I] |
| $NH_3$ | MP-LIF | $\tilde{C}\,^1A_1'$–$\tilde{X}\,^1A_1$ | 2 × 305 | $\tilde{A}\,^1A_2''$-$\tilde{X}\,^1A_1$ | 720 | $NH_3$–$O_2$ [P] | Wes & Ald 1990a [P] |
| | DFWM | $\tilde{B}\,^1E''$, $\tilde{C}\,^1A_1'$-$\tilde{X}\,^1A_1$ | 2 × 302–308 | Scattered beam | | $NH_3$–$O_2$ [P] | Geo & Ald 1993 [D] |
| | POL | $\tilde{B}\,^1E''$, $\tilde{C}\,^1A_1'$-$\tilde{X}\,^1A_1$ | 2 × 307–310 | Polarization change | | $NH_3$–$O_2$ [P] | Nyh et al. 1995b [P] |
| | CARS | $\omega_1$–$\omega_2$ | 3334 $cm^{-1}$ | $\omega_3$ beam | | Cell | Dre & Wol 1984 [D] |
| | TDL | $\nu_2$ band | 925–928 $cm^{-1}$ | Absorption | | Cell | Nec & Wol 1989 [S] |
| | | $\nu_1 + \nu_4$, $\nu_3 + \nu_4$ | 5005–5047 $cm^{-1}$ | | | Cell | Mih et al. 1998b [D] |
| | | $\nu_1 + \nu_3$, $2\nu_3$ bands | 6529–6678 $cm^{-1}$ | | | Cell | Web et al. 2001 [D] |
| *(C) Halogen-Containing Species* | | | | | | | |
| HF | DFWM | (1,0), (3,0) bands | 870, 2500 | Scattered beam | | Cell | Van et al. 1992b [D] |
| CCl | LIF | $A\,^2\Delta$-$X\,^2\Pi$ | 270–285 | $A\,^2\Delta$-$X\,^2\Pi$ | 278.4 | $CH_4 + C_2H_5Cl$ + He/air [D] | McE et al. 1994 [P] |
| | | | 277.8 | | 278 | $CH_4$–$O_2$–$N_2$ + $CH_3Cl$, ... [P] | Dev et al. 1998 [P] |
| CF | LIF | $A\,^2\Sigma^+$–$X\,^2\Pi_i$ | 224 | $A\,^2\Sigma^+$-$X\,^2\Pi_i$ | 254 | $CH_4$–$O_2$ + $CHF_3$, ... [P] | Esp et al. 1997 [D] |
| | | | 223.3 | | 255 | $CH_4$–$O_2$ + $CHF_3$, ... [P] | Esp et al. 1999 [P] |
| CHF | LIF | $\tilde{A}\,^1A''$–$\tilde{X}\,^1A'$ | 492.4 | $\tilde{A}\,^1A''$-$\tilde{X}\,^1A'$ | > 515 | $CH_4$–$O_2$ + $CHF_3$, $CH_2F_2$ [P] | Esp et al. 1997 [D] |
| | | | 492.4 | | > 515 | $CH_4$–$O_2$ + $CHF_3$, $CH_2F_2$ [P] | Esp et al. 1999 [P] |
| $CF_2$ | LIF | $\tilde{A}\,^1B_1$-$\tilde{X}\,^1A_1$ | 233 | $\tilde{A}\,^1B_1$-$\tilde{X}\,^1A_1$ | 290 | $C_2F_4$–$O_2$ [P] | Dou et al. 1996 [P] |
| | | | 250 | | 334 | $CH_4$–$O_2$ + $CHF_3$, $CH_2F_2$ [P] | Esp et al. 1999 [P] |
| FCO | CRD | $\tilde{A}\,^2\Pi(A'')$–$\tilde{X}\,^2A'$ | 316–338 | Absorption | | Photolysis | How et al. 2000 [S] |
| $CF_2O$ | LIF | ($n, \pi^*$) system | 216 | ($n, \pi^*$) system | ? | $C_2F_4$–$O_2$ [P] | Dou et al. 1996 [P] |
| | | | 211.0 | | 330–410 | $C_2F_4$–$O_2$ [P] | Esp et al. 1997 [D] |
| | TDL | $\nu_4$ band | 1250–1275 $cm^{-1}$ | Absorption | | $CH_4$–$O_2$–Ar + $CF_3Br$, ... [P] | Dan et al. 1996 [P] |
| $CF_4$ | TDL | $\nu_3$, $2\nu_4$ bands | 1250–1280 $cm^{-1}$ | Absorption | | $CH_4$–$O_2$–Ar + $CF_3Br$, ... [P] | Dan et al. 1996 [P] |
| $CF_3H$ | TDL | $\nu_2$ band | 1075–1100 $cm^{-1}$ | Absorption | | $CH_4$–$O_2$–Ar + $CF_3Br$, ... [P] | Dan et al. 1996 [P] |
| $CF_2H_2$ | TDL | $\nu_3$ band | 1075–1120 $cm^{-1}$ | Absorption | | $CH_4$–$O_2$–Ar + $CF_3Br$, ... [P] | Dan et al. 1996 [P] |

