TECHNISCHE UNIVERSITÄT MÜNCHEN Lehrstuhl für Energiesysteme

Validation of spectral gas radiation models under oxyfuel conditions

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Abstract

Combustion of hydrocarbon fuels with pure oxygen results in a different flue gas composition than combustion with air. Standard computational-fluid-dynamics (CFD) spectral gas radiation models for air combustion are therefore out of their validity range in oxyfuel combustion. This thesis provides a common spectral basis for the validation of new spectral models. A literature review about fundamental gas radiation theory, spectral modeling and experimental methods provides the reader with a basic understanding of the topic. In the first results section, this thesis validates detailed spectral models with high resolution spectral measurements in a gas cell with the aim of recommending one model as the best benchmark model. In the second results section, spectral measurements from a turbulent natural gas flame - as an example for a technical combustion process - are compared to simulated spectra based on measured gas atmospheres. The third results section compares simplified spectral models to the benchmark model recommended in the first results section and gives a ranking of the proposed models based on their accuracy. A concluding section gives recommendations for the selection and further development of simplified spectral radiation models.

Gas cell transmissivity spectra in the spectral range of $2.4 - 5.4 \,\mu\text{m}$ of water vapor and carbon dioxide in the temperature range from 727 °C to 1500 °C and at different concentrations were compared in the first results section at a nominal resolution of $32 \,\text{cm}^{-1}$ to line-by-line models from different databases, two statisticalnarrow-band models and the exponential-wide-band model. The two statisticalnarrow-band models EM2C and RADCAL showed good agreement with a maximal band transmissivity deviation of 3%. The exponential-wide-band model showed a deviation of 6%. The new line-by-line database HITEMP2010 had the lowest band transmissivity deviation of 2.2% and was therefore recommended as a reference model for the validation of simplified CFD models. In the second results section, spectral measurements $(2.4 - 5.4 \,\mu\text{m})$ of a 70 kW turbulent natural gas flame in air blown combustion and in wet and dry oxyfuel combustion were compared with simulated spectra based on measured gas atmospheres. The line-by-line database HITEMP2010 and the two statistical-narrow-band models EM2C and RADCAL were used for the numerical simulation. The measured spectra showed large fluctuations due to turbulence. The averaged experimental intensity was found to be up to 75 % higher than the simulated intensity, thus demonstrating the importance of the effect of turbulence-radiation-interaction in combustion simulations.

Finally, total emissivities were calculated with the most common spectral models and compared with benchmark calculations by the detailed spectral line-by-line model HITEMP2010. The models were compared at path lengths ranging from 0.001 m to 100 m and at temperatures from 800 °C to 1800 °C for atmospheres of pure gases and of various combustion processes (air blown and oxyfuel combustion with wet and dry recirculation) as well as with different fuels (natural gas, brown coal and anthracite). The statistical-narrow-band models RADCAL and EM2C, the exponential-wide-band model and the statistical-line-width model were chosen as models, which are valid for oxyfuel combustion without modifications. A number of weighted-sum-of-grey-gases models from different authors were chosen as computationally efficient models especially developed for oxyfuel combustion. The statisticalnarrow-band model EM2C had the highest accuracy with maximum deviations of up to 12 %. The weighted-sum-of-grey-gases model for computationally efficient simulations of spectral gas properties with an overall accuracy of 21 % or better.

Zusammenfassung

Die Verbrennung von Kohlenwasserstoffen mit reinem Sauerstoff (Oxyfuelverbrennung) resultiert in einer anderen Rauchgaszusammensetzung als bei der Verbrennung mit Luft. Die normalen spektralen Gasstrahlungsmodelle für Computational Fluid Dynamics (CFD) Berechnungen, die für die Verbrennung mit Luft verwendet werden, sind für Oxyfuel-Verbrennung nicht mehr gültig. Diese Arbeit schafft die Grundlage für eine vergleichbare Validierung von neuentwickelten Gasstrahlungsmodellen. Der Literaturüberblick erläutert die theoretischen Grundlagen der Strahlung, die verschiedenen Modellierungsansätze und die experimentellen Messmethoden. Im ersten Ergebniskapitel werden verschiedene detaillierte Modelle anhand spektraler Messungen in einer Gaszelle validiert, um ein detailliertes Modell als Referenz für die Validierung einfacher Strahlungsmodelle zu bestimmen. Das zweite Ergebniskapitel vergleicht spektrale Messungen an einer turbulenten Erdgasflamme mit auf Grundlage gemessener Gasatmosphären modellierten Spektren, um Auswirkungen realer Verbrennungsvorgänge aufzuzeigen. Das dritte Ergebniskapitel vergleicht einfache Spektralmodelle mit dem detaillierten Referenzmodell und listet die einfachen Modelle in Abhängigkeit ihrer Genauigkeit.

Spektrale Messungen im Bereich von $2.4 - 5.4 \,\mu\text{m}$ bei Temperaturen von $727 \,^{\circ}\text{C}$ bis 1500 °C und verschiedenen Konzentrationen von CO₂ und H₂O wurden im ersten Ergebniskapitel bei einer nominalen Auflösung von $32 \,\text{cm}^{-1}$ verglichen mit Linienmodellen basierend auf verschiedenen Datenbanken, zwei Statistical-Narrow-Band Modellen und dem Exponential-Wide-Band Modell. Die beiden Statistical-Narrow-Band Modelle EM2C und RADCAL zeigten eine gute Übereinstimmung mit einer maximalen Abweichung der Bandtransmissivitäten von 3%. Das Exponential-Wide-Band Modell zeigte eine maximale Abweichung von 6%. Das Linienmodell mit der Datenbank HITEMP2010 zeigte die geringsten Abweichungen von 2.2% und wurde als Referenzmodell für die Validierung von einfachen Strahlungsmodellen empfohlen. Im zweiten Ergebniskapitel wurden spektrale Messungen $(2.4 - 5.4 \,\mu\text{m})$ einer turbulenten Erdgasflamme mit einer thermischen Leistung von 70 kW unter verschiedenen Bedingungen (Verbrennung mit Luft und Oxyfuelverbrennung mit nasser und trockener Rezirkulation) verglichen mit auf der Grundlage von gemessenen Gasatmosphären simulierten Spektren. Das Linienmodell mit der Datenbank HITEMP2010 und die beiden Statistical-Narrow-Band Modelle EM2C und RADCAL wurden für die Simulation verwendet. Die gemessenen Spektren zeigten große Fluktuationen aufgrund der Turbulenz in der Flamme. Die durchschnittlich emittierte Strahlungsintensität war bis zu 75 % höher als die simulierten Werte. Diese Tatsache zeigte die Bedeutung des Einflusses der Turbulenz auf die korrekte Berechnung der emittierten Strahlung bei Verbrennungssimulationen auf.

Im letzten Ergebniskapitel wurden Totalemissivitäten berechnet mit den gebräuchlichsten Strahlungsmodellen und verglichen mit den Ergebnissen des Referenzlinienmodelles HITEMP2010. Die Modelle wurden verglichen für Weglängen von 0.001 m bis 100 m und bei Temperaturen von 800 °C bis 1800 °C für reine Gase und für Rauchgase von verschiedenen Verbrennungsprozessen (Verbrennung mit Luft und Oxyfuelverbrennung mit nasser und trockener Rezirkulation) und von verschiedenen Brennstoffen (Erdgas, Braun- und Steinkohle). Die Statistical-Narrow-Band Modelle RADCAL und EM2C, das Exponential-Wide-Band Modell und das Statistical-Line-Width Modell wurden ausgewählt, da sie auch für die Oxyfuelverbrennung gültig sind. Verschiedene Weighted-Sum-of-Grey-Gases Modelle wurden ausgewählt als numerisch effiziente Strahlungsmodelle, die speziell für Oxyfuelverbrennung entwickelt wurden. Das Statistical-Narrow-Band Modell EM2C zeigte die beste Genauigkeit mit maximal 12 % Abweichung. Das Weighted-Sum-of-Grey-Gases Modell von Johansson et al. [64] ergab die besten Ergebnisse der numerisch effizienten Modelle mit Abweichungen von maximal 21 %.

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List of Symbols

α	Integrated band intensity, page 36
β	Mean line width-to-spacing parameter, page 36
q	Heat flux vector, page 22
v	Velocity vector, page 22
$\Delta \omega$	Spectral resolution of the acquired spectrum $[cm^{-1}]$, page 53
δ	Mean spacing between two consecutive lines in a narrow band, page 33
δ_{air}	Air-broadened pressure shift $[cm^{-1}/atm]$, page 30
\dot{Q}	Heat source due to chemical reactions, page 22
ϵ	Emissivity [–], page 27
γ	Spectral line half width due to pressure/collisional broadening $[cm^{-1}/atm]$, page 19
λ	Wavelength $[\mu m]$, page 7
μ	Dynamic viscosity $[kg/ms]$, page 22
ν	Frequency [Hz], page 7
Ω	Maximum solid angle for collimation of light in FTIR [sr], page 55
ω	Wavenumber $[cm^{-1}]$, page 7
$\overline{\beta}$	Statistical degree of line overlapping = $2\pi\overline{\gamma}/\overline{\delta}$ [–], page 34
\overline{k}	Statistical line intensity $= \frac{\overline{S}}{\delta} [\mathrm{cm}^{-1} \cdot \mathrm{atm}^{-1}], \mathrm{page} 34$
Φ	Dissipation function, page 22
ρ	Density of the medium $[kg/m^2]$, page 22
σ	Mean line intensity in narrow band, page 33
σ	Stefan Boltzmann constant $\sigma = 5.670\cdot 10^{-8}\mathrm{W/m^2K^4},$ page 44
τ	Transmissivity [–], page 27
$ au_H$	Optical thickness / optical depth at band head, page 37
Θ	Optical throughput $[m^2 sr]$, page 55

θ	Phase Angle, page 58
ξ	Efficiency of the optical system [–], page 56
A	Absorbance, page 47
A	Area $[m^2]$, page 56
a	Empirical constant for soot absorption [-], page 13
a	Particle radius [m], page 11
A(OPD)	Apodization function, page 58
a_{ϵ}	Emissivity weighting factor, page 42
A_{ji}	Einstein probability coefficient for spontaneous emission for the molec-
	ular transition from upper energy state j to lower energy state i ,
	page 17
В	Phase corrected spectrum after Fourier transform, page 58
B'	Complex phase curve, the result of the Fourier transform of an inter-
	ferogram, page 58
b_{ϵ}	Emissivity gas temperature polynomial coefficient, page 39
B_{ij}	Einstein probability coefficient for absorption at the molecular tran-
U U	sition from lower energy state i to higher energy state j , page 17
B_{ji}	Einstein probability coefficient for induced emission for the molecular
	transition from upper energy state j to lower energy state i , page 17
C	Empirical constant for soot absorption [-], page 13
c	Clearance between two neighbouring particles [m], page 11
c	Speed of light = speed of light in vacuum = $2.99792458 \times 10^8 \text{ m/s}$,
	page 7
c_2	Second radiation constant $=1.4388 \mathrm{cm}\mathrm{K}$, page 31
c_v	Specific heat at constant volume $[kJ/kgK]$, page 23
C_{abs}	Absorption cross section $[mol/m^2]$, page 44
d	Diameter [m], page 55
d	Line spacing ratio, page 35
D^*	Specific detectivity $[\text{cm}\text{Hz}^{1/2}\text{W}^{-1}]$, page 53
E	Energy [J], page 7
E	Energy $[cm^{-1}]$, page 30
f	Factor [–], page 58
f_l	Focal distance of lens [m], page 55
f_v	Volume density [-], page 12

g	Statistical weight / degeneracy of a molecular energy level, i.e. the
	number of different arrangements with which a molecule can obtain
	this energy level, page 18
h	Planck's constant = $6.62526069 \times 10^{-34} \mathrm{J\cdot s}$, page 7
Ι	Radiation intensity per unit solid angle $[W/m^2 \cdot sr]$, page 9
j	Rotational quantum number, page 15
K	Total number of bands, page 38
k	Absorption coefficient $[1/m]$, page 29
k	Absorptive index [-], page 11
k_B	Boltzmann constant = $1.3806503 \times 10^{-23} \text{ J/K}$, page 9
k_t	Thermal conductivity $[W/mK]$, page 23
L	Total number of spectral intervals, page 38
M	Number of lines in narrow band, page 32
M	Number of resolution elements in the spectrum, page 52
m	Complex index of refraction [-], page 11
N	Molar density of absorbing gas molecules $[mol/m^3]$, page 44
N	Number of molecules per unit volume $[1/m^3]$, page 17
n	Coefficient of temperature dependence of the air-broadened half width
	[–], page 30
n	Refractive index [-], page 11
OPD	Optical path distance / retardation [m], page 53
Р	Probability distribution function, page 33
p	Pressure [bar], page 30
Q	Total internal partition sum, page 31
R	Maximum to minimum line intensity ratio, page 34
$R(\omega)$	Response function of optical system, page 59
R_g	Universal gas constant $R_g = 8.314472 \mathrm{J/molK}$, page 44
S	Line-integrated absorption coefficient / line intensity $[cm^{-1}/(molecule cm^{-2})]$,
	page 21
s	Path length [m], page 27
T	Temperature [K], page 9
t	Time [s], page 22
U	Voltage [V], page 56
u	Internal energy [J], page 22

V	Volume $[m^3]$, page 42
v	Vibrational quantum number, page 15
W	Equivalent black line-width, page 33
X	Absorber density path length product $[g m^{-2}]$, page 37
x	Molar fraction/volume concentration of species [–], page 35
x	Relative particle size [–], page 11

Subscripts

0	Property at wall / start of line-of-sight, page 114
λ	Property at specific wavelength, page 27
ν	Property at specific frequency, page 21
ω	Property at specific wavenumber, page 19
abs	Property of absorbing gases, page 36
air	air-broadened state, page 30
b	Property of a black body, page 9
band	Property of spectral band, page 75
C	Due to conduction, page 23
С	Property at the spectral line center, page 19
CBB	Cold black body in the background, page 72
corr	Corrected value, page 58
D	Detector property, page 56
e	Electronic quantum number, page 15
gas	Property of gas mixture, page 72
HBB	Hot black body in the background, page 70
i	Molecular quantum state i, page 13
i	Property of intermediate cell in the line of sight, page 115
i	Property of specific band, page 38
i	Property of specific spectral interval, page 37
i	Transition property of lower state, page 30
j	Molecular quantum state j, page 13
j	Transition property of upper state, page 30
k	Property of molecule/species, page 32
l	Property of spectral line/transition, page 31
linewidth	Property of absorption coefficient line width, page 74
loc	Local property / property in line-of-sight cell, page 46
lower	Property of lower band head, page 36
m	Property of molecule isotope, page 31
max	Maximum value, page 34
n	Property of last cell in the line of sight, page 115
par	Partial property, page 31
R	Due to Radiation, page 23

r	Rotational quantum number, page 15
ref	Reference state, page 30
sb	Property of self-broadening effect, page 44
self	Self-broadened state $[cm^{-1}/atm]$, page 30
symmetrical	Property of symmetrical band head, page 36
Т	Property at temperature T [K], page 72
t	Translational quantum number, page 15
tot	Total property, page 27
TRI	Property of turbulence/radiation interaction, page 25
upper	Property of upper band head, page 36
v	Vibrational quantum number, page 15
w	Property of band width, page 36
wall	Property of wall, page 114
WSGG	Property of WSGG model formulation, page 42
ZPD	Property with regard to the point of Zero Point Distance, page 56

List of abbreviations

3D	Three dimensional
ALBDF	Absorption line black body distribution function
CCS	Carbon capture and storage
CFD	Computational fluid dynamic
DC	Direct current
DLATGS	Deuterated lanthanum triglycine sulfate detector
DTGS	Deuterated triglycine sulfate detector
EWB	Exponential-wide-band model
FFT	Fast Fourier transform
FTIR	Fourier-transform infrared spectrometer
IFRF	International Flame Research Foundation
ILS	Instrumental line shape function
LBL	Line-by-line model
LTE	Local thermodynamic equilibrium
MCT	Mercury cadmium telluride detector
n.s.	not specified
OPD	Optical path difference
RTE	Radiative-transfer-equation
SLW	Statistical-line-width model
SNB	Statistical-narrow-band model
SNR	Signal-to-noise ratio
TRI	Turbulence-radiation interaction
WBCK	Wide-band-correlated-k model
WSGG	Weighted-sum-of-grey-gases model
ZPD	Zero path distance

Chapter 1

Introduction

Since the last century, the human population has grown exponentially due to the extremely fast rate of technological development. The effects of increased mechanization and the growth in productivity increased the economic output especially with regard to the production of food. This development has enabled the worlds population to grow while at the same time it has increased the overall material wealth of the people in the industrialized countries.

The economic growth began with the industrialization in the 19th century coupled with the development of new technologies, which enabled the people to exploit fossil resources such as ore, oil, gas and coal more efficiently. Todays level of prosperity and technology is based on the consumption of these non-renewable resources, where the current level of consumption cannot be sustained indefinitely in the future.

The consumption of resources such as oil, gas and coal have the additional negative effect of releasing large amounts of carbon dioxide into the atmosphere, which was previously chemically bound in the crust of the earth [61]. There is evidence that the climate system of our planet is increasingly affected by this man made increase of CO_2 concentration in the atmosphere, based on a pre-industrial value of about 280 ppm to the 390 ppm measured in 2010 [84, 114]. The measured increase of the average surface temperatures over the last decades can be explained by the higher radiative forcing on the earth's surface, which in turn is caused by the rising CO_2 and other greenhouse gas concentrations in the atmosphere [84].

The renewable energy technologies currently available are not yet able to satisfy the energy needs of the world's growing population and fossil energy use will be neccessary for some time. To mitigate the release of carbon dioxide from fossil power generation, the concept of carbon capture and storage (CCS) is under development, i.e. capturing and storing the carbon dioxide underground instead of releasing it into the atmosphere.

Three main technologies are currently in the process of development in order to apply CCS to power generation from fossil fuels [107]:

- 1. Pre-combustion
- 2. Post-combustion
- 3. Oxyfuel-combustion

The difference between the three technologies is the point in the process, where the oxidized carbon is separated (figure 1.1). The pre-combustion process consists of a gasification step before the combustion. The fuel is decomposed into its gaseous components (H_2, CO_2) and the CO_2 is separated. The remaining hydrogen diluted with nitrogen is combusted to water in a combined cycle power plant. The postcombustion process consists of a conventional combustion process and a downstream separation of CO_2 from the flue gases with the help of large washing columns. In the oxyfuel process the combustion air is separated into oxygen and nitrogen and the fuel is combusted with pure oxygen. The resulting flue gas is a mixture of carbon dioxide and water. The latter is condensed to get a carbon dioxide stream for storage. The combustion of the fuel occurs in a $CO_2/O_2/H_2O$ atmosphere not diluted with nitrogen as in air blown combustion. The exact gas composition in the furnace depends on the fuel type (or its combustion products) and the recirculation type (wet or dry flue gas recirculation / figure 1.1). For a new and thorough view of all fields of combustion science however a different perspective is necessary. A lot of research has been done over the last years in this field and quite a few reviews are available [16, 23, 32, 66, 77, 113, 119, 123, 124].

The timescale for the development of the oxyfuel technology from lab scale to full-scale power plants has to be extremely short compared with the mostly empirical development process of today's full scale power plants in order to reach the ambitious carbon dioxide reduction targets. In a pulverized coal furnace, over 50 % of the energy is transmitted via radiative exchange from the hot flames, particles and gases to the surrounding water membrane walls cooled by water evaporation. The convective transfer of heat is responsible for the smaller part of the transmitted energy in high temperature processes [121, p. ix]. The ability to make exact calculations of the radiative exchange is therefore a prerequisite for the successful design and development of large scale oxyfuel boilers and plants in the very near future. While the radiative properties of the particles (soot, coal, char and fly ash) do not differ to air blown combustion - only the particle densities might change the radiative properties of the furnace gases are significantly different compared to air blown combustion and are in the focus of this work.

1.1 Thesis structure

In this thesis, the changed radiative properties of the furnace gases were looked into more closely and new spectral models developed for the oxyfuel combustion process were validated. First an overview of the spectral radiation properties of gases and particles is presented in the literature review chapter. Based on a basic description of photon-gas-molecule interactions, the different spectral gas radiation models are explained as proposed in the literature. These models span from very detailed models, which account for every line in the spectrum and are based on large databases containing the properties of every spectral line, to more simplified models which calculate the average intensity over a narrow or wide band, to the most simplistic models with only a single value for the full spectrum. The experimental methodologies available for the measurement of the spectral radiative properties of gases are explained in more detail. After an overview of high temperature gas cell measurements and published modeling work concerning spectral gas radiation in oxyfuel combustion, the literature review section finishes with the objective of the work presented in this thesis, the validation of spectral gas radiation models under oxyfuel conditions.

Based on the knowledge gained from the literature review, experiments and simulations with spectral models are described in the following chapters. Chapter 3 describes the experiments in the hot gas cell and the validation of the detailed reference models. One model is recommended as a reference model. Experiments with turbulent natural gas flames are presented in chapter 4 together with numerical simulations of the spectral radiation. The final validation of the simplified models with the reference model from chapter 3 is presented in chapter 5.

The results are concluded in the last chapter of the thesis. The importance of the right choice of a spectral gas radiation model in oxyfuel combustion is emphasized

Pre-combustion



Figure 1.1: Technologies for the capture of carbon dioxide from fossil fuel power generation; (1) wet flue gases are recirculated; (2) dry flue gases are recirculated.

and a specific simplified model is recommended for use in large scale 3D furnace simulations.
Chapter 2

Literature review

2.1 Radiation fundamentals

In this first section of the literature review I describe the basic physical processes involved in the exchange of radiative energy. The focus is on the physics relevant to gas-molecule photon interactions. A more detailed treatment of radiation can be found in the text books from Viskanta [121], Modest [82] or Bernath [10], which were the basis for the following description.

Radiative energy exchange is the emission of photons from a source into space and vice versa. A source is any atom or molecule with a temperature higher as 0 K. A photon possesses the energy $h\nu$. The energy of two photons differs only, if the frequency ν is different as h is constant (Planck's constant $h = 6.626 \times 10^{-34} \,\mathrm{J} \cdot \mathrm{s}$). Every photon can also be seen as an electromagnetic wave traveling in space, the so called *duality of light* [50, 121]. Therefore the energy of a photon E can be expressed in different units.

$$E = h\nu = hc\,\omega = \frac{hc}{\lambda} \tag{2.1}$$

where E is the energy of the photon, $\omega = \nu/c = 1/\lambda$ is the wavenumber and $\lambda = c/\nu = 1/\omega$ is the wavelength. The speed of light c has in gases approximately the same value as in vacuum ($c = 2.99792458 \times 10^8 \text{ m/s}$).

Photons/electromagnetic waves with different frequencies constitute the full electromagnetic spectrum (see figure 2.1). Only the range from $0.1 \,\mu\text{m}$ to $100 \,\mu\text{m}$ is of interest for thermal radiation. Thermal radiation is defined as a method of production of radiation, where the photons are emitted by ions, electrons and molecules



Figure 2.1: Electromagnetic spectrum [121, p. 5].

excited by temperature, the nature of the matter does not change and the radiation stays constant if the temperature is kept constant by the addition of heat. The thermal radiation spectral range includes part of the ultraviolet, all visible and part of the infrared spectrum [121, p. 6].

2.1.1 Black body radiation

A body that absorbs all incoming thermal radiation is called a black body. If the black body is at thermal equilibrium with its surroundings, it emits the same energy as it absorbs. The spectral distribution of the emitted thermal energy of a black body (figure 2.2 and 2.3) can be described by Planck's blackbody function [90, 121]:

$$I_{b\lambda}(T) = \frac{2c^2 h/\lambda^5}{e^{hc/\lambda k_B T} - 1}$$
(2.2)



Figure 2.2: Black body emission spectra vs. wavelength, adapted from [121, p. 35].

where $I_{b\lambda}(T)$ is the emitted thermal energy (intensity) of the black body at a specific wavelength λ , in a specific unit angle and at a specific black body temperature T. k_B is the Boltzmann constant ($k_B = 1.3806503 \times 10^{-23} \text{ J/K}$). The refractive index is assumed to be equal to one for gases and is here neglected [121, p. 34].

As no body or molecule can emit more radiative energy as a black body, the emitted energy of any body can be expressed by a fraction of the emission of a black body at the same temperature.

$$I_{\lambda} = \frac{I_{\lambda}}{I_{b}\lambda} \cdot I_{b\lambda} = \epsilon_{\lambda} \cdot I_{b\lambda}$$
(2.3)

where I_{λ} is the emitted thermal energy of any body at a specific wavelength λ and ϵ_{λ} the emissivity at the specific wavelength λ [82, p. 64].

If the emissivity is not dependent on the wavelength, the body is called *grey* and the emitted thermal energy at a specific wavelength can be calculated with the well known black body intensity as

$$I_{\lambda} = \epsilon \cdot I_{b\lambda} \tag{2.4}$$

This simplification is widely used for the calculation of thermal radiation exchange for engineering purposes.



Figure 2.3: Black body emission spectra vs. wavelength (log.), adapted from [121, p. 35].

2.1.2 Photon - particle interaction

If a photon interacts with a particle, i.e. large solid particles as fly ash but also small particles as gas molecules, it is absorbed or scattered into another direction with a certain probability. Scattering into another direction in space occurs due to three different phenomena (figure 2.4) [82, p. 362]:

Reflection The photon is reflected of the particle sphere.

- **Refraction** The photon penetrates into the particle, is partly absorpted and reemerges out of the particle into a different direction.
- **Diffraction** The direction of propagation of the photon is altered due to the presence of the particle.

Most of the times, the photon is on the same energy level after the interaction with the particle as before (*elastic scattering*). Very seldomly, the energy is after the interaction less as before (*inelastic scattering*). This *Raman scattering* is not important for heat transfer and therefore here neglected, but is used for optical dignostic purposes [82, p. 362].



Figure 2.4: Interaction between photons and spherical particles [82, p. 362]

The effects of the vicinity of multiple particles on a single photon is called *dependent scattering*. In almost all combustion heat transfer applications, the particles are far enough apart, that there is no interaction of multiple particles on a single photon and we can speak of *independent scattering* [82, p. 362]. The effect of particle clouds is therefore simply additive of the effects of single particle scattering [82, p. 368].

Four particle properties are important for the calculation of scattering effects:

- 1. The **particle shape** is in most radiative calculations assumed to be spherical. This assumption has been shown to be a good average of all millions of particles in a particle cloud [82, p. 361].
- 2. The **particle size** x is expressed relative to the wavelength λ of the incoming photons (figure 2.4)

$$x = \frac{2 \cdot \pi \cdot a}{\lambda} \tag{2.5}$$

where a is the radius of the particle.

- 3. The **particle density** is expressed as clearance-to-wavelength ratio c/λ .
- 4. The material properties are accounted for in the **complex index of refrac-tion**

$$m(\lambda, T) = n - i k \tag{2.6}$$

where n is the refractive index and k the absorptive index. The complex index of refraction m is a function of the wavelength λ , the temperature T and the material. An additional complexity bring inhomogenities in the particle for example in fly ash particles from coal combustion. There exists only limited data about the complex index of refraction for particles within coal combustion atmospheres. The temperature dependence of the property is still unknown [82, p. 395].

The relative particle size x is the most important parameter for the calculation of the scattering effect. Independent scattering $(c/\lambda \gg 1)$ is assumed in the following treatment relevant for combustion applications [82, p. 362f].

The scattering of large particles $(x \gg 1 \text{ and } kx \gg 1)$ is calculated by the principles of geometric optics. In coal combustion are generally no large particles.

The scattering of particles with sizes similar to the wavelength of the incoming radiation ($x \approx 1$) is calculated with the Mie theory [79]. Coal, char and fly ash particles in coal combustion fall into this category. The exact calculation is quite complex and simplified models are used in 3D furnace calculations. Details about the mathematical principles are explained by Modest [82, p. 362f] and Viskanta [121, p. 112f].

If the particle size is much smaller than the incoming radiation ($x \ll 1$), the scattering and absorption can be calculated by the Rayleigh theory [91]. Soot particles as well as gas molecules fall into this regime in coal combustion. Soot particles are so small, that they have generally nearly the same temperature as the surounding gas [82, p. 398]. Their emitted radiation is visible to the human eye as they emit over a broad range of wavelengths. The luminosity of a flame is therefore an indication of the amount of soot existing and the flame temperature. The scattering effect is very minor compared to the absorption effect [82, p. 373], which is inverse proportional to the wavelength

$$\kappa_{\lambda} \propto \frac{1}{\lambda} \propto \nu$$
(2.7)

It was shown, that the absorption of particles in the Rayleigh regime is not dependent on the particle size, but only on the volume density of the particles f_v [82, p. 374]. In the literature, the absorption of soot particles is frequently described as

$$\kappa_{\lambda} = \frac{C \cdot f_v}{\lambda^a} \tag{2.8}$$

where C and a are empirical constants [82, p. 399][121, p. 130f].

The effect of scattering can be neglected for heat transfer calculations of gases as the gaseous molecules are very small $(x \to 0)$ and the application of the Rayleigh theory results in negligible scattering effects [82, p. 373].

As only the radiation behaviour of gas molecules is in the focus of this thesis, the radiation behaviour of larger particles is not look at in the following parts.

2.1.3 Photon - gas molecule interactions

The explanations in this section are based on Viskanta [121, p. 71ff]. In the following only bound-bound transitions are described, i.e. the molecule binding after the interaction with a photon does not break up. Bound-free and free-free transitions occur if the gases dissociate and get ionized. Significant dissociation of combustion gases occurs at temperatures over $1200 \,\mathrm{K}$ and has a significant effect (> 0.3 %) on the caloric properties [1, p. 19]. The bound-free and free-free transitions result in a continuum radiation in the ultraviolet and visible wavelength. The bound-bound transitions result in radiation in the infrared $(> 1 \,\mu\text{m})$. As the peak of the black body radiation lies in the infrared for temperatures less than 2624 °C (equation 2.2 and figure 2.3), the bound-bound transitions are most important for combustion processes in lower temperature ranges (< 2000 °C) [82, p. 290]. In high temperature ranges - as occur in oxyfuel combustion with high oxygen content - the bound-free and free-free transitions have to be accounted for. The author found evidence of this importance in an earlier article in the increasing luminosity of natural gas oxyfuel flames in the visible range with increasing oxygen content without finding evidence for continuus soot radiation in the near infrared [8, p. 1550].

A photon with the energy $h\nu$ can interact with a gas molecule in three different ways (figure 2.5):

- Absorption: The photon is absorbed by the molecule and the energy of the photon $h\nu$ increases the energy of the molecule from energy level E_i to energy level E_j . The molecule is in an excited state after the absorption process.
- Stimulated emission: The excited molecule emits a photon, if it is stimulated by another photon. The photon is emitted in the direction of the stimulation photon. The energy of the molecule decreases from E_j to E_i .



Figure 2.5: Schematic of elementary transitions [121, p. 77].

Spontaneous emission: The excited molecule emits a photon spontaneously. The probability of spontaneous emission increases with increasing gas temperature. The emission is isotropic in all space angles. The energy of the molecule decreases from E_j to E_i .

For all three gas-molecule interactions following equation is valid:

$$|E_j - E_i| = \Delta E = h\nu_{ij} \tag{2.9}$$

There is a direct relation between the molecular energy states before and after the interaction with the photon and the energy of the photon, i.e. its wavelength or wavenumber.

This is where quantum physics comes into play. Any closed atomic system, i.e. gaseous molcules, has only a certain number of discrete states according to Bohr's theory [14]. The molecule has a certain probability of being in a certain quantum state without emitting energy for a certain time interval. Without any external disturbance a molecule falls and stays in a normal state with the lowest binding

energy (figure 2.6). The total energy of a molecule can be written as

$$E = E_e + E_v + E_r + E_t (2.10)$$

where E_e is the electronic energy, E_v the vibrational energy, E_r the rotational energy and E_t the translational energy. Only the first three energies are quantized (figure 2.6). Each energy state is characterized by a quantum number for each energy type (v = 0, 1, 2, 3, ... and j = 0, 1, 2, 3, ...).

These discrete energy states result in absorption and emission of photons with the energy $h\nu$ by molecular transitions only at well defined energies. The result is not a continuous spectrum but a line spectrum, where each line, i.e. photon energy, can be characterized by a set of quantum numbers. The energies can be calculated using quantum theory. I restrict the description here to basic relationships. More details can be found in Bernath [10].

Molecular energy transitions result in distinct lines in different parts of the spectrum: **Electronic energy transitions** in the ultraviolet over visible to the near infrared spectrum ($\lambda \leq 1.5 \,\mu$ m), **vibrational energy transitions** in the infrared spectrum ($1.5 \,\mu m \leq \lambda \leq 20 \,\mu m$) and **rotational energy transitions** in the far infrared to microwave spectrum ($20 \,\mu m \leq \lambda \leq 1000 \,\mu m$) [118, p. 263].

Electronic transitions occur only if a very strong photon source such as a laser is used. They do not occur in normal combustion processes. According to quantum theory only rotational and vibrational transitions can occur which correspond to the selection rules $\Delta j = \pm 1$ and $\Delta v = \pm 1$. The energies necessary for vibrational transitions are much larger than for rotational transitions. Both transitions often occur as combined vibration-rotational transitions and result in many closely spaced lines or bands in the infrared spectrum (figure 2.6). The vibration-rotational lines are very closely spaced and form bands. These bands in the infrared spectrum are the main contributors to the exchange of thermal radiation by gases.

2.1.4 Emission and absorption probabilities

The probabilities for spontaneous and induced molecular transitions (figure 2.5) can be calculated from quantum mechanics by means of Einstein's probability coefficients



Figure 2.6: Schematic of quantum states and possible transitions [121, p. 72]

[35][121, p. 76f]. The total number of transitions due to absorption is

$$\left(\frac{dN_i}{dt}\right)_{i\to j} = N_i I_\lambda B_{ij} \tag{2.11}$$

where N_i is the number of molecules per unit volume in the energy state i, I_{λ} is the incoming radiation intensity at the transition wavelength and B_{ij} is the Einstein probability coefficient for absorption. The number of transitions is proportional to the incoming radiation intensity and the number of molecules.

The number of transitions due to induced and spontaneous emission can in the same manner be written as

$$\left(\frac{dN_j}{dt}\right)_{j\to i} = -N_j \left(A_{ji} + I_\lambda B_{ji}\right) \tag{2.12}$$

where A_{ji} is the Einstein probability coefficient for spontaneous emission and B_{ji} is the Einstein probability coefficient for induced emission. The number of spontaneous emission transitions is only dependent on the number of molecules while the number of induced emission transitions is also dependent on the intensity of the incoming radiation.

2.1.5 Local thermodynamic equilibrium

A molecule is in the condition of local thermodynamic equilibrium (LTE) if the distribution between the internal molecular energy states is in equilibrium for the temperature of the molecule. Gas molecules redistribute absorbed energy very rapidly and the molecules are always in normal combustion applications in LTE conditions [104, p. 541]. Hence LTE is always assumed in this thesis.

The principle of detailed balancing states that the number of downward transitions equals the number of upward transitions

$$\left(\frac{dN_i}{dt}\right)_{i\to j} + \left(\frac{dN_j}{dt}\right)_{j\to i} = 0$$
(2.13)

The populations of two molecular energy levels are for radiative equilibrium conditions, i.e. inside a black enclosure, related by the Boltzmann formula

$$\frac{N_j}{N_i} = \frac{g_j}{g_i} e^{-hc/\lambda kT}$$
(2.14)

Solving eq. (2.13) combined with (2.12), (2.11) and (2.14) for I_{λ} yields

$$I_{\lambda} = \frac{A_{ji}/B_{ji}}{\left(\frac{g_i}{g_j}\frac{B_{ij}}{B_{ji}}\right)e^{hc/\lambda kT} - 1}$$
(2.15)

As the incoming radiation intensity under radiative equilibrium conditions is always equal to the black body intensity, $I_{b\lambda}(T) = I_{\lambda}$, equation (2.15) can be combined with equation (2.2).

$$I_{b\lambda}(T) = I_{\lambda} = \frac{A_{ji}/B_{ji}}{\left(\frac{g_i}{g_j}\frac{B_{ij}}{B_{ji}}\right)e^{hc/\lambda kT} - 1} = \frac{2c^2h/\lambda^5}{e^{hc/\lambda kT} - 1}$$
(2.16)

Following relations between the Einstein coefficients can be deduced:

$$g_i B_{ij} = g_j B_{ji} \tag{2.17}$$

and

$$\frac{A_{ji}}{B_{ji}} = \frac{2c^2h}{\lambda^5} \tag{2.18}$$

Hence only one Einstein coefficient is necessary for every line as the other two can be calculated from the degeneracies of the transition.

2.1.6 Spectral line behavior

The specific energy levels of the vibration-rotational transitions are in reality not at a specific frequency, but are distributed ("broadened") over a very small range of frequencies. This effect is caused by a number of different mechanisms [121, p. 79]:

Natural line broadening: Unavoidable uncertainty in the energy levels.

Pressure broadening: Perturbation of the energy levels by collision.

Doppler broadening: Thermal motion of the emitting body relative to the absorber.

Stark broadening: Perturbation of the energy levels by strong electric fields.

Statistical broadening: Statistical perturbation of energy levels due to distribution of inter atomic distances that the various neighbors may assume with respect to the radiating molecule.

Homogeneous or Voigt broadening: Combined effects of collisional and Doppler broadening.

Interested readers can find more details about all effects in the books by Modest [82, p. 297ff], Bernath [10, p. 21ff] and Siegel and Howell [103, p. 438ff]. Under normal combustion conditions with higher pressures ($p \ge 1$ bar) and not extreme temperatures (T < 2000 K) pressure broadening is the dominating broadening mechanism [82, p. 298].

The shape of the pressure broadened spectral absorption coefficient by one molecular transition may be calculated by the *Lorentz* profile [75]

$$k_{\omega} = \left(\frac{S}{\pi}\right) \frac{\gamma}{(\omega - \omega_c)^2 + \gamma^2} \tag{2.19}$$

where γ is the pressure broadened half width and ω_c the wavenumber at the line center (figure 2.7).

2.1.7 Band radiation

As the energy levels of the vibration-rotation lines are very close (figure 2.6), socalled bands in the spectrum result, i.e. a gas absorbs and emits only in specific regions of the spectrum (figure 2.8). The band locations in the spectrum differ from molecule to molecule and overlap each other. The assumption of grey behaviour is not valid [82, p. 288].

2.1.8 Radiative-Transfer-Equation for absorbing-emitting media

Along a line-of-sight the absorption of the radiation intensity I_{ν} due to absorption and stimulated emission of photons can be written in the Radiative-Transfer-Equation (RTE) as [82, p. 291]

$$\frac{dI_{\nu}}{ds} = -(N_j B_{ji} - N_i B_{ij}) h \nu I_{\nu}$$
(2.20)



Figure 2.7: Spectral line shape for Lorentz profile.



Figure 2.8: Emitted intensity of a 70 cm gas column (50 vol. -% CO₂; 45 vol. -% H₂O; 5 vol. -% CH₄; SNB model RADCAL) at 1500 °C and of a black body at the same temperature.

where s is the length of a homogeneous gas column.

In reality the energies from a transition from upper state j to lower state i are "broadened" over a very small range of energies. The resulting absorption and emission occurs in a wavelength range (section 2.1.6). Therefore the *line intensity* or *line strength* S_{ν} is defined as the line-integrated absorption coefficient [82, p. 291][95, p. 708].

$$S_{\nu} = \int_{\Delta\nu} k_{\nu} d\nu = (N_j B_{ji} - N_i B_{ij}) h\nu = \frac{h\omega_{ij}}{c} \frac{N_i}{N_{tot}} \left(1 - \frac{g_i N_j}{g_j N_i}\right) B_{ij}$$
(2.21)

where k_{ν} is the frequency specific *effective absorption coefficient* (since it incorporates absorption and induced emission), ω_{ij} is the transition wavenumber and N is the molecular number density.

If equation (2.20) and equation (2.21) are combined we can write

$$\frac{dI_{\nu}}{ds} = -k_{\nu}I_{\nu} \tag{2.22}$$

A similar deduction can be made for the effect of spontaneous emission

$$\frac{dI_{\nu}}{ds} = k_{\nu}I_{b\nu} \tag{2.23}$$

where $I_{b\nu}$ is the radiation intensity of a black body at the frequency ν . This leads to the complete differential Radiative-Transfer-Equation (RTE) for an absorbingemitting (but not scattering) media [82, p. 267].

$$\frac{dI_{\nu}}{ds} = -k_{\nu}I_{\nu} + k_{\nu}I_{b\nu} = k_{\nu}(I_{b\nu} - I_{\nu})$$
(2.24)

where the first term on the right hand side accounts for the absorption and induced emission of photons and the second term on the right hand side for the spontaneous emission of photons. The solution to the equation of transfer for an isothermal gas layer of thickness s is

$$I_{\nu}(s) = I_{\nu}(0)e^{-k_{\nu}s} + I_{b\nu}(1 - e^{-k_{\nu}s}) = I_{\nu}(0)\tau_{\nu} + I_{b\nu}(1 - \tau_{\nu})$$
(2.25)

where the transmissivity τ_{ν} of the gas column of length s is defined as

$$\tau_{\nu} = e^{-k_{\nu}s} \tag{2.26}$$

Equation (2.26) is often referred to as *Beer's law* [9][33, p. 128].

2.2 Fundamentals of modelling radiation

Modeling radiative heat transfer is a complicated task. Not only the spectral dependency of the participating gases and particles (section 2.1), i.e. the variations of transmitted energy over the wavelength spectrum, but also the directional and spacial component, i.e. the variations of transmitted energy with space angle, have to be taken into account as photons travel in any direction in a multidimensional computational domain. Therefore the literature distinguishes between two different models:

- 1. Spectral models and
- 2. Directional models

For numerical investigations of heat transfer in 3D furnace simulations, models for both radiation properties have to be chosen. The models have to be the most computationally efficient for the purpose of the simulation and have to work together properly. Typical examples of simulation aims with different requirements are the accurate prediction of wall heat transfer rates or the prediction of the flame temperature structure.

This section will first summarize the coupling of the radiative transfer calculations with the energy equation of 3D furnace simulations. As the validation of spectral models is the focus of this thesis, the directional models are only briefly described with reference to further reading. Afterwards I give a summary of the importance of including turbulence effects in radiative heat transfer calculations.

2.2.1 Coupling of radiative-transfer-equation and energy equation

The temperature field in a reacting fluid flow simulation is found by numerical solution of the energy conservation equation [82, p. 281]

$$\rho \frac{Du}{Dt} = \rho \left(\frac{\partial u}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} u \right) = -\boldsymbol{\nabla} \cdot \boldsymbol{q} - p \boldsymbol{\nabla} \cdot \boldsymbol{v} + \mu \Phi + \dot{Q}^{\prime\prime\prime}$$
(2.27)

where u is the internal energy, v is the velocity vector, q is the total heat flux vector, μ is the dynamic viscosity, Φ is the dissipation function, and $\dot{Q}^{\prime\prime\prime}$ is the heat

generated within the medium (i.e. energy release due to chemical reactions). This general equation can be further simplified with the assumption

$$du = c_v dT \tag{2.28}$$

where c_v is the specific heat at constant volume and Fourier's law for heat conduction [46]

$$\boldsymbol{q} = \boldsymbol{q}_C + \boldsymbol{q}_R = -k_t \boldsymbol{\nabla} T + \boldsymbol{q}_R \tag{2.29}$$

where k_t is the thermal conductivity and \boldsymbol{q}_R the radiation heat flux vector to

$$\rho c_v \frac{DT}{Dt} = \rho c_v \left(\frac{\partial T}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} T \right) = -\boldsymbol{\nabla} \cdot (k_t \boldsymbol{\nabla} T) - p \boldsymbol{\nabla} \cdot \boldsymbol{v} + \mu \Phi + \dot{Q}^{\prime\prime\prime\prime} - \boldsymbol{\nabla} \cdot \boldsymbol{q}_R \quad (2.30)$$

The last term on the right hand side is the contribution of the radiation on the energy balance. For a line-of-sight similar to the formulation of the RTE (equation 2.24) the equation of energy conservation is

$$\rho c_v \frac{DT}{Dt} = \rho c_v \left(\frac{dT}{dt} + v_s \cdot \frac{dT}{ds} \right) = -\frac{d}{ds} \cdot \left(k_t \frac{dT}{ds} \right) - p \frac{dv_s}{ds} + \mu \Phi + \dot{Q}^{\prime\prime\prime} - \frac{dI}{ds} \quad (2.31)$$

2.2.2 Directional models

Directional models for the simulation of the directional and spacial properties of radiation can be divided into four different groups (figure 2.9) [122, p. 419]:

- 1. directional averaging approximations
- 2. differential approximations
- 3. energy balance methods
- 4. hybrid methods

The use of the two simple approximations of optically thin and thick conditions (Modest [82, p. 450f]) is very limited. From the other methods in figure 2.9 only the discrete ordinates method, the discrete transfer method, the P_n -approximations and the finite volume method are compatible with CFD codes [122, p. 420]. All models need the coefficient of absorption k_{ν} for inclusion of the spectral radiative properties of gases. More details about the different methods can be found in Viskanta [122], Viskanta and Menguec [120] and Modest [82].



Figure 2.9: Directional models [122, p. 419].

2.2.3 Radiation from turbulent flames

The effect of turbulence on radiation (turbulence-radiation interaction / TRI) from flames was a main research area in the field of radiation in the last decades. Two specific reviews are known to the author [21, 38] and two books, where TRI is described [121, p. 251ff][82, p. 707ff]. All conclude that turbulence enhances the mean radiation from turbulent flames compared with radiation calculations based on the mean properties by a factor f_{TRI} between 1.1 and 4.2 [121, p. 262f]. The values differ depending on optical thin or thick conditions and on luminous or nonluminous flames, i. e. the propensity for the formation of soot inside the flame. Non-luminous turbulent methane flames tend to have a lower factor f_{TRI} of 1.1 to 1.5 [21, p. 378], i.e. a 10 - 50% increase of radiation intensity due to turbulence. The effect of TRI is not important outside of flames in regions of non-reactive flows [21, p. 377].

One way of accounting for turbulence in reacting flows is the Reynolds averaging technique [121, p. 258]. The spectral absorption coefficient, Planck's black body function and the intensity are decomposed in mean and fluctuating parts.

$$k_{\nu} = \overline{k_{\nu}} + k_{\nu}', \ I_{b\nu} = \overline{I_{b\nu}} + I_{b\nu}' \text{ and } I_{\nu} = \overline{I_{\nu}} + I_{\nu}' \tag{2.32}$$

The resulting Radiative-Transfer-Equation for an absorbing-emitting and not-scattering medium is (compare equation 2.24)

$$\frac{d\overline{I_{\nu}}}{ds} = -\overline{k_{\nu}I_{\nu}} + \overline{k_{\nu}I_{b\nu}} + \overline{k_{\nu}'I_{b\nu}'} - \overline{k_{\nu}'I_{\nu}'}$$
(2.33)

where the last two terms are due to the interaction of radiation with turbulence.

The mean property model neglects the last two terms and assumes that the turbulence has no effect on radiation characteristics of combustion gases. This is the common approach in commercial CFD software and in most spectral radiation work up to now. Other researchers have argued that the fourth term on the right hand side, the correlation between the fluctuating absorption coefficient k'_{ν} and the fluctuating intensity I'_{ν} , can be neglected for most practical combustion systems [121, p. 258]. The calculation of the remaining third term is still a formidable task and not possible without simplifications, but is very important for the correct accounting of TRI in turbulent flames. The best TRI methods are able to predict radiative heat transfer from turbulent flames with 10 - 20% accuracy [21, p. 378],

but are generally not used for CFD simulations due to their extensive numerical costs.

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2.3 Spectral gas radiation models

The absorption and emission behavior of gaseous molecules is very irregular in the infrared spectrum (section 2.1) and its simulation is a difficult task. The main difference between the different spectral models with regard to complexity is the spectral discretization. The most simple grey models assume only one value (for the emissivity) over the whole spectrum (figure 2.10). The most complicated LBL-models calculate up to 10^6 values and are able to model the physics without simplifications (figure 2.11). The second difference is the modeled spectral gas property. Some models calculate the path length independent coefficient of absorption k_{λ} , others the path length dependent transmissivity $\tau_{\lambda}(s)$ or total emissivity $\epsilon_{tot}(s)$ (table 2.1). The models, which calculate the path independent absorption coefficient k_{λ} , are better suited for 3-D simulations as they allow a strict division between directional and spectral models. The path dependent models are generally not easy to implement as they need an assumption for the path length (e. g. cell-based or domain-based), which has no sound physical basis [20, p. 308]. The third difference is the possibility to account for varying partial and total pressures of multiple gases. The most simple spectral models (WSGG and grey) do not take these values into account, but are only valid in a gas atmosphere with a specific gas composition and total pressure. All other models presented here take the gas composition into account to the price of higher computational costs. The choice of the right model for a simulation is a trade-off between precision and computational effort. The simple models without the calculation of absorption bands are adequate for calculation of wall heat fluxes. To calculate flame and temperature structure more detailed models are necessary [121, p. 169].

2.3.1 Line-by-line models

The most complicated and most accurate model is the line-by-line (LBL) model. The model calculates the intensity and shape of each spectral line based on specific data for each vibration-rotational transition, the gas temperature and gas composition. The final absorption coefficient k_{ω} at a specific wavenumber ω is found by summation of the absorption of all lines in the vicinity. The spectral discretization should be high enough to discretize each spectral line shape (< 0.5 cm^{-1} / figure 2.7). The quality of the simulations depends almost only on the quality of the used transition



Figure 2.10: Spectral discretization of simplified spectral models; Natural gas - air combustion atmosphere, 700 °C, $s=0.7\,{\rm m}$



Figure 2.11: Spectral discretization of detailed spectral models; Natural gas - air combustion atmosphere, 700 °C, $s=0.7\,{\rm m}$

Туре	Name	Abbr.	Spectral intervals	Modeled property	Path length	Gas composi- tion
					depen-	
					dence	
detailed	Line-by-line	LBL	> 1E6	k_{λ}	no	Variable
models	Statistical-narrow-band	SNB	350-400	$ au_{\lambda}(s)$	yes	Variable
	Exponential-wide-band	EWB	≥ 16	$ au_{band}(s)$	yes	Variable
simplified	Statistical-line-width	SLW	≥ 10	k_{λ}	no	Variable
models	Weighted-sum-of-grey-gases	WSGG	4 or 5	k_{λ}	no	\mathbf{Fixed}^1
	Grey (EWB or WSGG based)		1	$\epsilon_{tot}(s)$	yes	See above

Table 2.1: Overview of spectral radiation models. k_{λ} is the absorption coefficient, τ_{λ} the transmissivity, s the path length and ϵ_{tot} the total emissivity.

database.