**Flame Measurements of Minor Species** *Continued*

| Species | Method | Excitation | | Detection | | Flame | Reference |
|---|---|---|---|---|---|---|---|
| | | Transition | Wavelength (nm)* | Transition | Wavelength (nm) | Premixed [P] Diffusion [D] | Profile [P] Detection [D] Image [I] Spectroscopy [S] |
| *(D) Other Species* | | | | | | | |
| Ar | 3 + 1 REMPI | $3p^5 4s4s' - 3p^6\ ^1S$ | 3 × 314.4 | Electrons | | $CH_4$/air [D] | Smy & Tjo 1990b [P] |
| Si | 2 + 1 REMPI | $4p^3P - 3p^2\ ^3p$ | 2 × 406–410 | Electrons | | $H_2 + Ar + SiH_4/O_2 + Ar$ [D] | Zac & Jok 1990 [P] |
| PO | LIF | $B^2\Sigma^+ - X^2\Pi_r$ | 324–327 | $B^2\Sigma^+ - X^2\Pi_r$ | 325.0 | Discharge | And et al. 1984 [D,S] |
| | | $A^2\Sigma^+ - X^2\Pi_r$ | 245.6–247.8 | $A^2\Sigma^+ - X^2\Pi_r$ | 240 | Discharge | Won et al. 1986 [D] |
| | 1 + 1 REMPI | $B^2\Sigma^+ - X^2\Pi_r$ | 302–334 | Electrons | | $C_2H_2$–air [P] | Smy & Mal 1982 [S] |
| $S_2$ | LIF | $B^3\Sigma_u^- - X^3\Sigma_g^-$ | 296.0 | $B^3\Sigma_u^- - X^3\Sigma_g^-$ | 302.5 | $H_2$–$O_2$–$N_2 + H_2S$ [P] | Mul et al. 1979 [P] |
| | DFWM | $B^3\Sigma_u^- - X^3\Sigma_g^-$ | 309.6 | Scattered beam | | $C_3H_8$–air + $SO_2$ [P] | Mis et al. 1996 [P] |
| | | | 309.6 | | | $H_2$–air + $SO_2$ [P] | Rad et al. 1999 [P] |
| SH | LIF | $A^2\Sigma^+ - X^2\Pi_i$ | 323.7 | $A^2\Sigma^+ - X^2\Pi_i$ | 328.0 | $H_2$–$O_2$–$N_2 + H_2S$ [P] | Mul et al. 1979 [P] |
| SO | LIF | $B^3\Sigma^- - X^3\Sigma^-$ | 266.5 | $B^3\Sigma^- - X^3\Sigma^-$ | 283.4 | $H_2$–$O_2$–$N_2 + H_2S$ [P] | Mul et al. 1979 [P] |
| SiO | LIF | $A^1\Pi - X^1\Sigma^+$ | 227.5–232.9 | $A^3\Pi - X^3\Sigma^-$ | 232 | $CH_4$–$O_2$ + $SiCl_4$ [P] | Hyn 1991 [S] |
| | | | 231.0 | | 237 | $H_2 + Ar + SiH_4/O_2 + Ar$ [D] | Zac & Bur 1994 [P] |
| | | | 231 | | 238 | $H_2$–$O_2$ + HMDS [P] | Glu 2001 [P] |
| $SO_2$ | LIF | $\tilde{A}\ ^1B_1 - \tilde{X}\ ^1A_1$ | 266.5 | $\tilde{A}\ ^1B_1 - \tilde{X}\ ^1A_1$ | 279.3 | $H_2$–$O_2$–$N_2 + H_2S$ [P] | Mul et al. 1979 [P] |

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