The most important LBL database is the HITRAN compilation [95, 96, 100]. HITRAN's main purpose is the calculation of the radiative transfer in the earth's atmosphere. The database is updated regularly. The last HITRAN edition is from 2008 [100]. As the temperatures in the atmosphere are only moderate, HITRAN is not valid for high temperatures. In the low temperature regions only transitions into and from the ground state are responsible for photon absorption and emission. Therefore HITRAN includes mostly ground state transitions and many excited state transitions (so called *hot lines*) are missing. The first edition of HITEMP was published 1995 by Rothman et al. [98], a LBL database especially for high temperature calculations ($T \leq 1000 \text{ K} / 727 \,^{\circ}\text{C}$). The HITEMP1995 database was based on extrapolated transitions for excited states at high temperatures and not on experimental observations. 2010 a new edition of HITEMP was published [101], which incorporated the existing high temperature BT2 database for H₂O lines [7] and an updated version of the high temperature CDSD-1000 database for CO₂ [115, 116]. Both databases are based on measurements and theoretical calculations.

The LBL databases give amongst others following parameter [95, Appendix A]:

Mol: Molecular species identification $(1 = H_2O, 2 = CO_2, 5 = CO, 6 = CH_4)$

¹Johansson et al. [64] gives a WSGG parameter set depending on the molar ratio of H_2O/CO_2 and therefore allows variable composition. All other authors give only parameter sets for specific molar ratios (section 2.3.4).

	HITE	MP		HITRAN			
	2010	1995	2008	2004	1996	1992	
H_2O	111,377,777	1,174,009	69,201	63,196	49,444	48,523	
$\rm CO_2$	$11,\!167,\!618$	$1,\!032,\!269$	312,479	62,913	60,802	60,790	
CO	$115,\!218$	113,022	$4,\!477$	$4,\!477$	$4,\!477$	3,600	

Table 2.2: Number of molecular transitions in LBL databases [95–98, 100, 101].

Iso: Isotope ID number. Iso = 1 for the most abundant, etc.

- ω_c : Transition wavenumber in vacuum at line center [cm⁻¹]
- S: Spectral line intensity $[cm^{-1}/(molecule cm^{-2})]$ at a reference temperature of 296 K for the natural terrestrial isotopic abundance
- γ_{air} : Air-broadened half width at half maximum [cm⁻¹/atm] at $T_{ref} = 296$ K and reference pressure $p_{ref} = 1$ atm
- γ_{self} : Self-broadened half width at half maximum [cm⁻¹/atm] at $T_{ref} = 296$ K and $p_{ref} = 1$ atm
- E_i : Lower state energy of the transition $[\text{cm}^{-1}]$
- n: Coefficient of temperature dependence of the air-broadened half width [-]
- δ_{air} : Air-broadened pressure shift [cm⁻¹/atm] at $T_{ref} = 296$ K and $p_{ref} = 1$ atm
- g_i : Statistical weight of the lower energy state (only given in the 160 char HITRAN format for the editions since 2002)
- g_j : Statistical weight of the upper energy state (only given in the 160 char HITRAN format for the editions since 2002)

With this data the temperature corrected line intensity S can be calculated [95, p. 710] as

$$S(T) =$$

$$S(T_{ref}) \frac{Q(T_{ref})}{Q(T)} \frac{\exp(-c_2 E_i/T)}{\exp(-c_2 E_i/T_{ref})} \frac{[1 - \exp(-c_2 \omega_c/T)]}{[1 - \exp(-c_2 \omega_c/T_{ref})]} \quad (2.34)$$

where c_2 is the second radiation constant ($c_2 = 1.4388 \,\mathrm{cm}\,\mathrm{K}$) and Q is the total internal partition sum, which can be calculated as

$$Q_m(T) = \sum_{l} g_{lm} \exp(-c_2 E_{ilm}/T)$$
 (2.35)

where l sums over all transitions of the molecule isotope m and g_l are the statistical weights of the transitions. Theoretically, the upper statistical weight g_j has to be used for the calculation of total internal partition sums for spontaneous emission and the lower statistical weight g_i for the total internal partition sums for absorption and induced emission. Both total internal partition sums are identical in the range of interest for thermal radiation i.e. the infrared with no electronic level transitions. To avoid the necessity of a summation of parameters from all lines, HITRAN2008 is accompanied by a FORTRAN routine called TIPS2009, which can be used for the calculation of the total internal partition sums in a temperature range of 70 - 3000 K for all molecules included in HITRAN [42, 100].

The wavenumber of the line center has to be corrected for pressure-shift by

$$\omega_c^*(p_{tot}) = \omega_c + \delta_{air}(p_{ref}) \cdot p_{tot} \tag{2.36}$$

where p_{tot} is the total gas pressure.

The Lorentz half width γ for a specific temperature T [K], total pressure p_{tot} [atm] and partial pressure p_{par} [atm] is calculated as

$$\gamma(p_{tot}, p_{par}, T) = \left(\frac{T_{ref}}{T}\right)^n \cdot \left[\gamma_{air}(p_{ref}, T_{ref}) \cdot (p_{tot} - p_{par}) + \gamma_{self}(p_{ref}, T_{ref}) \cdot p_{par}\right] \quad (2.37)$$

Under normal combustion conditions with higher pressures $(p \ge 1 \text{ bar})$ and not extreme temperatures (T < 2000 K) the dominating broadening mechanism is pressure broadening [82, p. 298]. The resulting line shapes have a Lorentz profile. The profile for the transition with line center at ω_c is calculated as

$$f(\omega, \omega_c, T, p_{tot}, p_{par}) = \frac{1}{\pi} \frac{\gamma(p_{tot}, p_{par}, T)}{\gamma(p_{tot}, p_{par}, T)^2 + [\omega - \omega_c^*(p_{tot})]^2}$$
(2.38)

The monochromatic absorption coefficient k_{ω} [1/cm] at wavenumber ω due to this

transition is given by

$$k_{\omega} = S(T) \frac{7.338933 \times 10^{21}}{T} \cdot f(\omega, \omega_c, T, p_{tot}, p_{par}) \cdot p_{par}$$
(2.39)

where the line intensity S(T) is converted from $[\text{cm}^{-1}/(\text{molecule cm}^{-2})]$ to $[\text{cm}^{-2}/\text{atm}]$ according to Bernath [10, p. 274f].

The final absorption coefficient k_{ω} is under the hypothesis of an isolated line, i.e. the transitions have no influence on each other,

$$k_{\omega} = \sum_{k} \sum_{l} k_{kl\omega} \tag{2.40}$$

where the first sum refers to all molecules k and the second sum to all the lines/transitions l of these molecules [121, p. 82]. The absorption coefficient k_{ω} is used directly in the differential RTE (equation 2.24).

2.3.2 Statistical narrow band models

The second detailed spectral model (table 2.1), I present here, is the statistical narrow band (SNB) model, which is based on assumptions for the spectral line distribution in a band narrow enough to regard the black body function as constant and wide enough to contain a large enough number of lines M for a statistical treatment (5 - 25 cm⁻¹). Tables with statistical variables describing the molecular absorption behavior in these bands are compiled based on experiments, theoretical calculations and LBL databases.

The application of the SNB model to multidimensional CFD calculations with the differential radiative-transfer-equation (RTE) (equation 2.24) is not possible as the SNB model yields the spectral transmissivity τ_{ω} (i.e. dependent on a spatial variable) and not the spectral absorption coefficient k_{ω} [122, p. 427]. The model is explained here nevertheless as it can be used as a more computationally efficient reference model compared to the LBL model for the validation of simple spectral models for CFD calculations.

All SNB models are based on the general expression for the average transmissivity $\overline{\tau}$ in a narrow band of width $\Delta \omega$ [112, p. 343]

$$\overline{\tau}_{\Delta\omega} = \exp\left(-\frac{\overline{W}}{\delta}\right) \tag{2.41}$$

where δ is the mean spacing between two consecutive lines, given by

$$\delta = \frac{\Delta\omega}{M} \tag{2.42}$$

where M is the number of lines in the narrow band. \overline{W} is the mean value of the equivalent black line-width W, i.e.

$$\overline{W} = \frac{1}{M} \sum_{l=1}^{M} W_l \tag{2.43}$$

with

$$W_l = \int_{-\infty}^{+\infty} [1 - \exp(-k_{l\omega}s)] d\omega \qquad (2.44)$$

where $k_{l\omega}$ is the absorption coefficient due to the line l in the narrow band.

As equation (2.43) cannot be calculated directly without knowledge of the column length s, the line intensity S_l , the line half width at half maximum γ_l and the partial pressure of the absorbing species p_{par} , the models assume that \overline{W} can be calculated with a probability distribution function P(S).

$$\overline{W} = \int_0^\infty P(S)W(S)dS \tag{2.45}$$

Two SNB models are readily available as FORTRAN computer codes with the book from Modest [82]: The EM2C model from Soufiani and Taine [106] and the RADCAL model from Grosshandler [54]. They differ in the formulation of the probability distribution function P(S) and the spectral data source. I will present the main equations and the parameter sources for these two models. For a more general description of narrow band models the interested reader is referred to Viskanta [121, p. 86ff], Taine and Soufiani [112, p. 347ff], Modest [82, p. 307ff] and Goody and Yung [51, p. 125ff].

2.3.2.1 RADCAL

The RADCAL model is based on the Goody exponential distribution function [53]:

$$P(S) = \frac{1}{\sigma} \exp\left(-\frac{S}{\sigma}\right) \tag{2.46}$$

where σ is the mean line intensity and is defined as

$$\sigma = \int_0^\infty SP(S) \, dS \tag{2.47}$$

After integration of equation (2.46) and considering of the weak and strong absorption limit for Lorentz shape lines we get [112, p. 346]

$$\frac{\overline{W}}{\delta} = \frac{p_{par} \, s \, \overline{k}}{\sqrt{1 + 0.5 \, p_{par} \, s \, \overline{k} / \overline{\beta}}} \tag{2.48}$$

where the average transmissivity depends only on the two statistical spectroscopic properties of absorption lines centered inside $\Delta \omega$

$$\overline{k} = \frac{1}{\delta} \frac{1}{M} \sum_{l=1}^{M} S_l = \frac{\overline{S}}{\delta}$$
(2.49)

and

$$\overline{\beta} = 2\pi\overline{\gamma}/\overline{\delta} \tag{2.50}$$

with

$$\overline{\gamma} = \frac{1}{M} \sum_{l=1}^{M} \gamma_l \tag{2.51}$$

and

$$\overline{\delta} = \delta \frac{S\overline{\gamma}}{\left[(1/M) \sum_{l=1}^{M} \sqrt{\gamma_l S_l} \right]^2}$$
(2.52)

The parameters \overline{k} , $\overline{\gamma}$ and $\overline{\delta}$ are tabulated for spectral intervals of 25 cm^{-1} in the spectral range from 50 cm^{-1} to $10,000 \text{ cm}^{-1}$ and are based on experimental data from the NASA moon landing project during the sixties [54, 76].

2.3.2.2 EM2C

The EM2C model is based on the Malkmus inverse-exponential tailed distribution function [78, 106]

$$P(S) = \frac{1}{S \ln R} \left[\exp(\frac{-S}{S_{max}}) - \exp(\frac{-RS}{S_{max}}) \right]$$
(2.53)

where R is the maximum to minimum intensity ratio and S_{max} is the maximum value of the line intensities.

The average transmissivity is calculated as

$$\overline{\tau}_{\Delta\omega} = \exp\left[-\frac{\overline{\beta}}{\pi}\left(\sqrt{1 + \frac{2\pi \, p_{par} \, s \, \overline{k}}{\overline{\beta}}} - 1\right)\right] \tag{2.54}$$

where $\overline{\beta}$ is calculated with equation 2.50.

The mean half widths $\overline{\gamma}$ in equation 2.50 are calculated as $(p_{ref} = 1 \text{ bar and} T_{ref} = 296 \text{ K})$

$$\overline{\gamma}_{CO_2} = \frac{p}{p_{ref}} \left(\frac{T_{ref}}{T}\right)^{0.7} \cdot \left[0.07 \, x_{CO_2} + 0.058 \left(1 - x_{CO_2} - x_{H_2O}\right) + 0.1 \, x_{H_2O}\right] \quad (2.55)$$

$$\overline{\gamma}_{H_2O} = \frac{p}{p_{ref}} \left\{ 0.462 \, x_{H_2O} \left(\frac{T_{ref}}{T} \right) + \left(\frac{T_{ref}}{T} \right)^{0.5} \right. \\ \left. \left. \left. \left[0.079 \left(1 - x_{CO_2} - x_{O_2} \right) + 0.106 \, x_{CO_2} + 0.036 \, x_{O_2} \right] \right\} \right\}$$
(2.56)

$$\overline{\gamma}_{CO} = \frac{p}{p_{ref}} \left\{ 0.075 \, x_{CO_2} \left(\frac{T_{ref}}{T} \right)^{0.6} + 0.12 \, x_{H_2O} \left(\frac{T_{ref}}{T} \right)^{0.82} + 0.06 \, \left(\frac{T_{ref}}{T} \right)^{0.7} \left(1 - x_{CO_2} - x_{H_2O} \right) \right\} \quad (2.57)$$

where x is the molar fraction of the species.

The remaining statistical properties \overline{k} and $1/\overline{\delta}$ depend in a first approximation only on the temperature T and are tabulated for 25 cm^{-1} intervals in the ranges of 300 - 2900 K and $150 - 9300 \text{ cm}^{-1}$. They are based on the 1992 edition of the HITRAN database [97], on additional data for H₂O from Flaud et al. [43] and on additionally generated hot lines for temperatures up to 2500 K.

2.3.3 Exponential-wide-band model

One possibility of obtaining more simplicity for spectral modelling is the calculation of one value for every spectral band (figure 2.10). The model is less computational demanding as the whole spectrum is discretized more roughly as for the LBL and SNB models and the solution of less RTEs is necessary (table 2.1). These types of models are called *wide band models*. The most popular wide band model is the exponential wide band (EWB) model from Edwards and Balakrishnan [34]. The model assumes each band to have a band shape S/d with a defined band head and exponentially decreasing band wings (figure 2.12), where S is the mean line intensity and d the line spacing ratio.



Figure 2.12: Band shapes for exponential wide band model [82, p. 326].

The band can have an **upper band head**,

$$\frac{S}{d} = \frac{\alpha}{\omega_w} e^{-(\omega_{upper} - \omega)/\omega_w}$$
(2.58a)

be $\mathbf{symmetrical}$

$$\frac{S}{d} = \frac{\alpha}{\omega_w} e^{-2\left|\omega_{symmetrical} - \omega\right|/\omega_w} \tag{2.58b}$$

or have a lower band head

$$\frac{S}{d} = \frac{\alpha}{\omega_w} e^{-(\omega - \omega_{lower})/\omega_w}$$
(2.58c)

where α is the integrated band intensity, ω_w the band width at 1/e of maximum intensity, ω_{upper} the wavenumber position of the upper band head, ω_{lower} the wavenumber position of the lower band head and $\omega_{symmetrical}$ the wavenumber position of the symmetrical band head.

The spectral transmissivity τ_{ω} of the band through a gas layer s with the density ρ_{abs} of the absorbing gases is calculated as

$$\tau_{\omega} = \exp\left(\frac{-(S/d)X}{(1+(S/d)X/\beta)^{1/2}}\right)$$
(2.59)

where β is the mean line width-to-spacing parameter and

$$X = \rho_{abs} \cdot s \tag{2.60}$$

is the absorber density path length product, which accounts for the gas composition x and the path length s.

To calculate the total band absorption A_{band} Edwards and Balakrishnan [34] introduced the so called four-region method. The dimensionless band absorption $A^* = A_{band}/\omega_w$ is calculated with four different expressions depending on β and the optical thickness at the band head $\tau_H = \alpha X/\omega_w$:

$$A^* = \tau_H \qquad \text{for } \tau_H \le 1, \tau_H \le \beta \qquad (\text{linear region}) \quad (2.61a)$$
$$A^* = 2\sqrt{\tau_H \beta} - \beta \qquad \text{for } \beta \le \tau_H \le 1/\beta \ \beta \le 1 \qquad (\text{Square root region}) \quad (2.61b)$$

$$A^{*} = \ln(\tau_{H}\beta) + 2 - \beta \quad \text{for } 1/\beta \leq \tau_{H} \leq 1/\beta, \beta \leq 1 \quad \text{(Square root region)} \quad (2.61c)$$
$$A^{*} = \ln\tau_{H} + 1 \quad \text{for } \tau_{H} \geq 1/\beta, \beta \geq 1 \quad \text{(Logarithmic region)} \quad (2.61d)$$

The parameter α , β and ω_w are dependent on temperature and empirical data for each spectral band [82, p. 327ff]. The calculation of α and β involves complicated numerical expressions. These were simplified by a computationally efficient algorithm by Lallemant and Weber [71]. The band transmissivity τ_{band} is calculated from

$$\tau_{band} = \frac{\tau_H}{A} \frac{dA_{band}}{d\tau_H} \tag{2.62}$$

and the width of the band ω_w by

$$\omega_w = \frac{A_{band}}{1 - \tau_{band}} \tag{2.63}$$

Edwards [33, p. 157] proposed a block calculation procedure to calculate the total properties for homogeneous gas mixtures. He proposed to limit the band transmissivity τ_{band} to an upper value of 0.9 as the grey band approximation breaks down at small optical depth. This upper limit is not mentioned by later authors [82, 103] and leads to serious errors for very small grids, if the optical path length is cell based [110, p. 2133]. The band upper and lower limits are found with the band head position (table 10.3 in Modest [82, p. 328f]) under consideration of the band shape (figure 2.12). All band limits are sorted in ascending order and the bands are distributed to the corresponding spectral intervals *i*. Where two bands overlap each other, the resulting transmissivity is found from the product of the transmissivities

$$\tau_i = \prod_{n=1}^K \tau_{ni} \tag{2.64}$$

where K is the total number of bands n in the spectral interval i.

The total emissivity ϵ_{tot} is found by summation of the product of the emissivity $\epsilon_i = 1 - \tau_i$ and the fraction of the black body radiation $f_{b,i}$ in each spectral interval *i*.

$$\epsilon_{tot} = \sum_{i=1}^{L} \epsilon_i f_{b,i} \tag{2.65}$$

where L is the total number of spectral intervals i.

The block calculation procedure leads to a grey model, as only one RTE is solved. The absorption coefficient k_{tot} is calculated from the total emissivity as

$$k_{tot} = -\frac{\ln(1 - \epsilon_{tot})}{s} \tag{2.66}$$

A direct coupling of the EWB model with a directional model to solve more than one RTE is complicated as the width of the bands, i.e. the spectral discretization and therefore the number of RTEs to be solved, depend on path length, gas concentrations and gas temperature. The directional and the spacial model are not strictly divided similar to the SNB model (section 2.3). The path length is normally selected as the length of the computational cell (cell based) or a length characteristic for the whole computational domain (domain based). A number of authors proposed solutions for the coupling of the spectral EWB model with different directional models [22, 68, 110].

The wide band model parameters given by Modest [82, p. 328f] are based mostly on experiments from Edwards [33]. Only the parameter for the pure rotational water band are from Modak [80]. Detailed summaries about the EWB model were published by a number of authors [33, 82, 103, 108, 110].

2.3.4 Weighted-sum-of-grey-gases model

The weighted-sum-of-grey-gases (WSGG) model accounts for the non-grey nature of gases even more simply as the EWB model (table 2.1) with the replacement of the non-grey gas with of a number of grey gases with different absorption coefficients $k_{i,WSGG}$. One "clear gas" ($k_{0,WSGG} = 0$) is used to model the clear windows in the gas spectrum without absorption (figure 2.10). The total absorption is found by a summation of all grey and clear gases with emissivity weighting factors $a_{\epsilon,i}$. The

model is limited to non scattering media confined within a black walled enclosure [81].

The values of $a_{\epsilon,i}$ and $k_{i,WSGG}$ are dependent on the gas temperature and the ratio of partial pressures p_{par} of steam to carbon dioxide. Most authors (table 2.3) give polynomial coefficients $b_{\epsilon,i,j}$ (equation 2.67) for the dependency of $a_{\epsilon,i}$ on the gas temperature T and constant values of $k_{i,WSGG}$ for each grey gas.

$$a_{\epsilon,i} = \sum_{j=1}^{J} b_{\epsilon,i,j} T^{j-1}$$
(2.67)

The dependency on steam to carbon ratio is accounted for by various sets of the parameters $b_{\epsilon,i,j}$ and $k_{i,WSGG}$ for specific ratios.

total pressure of 1.01325	bar.			
Source	$\rm H_2O/CO_2$ ratios	Pressure path length [bar m]	Temperature [°C]	Reference model
Lallemant et al. [72]	Review of various WSGG models with pr	essure path length	< 10 bar m	
Smith et al. $[105]$	1; 2; two sets for traces of CO_2 or H_2O ;	0.001 - 9.87	327 - 2127	EWB
	one set for pure H_2O			
Khare $[67]$	0.1; 0.2; 0.48	0.001 - 59.22	327 - 2127	EWB
Yin et al. $[126]$	0.125; 0.25; 0.5; 0.75; 1; 2; 4; three sets	0.001 - 60	227 - 2727	EWB
	for air blown combustion			
Johansson et al. [63]	0.125; 1	0.01 - 60	227 - 2227	SNB (EM2C)
Johansson et al. [64]	0.125 - 2 (one set depending on ratio)	0.01 - 60	227 - 2227	SNB (EM2C)
Krishnamoorthy et al.	0.111; 0.5; one set for air blown combus-	n.s.	n.s.	SNB (RADCAL)
[20]	tion			

Table 2.3: Published parameter for WSGG model with their validity range and reference model. All models are valid for a to to The common parameters used for CFD air blown combustion at atmospheric pressure [45, p. 13-64ff] are from Smith et al. [105] for temperatures up to 2400 K. Smith gives parameters for H_2O/CO_2 ratios of 1 and 2, for pure water and for traces of water or carbon dioxide. The given parameters are valid for atmospheric total pressure and partial pressure path length products between 0.001 and 9.87 bar m. The parameter sets were generated based on total emissivities calculated with the EWB model from Edwards [33]. Lallemant et al. [72] published an extensive review about total emissivity correlations and compared various models with the EWB model as benchmark. All models compared by Lallemant et al. [72] are only valid for a pressure path length up to 10 bar m. As in oxyfuel combustion the pressure path length can reach far higher values (table 2.7), later authors published model parameters for longer path lengths (table 2.3).

Recently, Johansson et al. [64] proposed a different method for the calculation of the two model parameters $a_{\epsilon,i}$ and $k_{i,WSGG}$. Instead of different parameter sets for specific steam to carbon dioxide ratios, they give only one parameter set of polynomial coefficients, where both $k_{i,WSGG}$ and $a_{\epsilon,i}$ are dependent on the steam to carbon dioxide ratio.

$$k_{i,WSGG} = f(\frac{p_{H_2O}}{p_{CO_2}})$$
(2.68)

$$a_{\epsilon,i} = f(T, \frac{p_{H_2O}}{p_{CO_2}})$$
 (2.69)

The absorption coefficient $k_{0,WSGG}$ for i = 0 (the so called clear gas) is assumed to be zero in all WSGG models. The weighting factor for the clear gas $a_{\epsilon,0}$ is calculated under the assumption that the sum of all emissivity weighting factors has to be unity.

$$a_{\epsilon,0} = 1 - \sum_{i=1}^{I} a_{\epsilon,i} \tag{2.70}$$

Different formulations were developed to apply the WSGG model to directional models.

2.3.4.1 Grey formulation

The WSGG model was originally proposed in its *grey formulation* by Hottel and Sarofim [57] for the calculation of the total gas emissivity as

$$\epsilon_{tot} = \sum_{i=0}^{I} a_{\epsilon,i}(T) \left(1 - \exp(-k_i s)\right) \tag{2.71}$$

$$k_i = p_{abs} k_{i,WSGG} \tag{2.72}$$

where $a_{\epsilon,i}$ are the emissivity weighting factors for the *i*th fictitious grey gas, k_i is the absorption coefficient of the *i*th grey gas, p_{abs} the sum of all partial pressures of the absorbing gases, *s* the path length and $k_{i,WSGG}$ the partial pressure independent absorption coefficient. The formulation is called grey as the gas is assumed grey with the total absorption coefficient k_{tot} calculated by equation (2.66) and one RTE is solved for the whole spectrum (section 2.3.5).

The choice of the path length s is critical for the model as the resulting total emissivity ϵ_{tot} is very sensitive to s. One common approach is to use the characteristic cell size (cell based approach). The resulting total absorption coefficient k_{tot} is grid dependent [45, p. 13-66]. The most frequently used approach is the calculation with a domain based path length (also called mean beam length). This approach has been demonstrated to result in wall heat fluxes with errors as low as 5% [82, p. 586] if the mean beam length is calculated correctly. A mean beam length s for geometries where no specific formula is available has been recommended as

$$s = 3.6 \frac{V}{A} \tag{2.73}$$

where V is the volume and A the surface of the domain [57, 58, 82].

2.3.4.2 Banded formulation

A more general implementation method for the WSGG model was proposed by Modest [81], the so called *banded formulation*, where the heat flux of each grey and clear gas is calculated separately as

$$\frac{dI_i}{ds} = k_{i,WSGG} \left(a_{\epsilon,i} I_b - I_i \right) \tag{2.74}$$
The total transmitted intensity is calculated by a summation of the heat fluxes from all grey and clear gases as

$$I_{tot}(s) = \sum_{i=0}^{I} I_i(s)$$
 (2.75)

with the boundary condition at the wall (s = 0)

$$I_i(0) = \epsilon_{wall} \, a_{\epsilon,i}(T_{wall}) \, I_b(T_{wall}) \tag{2.76}$$

This approach is not dependent on the correct choice of a path length s and therefore more physically correct to use with any directional model implementation. The method can be seen as spectral discretization of the RTE based on different weighted absorption coefficients. While the grey formulation of the WSGG model results in correct wall heat fluxes with the correct choice of the path length s and in incorrect intensity profiles of non-homogeneous temperature gas columns, the banded formulation of the WSGG model results in correct wall heat fluxes and correct intensity profiles [63, 74] with the additional computational cost of having to solve four or five RTEs for each grey and clear gas instead of one for the total absorption coefficient (equation 2.72).

2.3.4.3 Spectral line-based formulation

A further refinement of the banded formulation was proposed by Denison and Webb [24, 26] as the absorption line black body distribution function (ALBDF) commonly called the spectral line-based weighted-sum-of-grey-gases (SLW) model. The SLW model calculates the two WSGG model parameter $k_{i,WSGG}$ and $a_{\epsilon,i}$ with more functions. More grey gases are used as in the standard WSGG models and variable gas compositions can be calculated. The SLW method is computationally demanding, but still less than with the SNB or the LBL models (table 2.1).

The SLW model is based on the ALBDF, which is defined as

the fraction of the black body energy in the portions of the total spectrum where the high resolution spectral molar absorption cross section of the gas $\bar{C}_{abs,\lambda}$ is less than a prescribed value \bar{C}_{abs} [103, p. 460].

$$F(\bar{C}_{abs}, T_b, T_{gas}, p_{tot}, x_{abs}) = \frac{\pi}{\sigma T_b^4} \sum_j \int_{\Delta\lambda_j(C_{abs}, T_{gas}, p_{tot}, x_{abs})} I_{b,\lambda}(\lambda, T_b) d\lambda \qquad (2.77)$$

where x_{abs} is the molar fraction of the absorbing species and σ the Stefan Boltzmann constant ($\sigma = 5.670 \cdot 10^{-8} \,\mathrm{W/m^2K^4}$). The subscript j refers to the jth spectral segment and the summation is performed over the whole spectrum. The SLW method replaces the discretization of the wavenumber ω as in the SNB and the LBL models with a discretization of the absorption cross section C_{abs} .

The absorption cross section C_{abs} [mol/m²] is also called the molar absorptivity and is related to the absorption coefficient k as

$$k = C_{abs} N = C_{abs} \frac{p_{abs}}{R_g T_{gas}}$$
(2.78)

where $N \text{ [mol/m^3]}$ is the molar density of absorbing gas molecules and R_g is the universal gas constant ($R_g = 8.314472 \text{ J/molK}$).

The ALBDF is approximated by [26] as

$$F = \frac{1}{2} \tanh\left(P_F(T_{gas}, T_b, \xi - \xi_{sb})\right) + \frac{1}{2}$$
(2.79a)

where the function P_F is

$$P_F(T_{gas}, T_b, \xi - \xi_{sb}) = \sum_{l=0}^{3} \sum_{m=0}^{3} \sum_{n=0}^{3} c_{lmn} \left(\frac{T_{gas}}{2500}\right)^n \left(\frac{T_b}{2500}\right)^m (\xi - \xi_{sb})^l \qquad (2.79b)$$

$$\xi = \ln(\bar{C}_{abs}) \tag{2.79c}$$

and

$$\xi_{sb} = \sum_{l=0}^{3} \sum_{m=0}^{3} \sum_{n=0}^{2} d_{lmn} \left(\frac{T_b}{2500}\right)^m \xi^m x_{abs}^{l+1}$$
(2.79d)

The function and the parameter c_{lmn} and d_{lmn} are given for H₂O [26] and CO₂ [25]. ξ_{sb} represents the self-broadening effect, which is important for H₂O. For CO₂ self-broadening is neglected and $\xi_{sb} = 0$. The parameters were generated based on the 1992 edition of HITRAN [97] with additions for the missing hot lines and selfbroadening of H₂O. FORTRAN codes with the implementation of the ALBDF are given by Modest [82].

The black body weighting coefficient a_i in equation (2.74) is calculated in the absorption cross section interval i as

$$a_i = F(\bar{C}_{abs,i+1}, T_b, T_{gas}, x_{abs}) - F(\bar{C}_{abs,i}, T_b, T_{gas}, x_{abs})$$
(2.80)

The gas temperature T_{gas} and the black body temperature T_b are equal to the gas temperature for total emissivity calculations. The corresponding absorption

Table 2.4: Recommended domain limits for absorption cross section C_{abs} of SLW model [25, 26].

Molecule	Absorption cross section domain
H ₂ O	$3E^{-5} - 60 \mathrm{m^2/mol}$
$\rm CO_2$	$3E^{-5} - 120 m^2/mol$

coefficient k_i in equation (2.74) is found from a mean value $\bar{C}^*_{abs,i}$ in each interval as

$$k_{i} = N\bar{C}_{abs,i}^{*} = N \exp\left(\frac{\ln(\bar{C}_{abs,i}) + \ln(\bar{C}_{abs,i+1})}{2}\right)$$
(2.81)

The sum of all black body weighting coefficients a_i has to be one as in the standard WSGG model. The black body weighting coefficient a_0 for the clear gas ($k_0 = 0$) is calculated with equation (2.70) after the domain limits (table 2.4) and the discretization of the absorption cross section C_{abs} are calculated. Denison and Webb [26] recommended a logarithmic spacing with 10 intervals. More intervals were found to get unimproved results. The number of intervals can be further reduced down to three grey gases if the interval limits are optimized [25].

For non homogeneous and non isothermal media with one absorbing species, Denison and Webb [27] suggested an approximation procedure:

- 1. The reference state is calculated as a spatial average of temperature, total pressure and mole fraction over the whole line-of-sight.
- 2. The cross section domain is divided into 10 or more logarithmically spaced intervals *i* and the reference absorption cross section $\bar{C}^*_{abs,i,ref}$ is calculated in each interval with equation (2.81).
- 3. In each spatial location the local absorption cross section $\bar{C}^*_{abs,i,loc}$ and the local absorption coefficient $k_{i,loc}$ are calculated from equation (2.82) and (2.83). Equation (2.82) needs to be solved with an interactive method as bisection or Newton-Raphson.

$$F(C^*_{abs,i,loc}, T_b = T_{loc}, T_{gas} = T_{ref}, x_{abs} = x_{abs,ref})$$

= $F(\bar{C}^*_{abs,i,ref}, T_b = T_{ref}, T_{gas} = T_{ref}, x_{abs} = x_{abs,ref})$ (2.82)

$$k_{i,loc} = N(T_{loc}, x_{abs,loc})\bar{C}^*_{abs,i,loc}$$

$$(2.83)$$

4. The local black body weight is calculated with equation (2.84), for the wall with equation (2.85).

$$a_{i,loc} = F(\bar{C}_{abs,i+1}, T_b = T_{loc}, T_{gas} = T_{ref}, x_{abs} = x_{abs,ref}) - F(\bar{C}_{abs,i}, T_b = T_{loc}, T_{gas} = T_{ref}, x_{abs} = x_{abs,ref})$$
(2.84)

$$a_{i,wall} = F(\bar{C}_{abs,i+1}, T_b = T_{wall}, T_{gas} = T_{ref}, x_{abs} = x_{abs,ref}) - F(\bar{C}_{abs,i}, T_b = T_{wall}, T_{gas} = T_{ref}, x_{abs} = x_{abs,ref})$$
(2.85)

5. Equations (2.74) to (2.76) are solved for the whole path.

For binary mixtures of two absorbing species (e.g. CO_2 and H_2O) Denison and Webb [28] proposed to modify equation (2.74) with a second index j for the second species as

$$\frac{dI_{i,j}}{ds} = k_{i,j} \left(a_{i,j} I_b - I_{i,j} \right)$$
(2.86)

The combined absorption coefficient $k_{i,j}$ is calculated as

$$k_{i,j} = k_{CO_2,i} + k_{H_2O,j} \tag{2.87}$$

The combined black body weight $a_{i,j}$ is approximated as

$$a_{i,j} = a_i a_j \tag{2.88}$$

The sum of all black body weights including the clear gases has to be unity

$$\sum_{i} \sum_{j} a_{i,j} = 1 \tag{2.89}$$

and the total intensity I_{tot} is found as (compare equation 2.75)

$$I_{tot}(s) = \sum_{i} \sum_{j} I_{i,j}$$
(2.90)

The method for binary mixtures results in $(n_i + 1) \cdot (n_j + 1)$ RTEs, where n is the number of cross section intervals.

2.3.5 Grey model

A spectral gas radiation model is called a grey model if it assumes grey radiation behaviour and solves only one radiative transfer equation (RTE)

$$\frac{dI_{tot}}{ds} = k_{tot}(I_b - I_{tot}) \tag{2.91}$$

where I_{tot} is the total transmitted thermal energy (intensity) per unit solid angle and I_b is the intensity emitted from a black body.

The total or mean absorption coefficient k_{tot} can be calculated with all spectral gas models, i.e. the EWB model (equations 2.65 and 2.66) or the WSGG model (equations 2.71 and 2.72). Another possibility is the application of a constant absorption coefficient based on experience. Viskanta [122, p. 432] reviews original research papers, which used a mean absorption coefficient k_{tot} for non-sooty natural gas flames in the range of $0.05 - 0.15 \, 1/m$.

2.4 Spectral radiation measurements

Measurements of spectral gas properties are very common in the literature. The most important methods and types of equipment for the optical setup are explained in the following section to give an overview: the optical principle, the used test rig that contains the gas sample and the spectroscopic equipment for recording the intensity vs. wavelength spectrum.

2.4.1 Optics

The optical principle for spectral measurements is either transmission/absorption or emission of radiation (figure 2.13).

Transmission/absorption measurements are based on the fact that the light emitted from a source is partly absorbed while traveling through the gas containment. The source has to be at a higher temperature than the gas in containment in order to avoid problems with the emitted radiation from the hot gases and needs to emit radiation at all wavelengths of interest. This setup is nearly always used for the quantitative analysis of gas concentrations or other molecular spectroscopic applications, as the absorbance $A_{\omega k}$ of each gas species k in the sample is proportional to its concentration [52, p. 13].

$$A_{\omega k} = \log_{10} \frac{1}{\tau_{\omega k}} \tag{2.92}$$

The transmissivity of the sample is therefore the raw measurement value for the species concentration, if the sample temperature is constant. Another advantage of transmission measurements is the easy calibration of the measured radiation intensity. If the light source is very stable and of known power, the spectrometer can be calibrated by a purging of the gas containment with non-absorbing gases as nitrogen.

Emission measurements are only very seldomly carried out. As the spectral behavior of molecular gases is very complex (section 2.1), the analysis of the recorded spectrum is not easy [52, p. 363]. The sample temperature has to be above or below the temperature of the cooled target. If the temperatures are comparable, no spectrum can be recorded. Back reflection of radiation on the opposite wall and reflection of the surroundings into the optical path have to be avoided. The calibration of the spectrometer is difficult, as the emitting gas sample has to be replaced by a light source with defined light intensity.

One general principle is to make sure that the same optical parts are used during measurement and calibration, as all parts have specific spectral optical properties. The calibration procedure has to take these spectral properties into account and eliminate their effects on the measured spectrum. The optical path outside the gas containment should be purged with non absorbing gases as nitrogen or dry and CO_2 -free air to avoid additional absorption.

2.4.2 Test rigs for high temperature measurements

The purpose of the test rig is to provide a gas sample under more or less controlled temperature and pressure conditions. It can be a heated gas cell with minimal temperature, pressure and composition gradients for gas absorption measurements or a burner inside a combustion chamber for radiation measurements of real flames. The light path crosses the test rig at least once. More crossings enlarge the optical path length of the test rig and can be realized with mirrors outside of the test rig.

2.4.2.1 Gas cells

Modest [82, p. 347] distinguishes between the following types:



Figure 2.13: Principles of spectral gas measurements.

- Hot window cell
- Cold window cell
- Nozzle seal cell
- Free jet device

The difference between the different types is the method of separating the gas from its surroundings and the type of the gas flow inside the test rig. The hot window cell, where the windows are kept at the same temperature as the gas sample, has material problems regarding strength, transmissivity and chemical attack from the test gases at high temperatures. The cold window cell avoids these problems with water-cooled windows but has temperature and density variations inside the gas cell. The nozzle seal cell has no windows and separates the gas sample cell from the surroundings with a flow of inert gases as nitrogen or argon. Close to the nozzle is a concentration gradient causing scattering due to turbulent eddies of the mixing flows. Free jet test rigs are basically laminar burner test rigs with a spectrometer attached. They have temperature and concentration gradients and are therefore not useful for the determination of spectral properties of gases. Their usefulness lies in the verification of complete models for non-homogeneous and non-isothermal models. Another option is the use of supersonic burners or shock tubes. They were used during the 1960's for the measurements of spectral gas properties at very high temperatures. More details and schematics to all test rig types can be found in Modest [82, p. 346ff] and in Ludwig [76, p. 291ff].

2.4.2.2 Flames

Radiation measurements of flames were done with different types of fuels, burners and radiation probes. The most important **types of fuels** are:

- **Gases** such as natural gas, methane, propane, ethylene, acetylene, carbon monoxide, hydrogen. The main distinction between them lies in the fact that higher hydrocarbons tend to form more soot in the flame with a continuous spectrum and lower hydrocarbon flames radiate only a molecular gas spectrum [121].
- Liquid fuels such as oil gasoline. They burn in droplet combustion and are a complete research area of their own.
- **Solid fuels** such as pulverized coal or biomass. Flames from solid fuels exhibit continuous particle radiation, which blur the gaseous radiation. The processes in a solid fuel flame are the most complex. For example, soot is formed but the amount is very difficult to measure due to the burning fuel particles, which exist at the same time [121, p. 349ff].

The next type of distinction is the **burner type**. Gaseous fuels can be burned in a laminar flow diffusion or pre-mixed burner. Solid, liquid and gaseous fuels are burned in a turbulent diffusion flame in most technical processes. Radiation from laminar flames is more easy to simulate as the added complication of the turbulence/radiation interaction is missing (section 2.2.3). Most spectral measurements were done with lab scale burners, which are the most easy to characterize regarding the temperature and composition field. Measurements of the processes on a technical scale are found more seldomly in the literature as they require a greater effort in terms of measuring equipment and other resources [121, p. 265].

The last distinction for radiation measurements is the **type of probe**. There exist a wide variety of total radiation probes, which measure the total radiation not spectrally resolved. They can be constructed as a hemispherical probe with measuring radiation over a solid angle of 2π [47] or as a narrow angle probe [3–6, 48, 72], that measures only the incoming radiation in a narrow solid angle. One common problem in refractory lined combustion chambers is the background radiation. The

refractory is typically at similar temperatures as the gas atmosphere, but radiates as a grey body continuously over the spectrum. The background radiation can easily blur the emitted radiation from the flame and renders the results useless. This is particularly a problem for hemispherical probes. A cold target on the opposite wall avoids these problems for narrow angle measurements. All spectrometers, which measure the emission spectrally resolved, work based on the principle of narrow angle probes.

2.4.3 Spectroscopic equipment

Spectrometers consist of a spectral separator and a detector. The former performs the separation of the spectrum in the various wavelengths, while the latter detects the quantity of the incoming separated photons.

2.4.3.1 Spectral separators

The spectral separator can be either a monochromator or a Fourier-transform infrared spectrometer (FTIR). Optical filters and lasers (monochromatic light sources) are also used to measure a certain wavelength range. I restrict the following description to the first two types of instruments as only they are able to record a full intensity vs. wavelength spectrum.

- Monochromators consist of an entrance slit, where only a part of the light is let through, a prism or grating for separating the polychromatic incoming light into spectral components, and an exit slit that lets only a specific wavelength pass through (figure 2.14). The detector is positioned after the exit slit. The angle of the prism or grating has to be changed for detection of a full spectrum. Another possibility is the use of a linear photo diode array for the simultaneous detection of different wavelengths.
- **FTIR spectrometer** work after the principle of interference of two beams of light. The incoming light is divided by a beam splitter into two paths. One path has a fixed length due to a fixed mirror and the other path has a variable length with a moving mirror (figure 2.15). Both paths are again combined at the beam splitter and an interferrogram results on the detector. Half of the incoming light is reflected back towards the source and the other half reaches



Fixed mirror Source Beamsplitter Detector

Figure 2.14: Principle of a monochromator [82, p. 110].

Figure 2.15: Principle of a Michelson interferometer, the most basic FTIR design [52, p. 20].

the detector. The beam splitter is made of a special optical material that partially reflects and partially transmits the incoming light. The resulting interferogram is converted by a computer with a fast-Fourier-transformation in an intensity vs. wavelength spectrum.

FTIR detectors have following advantages over monochromators [52, p. 171]:

- Fellgett's (multiplex) advantage The FTIR is able to measure all wavelengths simultaneously. This results in a higher signal-to-noise ratio (SNR) for a spectrum with the same resolution, optical throughput and efficiency compared to a monochromator. The SNR is higher by a factor of \sqrt{M} , where M is the number of resolution elements in the spectrum, or the acquisition time for a spectrum with the same SNR is M-times shorter [41].
- Jacquinout (throughput) advantage The FTIR spectrometer allows more light to reach the detector (throughput) as in a monochromator. This advantage is dependent on wavelength, resolution and the constants of the used monochromator gratings. Typical values range from 20 - 300 for the throughput of FTIR spectrometer compared to grating spectrometer [62][52, p. 173].

2.4.3.2 Detectors

Two kinds of infrared detectors exist: Thermal and quantum detectors [52, p. 146]. The former sense a change in the temperature of an absorbing material, the latter are based on the interaction of radiation with the electrons in a solid, causing the electrons to be exited to a higher state and an electrical current to flow. Solar panels for the production of electricity work by the same principle. The main parameters of the detectors are the area of incident radiation A_D and the specific detectivity D^* of the detector.

Most thermal detectors are too slow for FTIR systems. The only thermal detectors fast enough for modern FTIR systems, i.e. with a response time of less than 1 ms, are pyroelectric bolometers such as deuterated triglycine sulfate (DTGS) or deuterated lanthanum triglycine sulfate (DLATGS) detectors.

Quantum detectors normally have a higher sensitivity than thermal detectors, but require cooling to temperatures as low as -196 °C to reduce the level of noise. They have a sensitivity in a small wavelength range (figure 2.16). The higher the sensitivity and the lower the value of λ_{min} required, the lower the temperature to which the detector must be cooled. A lot of different semiconductor materials can be used for quantum detectors. For mid-infrared applications mercury cadmium telluride (MCT) detectors are the most common type. Their sensitivity D^* is normally 10 to 50 times greater than the sensitivity of DTGS detectors. They can be cooled thermo electrically to -20 °C or with liquid Nitrogen to -196 °C. Other common quantum detector types are InSb, InAs, Ge and InGaAs.

2.4.3.3 Characteristics of FTIR spectrometer

The spectral **resolution** is given in FTIR spectrometry in wavenumber $[\text{cm}^{-1}]$ as the Fourier-transformations are done in the frequency domain, i.e. to and from wavenumbers. If the spectrum is converted from wavenumber to wavelength, the constant wavenumber resolution results in a wavelength resolution dependent on the spectral position (table 2.5). As in spectral modelling the models are calculated in wavenumbers with a constant wavenumber resolution, the resulting spectra do not have a constant resolution if converted to wavelength (SNB model with resolution of 25 cm^{-1} in figure 2.10).

The highest possible resolution of a FTIR spectrometer $\Delta \omega_{min}$ is a function of the maximum optical path difference OPD_{max} [52, p. 28].

$$\Delta\omega_{min} = (OPD_{max})^{-1} \tag{2.93}$$

This means that the maximum traveling distance of the moving mirror restricts the minimal possible resolution. For a Michelson interferometer (figure 2.15) the



Figure 2.16: Plots of specific detectivity D^* as a function of wavelength for different detector types [117].

Spectral position		Resolution		
$[\mu\mathrm{m}]$	$[\mathrm{cm}^{-1}]$	[nm]	$[\mathrm{cm}^{-1}]$	
1	10000	2.5	25	
2	5000	10	25	
5	2000	63	25	
10	1000	256	25	
20	500	1053	25	

Table 2.5: Spectral resolution for wavenumber and wavelength spectra

maximum OPD is twice the maximum traveling distance of the moving mirror. The factor is dependent on the interferometer design.

Another restriction of FTIR spectrometry is the **collimation of light**. Only parallel light travels "correctly" through the interferometer. Divergence results in different OPD within the beam entering the instrument and distorts the interferogram. The maximum solid angle $\Omega_{max,Resolution}$, which can be tolerated, is [52, p. 44]

$$\Omega_{max,Resolution} = 2\pi \frac{\Delta\omega}{\omega_{max}} \tag{2.94}$$

and is therefore a function of the spectral resolution and the maximal wavenumber. A collimator with a Jacquinot stop in the optical path before the interferometer can be used to restrict the maximum solid angle. A Jacquinot stop consists of two planoconvex lenses spaced exactly at the sum of the two focal lengths with an aperture in the focal point (figure 2.17). The size of the aperture restricts the maximum possible solid angle $\Omega_{max,Jacquinot}$ as [31, p. 612]

$$\Omega_{max,Jacquinot} = \frac{d_{aperture}^2}{d_{inlet}^2 \cdot f_{l,collimator}^2}$$
(2.95)

where d_{inlet} is the diameter of the beam entering the collimator, $d_{aperture}$ is the diameter of the aperture in the Jacquinot stop and $f_{l,collimator}$ is the focal distance of the lens before the aperture.

The maximal size of the Jacquinot aperture can be calculated by combining equations (2.94) and (2.95):

$$d_{aperture,max} = d_{inlet} \cdot f_{l,collimator} \sqrt{2\pi \frac{\Delta\omega}{\omega_{max}}}$$
(2.96)

Every FTIR has a certain amount of noise, i.e. random fluctuations, that are independent from the incoming light spectrum. The main source for the noise should be the detector noise. The optical path components can generate noise as well, but this noise can be reduced. The theoretical SNR of a FTIR system can be calculated as [52, p. 162]

$$SNR_{\omega} = \frac{I_{\omega} \Theta \Delta \omega \sqrt{t} D_{\omega}^* \xi_{\omega}}{\sqrt{A_D}}$$
(2.97)

where I_{ω} is the incoming intensity, Θ is the optical throughput of the system, i.e. the product of the area of the beam and its solid angle Ω at the limiting aperture



Figure 2.17: Collimator with Jacquinot stop.

of the system, t is the acquisition time, D^*_{ω} is the sensitivity of the detector, ξ_{ω} is the efficiency of the system and A_D is the illuminated area of the detector. It can be seen, that the SNR is linearly dependent on the optical throughput, the system efficiency and the resolution of the system. Longer acquisition times, i.e. averaging of scans, increases the SNR with the square root of the number of scans.

The shape of the spectrum from the FTIR is distorted by the instrumental line shape (ILS) function of the system. The ILS is important for measurements of high ($< 0.5 \text{ cm}^{-1}$) and medium ($< 8 \text{ cm}^{-1}$) resolution, but can be neglected for low resolution measurements [18].

The signal from the FTIR detector has the form of a double sided interferogram. The center burst or maximum detector signal is at the point of zero path distance (ZPD), where no destructive interference occurs (figure 2.18).

Sampling of the detector voltage U_D is triggered if the sinusoidal interferogram from a reference laser has a negative zero crossing. Most systems use a HeNe laser with a wavelength of 0.632816 µm. This frequency can be increased with the oversampling factor. An oversampling factor of two results in triggering a sampling at positive and negative zero crossings.

A few correction methods have to be applied during the transformation from an interferogram to a full intensity vs. wavelength spectrum. The common procedure is [52, p. 88ff]:

1. Zero filling: Zero filling is a useful method for interpolation of the spectrum



Figure 2.18: An example of a raw interferogram. The y-axis shows the detector voltage U_D . The x-axis variable is the optical path distance *OPD* as a multiple of the reference laser wavelength and the oversampling factor.

[52, p. 227]. A double sided spectrum with $2 \times M$ data points is interpolated by the zero filling factor $f_{zerofilling}$ to $2 \times M \times (f_{zerofilling} + 1)$ data points with the addition of $f_{zerofilling} \times M$ zeros at both ends of the interferogram.

2. Apodization of the interferogram: The interferogram is numerically weighted with an apodization function to suppress side lobe oscillations [52, p. 32]

$$U_{D,corr}(OPD) = U_D(OPD) \cdot A(OPD)$$
(2.98)

where A(OPD) is the apodization function. Possible functions can be found in Griffiths and Haseth [52, p. 33ff]. The most used ones are the Boxcar and the Norton-Beer function.

- 3. Shift of interferogram: The maximum value is shifted in order to the first position to reference the function as close as possible to zero the phase.
- 4. Fast Fourier transform (FFT): The complex phase curve $B'(\omega)$ is produced as the original function has both cosine and sine components.

$$B'(\omega) = FFT(U_{D,corr}(OPD))$$
(2.99)

The central point has the highest wavenumber ω_{max} calculated by the wavenumber of the reference laser ω_{ref} and the oversampling factor $f_{oversampling}$:

$$\omega_{max} = \frac{2\,\omega_{ref}}{f_{oversampling}}\tag{2.100}$$

while the two endpoints correspond to 0 cm^{-1} . All FFT-algorithms are most computationally efficient, if the number of data points is 2^x .

5. **Phase correction** with the Mertz method: The phase angle θ is calculated as [52, p. 86]:

$$\theta_{\omega} = \arctan \frac{\mathrm{Im}(B'(\omega))}{\mathrm{Re}(B'(\omega))} \tag{2.101}$$

The final spectrum $B(\omega)$ is calculated from the cosine and sine of the phase angle and the real and imaginary part of the phase curve $B'(\omega)$:

$$B(\omega) = \operatorname{Re}(B'(\omega))\cos\theta_{\omega} + \operatorname{Im}(B'(\omega))\sin\theta_{\omega}$$
(2.102)

- 6. **Deletion of the left half of the spectrum** as both halves include the same information
- 7. Cut to selected upper and lower limits as the optical system only has sensitivity in a certain range of the spectrum.
- 8. Calibration with response function of the system: The optical response function $R(\omega)$ of the system is calculated with a recorded spectrum of a black body source $B_b(\omega)$ through the same optical path as the measured spectrum with known emissivity ϵ_b and known temperature T_b .

$$R(\omega) = \frac{B_{b,T_b}(\omega)}{\epsilon_b \cdot I_{b,T_b}(\omega)}$$
(2.103)

The response function includes all absorption and transmission effects of the used equipment such as the sensitivity of the detector and the transmissivity of the beam splitter, the windows and lenses. The final calibrated spectrum $I(\omega)$ is then calculated as:

$$I(\omega) = \frac{B(\omega)}{R(\omega)} \tag{2.104}$$

2.5 Experimental validation of spectral models at high temperatures

The experimental validation of spectral radiation models has been the topic of various research projects. The projects can be divided into gas cell experiments with a very defined temperature and gas concentration and in flame measurements (section 2.4.2). I will summarize in the following section the most important projects and their results.

Gas cell experiments were done mostly for one gas species at a time due to the independence of the spectral gas properties (compare the hypothesis of an isolated line / equation 2.40 on page 32). As the main products of combustion are water vapor and carbon dioxide, only these two gases are considered in the following section:

The first systematic measurements for spectral properties of combustion gases were done by C. H. Hottel during the 1940s [58–60]. He made his own experiments and took data from the literature to derive a total emissivity model. This model was further improved by Leckner [73] and is still in use today for engineering calculations [94].

The next large project was stimulated by the moon landing projects carried out by the USA during the 1960's. The NASA financed systematic experiments and the development of spectral models of combustion gases, which were necessary for the design of space rocket propulsion systems. A good review of the work done was written by Ludwig [76]. The statistical narrow band model RADCAL from Grosshandler [54] is a direct result of this project.

In the 1990's, Phillips carried out experiments in the range from 300 - 1000 K for the 4.3 µm CO₂ band and the 2.7 µm H₂O band [87, 88]. He validated a band model from Young [127], which was extrapolated from low temperature data and the 1986 edition of HITRAN [99]. He found poor agreement between his high temperature experiments and both models, and proposed new narrow band model parameters for the two bands.

The most recent experiments were done during the master and PhD thesis of Sudarshan Bharadwaj [11–13, 83]. He made CO_2 and H_2O measurements in a drop tube gas cell at temperatures up to $1550 \,\mathrm{K}$ with a resolution of $4 \,\mathrm{cm}^{-1}$ (figure 2.19). The measurements of water vapor were similar to the carbon dioxide measurements with a different gas supply and an additional gas chromatograph for measuring the gas atmosphere. In one paper from 2002 [83] he validated the statistical narrow band models RADCAL and EM2C and the LBL models HITEMP1995 and HI-TRAN96 with CO_2 experimental data. He found large differences between the two LBL models compared to the experiments at high temperatures and at the band wings. RADCAL deviated for optically intermediate conditions at the band centers but was otherwise in good agreement. The EM2C model showed good agreement up to 1300 K but missed some hot lines at higher temperatures. The two later articles validated the LBL models with new experimental data. In the first article Bharadwaj et al. [13] were comparing experimental data from H_2O with the LBL database HITEMP1995 [98] and in the second article Bharadwaj and Modest [11] compared new CO_2 experimental data with the LBL database HITEMP1995 and the LBL database CDSD-1000 [116]. The results for the H_2O data were in a good agreement between the experiments and the HITEMP1995 data for temperatures up to 1600 K. The modeled absorption was slightly less than from the experiments indicating the absence of hot lines. The new CO_2 data [11] showed a very good



Figure 2.19: Setup of the CO_2 measurements from Bharadwaj and Modest [11].

agreement of CDSD-1000 data with the experimental data. The HITEMP1995 data showed overprediction of absorption in most bands. The CDSD-1000 database was recommended as a good choice for the simulation of CO_2 absorption up to temperatures of 1600 K.

2.6 Spectral gas radiation modeling for oxyfuel combustion

The spectral modelling approaches proposed specifically for oxyfuel were either implementing the EWB model into CFD simulations or generating a new set of WSGG model parameter valid for the new combustion atmospheres under oxyfuel conditions (table 2.6). In the following section, all approaches are briefly described while I start with the group of EWB implementations.

Kakaras et al. [65] made a comparison of different spectral codes for the use in oxyfuel combustion based on the literature and model properties. They concluded that the EWB model is the best compromise between accuracy and computational effort. They wrote a standalone code of the EWB and validated the code with values presented by Edwards [33]. Various total absorptivity results were presented but not

Main author	Type	Adapted	Validated by	References
E. Kakaras	EWB	no	EWB	[65]
J. Erfurth	EWB	no	EWB	[36, 37]
J. Ströhle	WBCK	no	EWB	[109, 111]
S. P. Khare	WSGG	yes	EWB	[55, 67, 123]
C. Yin	WSGG	yes	EWB	[126]
S. Rehfeldt	WSGG	yes	EWB	$\left[92,\;93\right]$ / model parameters not
				published
R. Johansson	WSGG	yes	SNB (EM2C)	[4-6, 63, 64]
G. Krishnamoorthy	WSGG	yes	SNB (RAD-	[69, 70, 85]
			CAL)	

Table 2.6: Spectral gas radiation models proposed for oxyfuel CFD-simulation.

compared to other models. They did not mention which beam length s (cell-based or domain-based) should be used for the implementation of the EWB model into a CFD code.

Erfurth et al. [37] compared 3D CFD simulations in a 1210 MW pulverized coal unit using the WSGG model from Smith et al. [105] with both domain-based path length and cell based path length and a simulation with the EWB model discretized in 10 beforehand defined spectral intervals. The EWB implementation solved 10 RTE's, while a mean beam length based on each cell's dimension was used as optical path length s. The resulting wall heat fluxes showed a very high heat flux by the cell-based WSGG model. The domain-based WSGG model showed very uniform heat flux profiles. The EWB model implementation showed higher fluxes compared to the domain-based WSGG model but more pronounced profiles according to the flow field characteristics. The EWB model implementation was assumed to be the reference case as the parameters of the WSGG model from Smith et al. [105] were generated originally from the EWB model. A further study focused on the total heat transfer characteristics of different recirculation rates and types (wet or dry) and used the EWB model to find oxygen concentrations respectively recirculation rates with similar heat transfer to air blown combustion [36].

The third group proposing a wide band model for oxyfuel combustion was Ströhle et al. [111]. They compared different numerical implementations of the wide band correlated-k (WBCK) model [109] under oxyfuel conditions with the standard WSGG



Figure 2.20: Comparison of emissivities at 1500 K for air-fired and oxy-fired systems estimated from WSGG (GGM) with Smith's parameters and EWB (WBM) models [55].

model of Smith et al. [105] implemented as in the grey and the banded formulation (section 2.3.4). The WBCK is based on the EWB model (section 2.3.3). The authors concluded that the optimized "Multiple Gases Formulation" is the best compromise with regard to the accuracy and efficiency of 3D calculations for oxyfuel combustion.

The first author who generated new WSGG model parameters for specific oxyfuel conditions (table 2.3) was Khare [67, p. 83-100]. He showed for the first time the consequences of being outside the validity range of the parameter from Smith [55] for a path length larger than 10 m with a comparison of path length dependent total emissivity ϵ_{tot} calculated with the EWB model and the WSGG model (figure 2.20). The EWB results were regarded as a reference. He concluded that the true gas emissivity in oxyfuel combustion is underestimated especially for large path lengths when using the standard model. Therefore, based on his EWB model calculations he generated new sets of WSGG parameters with an additional 4th grey gas for H₂O/CO₂ ratios of 0.1, 0.2 and 0.48 typical for oxyfuel combustion [67, p. 96].

A similar approach was followed by Yin et al. [126]. The authors gave ten sets of WSGG parameters for different steam to carbon dioxide ratios to account both for air and oxyfuel combustion in CFD calculations. They introduced a 4th grey gas and used the EWB model as a reference model similar to the WSGG model parameter generated by [105]. As the parameter source of the model from Smith et al. [105] and the model from Yin et al. [126] were the same, the resulting total emissivity values of both models were shown to be similar for the simulation of a small 0.8 MW oxy-natural gas furnace. The total emissivity for large beam lengths was shown to be different with CFD results from an 609 MW utility boiler in oxyfuel conditions.

Rehfeldt et al. [92, 93] implemented the EWB model in 3D CFD calculations and generated a new set of WSGG model parameters based on the EWB model. A variable for the molar ratio of H_2O/CO_2 was used resulting in a model applicable for most industrial oxyfuel processes. They did not publish their WSGG parameters. Wall heat flux calculations with radiating particles mixed to nitrogen or to oxyfuel flue gases showed that the gas radiation is responsible for 15% of the radiative heat transfer and therefore cannot be neglected. 3D CFD simulations showed a good aggreement of their new WSGG model and the EWB model.

Johansson et al. [63] compared different SNB models (EM2C, RADCAL, Leckner [73]) with the SLW model and the WSGG model in both the grey and the banded formulation. The authors concluded, that only the WSGG model can be used in large scale 3D simulations due to computational costs. If temperature gradients were present, the banded formulation gave good results, but to higher computational costs compared to the grey model formulation. The grey model formulation was recommended if small temperature gradients existed and the computational effort should be reduced. To overcome the invalidity of the WSGG model parameter from Smith et al. [105] for oxyfuel conditions, the authors gave new WSGG model parameter sets for H_2O/CO_2 ratios of 0.125 and 1 for three and four grey gases based on total emissivity calculations of the SNB model EM2C. The maximal deviations of total emissivity to the reference model are stated to be 20%. In a second paper, Johansson et al. [64] published a WSGG model with parameters dependent on gas temperature and steam to carbon dioxide ratio in a range from 0.125 to 2 (section 2.3.4.1). They were the first group giving one set of parameters dependent not only on gas temperature but also on the composition of the gases. This approach simplifies the usage of the WSGG model. The authors showed, that the total emissivities calculated with the new model were within 5% of the SNB model EM2C, which was used as a reference model.

Another study concerned with the generation of new sets of WSGG model parameters was published by Krishnamoorthy et al. [70]. The authors compared total emissivity values calculated with the SNB model RADCAL, the EWB model, a total emissivity model from Perry and Green [86] and the WSGG model from Smith et al. [105]. They found the same invalidity of the Smith et al. [105] model for large path length and low H_2O/CO_2 ratios as the other authors. The model from Perry and Green [86], which is based on the work from Hottel and Sarofim [57] with later adaptions according to the SNB model RADCAL, was found to give large errors for low H_2O/CO_2 ratios, as the correlations for traces of pure CO_2 are used. The Perry and Green [86] model was complemented by the authors with new correlations for low H_2O/CO_2 ratios based on the RADCAL model. These correlations were not published. Based on the supplemented Perry and Green [86] model a new set of WSGG model parameters was developed with three sets for air, oxyfuel wet and oxyfuel dry conditions with three grey gases. The influence of the new model was seen to be small in a simulated pulverized coal fired lab scale furnace due to the domination of particle radiation by an average factor of 2.7 - 5.5. Nevertheless, pockets were found in a full-scale boiler, where gas radiation dominated the particle radiation.

2.7 Objective of the thesis

The main difference between the furnace atmosphere for radiation processes in oxyfuel combustion compared with air blown combustion is the higher percentage of the radiatively active gas fraction and the changed H_2O/CO_2 ratio in case of a dry recirculation process (table 2.7).

The H_2O/CO_2 ratio is important for modeling the spectral gas radiation behavior as the standard simplified model for computationally fluid dynamic (CFD) calculations, the weighted-sum-of-grey-gases (WSGG) model of Smith et al. [105], is defined only for the specific ratios of 1 and 2. More complex spectral models are not limited to predefined ratios, i.e. allow variable gas compositions (table 2.1). The increase in partial pressure of the radiatively active gases from 25 vol. -% up to nearly 100 vol. -% results in another limiting factor for the use of the WSGG model. The maximal partial pressure path length products in large scale oxyfuel boilers are far above the range of validity of the Smith model (0.01 - 9.87 barm) with optical

Table 2.7: Exemplary calculated gas properties with different fuels and combustion processes; air: air blown combustion; wet: oxyfuel combustion with wet recirculation; dry: oxyfuel combustion with dry recirculation; all oxyfuel processes were calculated with 67 % recirculation rate; equivalence ratio oxygen to fuel: 1.2

	Natural gas		Brown coal			Anthracite			
	air	dry	wet	air	dry	wet	air	dry	wet
CO_2 [vol%]	8.1	55.8	31.9	14.6	76.7	57.3	15.1	83.4	70.7
H_2O [vol%]	16.1	36.8	63.8	9.6	16.6	37.7	4.8	8.8	22.6
O_2 [vol%]	3.2	7.3	4.2	3.3	5.8	4.3	3.5	6.4	5.4
N_2 [vol%]	72.6	0.1	0.1	72.5	0.9	0.7	76.6	1.4	1.3
Radiatively active [vol%]	24.2	92.6	95.7	24.2	93.3	95	19.9	92.2	93.3
H_2O/CO_2 [-]	2.0	0.7	2.0	0.7	0.2	0.7	0.3	0.1	0.3
Partial pressure path length									
product $(s = 40 \text{ m})$ [bar m]	9.6	36.6	37.8	9.6	36.8	37.5	7.9	36.4	36.8

path length up to 40 bar m (table2.7).

In the literature, there are quite a few solutions published for this specific problem (tables 2.3 and 2.6). All authors were either using a more detailed model as the exponential-wide-band (EWB) model from Edwards [33] or a more modern wide-band-correlated-k (WBCK) model, or they generated a new set of parameters for the WSGG model based on more detailed models such as the EWB or statistical-narrow-band (SNB) models [54, 106]. All proposed models were developed based on other detailed models using reference calculations under oxyfuel combustion conditions rather than models developed and validated based on experimental data.

The research question I wanted to answer was:

How valid are the existing spectral gas radiation models for oxyfuel combustion?

To answer this question I first validated detailed spectral models (with a spectral resolution of 25 cm^{-1} or better / table 2.1) with experimental data using a systematic approach (figure 2.21). I validated the models with spectral measurements from a hot gas cell, where the gas composition and temperature were well known. Spectral measurements from a turbulent natural gas flame, as for example in the



Figure 2.21: Method for the validation of spectral gas radiation models under oxyfuel conditions.

case of a technical combustion process, were compared to simulated spectra based on measured temperature and gas composition profiles. With the results I selected a detailed model as a reference model for the validation of more simplified models which are based on a smaller number of spectral discretization equations. The final aim was the recommendation of the best simplified model for the calculation of spectral gas radiation under oxyfuel conditions that can be used readily in large scale 3D furnace CFD-simulations.

Chapter 3

Gas cell experiments

In the following chapter new experiments in a hot gas cell are described with the aim to validate detailed spectral models with experimental spectral data from a well controlled atmosphere.

3.1 Materials and methods

3.1.1 Experimental setup

The author used unpublished measurements from the Optical Diagnostics Group in the Riso National Laboratory of DTU. S. Clausen and A. Fateev made measurements of H_2O and CO_2 in various concentrations and temperatures in a hot gas cell [19, 39, 40].

The gas cell (figure 3.1) had nozzle seals in the hot temperature zone and could be used for measurements of slabs of a defined gas mixture of up to 1600 °C [19, 39, 40]. The path length s [m] of the uniform gas mixture slab was dependent on the temperature T [K] according to

$$s(T) = 0.533 \cdot \left[1 + 0.00000725 \cdot (T - 273.15) + 1.047 \cdot 10^{-9} \cdot (T - 273.15)^2 \right] \quad (3.1)$$

The preheated sample gas flowed from two sides (only from one side in the H_2O experiments) concentrical around the inner ceramic tube and entered the gas sample cell in the middle of the cell. The flow turned outwards to the nozzle seals, where it mixed with nitrogen and flowed first radial and then axial out of the setup. The nitrogen and the sample gas flow were carefully maintained at the same flow rate

of around 2 L/min to keep the mixing layer in the nozzle stable and as plane as possible.

The sample gas was supplied by a premixed gas bottle of N₂ (quality 4.8 = 99.998 vol. -%) and CO₂ in the different concentrations for the CO₂ experiments and by an evaporator connected to a water syringe dosing pump system and a nitrogen bottle (quality 4.8 / figure 3.2) for the H₂O experiments. The water syringe dosing pump system had an uncertainty of $\pm 1.5 \%$ of the flow.

The optical setup was based on the principle of transmission (figure 3.3 / section 2.4.1). Either a hot $(800 \,^\circ\text{C})$ or a cold $(25 \,^\circ\text{C})$ black body was used as a light source. A flipping mirror made by metal substrate coated by Al allowed a fast change between both black bodies without a disturbance of the alignment. The black bodies and the space up to the outer cold window of the hot gas cell were purged by dry, CO_2 -free air. The light traveled through the cold outer KBr window (34 mm free aperture), which was tilted and wedged to minimize reflections. The aperture of the gas sample cell had a diameter of 15 mm. A variable aperture (aperture 1 in figure 3.3) was placed in the optical path after the hot gas cell. A Jacquinot stop with two off-axis parabolic mirrors (gold coated) and an aperture (aperture 2) in a metal housing fixed to the FTIR housing were placed before the emission port of the FTIR. The diameters of the two apertures were variable. Aperture 2 was normally set to a diameter of 1.3 mm and aperture 1 was opened less than 15 mm in order to minimize any wall effects. The spectrum was recorded with a FTIR Nicolet 5700 from ThermoFisher in emission mode operated with an external source. It was equipped with an InSb detector which was sensitive in the range of $1.7 - 5.6 \,\mu m$ $(1800 - 5900 \,\mathrm{cm}^{-1})$ and a KBr beam splitter. A thorough description and analysis of the hot gas cell and its measurements uncertainty is given by Clausen et al. [19].

Single sided interferograms with a nominal resolution $\Delta \omega$ of $0.125 \,\mathrm{cm}^{-1}$ were recorded at an optical retardation velocity of $9.494 \,\mathrm{mm/s}$. The number of averaged scans for one recorded spectrum was typically 144, which corresponded to an acquisition time of 14 min. The interferograms were converted by the OMNIC software from ThermoFisher to spectra with a Fast-Fourier-Transformation with the Mertz phase correction and the boxcar apodization function.

The methodology of the experiments used four measured net emission spectra for calculation of the transmissivity and the absorption coefficient:

1. Net emission spectrum $I_{N_2,T,HBB}(\lambda)$ from the hot black body and the hot gas



Figure 3.1: Hot gas cell, arrows show the flow directions [40].



Figure 3.2: Schematic of the H_2O/N_2 gas mixing system.



Figure 3.3: Optical path of the hot gas cell measurements (solid red lines). The shaded areas were purged either with nitrogen (dark grey) or dry, CO_2 -free air (light grey).

cell at temperature t purged with nitrogen.

- 2. Net emission spectrum $I_{N_2,T,CBB}(\lambda)$ from the cold black body and the hot gas cell at temperature t purged with nitrogen.
- 3. Net emission spectrum $I_{gas,T,HBB}(\lambda)$ from the hot black body and the hot gas cell at temperature t filled with sample gas.
- 4. Net emission spectrum $I_{gas,T,CBB}(\lambda)$ from the cold black body and the hot gas cell at temperature t filled with sample gas.

where I is the emitted thermal energy (intensity) per unit solid angle.

The transmissivity τ was calculated as

$$\tau_{gas,T}(\lambda) = \frac{I_{gas,T,HBB}(\lambda) - I_{gas,T,CBB}(\lambda)}{I_{N_2,T,HBB}(\lambda) - I_{N_2,T,CBB}(\lambda)}$$
(3.2)

The advantages of this measurement methodology are according to Clausen et al. [19] a simple alignment of the setup, an increased signal level when the gas temperature is larger than the black body temperature in the background, and that the DC signal due to thermal radiation is minimized. The exact temperatures of the hot and cold black bodies are not needed for the calculation of the spectral gas properties as the correction of the emitted spectrum with the response function of the system is already implied in the calculation of the transmissivity τ . The drawbacks are a doubled measurement time compared to traditional transmissivity measurements and the requirement of a highly temperature stable setup. The hot gas cell showed temperature uniformity better than ± 2 K within 0.45 m and a temperature stability of better than ± 0.1 K/h [19]. The hot black body had a temperature stability of ± 0.2 K. The transmission measurements were done at temperatures from 727 °C up to 1500 °C and different gas concentrations (table 3.1 and table 3.2).

3.1.2 Numerical simulation

All numerical simulations were done with a MATLAB based program called RADE-VAL (http://www.es.mw.tum.de/radeval), which was developed during the project. The aim of the program was the comfortable evaluation of experimental radiation spectra and simulation with different spectral models. MATLAB was chosen as the programming language due to the large library of functions and graphical user interfaces and the possibility of calling on external FORTRAN and C programs.

Description	Value					
Temperature	800 °C		$1000^{\circ}\mathrm{C}$	$1400^{\circ}\mathrm{C}$		
H_2O concentration	10 vol. -%	$35 \operatorname{vol.} -\%$	35 vol. -%	35 vol. -%		
Nitrogen flow	$2.0\mathrm{L/min}$					
Sample gas flow	$2.0\mathrm{L/min}$					
Gas cell absolute pressure	$1012.0\mathrm{mbar}$	$1089.2\mathrm{mbar}$	$1082.3\mathrm{mbar}$	$1089.3\mathrm{mbar}$		
Nominal spectral resolution		0.125	cm^{-1}			

Table 3.1: Experimental data from the hot gas cell measurements of H_2O .

Table 3.2: Experimental data from the hot gas cell measurements of CO_2 .

Description	Value
Temperature	727 °C / 1100 °C / 1500 °C
CO_2 concentration	$1\mathrm{vol.}-\%$ / $10\mathrm{vol.}-\%$ / $100\mathrm{vol.}-\%$
Nitrogen flow	$2.0\mathrm{L}/\mathrm{min}$
Sample gas flow	$2.0\mathrm{L}/\mathrm{min}$
Gas cell absolute pressure	$1089.0\mathrm{mbar}$
Nominal spectral resolution	$0.125{ m cm^{-1}}$

The line-of-sight through the hot gas cell was discretized as one cell. The temperature T and the volume concentrations x_k of the radiatively active species k (H₂O and CO₂) from the experiments were the input variables. The partial pressure of the species was calculated with the given total pressure p_{tot} :

$$p_{par,k} = x_k \cdot p_{tot} \tag{3.3}$$

3.1.2.1 Line-by-line modeling

In the LBL modelling approach, the first step was the discretization of the spectral domain, i.e. a selection of the lower and upper limit and of a spectral resolution of $0.125 \,\mathrm{cm}^{-1}$ similar to the experimental measurements. For each spectral discretized wavelength λ or wavenumber ω , the absorption coefficient k_{λ} was calculated according to section 2.3.1 (equations 2.34 to 2.40). The FORTRAN TIPS2009 routine from Fischer et al. [42] was used for the calculation of the total internal partition sums Q(T) (equation 2.35). To avoid the calculation of all molecular lines in the database (up to 111 mio. lines / table 2.2) for each spectral discretization point, it was assumed, that a transition has negligible influence on the absorption coefficient k_{λ} , if the wavelength of the pressure corrected line center ω_c^* (equation 2.36 and figure 2.7) has a distance $\Delta \omega_{line width}$ of more than $10 \,\mathrm{cm}^{-1}$ to the spectral discretization point.

The final gas transmissivity was calculated with the length of the gas sample cell:

$$\tau_{\lambda} = e^{-k_{\lambda} \cdot s} \tag{3.4}$$

where λ is the wavelength $(=1/\omega)$.

3.1.2.2 Statistical narrow band modeling

Two FORTRAN routines were used for modeling of the SNB models RADCAL and EM2C (section 2.3.2), which were available from the companion website of [82]. They calculate the spectral transmissivity over the path length and the emitted spectral intensity. The transmissivity was directly used as simulation result. Both routines work with a minimal spectral resolution of 25 cm^{-1} .

3.1.2.3 Exponential wide band modeling

The EWB model was implemented according to section 2.3.3. The band paramaters were taken from table 10.3 in Modest [82, p. 328f]. Modest [82] gives FORTRAN routines for the calculation of the parameter α and β in the appendix. The parameter for the 9.4 µm and 10.4 µm CO₂ band were calculated with the numerical approximations given by Lallemant and Weber [71]. The band transmissivities τ_{band} were computed without an upper transmissivity limit and the total emissivity ϵ_{tot} calculated with the block calculation procedure. A comparison of the results from the code against the validation case from Yin et al. [126] yielded a total emissivity of 0.1682 against a value of 0.1673 in the cited paper. This is a relative numerical deviation of 0.5 % and within the range of the relative deviations given by Lallemant and Weber [71] for the difference between their approximations and the original model.

3.1.3 Comparison of experimental spectra with numerical simulations

The aim of the gas cell experiments was the validation of the detailed spectral models (table 2.1). The newest LBL databases of the HITRAN series HITRAN2008 [100] and HITRAN2004 [96] for atmospheric calculations, which are valid up to temperatures of 700 K, as well as both available high temperature HITEMP editions 1995 and 2010 [98, 101], the two SNB models RADCAL [54] and EM2C [106] and the EWB model from Edwards [33] were compared with the experimental data.

All transmissivity spectra were downgraded down to a nominal spectral resolution of 32 cm^{-1} according to the procedure of Fleckl et al. [44]. The resolution downgrading was done with an inverse Fast-Fourier-Transformation, a truncation of the interferograms to the new resolution, a zero filling with a factor of one and a Fast-Fourier-Transformation to the final spectrum with lower resolution. The strong Norton-Beer function was used for the apodization function in order to smooth the spectrum [52, p. 33].

The main evaluation of the transmissivity model spectra was done with the band model transmissivity τ_{band} , which was calculated from the transmissivity spectra in downgraded nominal resolution of $32 \,\mathrm{cm}^{-1}$ as

$$\tau_{band} = \frac{\int_{\lambda_1}^{\lambda_2} \tau_{\lambda}}{\lambda_2 - \lambda_1} \tag{3.5}$$



Figure 3.4: Comparison of measured spectrum with high resolution and downgraded low resolution spectrum; $100 \text{ vol.} -\% \text{ CO}_2$ at $1500 \,^{\circ}\text{C}$.

where λ_1 is the left band limit and λ_2 the right band limit.

3.2 Results

3.2.1 Spectral resolution downgrading

The effect of the downgrading of all spectra with different original resolutions (LBL, measurements: $\Delta \omega = 0.125 \,\mathrm{cm}^{-1}$; SNB: $\Delta \omega = 25 \,\mathrm{cm}^{-1}$) to the same resolution of nominal $32 \,\mathrm{cm}^{-1}$ resulted in smoothed spectra (figures 3.4 to 3.6). Especially the sharp band heads were not as sharp as in the original resolution.

3.2.2 Water vapor

As the experimental setup could measure thermal radiation in the range from $1.7 \,\mu\text{m}$ to $5.6 \,\mu\text{m}$ (section 3.1.1), the $1.87 \,\mu\text{m}$, the $2.7 \,\mu\text{m}$ and the left wing of the $6.3 \,\mu\text{m}$ band of water vapor could be detected for the measurement cases (figures 3.7 and 3.8 and table 3.1). All three bands were not very sensitive to an increase in temperature (figure 3.7). Only the right wing (the so called *hot lines*) of the $1.87 \,\mu\text{m}$ and



Figure 3.5: Comparison of simulated (HITEMP2010) spectrum with high resolution and downgraded low resolution spectrum; $100 \text{ vol.} -\% \text{ CO}_2$ at $1500 \degree \text{C}$.



Figure 3.6: Comparison of simulated (EM2C) spectrum and downgraded spectrum; $100 \text{ vol.} -\% \text{ CO}_2$ at $1500 \degree \text{C}$.



Figure 3.7: Measured transmissivity spectra in the hot gas cell for $35 \text{ vol.} -\% \text{ H}_2\text{O}$ at different temperatures at a downgraded nominal resolution of 32 cm^{-1} .

of the 2.7 μ m band showed a widening of the bands due to increased absorption as an increase in temperature increases the probability of vibration-rotational transitions to higher states as opposed to mostly to ground states for lower temperatures (figure 2.6). The peak values of the 2.7 μ m band decreased with increasing temperature. The change of H₂O concentration lead to a strongly pronounced increase in absorptivity for all observed bands (figure 3.8).

While comparing the direct high resolution measurement results with the high resolution LBL simulation results, a good line position agreement between the newest LBL database HITEMP2010 and the experiments could be seen (figure 3.9). The LBL/HITEMP2010 model resulted in four artificial lines, which were not observed in the experimental spectra (three in figure 3.10 and one in figure 3.11).

Direct comparison of the transmissivity spectra and the integrated band transmissivity of the experiment and the different numerical simulations showed a large predictive capability range between the models (figures 3.12 to 3.15 and tables 3.3 to 3.5).

The two HITRAN databases were in good agreement for the $800 \,^{\circ}\text{C}$ (1073.15 K) experiments, but for higher temperatures the missing of the hot lines was evident.


Figure 3.8: Measured transmissivity spectra in the hot gas cell for H₂O at 800 °C for different concentrations at a downgraded nominal resolution of 32 cm^{-1} .



Figure 3.9: Comparison of experimental spectrum and LBL simulation (HITEMP2010) for $35 \text{ vol.} -\% \text{ H}_2\text{O}$ at $1400 \,^{\circ}\text{C}$ at the original resolution of $0.125 \,\mathrm{cm}^{-1}$ in randomly selected spectral range.



Figure 3.10: Three artificial lines near $3.9\,\mu\text{m}$ in LBL simulation spectrum (HITEMP2010) for $35\,\text{vol.} -\%$ H₂O at 1400 °C at the original resolution of $0.125\,\text{cm}^{-1}$.

The HITRAN2008 database was always an improvement over the HITRAN2004 database. The band transmissivity deviations were up to 10% at the 2.7 µm band for 1400 °C.

HITEMP1995 was in a similar deviation range as the two HITRAN databases for high temperatures. The deviations were even worse as the HITRAN databases for low temperatures and high H₂O concentrations. Especially the 2.7 μ m-band had a high band transmissivity deviation of 6.1 – 7.3 % for a H₂O concentration of 35 vol. –%.

The HITEMP2010 predictions matched the experimental results best. The band transmissivity deviated at a maximum of 2.2% from the measured values for high temperatures (1400 °C). The deviations were lower than 0.6% at lower temperatures.

The two SNB models EM2C and RADCAL did not reach the good spectrum agreement of the HITEMP2010 model but the band transmissivities were predicted similarly good or better. The RADCAL model had a maximum deviation of 1.2%. The lower temperatures for high concentrations were predicted worse than for high



Figure 3.11: One artificial line near $4.4 \,\mu\text{m}$ in LBL simulation spectrum (HITEMP2010) for $35 \,\text{vol.} -\% \,\text{H}_2\text{O}$ at $1400 \,^\circ\text{C}$ at the original resolution of $0.125 \,\text{cm}^{-1}$.

temperatures. The EM2C model behaved very similar to the HITEMP2010 model. The band transmissivity deviations were under 1.0% for temperatures up to 1000 °C and 2.9% for higher temperatures (1400 °C).

The accuracy of the EWB model could only be validated for the 1.87 μ m and the 2.7 μ m band of H₂O as the 6.3 μ m band was only partially in the measurement range (figure 3.16). Both bands showed a good agreement of total band transmissivity between the experiment and the simulated values with a maximal absolute deviation of 2.4 %.

The best models for the $1.8 \,\mu\text{m}$ and $2.7 \,\mu\text{m}$ bands of H₂O at high temperatures were (the maximum absolute deviation of measured band transmissivity are shown in brackets):

- 1. SNB/RADCAL $(\pm 1.2\%)$
- 2. LBL/HITEMP2010 ($\pm 2.2\%$), best spectrum agreement, i.e. less visual deviation from measurements as SNB/RADCAL
- 3. EWB $(\pm 2.4\%)$



Figure 3.12: Comparison of experimental and modeled transmissivity spectra for $10 \text{ vol.} -\% \text{ H}_2\text{O}$ at 800 °C and a nominal resolution of 32 cm^{-1} .



Figure 3.13: Comparison of experimental and modeled transmissivity spectra for $35 \text{ vol.} -\% \text{ H}_2\text{O}$ at 800 °C and a nominal resolution of 32 cm^{-1} .



Figure 3.14: Comparison of experimental and modeled transmissivity spectra for $35 \text{ vol.} -\% \text{ H}_2\text{O}$ at $1000 \,^{\circ}\text{C}$ and a nominal resolution of $32 \, \text{cm}^{-1}$.



Figure 3.15: Comparison of experimental and modeled transmissivity spectra for $35 \text{ vol.} -\% \text{ H}_2\text{O}$ at 1400 °C and a nominal resolution of 32 cm^{-1} .



Figure 3.16: Comparison of experimental measured transmissivity spectrum (nominal resolution $32 \,\mathrm{cm}^{-1}$) and exponential wide band model simulation.

Table 3.3:	$1.87\mu\mathrm{m}$	H_2O -band	$(1.7 - 2.2 \mu)$	n) trans	smissivity	and	absolute	deviation
of spectral	models							

H_2O conc. [vol%]	10		35		
Temperature $[^{\circ}C]$	800	800	1000	1400	
Exp. transmissivity [-]	0.9726	0.9272	0.9229	0.9067	
	Nu	merical de	viation (ab	os.)	Max. dev.
EM2C	0.51%	0.29%	1.04%	2.87%	$\pm 2.87\%$
RADCAL	0.02%	-1.17%	-0.61%	1.08%	$\pm 1.17\%$
HITEMP2010	0.01%	-0.59%	0.18%	2.17%	$\pm 2.17\%$
HITEMP1995	0.36%	1.71%	2.13%	3.58%	$\pm 3.58\%$
HITRAN2008	0.33%	0.49%	1.91%	5.18%	$\pm 5.18\%$
HITRAN2004	0.38%	0.74%	2.12%	5.30%	$\pm 5.30\%$
EWB	0.42%	0.68%	0.87%	2.03%	$\pm 2.03\%$

H_2O conc. [vol%]	10		35		
Temperature [°C]	800	800	1000	1400	
Exp. transmissivity [–]	0.9236	0.8113	0.8057	0.7869	
	Nu	merical de	viation (ab	os.)	Max. dev.
EM2C	-0.21%	-0.71%	-0.37%	0.83%	$\pm 0.83\%$
RADCAL	-0.72%	-1.15%	-1.18%	-0.36%	$\pm 1.18\%$
HITEMP2010	0.02%	-0.54%	-0.04%	1.65%	$\pm 1.65\%$
HITEMP1995	1.64%	6.09%	6.29%	7.30%	$\pm7.30\%$
HITRAN2008	0.90%	1.98%	4.19%	9.38%	$\pm 9.38\%$
HITRAN2004	1.24%	2.67%	4.93%	10.10%	$\pm 10.10\%$
EWB	-0.98%	-2.37%	-2.32%	-0.99%	$\pm 2.37\%$

Table 3.4: 2.7 μm H₂O-band (2.2 - 3.8 $\mu m)$ transmissivity and absolute deviation of spectral models.

Table 3.5: Partial 6.3 μ m H₂O-band (3.8 - 5.5 μ m) transmissivity and absolute deviation of spectral models. The EWB model was not evaluated as not the whole spectral band range was measured.

H_2O conc. [vol%]	10		35		
Temperature [°C]	800	800	1000	1400	
Exp. transmissivity [–]	0.9451	0.8539	0.8483	0.8438	
	Nu	merical de	viation (ab	os.)	Max. dev.
EM2C	-0.25%	-0.62%	-0.06%	0.38%	$\pm 0.62\%$
RADCAL	0.07%	0.43%	0.24%	-0.45%	$\pm 0.45\%$
HITEMP2010	-0.13%	-0.75%	-0.74%	-0.46%	$\pm 0.75\%$
HITEMP1995	0.60%	1.51%	2.04%	2.77%	$\pm 2.77\%$
HITRAN2008	0.49%	1.17%	2.48%	5.19%	$\pm 5.19\%$
HITRAN2004	0.94%	2.36%	3.85%	6.60%	$\pm 6.60\%$



Figure 3.17: Measured transmissivity spectra in the hot gas cell for $1 \text{ vol.} -\% \text{ CO}_2$ at different temperatures at a nominal resolution of 32 cm^{-1} .

- 4. SNB/EM2C $(\pm 2.9\%)$
- 5. LBL/HITEMP1995 ($\pm 7.3\%$), wrong at H₂O concentrations ≥ 35 vol. -%
- 6. LBL/HITRAN2008 ($\pm 9.4\%$), missing hot lines at temperatures > 800 °C
- 7. LBL/HITRAN2004 ($\pm 10.1\%$), missing hot lines at temperatures > 800 °C

3.2.3 Carbon dioxide

The experimental setup was capable of detecting the 2.7 μ m and the 4.3 μ m band of carbon dioxid for all measured cases (table 3.2). Both bands have sharp band heads at the lower wing (figure 3.4).

The experimental results revealed a similar dependence on temperature as in the H_2O experiments (figure 3.17 to 3.19). The peak band absorptivity was decreasing with increasing temperature while the hot lines at the right band wings lead to an increase in absorptivity. The latter effect was most pronounced at the right wing of the 4.3 µm band. An increase in CO_2 concentration lead to a more pronounced increase in absorptivity (figure 3.20 to 3.22).



Figure 3.18: Measured transmissivity spectra in the hot gas cell for $10 \text{ vol.} -\% \text{ CO}_2$ at different temperatures at a nominal resolution of 32 cm^{-1} .



Figure 3.19: Measured transmissivity spectra in the hot gas cell for $100 \text{ vol.} -\% \text{ CO}_2$ at different temperatures at a nominal resolution of 32 cm^{-1} .



Figure 3.20: Measured transmissivity spectra in the hot gas cell for $727 \,^{\circ}\text{C CO}_2$ at different concentrations at a nominal resolution of $32 \,\mathrm{cm}^{-1}$.



Figure 3.21: Measured transmissivity spectra in the hot gas cell for $1100 \,^{\circ}\text{C CO}_2$ at different concentrations at a nominal resolution of $32 \,\mathrm{cm}^{-1}$.



Figure 3.22: Measured transmissivity spectra in the hot gas cell for $1500 \,^{\circ}\text{C CO}_2$ at different concentrations at a nominal resolution of $32 \,\mathrm{cm}^{-1}$.



Figure 3.23: Comparison of experimental spectrum and LBL simulation (HITEMP2010) for 100 vol. -% CO₂ at 1500 °C at the original resolution of $0.125 \,\mathrm{cm}^{-1}$ in randomly selected spectral range.

The line positions at original resolution of the LBL model with the HITEMP2010 database were, similar to the H_2O results, in very good agreement with the experimental measurements (figure 3.23).

The visual comparison of the experimental with the simulated spectra at a nominal resolution of 32 cm^{-1} (figure 3.23 to 3.32) and the deviations of the simulated band transmissivities from the experimentally measured values (table 3.6 and 3.7) showed following results, similar to the results from the water vapor comparisons.



Figure 3.24: Comparison of experimental and modeled transmissivity spectra for $1 \text{ vol.} -\% \text{ CO}_2$ at $727 \,^{\circ}\text{C}$ and a nominal resolution of $32 \, \text{cm}^{-1}$.



Figure 3.25: Comparison of experimental and modeled transmissivity spectra for $10 \text{ vol.} -\% \text{ CO}_2$ at $727 \,^{\circ}\text{C}$ and a nominal resolution of $32 \, \text{cm}^{-1}$.



Figure 3.26: Comparison of experimental and modeled transmissivity spectra for $100 \text{ vol.} -\% \text{ CO}_2$ at $727 \,^{\circ}\text{C}$ and a nominal resolution of $32 \,\text{cm}^{-1}$.



Figure 3.27: Comparison of experimental and modeled transmissivity spectra for $1 \text{ vol.} -\% \text{ CO}_2$ at $1100 \,^{\circ}\text{C}$ and a nominal resolution of $32 \, \text{cm}^{-1}$.



Figure 3.28: Comparison of experimental and modeled transmissivity spectra for $10 \text{ vol.} -\% \text{ CO}_2$ at $1100 \,^{\circ}\text{C}$ and a nominal resolution of $32 \, \text{cm}^{-1}$.



Figure 3.29: Comparison of experimental and modeled transmissivity spectra for $100 \text{ vol.} -\% \text{ CO}_2$ at $1100 \,^{\circ}\text{C}$ and a nominal resolution of $32 \, \text{cm}^{-1}$.



Figure 3.30: Comparison of experimental and modeled transmissivity spectra for $1 \text{ vol.} -\% \text{ CO}_2$ at $1500 \,^{\circ}\text{C}$ and a nominal resolution of $32 \, \text{cm}^{-1}$.



Figure 3.31: Comparison of experimental and modeled transmissivity spectra for $10 \text{ vol.} -\% \text{ CO}_2$ at $1500 \,^{\circ}\text{C}$ and a nominal resolution of $32 \, \text{cm}^{-1}$.



Figure 3.32: Comparison of experimental and modeled transmissivity spectra for $100 \text{ vol.} -\% \text{ CO}_2$ at $1500 \,^{\circ}\text{C}$ and a nominal resolution of $32 \, \text{cm}^{-1}$.

CO_2 conc. [vol%]		1			10			100		
Temperature [°C]	727	1100	1500	727	1100	1500	727	1100	1500	
Exp. transmissivity [–]	0.9919	0.9874	0.9929	0.9300	0.9295	0.9304	0.7718	0.7371	0.7120	
				Numer	ical deviat.	ion (abs.)				Max. dev
EM2C	-0.11%	0.49%	0.03%	0.08%	0.63%	0.91%	0.08%	1.77%	2.25%	$\pm 2.25\%$
RADCAL	-0.24%	0.31%	-0.19%	-0.96%	-0.82%	-0.90 %	-0.96%	-1.20%	-2.40%	$\pm 2.40 \%$
HITEMP2010	-0.13%	0.43%	-0.04%	0.09%	0.25%	0.39%	0.09%	0.54%	0.37%	± 0.54 %
HITEMP1995	-0.16%	0.24%	-0.73%	-0.08%	-1.37%	-4.96%	-0.08%	-5.63%	-13.12%	$\pm 13.12\%$
HITRAN2008	-0.08%	0.61%	0.30%	0.55%	1.77%	3.26%	0.55%	5.99%	10.96%	$\pm 10.96\%$
HITRAN2004	0.01%	0.77%	0.44%	1.32%	3.07%	4.55%	1.32%	10.28%	16.34%	$\pm 16.34\%$
EWB	-0.22%	0.37%	-0.10%	-1.99%	-1.48%	-0.11%	-1.99%	2.74%	3.58%	$\pm 3.58\%$

CO ₂ conc. [vol%]		1			10			100		
Temperature [°C]	727	1100	1500	727	1100	1500	727	1100	1500	
Exp. transmissivity [–]	0.8458	0.8315	0.8368	0.7465	0.6941	0.6572	0.6654	0.5902	0.5305	
				Numeri	cal deviation	on (abs.)				Max. dev
EM2C	0.33%	0.83%	0.18%	0.70%	1.21%	0.48%	0.70%	2.31%	2.61%	$\pm 2.61 \%$
RADCAL	-2.04%	-2.34%	-3.39%	0.08%	-0.42%	-2.19%	0.08%	2.51%	0.64%	$\pm 3.39~\%$
HITEMP2010	0.13%	0.55%	0.00%	-0.01%	0.15%	-0.64%	-0.01%	0.41%	1.02~%	$\pm 1.02~\%$
HITEMP1995	0.28%	-0.26~%	-4.00%	0.01%	-1.26%	-7.27%	0.01%	-6.77%	-18.21%	$\pm 18.21\%$
HITRAN2008	0.83%	2.89%	4.75~%	2.03%	6.68%	10.95%	2.03%	12.03%	18.82%	$\pm 18.82\%$
HITRAN2004	1.79%	4.94%	7.35~%	4.32%	9.94%	14.80%	4.32%	16.04%	23.18%	$\pm 23.18\%$
EWB	1.50%	2.87%	2.57%	0.58%	3.79~%	5.87%	0.58%	0.14%	2.28%	$\pm 5.87\%$

Table 3.7: 4.3 μm CO₅-band (3.9 – 5.4 μm) transmissivity and absolute deviation of spectral models.

The HITRAN2008 simulations resulted in all experimental cases in less band transmissivity deviations as the HITRAN2004 simulations. Both models are aimed at calculating atmospheric radiation and were therefore not valid for the measured temperatures ($\geq 727 \,^{\circ}$ C / 1000 K). Many hot lines were missing in both bands, which lead to deviations as much as 23 % for high temperatures.

HITEMP1995 had many artificial overpredicted lines in the 2.7 μ m and the 4.3 μ m band for temperatures higher than 727 °C (1000 K). This lead to deviations as much as 18 %. At 727 °C the absolute model deviation was lower than 0.3 %.

The HITEMP2010 spectra had in all bands a deviation below 1.0%. The only flaw were some missing hot lines in the right 4.3μ m-band wing at high temperatures (1500 °C) and high concentrations (100 vol. -%). This accounted for an absolute band transmissivity deviation of 1.0% between the measured and the simulated values.

For the SNB model RADCAL, the only flaws were the over prediction of the 4.3 μ m band peak at low concentrations of 1 vol. -% CO₂ and an under prediction of the right wing of the same band at high concentrations (100 vol. -%). These flaws lead to deviations of 3.4 %.

The SNB model EM2C was missing hot lines in the right wings of the 2.7 μ m and the 4.3 μ m bands for high concentrations and high temperatures (figures 3.31 and 3.32). The maximum deviation was 2.6 %.

The comparison of the band transmissivities predicted by the EWB model and the experiments (figure 3.33 and tables 3.6 and 3.7) showed a worse predictive capability than the SNB models. The deviations were up to 5.9% while the worst deviations could be seen for $10 \text{ vol.} -\% \text{ CO}_2$ and high temperatures ($1100 \,^{\circ}\text{C}$).

The best models for the 2.7 μ m and 4.3 μ m CO₂ bands were (maximum absolute band transmissivity deviation is shown in brackets):

- 1. LBL/HITEMP2010 (±1.0%)
- 2. SNB/EM2C ($\pm 2.6\%$)
- 3. SNB/RADCAL $(\pm 3.4\%)$
- 4. EWB $(\pm 5.9\%)$

5. LBL/HITEMP1995 (±18.2%), wrong at temperatures $\geq 1100 \,^{\circ}\text{C}$



Figure 3.33: Comparison of experimental band transmissivity (nominal resolution 32 cm^{-1}) and EWB model (1500 °C, 100 vol. -% CO₂).

- 6. LBL/HITRAN2008 (±18.8%), missing hot lines at temperatures $\geq 727 \,^{\circ}\text{C}$
- 7. LBL/HITRAN2004 ($\pm 23.2\%$), missing hot lines at temperatures ≥ 727 °C

3.3 Discussion

The differences of band transmissivities between the models showed the importance of the source of spectral data, the models are generated from. Even if the SNB models were generated based on LBL data, the LBL data source was not the same as the data source of HITEMP2010 and therefore the deviations between the models. Nevertheless, both SNB models and the LBL HITEMP2010 model showed maximum deviations of 3.4% from the experimental measurements for all cases. The slight decrease in prediction accuracy of the SNB models has to be weighted against the large computational effort of the LBL simulations. This effort increases with the number of lines in the LBL databases (table 2.2), where HITEMP2010 has ten times more lines for H₂O as for CO₂.

The better visual spectrum agreement of the LBL HITEMP2010 model as the SNB models - even after the resolution downgrading procedure - might be due to dif-

ferent resolutions of the simulations. The evaluation of the total band transmissivity canceled out this effect in the accuracy comparison.

The LBL model with the HITEMP2010 database had the least devations for CO_2 and H_2O . Its worst band transmissivity deviation was 2.2%. The spectra agreed better visually with the experimental results than the other predictions. Therefore HITEMP2010 is recommended as a reference model for the development and validation of simplified spectral gas radiation models. The accuracy of prediction of radiation from high temperature gases by the model is more than enough for the simulation of total radiative heat transfer and not much further improvement can be done in the temperature range looked at (<1600 °C).

Chapter 4

Natural gas flame experiments

The following chapter presents the experimental measurements and simulations of emitted radiation from a turbulent natural gas flame as an example for a technical combustion process.

4.1 Materials and methods

4.1.1 Experimental setup

4.1.1.1 Air cooled combustion chamber

A 3 x 70 kW multi burner test rig at the Technische Universität München was used (figure 4.1). The combustion chamber was cylindrical with a dimension of 700 mm in diameter and a height of 4000 mm. The walls were cooled by air. A detailed description can be found elsewhere [8]. Only the modifications compared to the reference are described in the following chapter.

The combustion chamber was modified for optional coal combustion with a change of the flue gas direction from upwards to downwards and the addition of flue gas cleaning devices. A cyclone was added downstream of the outlet of the chamber, followed by a flue gas cooler, a bag filter and a flue gas fan. The fan controlled the pressure in the combustion chamber (atmospheric). The point of recirculation could be switched from before the flue gas condenser for wet recirculation to after the flue gas condenser for dry recirculation. The amount of recirculated flue gas was controlled by a fan in the recirculation line. The oxygen was supplied from a liquid oxygen tank and had a purity of 99.5 vol. -%.



Figure 4.1: 3 x 70 kW air cooled multi burner test rig.



Figure 4.2: Natural gas burner for oxyfuel and air operation. All dimensions are given in mm [8].

A modified natural gas ignition burner was used (figure 4.2), which is described in detail elsewhere [8]. The natural gas had a methane concentration of 97.12 vol. -%, an ethane concentration of 1.28 vol. -% and a propane concentration of 0.41 vol. -%.

The burners were arranged with a vertical distance of 1 m between one another (figure 4.1). The bottom burner was placed 1.25 m above the chamber bottom and the top burner 0.75 m below the furnace roof.

4.1.1.2 Measurement equipment

The dry flue gas composition (CO, CO₂, NO, NO₂, SO₂ and O₂) was measured at the furnace exit with an extractive on-line ABB Gas-Analyzer type AO2000 (URAS 26 / ultraviolett, LIMAS 11 / infrared, MAGNOS 206 / paramagnetic). The steam content in the flue gas at the furnace exit was measured by an on-line extractive process hygrometer type BARTEC HYGROPHIL H 4230.

Temperature and composition profiles were measured in the flame of the middle burner (flame / 2.25 m above the chamber bottom / figures 4.1 and 4.3). The flue gases were not measured with the intrusive technique. The profiles were traversed from the wall to the middle axis of the combustion chamber. The other side of the profile was assumed to be symmetrical. The temperature measurements were done with an International Flame Research Foundation (IFRF) type suction pyrometer [49]. Composition profiles were taken with a portable gas sample probe type M&C PSP4000 H/C/T. The gases were led through an online gas analyzer type SICK MAIHAK Sidor 700 (CO, CO₂ / both IR) and a M&C PMA30 analyzer (O₂ /



Figure 4.3: Cross section of temperature measurements with the IFRF type suction pyrometer [8].

paramagnetic). The steam content was measured with the BARTEC HYGROPHIL H 4230 connected to the second connection at the portable gas sample probe.

Radiation spectra emitted along a line-of-sight were measured with Fourier Transform Infrared Emission Spectroscopy in a very narrow angle (figure 4.4). An ORIEL MIR8025 Modular Infrared Fourier Interferometer was used with an InSb detector. The FTIR measurements were taken in the same port at the middle burner as the intrusive temperature and composition profiles as representation of a flame and in the port 500 mm below as representation of the flue gases (1.75 m above the chamber bottom / figure 4.1).

The measurements were done through an open path optical setup (figure 4.4). For windows and lenses CaF₂ (planoconvex focusing lens in measurement port / $f_l = 500$ mm, windows and beam splitter in MIR8025) was used. The focal point of the focusing lens was chosen to be in the middle axis of the combustion chamber. Sapphire (windows combustion chamber and lens detector) was used due to its high transmissivity in the measured spectral range from 2.4 to 5.4 µm and its heat resistance [56]. The measurement port with the FTIR optics and the sapphire window was water cooled. Two apertures with variable openings were in the optical path to avoid saturation of the detector, one before the light entered the FTIR and one



Figure 4.4: Setup of FTIR emission measurements at natural gas test rig.



Figure 4.5: FTIR calibration setup.

between the FTIR and the detector. Both aperture openings were fixed during calibration at a black body before the measurements at the test rig. A black background probe was mounted in the measurement port of the test rig on the opposite side of the FTIR port. The background probe consisted of an 1200 mm deep cylindrical hole (24 mm diameter) with a plug at the end outside of the chamber. Concentrically around the cylindrical inner tube were two larger tubes through which cooling water was flowing. The outer tube had an outer diameter of 76.7 mm. The probe tip was aligned to the chamber wall. Reflections from other furnace parts into the optical path were assumed to be negligible due to the low temperature (around 30 °C) and the geometry of the background probe. The optical path was aligned during the set up with a laser pointer connected to the detector port of the FTIR. The optical setup yielded a spectral sensitivity of the measurement equipment in the range from $2.4 - 5.5 \,\mu\text{m}$. A black body furnace type Cyclops 878 from Isothermal Technology Ltd was used for calibration of the setup. The calibrations were done before and after the measurements at the test rig at a constant black body temperature of 900 ± 0.25 °C (figure 4.5). Double sided interferograms were recorded with a resolution of $16 \,\mathrm{cm}^{-1}$, an oversampling factor of four and a mirror speed of $25.3 \,\mathrm{mm/s}$. For each measurement point a measurement with 100 averaged scans was done and 10 separate single scans. The resulting acquisition times were in the range of milliseconds (table 4.1).

Resolution	No. of scans	Acquisition time
$16\mathrm{cm}^{-1}$	1	$24.7\mathrm{ms}$
$32\mathrm{cm}^{-1}$	1	$12.4\mathrm{ms}$
$16{\rm cm}^{-1}$	100	$2.47\mathrm{s}$

Table 4.1: Acquisition times for FTIR interferograms.

The recorded interferograms were shortened to a nominal resolution of 32 cm^{-1} and weighted with the strong Norton-Beer apodization function [52, p. 33]. The final spectrum resulted after a fast Fourier transformation and a phase correction with the Mertz method [52, p. 88ff].

4.1.1.3 Measurement errors

Measurement errors of the test rig sensors were calculated according to DIN 1319 [29, 30]. The resulting uncertainty was compared with the maximal deviation of the value during stationary times of the test rig. The given uncertainty is the maximum value of both. The uncertainty of the FTIR emission measurements was $\pm 4\%$ due to the optical alignment [125].

4.1.1.4 Test cases

Three different combustion cases were characterized:

- **Air blown combustion:** Slightly fuel lean operation of all three burners. The oxidant was air.
- **Dry oxyfuel combustion:** Slightly fuel lean operation of all three burners. The oxidant was a mixture of dry recirculated flue gas and oxygen. The recirculation rate of 70 % was the maximum possible recirculation rate while maintaining stable flames.
- Wet oxyfuel combustion: Slightly fuel lean operation of all three burners. The oxidant was a mixture of wet recirculated flue gas and oxygen. The recirculation rate of 65 % was the maximum possible recirculation rate while maintaining stable flames.

The total stoichiometries (primary and secondary oxidant to fuel) were set to an optimum between low remaining oxygen and low CO emissions in the flue gas. The primary burner stoichiometry (primary oxidant to fuel) was set to 0.65 to get a flame length well into the measurement line. All burners had the same thermal power of 70 kW. The wall cooling was kept constant for all cases with a constant cooling air mass flow.

4.1.2 Numerical simulation

All numerical simulations and spectral calculations were implemented into the MAT-LAB program RADEVAL (http://www.es.mw.tum.de/radeval). The numerical theory of the compared detailed spectral models can be found in section 2.3. The implementation in RADEVAL is described in section 3.1.2. Only the differing implementation details compared to section 3.1.2 are described in the following section.



Figure 4.6: Discretization of a line-of-sight (adapted from Johansson et al. [63]).

4.1.2.1 Line-of-sight modeling

A one dimensional line-of-sight directional model was implemented for the simulation of the experimentally measured spectra in the flames, where intrusive gas atmosphere measurements were available as input for the simulations. The experimental mesh consisted of a grey wall emitter at the beginning of the virtual light ray (figure 4.6 and equation 4.1). Reflections from incoming radiation on this wall element were not included. During the experiments a black and cold target was placed at this position which minimized the reflection of stray light (section 4.1.1.2).

$$\bar{I}_{\lambda,0} = \bar{I}_{b\lambda}(T_{wall}) \cdot \epsilon_{wall} \tag{4.1}$$

where $\bar{I}_{\lambda,0}$ is the averaged radiation intensity per solid angle emitted from the wall, $\bar{I}_{b,\lambda}$ is the averaged black body radiation intensity per solid angle at wavelength λ , T_{wall} the wall temperature and ϵ_{wall} the wall emissivity.

The discretization of the line-of-sight was done similar to Johansson et al. [63]. The correlated formulation of the discretized RTE was used for the transmissivity models as

$$\bar{I}_{\lambda,n} = \bar{I}_{\lambda_0} \cdot \bar{\tau}_{\lambda,0 \to n} + \sum_{i=0}^{n-1} \left(\bar{\tau}_{\lambda,i+1 \to n} - \bar{\tau}_{\lambda,i \to n} \right) \cdot \bar{I}_{b\lambda,i+1/2}$$
(4.2)
where the first term on the right hand side is the transmitted radiation from the wall and the second term is the emitted radiation from each element in the line of sight $\bar{I}_{b\lambda,i+1/2} \cdot \bar{\alpha}_{\lambda,i+1/2}$ multiplied by the product of the transmissivities of the remaining elements towards $n \ \bar{\tau}_{\lambda,i+1 \to n}$ [112, p. 298ff].

The non-correlated formulation of the discretized RTE was used for the absorption coefficient models as

$$\bar{I}_{\lambda,n} = \bar{I}_{\lambda,n-1} \cdot \bar{\tau}_{\lambda,n-1 \to n} + \bar{I}_{b\lambda,n-1/2} \cdot (1 - \bar{\tau}_{\lambda,n-1 \to n})$$
(4.3)

where the first term on the right hand side is the transmitted radiation from the element before and the second term is the emitted radiation from the element.

The main difference between both approaches is the number of nodes in the line-of-sight necessary for the calculation of the intensity at the last node (figure 4.6). The correlated formulation needs all nodes from the beginning of the line-of-sight to the current position, the non-correlated formulation employs only the two last nodes. The correlated formulation is computationally demanding due to the summation term and therefore not usable for CFD three dimensional simulations. The correlated approach is strongly recommended for one dimensional simulations of transmissivity models, i.e. the SNB models. The less computationally demanding non-correlated formulation (eq. 4.3) is suitable for absorption coefficient models, i.e. the LBL model, as the absorption coefficient is not path dependent.

The transmissivity in each cell was calculated with the length of the corresponding cell in the case of the absorption coefficient models.

$$\tau_{\lambda,n-1\to n} = e^{-k_{\lambda,n-1/2} \cdot \Delta s_{n-1/2}} \tag{4.4}$$

The temperature T and the volume concentrations x_k of the main radiatively active species k (H₂O, CO₂, CO and CH₄) in each cell were defined according to the measured profiles. The partial pressure of the species $p_{par,k}$ was calculated with the total pressure p_{tot} , which was assumed constant over the whole path:

$$p_{par,k} = x_k \cdot p_{tot} \tag{4.5}$$

4.1.2.2 Line-by-line modeling

The spectral LBL model was implemented in RADEVAL according to section 3.1.2.1. The FORTRAN TIPS2009 routine from Fischer et al. [42] was used for the calculation of the total internal partition sums Q(T). The line parameters of the HITEMP2010 database [101] were used as this database was found to be the best reference model in the gas cell experiments (section 3.3).

4.1.2.3 Statistical narrow band modeling

Two FORTRAN routines were used for the modeling of the SNB models RADCAL [54] and EM2C [106], which were available from the companion website of Modest [82]. Details concerning the SNB models and the implementation can be found in sections 2.3.2 and 3.1.2.2. The routines included the directional discretization with the correlated formulation of the RTE (eq. 4.2) and calculated the total transmissivity over the path length and the emitted intensity. The output of the routines were directly used as results for the simulation of the spectra. Both routines work with a minimal spectral resolution of $25 \,\mathrm{cm}^{-1}$ and a maximum number of 50 (RADCAL) or 100 (EM2C) path length cells.

4.1.3 Comparison of experimental spectra with numerical simulations

The path length of the line-of-sight was discretized according to the steps of the measured profiles. The total pressure was assumed to be 1 bar. The simulated intensity spectra were calculated with these assumptions with the three best models from the gas cell experiments (LBL/HITEMP2010, SNB/RADCAL and SNB/EM2C - section 3). The LBL model was spectrally discretized with a resolution of 0.125 cm^{-1} and a maximum line with of 10 cm^{-1} as in the gas cell experiments (section 3.1.2.1). The two SNB models resulted in intensity spectra with a resolution of 25 cm^{-1} .

All intensity spectra were downgraded down to a nominal spectral resolution of 32 cm^{-1} according to the procedure of Fleckl et al. [44]. The spectral downgrading was done with an inverse Fast-Fourier-Transformation, a truncation of the interferograms to the new resolution, a zero filling with a factor of one and a Fast-Fourier-Transformation to the final spectrum. The strong Norton-Beer function was applied as apodization function for a smoothing of the spectra [52, p. 33].

The main evaluation of the model spectra was done with the integrated band intensity I_{band} , which was calculated from the intensity spectra in a downgraded nominal resolution of $32 \,\mathrm{cm}^{-1}$ as

$$I_{band} = \frac{\int_{\lambda_1}^{\lambda_2} I_{\lambda}}{\lambda_2 - \lambda_1} \tag{4.6}$$

where λ_1 is the left band limit and λ_2 the right band limit.

4.2 Results

The dry oxyfuel flame had the highest peak flame temperatures (table 4.2 and figures 4.7 to 4.9) followed by the wet oxyfuel and the air blown flame. This tendency was also observed in the spectra (figures 4.10 and 4.11) and in the integrated band intensity of the 2.7 μ m band (table 4.4). The highest temperatures occurred with the highest oxygen concentration in the oxidant (table 4.3). Of further interest were the higher temperatures and the higher oxygen concentration of the dry oxyfuel case compared to the wet oxyfuel case even with a higher recirculation rate. The reduced temperature was a result of the high water concentrations, which acted as a flame temperature moderator due to the higher heat capacity compared to carbon dioxide (figure 4.12).

Combustion conditions	Air	Oxyfuel dry	Oxyfuel wet	
Average peak gas temperature [°C]	1203	1382	1305	
	Experimental deviations			
Max. peak gas temperature	0.88%	0.49%	0.90%	
Min. peak gas temperature	-0.82%	-0.62%	-0.86%	

Table 4.2: Peak gas temperatures in the flames from intrusive measurements.

The 4.3 µm CO₂ band saturates for CO₂ concentrations of $\geq 10 \text{ vol.} -\%$ and at the temperatures occuring ($\geq 550 \text{ °C}$ / figures 3.18 and 3.19). The band head at 4.2 µm does not change with increasing temperature or CO₂ concentration, but the upper band limit is shifted with increasing temperature and concentration towards higher wavelengths. For longer path length and temperatures, this characteristic of the band allows conclusions about the gas temperature and CO₂ concentration profile in the line of sight, as water vapor, the other main contributor to gas radiation transmitts over 90% of the radiative energy in this spectral range (figure 3.7 and 3.8).



Figure 4.7: Gas atmosphere in air blown flame measured with intrusive suction technique.



Figure 4.8: Gas atmosphere in oxyfuel flame with dry recirculation measured with intrusive suction technique.



Figure 4.9: Gas atmosphere in oxyfuel flame with wet recirculation measured with intrusive suction technique.



Figure 4.10: Comparison of averaged (100 scans) emitted radiation from flames.

Value	Unit	Air	Dry oxyfuel	Wet oxyfuel
Oxidant composition (wet)				
CO_2	vol. $-\%$	-	$52.7 (\pm 3.7)$	$23.6 (\pm 2.0)$
O_2	vol. $-\%$	$20.9 (\pm 0.1)$	$32.5 (\pm 1.1)$	$29.3 (\pm 1.0)$
H_2O	vol. $-\%$	-	$6.8 (\pm 3.1)$	$43.4 \ (\pm 2.6)$
N_2	vol. $-\%$	$79.1 \ (\pm 0.1)$	$8.8 (\pm 2.5)$	$3.8 (\pm 1.2)$
Flue gas composition at furnace exit (wet)				
CO_2	vol. $-\%$	$8.7 (\pm 3.3)$	$58.1 (\pm 2.0)$	$32.3 (\pm 2.9)$
O_2	vol. $-\%$	$2.6 (\pm 8.2)$	$3.15 (\pm 0.4)$	$3.15~(\pm 0.4)$
H_2O	vol. $-\%$	$16.5 (\pm 0.9)$	$29.0 (\pm 1.4)$	$59.3 (\pm 3.3)$
N_2	vol. $-\%$	$72.3 (\pm 1.6)$	$9.7 (\pm 2.3)$	$5.2 (\pm 1.6)$
Flue gas composition at furnace exit (dry)				
CO_2	vol. $-\%$	$10.4 (\pm 4.0)$	$81.8 (\pm 2.8)$	$79.5~(\pm 1.6)$
O_2	vol. $-\%$	$3.1 \ (\pm 9.9)$	$4.4 \ (\pm 0.5)$	$7.6~(\pm 0.5)$
CO	ppm	$143 \ (\pm 75)$	$96 \ (\pm 75)$	$196 \ (\pm 75)$
NO	mg/m^3	$21 \ (\pm 75)$	$17 \ (\pm 75)$	$7 (\pm 75)$
Flue gas furnace exit temperature	$^{\circ}\mathrm{C}$	$547 (\pm 14)$	$481 (\pm 7)$	$594 (\pm 5)$
Mass flow of middle burner natural gas	$\rm kg/h$	$5.1 (\pm 0.1)$	$5.1 \ (\pm 0.1)$	$5.1 \ (\pm 0.1)$
Mass flow of middle burner primary oxidant	$\rm kg/h$	$59.2 (\pm 2.7)$	$47.3 (\pm 1.0)$	$40.9~(\pm 0.6)$
Mass flow of middle burner secondary oxidant	$\rm kg/h$	$42.4 (\pm 3.7)$	$32.7~(\pm 0.7)$	$28.2 (\pm 0.4)$
Flue gas flow at end of furnace	$\rm kg/h$	$320.2 (\pm 20.1)$	$255.1 \ (\pm 5.6)$	$222.4 (\pm 3.2)$
Recirculated flue gas flow	$\rm kg/h$	-	$177.3 (\pm 5.5)$	$142.1 \ (\pm 2.5)$
Additional oxygen	$\rm kg/h$	-	$61.7 (\pm 1.6)$	$62.3 (\pm 1.2)$
Overall combustion stoichiometry	-	$1.15~(\pm 0.05)$	$1.09 \ (\pm 0.03)$	$1.10~(\pm 0.03)$
Recirculation rate	$\mathrm{mass\%}$	-	$69.7~(\pm 0.8)$	$64.7 (\pm 0.3)$

Table 4.3: Test rig values with absolute uncertainties.



Figure 4.11: Comparison of averaged (100 scans) emitted radiation from flue gases.

Table 4.4: Integrated band intensity in the range from $2.4 - 4 \,\mu\text{m}$. The average experimental intensity is from 100 scans and the maximum and minimum experimental intensity from 10 separate single scans.

Combustion conditions	Air		Oxyfuel dry		Oxyfuel wet	
Measurement position	Flame	Flue gas	Flame	Flue gas	Flame	Flue gas
Avg. exp. intensity $[W/(m^2\cdot sr)]$	1714 (±4%)	$647 (\pm 4\%)$	2790 ($\pm 4\%$)	$1366 (\pm 4\%)$	2343 $(\pm 4\%)$	1336 (±4%)
	Experimental deviations (rel. to avg. exp. intensity)					
Max. exp. intensity	22%	37%	34%	11%	33%	21%
Min. exp. intensity	-25%	-13%	-34%	-15%	-32%	-14%
Deviation range	47%	50%	67%	26%	65%	35%
	Numerical deviations (rel. to avg. exp. intensity)					
LBL HITEMP 2010	-25%		-16%		-12%	
SNB EM2C	-24%		-16%		-12%	
SNB RADCAL	-19%		-10%		-8%	
	Avg. exp. deviations (rel. to numerical calculations)					
LBL HITEMP 2010	34%		20%		13%	
SNB EM2C	31%		18%		13%	
SNB RADCAL	23%		11%		9%	



Figure 4.12: Comparison of isobaric heat capacity from CO_2 and H_2O over different temperatures.

The intensity emitted by the hot central flame was fully absorbed by the boundary layer and the temperature of the boundary layer defined the intensity reaching the wall and the FTIR. This fact was the reason that the evaluation of the band transmissivity was done separately for the left (lower band limit with band head) and the right part of the band (upper band limit with hot lines). The left part of the band (table 4.5) characterized the boundary layer and the right part the hot flame as the right wing of the band widenend with the increasing temperature, while at lower temperatures (i.e. at the boundary layer) CO_2 is transparent in this spectral region (table 4.6).

The effect of the increasing flame temperatures and the increasing CO_2 concentration from the different test cases could be seen in the right wing of the 4.3 µm CO_2 band (figure 4.10 and figure 4.11). The band peak increased with the increasing peak gas temperature and the right wing shifted to higher wavelength due to more hot lines. The result is a window on the hot flame, not disturbed by absorption in the cold gas boundary layer. This effect was additionally intensified with higher CO_2 concentration in the dry and wet oxyfuel combustion cases (figure 4.14 and 4.15).

The comparison of the averaged and the single FTIR scans from the flames showed high fluctuating behavior of the emitted radiation due to flame turbulence (figures 4.13 to 4.15). The integrated band intensities of the single scans varied between

Table 4.5: Integrated band intensity in the range from $4.0 - 4.5 \,\mu\text{m}$ characteristic for the cold boundary layer. The average experimental intensity is from 100 scans and the maximum and minimum experimental intensity from 10 separate single scans.

Combustion conditions	А	ir	Oxyfu	el dry	Oxyfu	el wet
Measurement position	Flame	Flue gas	Flame	Flue gas	Flame	Flue gas
Avg. exp. intensity $[W/(m^2 \cdot sr)]$	$749(\pm 4\%)$	$455 (\pm 4\%)$	$426 (\pm 4\%)$	$396 (\pm 4\%)$	$464 (\pm 4\%)$	419 (±4%)
		Experimenta	l deviations (rel. to avg. ex	p. intensity)	
Max. exp. intensity	12%	17%	7%	2%	-5%	6%
Min. exp. intensity	-7%	11%	-24%	-10%	-11%	-6%
Deviation range	19%	6%	31%	12%	6%	11%
	Numerical deviations (rel. to avg. exp. intensity)					
LBL HITEMP 2010	-5%		41%		19%	
SNB EM2C	-12%		48%		28%	
SNB RADCAL	-20%		17%		1%	
	Avg. exp. deviations (rel. to numerical calculations)					
LBL HITEMP 2010	5%		-29%		-16%	
SNB EM2C	14%		-33%		-22%	
SNB RADCAL	25%		-15%		-1%	

Table 4.6: Integrated band intensity in the range from $4.5 - 5.4 \,\mu\text{m}$ characteristic for the hot central flame with transparent cold boundary layer. The average experimental intensity is from 100 scans and the maximum and minimum experimental intensity from 10 separate single scans.

Combustion conditions	Ai	r	Oxyfue	el dry	Oxyfue	el wet
Measurement position	Flame	Flue gas	Flame	Flue gas	Flame	Flue gas
Avg. exp. intensity $[W/(m^2\cdot sr)]$	$1072 (\pm 4\%)$	$443 (\pm 4\%)$	$2058~(\pm 4\%)$	776 $(\pm 4\%)$	$1754~(\pm 4\%)$	750 (±4%)
		Experimenta	al deviations (r	el. to avg. exp	p. intensity)	
Max. exp. intensity	21%	28%	28%	4%	30%	13%
Min. exp. intensity	-26%	-14%	-32%	-10%	-27%	-12%
Deviation range	48%	42%	60%	13%	57%	25%
	Numerical deviations (rel. to avg. exp. intensity)					
LBL HITEMP 2010	-43%		-34%		-31%	
SNB EM2C	-36%		-22%		-26%	
SNB RADCAL	-30%		-24%		-27%	
	Avg. exp. deviations (rel. to numerical calculations)					
LBL HITEMP 2010	75%		51%		45%	
SNB EM2C	56%		27%		35%	
SNB RADCAL	43%		32%		36%	



Figure 4.13: Comparison of measured and simulated spectral radiation of air blown flame $(32 \text{ cm}^{-1} \text{ nominal resolution}).$

 $\pm 20\%$ (air) and $\pm 30\%$ (both oxyfuel cases) around the average (table 4.4 and table 4.6). The 4.0 – 4.5 µm range showed less turbulence as it characterized the less turbulent cold boundary layer. The spectral measurements of the flue gases showed turbulent behavior as well (figures 4.16 to 4.18). The deviations were not as large as for the flames but still around $\pm 20\%$.

All three models with their different implementations showed similar behavior in their deviation from the average measured intensity (figure 4.19 and tables 4.4 to 4.6). Only in the strong absorption region of the $4.3 \,\mu\text{m}$ CO₂ band occured a difference between the SNB/RADCAL and the two other models (table 4.5). The LBL model with the HITEMP2010 database was asumed to be the most valid model (section 3.3) and is shown in the spectra.

The modeling of the emitted radiation intensity always resulted in a lower radiation intensity than the measured averaged intensity (figures 4.13 to 4.15 and tables 4.4 and 4.6). The most precise spectral model (LBL/HITEMP2010) always simulated emitted intensities below or similar to the minimal measured intensity from the single scans. The simulated value was between 10 % and 40 % lower compared to the measured average intensity or otherwise the measured average intensity was between



Figure 4.14: Comparison of measured and simulated spectral radiation of flame for oxyfuel combustion with dry recirculation $(32 \text{ cm}^{-1} \text{ nominal resolution})$.



Figure 4.15: Comparison of measured and simulated spectral radiation of flame for oxyfuel combustion with wet recirculation $(32 \text{ cm}^{-1} \text{ nominal resolution})$.



Figure 4.16: Measured spectral radiation of flue gas from air blown flame $(32 \text{ cm}^{-1} \text{ nominal resolution})$.



Figure 4.17: Measured spectral radiation of flue gas from flame for oxyfuel combustion with dry recirculation $(32 \text{ cm}^{-1} \text{ nominal resolution})$.



Figure 4.18: Measured spectral radiation of flue gas from flame for oxyfuel combustion with wet recirculation $(32 \text{ cm}^{-1} \text{ nominal resolution})$.



Figure 4.19: Comparison of simulations from different models and average measured intensity for air flame.

13% to 75% higher than the simulated value. The intensity was overpredicted in the $4.0 - 4.5 \,\mu\text{m}$ range for both oxyfuel cases (figures 4.14 and 4.15 and table 4.5). Air blown combustion lead to the largest deviations, both flames of oxyfuel combustion showed less deviations between the averaged measured and the simulated intensity (tables 4.4 and 4.6).

4.3 Discussion

The results highlighted the differences between dry and wet recirculation for oxyfuel combustion. The higher heat capacity of water had a large influence on the combustion temperatures and the flame stability. The wet oxyfuel case needed more oxygen for stable flames and - despite higher oxygen content - a lower maximum flame temperature resulted. This effect was very pronounced for the natural gas combustion experiments with a low carbon-to-hydrogen ratio in the fuel and high H_2O content in the flue gases (table 4.3).

The gas temperature was a main driver for higher radiative transfer as the higher measured maximum gas temperature in the dry oxyfuel case compared with the wet oxyfuel case correlated with higher measured average spectral radiative intensity in the flames (table 4.2 and 4.4). The measured radiation in the flue gases showed no large differences between oxyfuel dry and oxyfuel wet as the temperatures were more similar.

The most important result was the observed deviation between the averaged nonintrusively measured radiative intensity and the simulated intensity calculated from the averaged intrusively measured gas temperature and composition profiles (table 4.4 and 4.6). A lot of factors with complex uncertainties played a role:

- The FTIR emission measurement setup had a measurement uncertainty of 4 % [125]. The correct alignment of the optical components had the biggest impact on the uncertainty of the FTIR system.
- The spectral gas radiation model LBL/HITEMP2010 [101] had a maximum uncertainty of 2.2% as shown in the gas cell experiments (section 3).
- The suction gas temperature measurements were within a few degrees of the true gas temperature [17, 49]. Nevertheless, the technique measured a gas volume in front of the probe tip and not the gas temperature at a single point in

space (figure 4.3). During the experiments only negligible fluctuations of less than 1% were observed (table 4.2). The thermal inertia of the three ceramic shields around the thermocouple dampened the turbulent flame fluctuations strongly and the averaged temperature was assumed to be measured. Whether the strong temperature fluctuations within a turbulent flame had an increasing or decreasing effect on the measured average temperature of a suction pyrometer was not known to the authors.

- The suction gas concentration measurements had a measurement uncertainty below 1 vol. -% for CO and CO₂ [102] and below 3 vol. -% for H₂O [2]. The measured values had very low fluctuations and were assumed to be averaged values. The technique measured a gas volume similar to the temperature measurements, but the volume was smaller as the suction velocity was considerably less.
- The non-homogenous line-of-sight with temperature and compositions variations was accounted for by the discretization with the profile measurements (section 4.1.2.1). The non-correlated formulation of the RTE in the LBL modelling has no physical simplifications and was therefore assumed to be correct. The SNB models give the same accuracy as the LBL models, if the same spectral database is used [89].
- Discrete steps for intrusive measurements for gas temperature and composition lead to simplified temperature and composition profiles, but were assumed to have had a negligible effect on the numerical results in the middle of the flame. The most pronounced effect was the not simulated cold gas boundary layer directly in front of the water cooled window, which was not measured by the gas temperature profiles. This has been previously observed [8]. The effect of the missing cold gas boundary layer was assumed to be the additional absorption of radiation not accounted for by the numerical simulations and could be seen clearly in the overprediction of intensity in the 4.0 4.5 µm band for the oxyfuel cases (figure 4.14 and 4.15 and table 4.5). The absorption in the cold gas boundary layer was not as pronounced in the air blown combustion case. This is due to the lower concentration of radiatively active gases which was only 25.2 vol. -% as compared to the 87.1 vol. -% and 91.6 vol. -% in the two oxyfuel cases (table 4.3). The estimated effect in the 2.4 4 µm band was

a further decrease of calculated intensity and therefore even more deviation of measured average spectral radiation and calculated radiation. The effect on the right wing of the 4.3 μ m CO₂-band (4.5 - 5.5 μ m) was assumed to be negligible, as most radiation is caused by the widended band at hot temperatures and only minimal absorption occurs at cold temperatures in this spectral range (figures 3.8 and 3.18).

Turbulence-Radiation-Interaction (TRI) The effect of turbulence on radiation from flames has been a major area of research in the field of radiation over the past few decades. Two specific reviews [21, 38] and two books [121, p. 251ff [82, p. 707ff] were published in the literature describing the effect of TRI. A recent oxyfuel modeling review by Edge et al. [32] mentioned the importance of TRI especially for oxyfuel. Turbulence enhances the radiation from turbulent flames compared with radiation calculations based on the mean scalar properties between 10% and 320% [121, p. 262f]. The values differ depending on optical thin or thick conditions and on luminous or non-luminous flames, i. e. the propensity for the formation of soot inside the flame. In nonluminous turbulent methane flames an increase of radiation intensity due to turbulence between 10% and 50% can be observed [21, p. 378]. The effect of TRI is not important in regions of non-reactive flows, i.e. outside of flames [21, p. 377]. TRI is neglected normally in combustion simulations due to its complexity. The effect of TRI was very likely to occur in the observed flames as the spectral measurements showed a high turbulent behaviour (table 4.4 and 4.6).

Of all these factors TRI was assumed to be the main reason for the large systematic deviation between the calculated radiation and the measured averaged band radiation of up to 75% (table 4.4 and 4.6).

One hint of the complexity of TRI were two opposing observations during the experiments. On the one side the fluctuations of measured radiation intensity were higher in both oxyfuel cases with up to $\pm 30\%$ compared with up to $\pm 20\%$ in the air blown combustion case (table 4.4 and 4.6). On the other side, the deviations between the measured averaged radiation and the calculated radiation were higher for the air blown case than for the oxfuel cases (table 4.4 and 4.6).

The experiments did not allow an evaluation of the different spectral models used

in the simulation, as the deviations of all models were of similar magnitude and TRI lead to unpredictable differences between the simulations and the measurements.

The Single Scan Fourier Transform Emission Spectroscopy proved to be a valuable tool for performing time resolved radiation measurements in a highly turbulent domain. It gives information about turbulent values and additionally about gas temperatures and compositions, if inverse radiative heat transfer is applied to each single scan spectra [82, p. 729f][128, p. 253].

The experimental setup can be optimized with an in-place calibration procedure, an automatized data aquisition and analysis program and a more robust FTIR. The development of a commercial multi value flame sensor for harsh industrial applications is possible.

Chapter 5

Validation of simplified models

5.1 Materials and methods

5.1.1 Validation procedure and test cases

The aim of the following chapter is the comparison and validation of different simplified models. The models and model parameters were formulated by the respective authors based on different spectral databases and accuracies were given for deviations from the reference models (tables 2.3 and 2.6). I compared all models by calculation of the deviations of the total emissivity ϵ_{tot} between the model and the detailed reference model LBL/HITEMP2010 (section 3) similar to an older comparison from Lallemant et al. [72], where simplified models were compared with the EWB model as a benchmark. For every model, respective parameter set, the deviations were calculated for different path lengths, gas temperatures and gas concentrations (tables 2.7 and 5.1). The variable composition models were tested for various concentrations of the single gases H_2O and CO_2 with the balance N_2 . All models were tested with various calculated combustion atmospheres from different fuels and combustion processes (table 2.7). The path length was varied from very low values of 0.00126 m up to values as high as 100 m to include the very fine grids in the near burner field $(\geq 0.005 \text{ m})$ [72, p. 545] in cell based spectral modeling implementations and the long path length in flue gas sections in domain based mean beam length implementations.

Another reason for choosing the method of comparing total emissivities was that the WSGG model parameters were all generated by fitting the polynomial coeffi-

Variable [Unit]	Values
Path length [m]	0.00126 - 100 (50 logarithmically spaced intervals)
Temperature [°C]	800, 1300, 1800
Single gases [vol%]	10, 50, 80 (Balance N_2 / for CO_2 and for H_2O separately)
Combustion process type	Air blown, oxyfuel with dry and with wet recirculation
Fuel	Natural gas, brown coal, anthracite (calculated atmospheres as in table 2.7)

Table 5.1: List of variables for simplified model validation.

Spectral model	Test cases			
	Single gases	Combustion atmospheres		
SNB (EM2C)	х	Х		
SNB (RADCAL)	Х	Х		
EWB	Х	Х		
SLW	Х	Х		
WSGG $[63]$ 3GG		Х		
WSGG $[63]$ 4GG		Х		
WSGG $[64]$		Х		
WSGG $[105]$		Х		
WSGG $[67]$		Х		
WSGG $[126]$		Х		
WSGG [70]		Х		

Table 5.2: Tested models for total emissivity validation and calculated test cases.

cients to total emissivities from the respective reference models. Other radiative properties, such as spectral intensity, wall heat flux or source function, are more dependent on the type of model and the implementation. A comparison of intrinsic models and their specific properties based on the same spectral database can be found elsewhere [89].

5.1.2 Numerical implementation

All numerical simulations were done with the MATLAB based program RADEVAL (http://www.es.mw.tum.de/radeval).

The total pressure p_{tot} was assumed to be atmospheric (1.013 bar). The temperature T, the volume concentrations x_k of the radiatively active species k (H₂O and CO₂) and the path length were varied (table 5.1). The partial pressures of the molecules was calculated with the total pressure p_{tot} as

$$p_{par,k} = x_k \cdot p_{tot} \tag{5.1}$$

The LBL, SNB and EWB models were implemented in RADEVAL according to section 3.1.2. The total emissivity ϵ_{tot} for the LBL and SNB models was found similar to the box calculation procedure from the EWB model (equation 2.65).

The WSGG model was implemented according to section 2.3.4 with the grey formulation and parameter sets from various authors (table 2.3 on page 40).

The SLW model from Denison and Webb [26] was implemented according to section 2.3.4 while the ABDLF for water and carbon dioxide was taken as C-routine from Modest [82]. Equation (2.82) for the calculation of the local mean absorption coefficient was calculated with the help of the **fzero** function in Matlab. The starting point for the iteration was the right limit of the absorption cross section interval $\bar{C}_{abs,i+1}$.

The total emissivity ϵ_{tot} of the WSGG and the SLW model was calculated with equation (2.71).

5.2 Results

In the following section the results of the calculations are presented for each model separately. The comparison between the models will be done in the discussion section. I start with the more detailed variable composition models, which allowed total emissivity calculations of atmospheres with one radiating gas species as well as of combustion atmospheres (table 5.2).

5.2.1 Exponential wide band model

The EWB model showed a very discontinuous trend of the deviation over the path length both for H_2O and for CO_2 (figure 5.1 and 5.2). The total emissivity of H_2O was overpredicted at short path lengths and underpredicted at longer path lengths with a peak in the middle. The range of overprediction was shifted towards longer path lengths with higher temperatures and towards smaller path lengths with higher concentrations. A discontinuity was observed shortly before the intermediate peak at high temperatures and/or concentrations of H_2O .

The trend of total emissivity deviation from the reference model HITEMP2010 was for the test cases with pure CO_2 even more discontinuous than for H_2O (figure 5.2). Two or three peaks could be observed. The deviations were decreasing to underprediction at long path lengths of 100 m with a negative gradient at the end of the tested path length domain. The underprediction at long path lengths was more pronounced at higher concentrations. Lower temperatures lead to better accuracy.

The strong discontinuities in the deviation at short path lengths led to strong underpredictions of up to -57% for the combustion atmospheres (figure 5.3 and 5.4). The deviations of all combustion atmosphere calculations were within $\pm 10\%$ of the reference calculations up to a path length of 0.1 m. The total emissivity was overpredicted between 0% and 17% at 1 m path length and underpredicted between 10% and 20% at a path length of 100 m (figure 5.3).

The predictive capability was best for temperatures up to $1300 \,^{\circ}\text{C}$ and for pressure path lengths of 0.004 - 3.4 bar m. Higher pressure path lengths lead to a general underprediction, and shorter path lengths to underpredictions due to the discontinuities in the model functions.

5.2.2 Statistical narrow band model RADCAL

The SNB model RADCAL showed for the calculation of H_2O a similar trend as the EWB model only with better accuracy: Overprediction of around 10% for short path lengths, decreasing deviation with increasing path lengths until the total emissivity



Figure 5.1: Relative deviation of the EWB model of total emissivity from HITEMP2010 over path length at 800°C for different concentrations of H_2O and at 50 vol. -% H_2O for different temperatures.



Figure 5.2: Relative deviation of the EWB model of total emissivity from HITEMP2010 over path length at 800°C for different concentrations of CO_2 and at 50 vol. -% CO_2 for different temperatures.



Figure 5.3: Relative deviation range over path length from the EWB model for all combustion cases.



Figure 5.4: Relative deviation of total emissivity from HITEMP2010 for selected cases of the EWB model with artificial peaks at short path lengths; BC: fuel brown coal; AN: fuel anthracite.

was slightly underpredicted (2%) at long path lengths (figure 5.5). There was no or even a positive gradient at the upper end of the path length domain. The deviation curve shifted towards shorter path lengths with increasing H₂O concentration and to higher path lengths with increasing temperatures.

 CO_2 was predicted similar accurate as H_2O with a continuously decreasing deviation with increasing path lengths and an intermediate gradient with no deviations of total emissivities to the reference model around a path length of 0.5 m (figure 5.6). The total emissivity was 20 % overpredicted at short path lengths and around 30 % underpredicted at long path lengths. An increase of the CO_2 concentration shifted the curve towards shorter path lengths. An increase in temperature shifted the curve towards longer path lengths and the horizontal level increased to higher deviations.

The combustion atmosphere test cases mirrored these effects of the single gases (figure 5.7). At path lengths shorter than 10 m the accuracy was over 10% with values as high as 25% at very short path lengths of 0.001 m. The overprediction of total emissivity increased with increasing temperature (figure 5.8).



Figure 5.5: Relative deviation of the SNB model RADCAL of total emissivity from HITEMP2010 over path length at 800°C for different concentrations of H₂O and at 50 vol. -% H₂O for different temperatures (table 2.7).



Figure 5.6: Relative deviation of the SNB model RADCAL of total emissivity from HITEMP2010 over path length at 800°C for different concentrations of CO_2 and at 50 vol. -% CO_2 for different temperatures.



Figure 5.7: Relative deviation range over path length from the SNB model RADCAL for all combustion cases.



Figure 5.8: Relative deviation of the SNB model RADCAL of total emissivity from HITEMP2010 over path length for wet oxyfuel combustion of anthracite for different temperatures.

5.2.3 Statistical narrow band model EM2C

The SNB model EM2C showed a decreasing deviation with increasing path length for H_2O (figure 5.9). The total deviations were around $\pm 5\%$ for temperatures of 800 °C. An increase of concentrations leads to a slightly steeper gradient. An increase in temperatures leads to steeper gradients and more extreme deviations for short and long path lengths (-10% to 5%).

The total emissivity of CO₂ was best predicted by the SNB model EM2C for path lengths of up to 1 m with deviations of up to $\pm 5\%$ (figure 5.10). The total emissivity was strongly underpredicted at longer path lengths. The underprediction over 5% was more pronounced for temperatures higher than 800 °C. Deviations of more than -10% were observed for path lengths longer than 2.5 m and reached values of 40% underprediction for temperatures of 1800 °C and path lengths of 100 m.

The total emissivity of the combustion cases was predicted up to a path length of 1 m with -4% to 6% accuracy (figure 5.11). The accuracy got worse at higher path lengths with an increase in underprediction of up to 12% at 100 m. The trend of increased underprediction from the CO₂ test cases could be observed in the combustion cases as well (figure 5.12).



Figure 5.9: Relative deviation of the SNB model EM2C of total emissivity from HITEMP2010 over path length at 800°C for different concentrations of H_2O and at 50 vol. -% H_2O for different temperatures.



Figure 5.10: Relative deviation of the SNB model EM2C of total emissivity from HITEMP2010 over path length at 800°C for different concentrations of CO_2 and at 50 vol. -% CO₂ for different temperatures.



Figure 5.11: Relative deviation range over path length from the SNB model EM2C for all combustion cases.



Figure 5.12: Relative deviation of total emissivity from HITEMP2010 for various temperatures and anthracite dry oxyfuel combustion of the SNB model EM2C.

5.2.4 Spectral line-based weighted-sum-of-grey-gases model

The SLW model showed a decrease in the deviation of total emissivity from the reference model HITEMP2010 for H_2O from very strong overprediction at short path lengths (50 - 70%) to slight underprediction at longer path lengths (figure 5.13). An increase of the H_2O concentrations lead to higher overprediction at short path lengths, but no change at long path lengths. An increase in the temperatures leads to less overprediction at short path lengths and more underprediction at long path lengths.

The deviation of the prediction of CO_2 total emissivity increased with increasing path length (figure 5.14). Path lengths longer than 6 cm for 10 vol. -% and 1.5 cm for 50 vol. -% or more lead to deviations of less than 10%. The deviations were constant around 10% at longer path lengths. An increase in concentration shifted the curve towards shorter path lengths. An increase in temperature reduced the deviations at short path lengths and led to a more fluctuating deviation curve over path length.

The overprediction from H_2O was evened out by the underprediction of CO_2 in the combustion cases at short path lengths (figure 5.15). The deviations were not so extreme as with the single gas calculations. For natural gas combustion, the model was more accurate at shorter pressure path lengths (figure 5.16).



Figure 5.13: Relative deviation of the SLW model of total emissivity from HITEMP2010 over path length at 800°C for different concentrations of H_2O and at 50 vol. -% H_2O for different temperatures.



Figure 5.14: Relative deviation of the SLW model of total emissivity from HITEMP2010 over path length at 800°C for different concentrations of CO_2 and at 50 vol. -% CO₂ for different temperatures.


Figure 5.15: Relative deviation range over path length from the SLW model for all combustion cases.



Figure 5.16: Relative deviation range over path length from the SLW model for natural gas combustion cases.



Figure 5.17: Relative deviation range over path length from the WSGG model with parameters from Smith et al. [105] for all combustion cases.

5.2.5 WSGG model from Smith

The WSGG model with the parameters from [105] had bad accuracy for the combustion cases at path lengths of 0.1 - 10 m of up to 60% overprediction (figure 5.17). These high deviations were due to the combustion atmospheres with a H₂O/CO₂ ratio far away from the values of 1 and 2 given by the model. For wet oxyfuel and air blown natural gas combustion, the deviations were between -10% and 20% within the maximum pressure path length given by the authors of 9.87 bar m (figure 5.18). For longer pressure path lengths, the total emissivity was strongly underpredicted. The total emissivity was very well predicted at very short path lengths.



Figure 5.18: Relative deviation range over path length from the WSGG model with parameters from Smith et al. [105] for natural gas combustion cases with oxyfuel wet and air blown combustion (H_2O/CO_2 ratio of 2).



Figure 5.19: Relative deviation range over path length from the WSGG model with 3 grey gases with parameters from [63] for all combustion cases.

5.2.6 WSGG models from Johansson

All WSGG models from Johansson et al. [63, 64] showed an increase in deviation for path lengths shorter than 0.1 m (figure 5.19, 5.20 and 5.21). This increase was up to -50% to 25% at the lower path length domain boundary. The underprediction was worst for the lowest temperatures. These values were outside of the validity range given by the authors (figure 5.22 and 5.23). The trend was different for longer path lengths. Higher temperatures lead to more underprediction as the reference SNB model EM2C underpredicted the total emissivity there as well (figure 5.22 and 5.24). The model accuracy became worse above the upper path length limit and should not be used there (figure 5.22 and 5.24). The accuracy in the validity range was between -20% and 10%. The latest model from Johansson et al. [64] had the best accuracy, the model with three grey gases from Johansson et al. [63] the worst. The maximum deviation of the newest model was between -10% and 0% for temperatures of 800 °C (figures 5.23 and 5.25). For higher temperatures, the model underpredicted the total emissivity up to -20% (figure 5.24).



Figure 5.20: Relative deviation range over path length from the WSGG model with 4 grey gases with parameters from [63] for all combustion cases.



Figure 5.21: Relative deviation range over path length from the WSGG model with parameters from [64] for all combustion cases.



Figure 5.22: Relative deviation of total emissivity for natural gas wet oxyfuel combustion atmosphere at various temperatures from the WSGG model with parameters from Johansson et al. [64].



Figure 5.23: Relative deviation range over path length from the WSGG model with parameters from [64] for all combustion cases at 800 °C.



Figure 5.24: Relative deviation of total emissivity for 1800°C natural gas wet oxyfuel combustion atmosphere from the WSGG models with parameters from Johansson.



Figure 5.25: Relative deviation of total emissivity from HITEMP2010 predictions for 800°C anthracite air blown combustion atmosphere from the WSGG models with parameters from Johansson.



Figure 5.26: Relative deviation range over path length from the WSGG models with parameters from [67] for all combustion cases.

5.2.7 WSGG model from Khare

The WSGG model with the parameters from Khare [67] lead to an overprediction of total emissivity of up to 50 % (figure 5.26). The model underpredicted in the short path length ranges the total emissivity more than 30 %. Atmospheres with a H₂O/CO₂ ratio far away from the given parameter sets (table 2.3) lead to an underprediction of up to -20 % (figure 5.27). At given ratios, strong deviations were observed from the reference model EWB (figure 5.28). The model overpredicted the total emissivity for long path lengths. The best accuracy was reached for brown coal and anthracite combustion atmospheres up to 800 °C for path lengths longer than 0.01 m (figure 5.29).



Figure 5.27: Relative deviation of total emissivity for natural gas wet oxyfuel combustion atmosphere (H_2O/CO_2 ratio 2.0) at various temperatures for the WSGG model with parameters from Khare [67].



Figure 5.28: Relative deviation of total emissivity for brown coal dry oxyfuel combustion atmosphere (ratio 0.1) at 1800 °C for the WSGG model with the parameters from Khare [67] and for its reference model EWB.



Figure 5.29: Relative deviation range over path length from the WSGG model with the parameters from [67] for brown coal and anthracite combustion cases at 800 °C.



Figure 5.30: Relative deviation range over path length from the WSGG model with the parameters Yin et al. [126] for all combustion cases.

5.2.8 WSGG model from Yin

The WSGG model with the parameters from Yin et al. [126] had a similar accuracy as the WSGG model with the parameters from Khare [67] (figure 5.30), but the overprediction was not as high. The best accuracy was for a path length of 0.1 m. The accuracy was less before and after this path length. The peak of overprediction at 2 m path length was due to a peak from the EWB reference model (figure 5.31). At very long path lengths of 100 m, the model underpredicted the total emissivity like its reference model EWB (figure 5.30 and 5.3).



Figure 5.31: Relative deviation of total emissivity for anthracite air blown combustion atmosphere at 1800 °C for the WSGG model with the parameters from Yin et al. [126] and the reference model EWB.



Figure 5.32: Relative deviation range over path length from the WSGG model with the parameters from Krishnamoorthy et al. [70] for all combustion cases.

5.2.9 WSGG model from Krishnamoorthy

The WSGG model with the parameters from Krishnamoorthy et al. [70] had deviations of up to 130% at short path length (< 0.1 m) (figure 5.32). The same overprediction, but not as high, was observed at its reference model SNB/RADCAL (figure 5.7 and 5.33). The highest deviations were observed for natural gas combustion cases with a H₂O/CO₂ ratio far higher than the ratio of the given parameter sets (table 2.3 and figure 5.34). The deviations were lower for coal combustion atmospheres (figure 5.35).



Figure 5.33: Relative deviation of total emissivity for anthracite dry oxyfuel combustion atmosphere at 800 °C for the WSGG model with the parameters from Krishnamoorthy et al. [70] and the reference SNB model RADCAL.



Figure 5.34: Relative deviation of total emissivity for natural gas wet oxyfuel combustion atmosphere at various temperatures for the WSGG model with the parameters from Krishnamoorthy et al. [70].



Figure 5.35: Relative deviation range over path length from the WSGG model with the parameters from Krishnamoorthy et al. [70] for coal combustion cases.

5.3 Discussion

5.3.1 Pure gases

For the prediction of H_2O radiation the following ranking of the variable composition models was found (figure 5.36 and table 5.3):

- 1. The SNB model EM2C had the best predictive capability for H_2O radiation with a very continuous trend of total emissivity deviation from the HITEMP2010 benchmark predictions over path length. The accuracy was always better as 11%.
- 2. The SNB model RADCAL was slightly worse than EM2C with similar independence from path length. The model overpredicted the total emissivity at most test calculations. The maximum overprediction was 17%.
- 3. The EWB model had a very discontinuous trend of total emissivity deviation over path length. The maximum deviation was 28 %.
- 4. The SLW model had the largest deviations of up to 73% overprediction for short path length. Slight underpredictions were observed at long path length up to -21%.

For the prediction of carbon dioxide radiation, the ranking was as follows (figure 5.37 and table 5.3):

- 1. The EWB model had the best predictive capability of total emissivity. The values were always within 13% of the reference calculations. The highest deviations were at long path length.
- 2. The second best predictions were from the SLW model. It had a maximum deviation of -28% to 10% at short path length (< 6 cm).
- 3. The SNB model RADCAL had maximum deviations of up to 36%. The total emissivity was overpredicted at short path length and underpredicted at long path length.
- 4. The SNB model EM2C had the worst mean predictive capability. The deviations were below 10% for path length up to $2.5\,\mathrm{m}$. Deviations of up to

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Figure 5.36: Relative deviation ranges for the variable composition spectral models from HITEMP2010 total emissivity for the different concentrations and temperatures of H_2O .

-43% were observed for high temperatures and long path length and can be explained with the missing of hot CO₂ lines (section 3).

Table 5.3: Maximum and minimum deviation of total emissivity from the HITEMP2010 reference calculations for test cases with single gases.

	H_2	С	CO_2		
	Min.	Max.	Min.	Max.	
EWB	-27.9%	26.8%	-13.2%	9.2%	
SNB (RADCAL)	-2.3%	16.5%	-36.2%	26.9%	
SNB (EM2C)	-10.5%	6.3%	-42.5%	4.0%	
SLW	-21.3%	73.2%	-28.4%	9.8%	



Figure 5.37: Relative deviation ranges for the variable composition spectral models from HITEMP2010 total emissivity for the different concentrations and temperatures of CO_2 .

5.3.2 Combustion atmospheres

The combustion atmosphere cases brought a similar result for the variable composition models (figure 5.38 and 5.39 and table 5.4).

- 1. The SNB model EM2C had the best accuracy with maximum accuracy of 12% at long path lengths (figure 5.11). The model can be improved with an consideration of the hot CO₂ lines in the HITEMP2010 database.
- 2. The SLW model had the second best accuracy of maximum 19%. The maximum deviations could be improved to 12% if a lower limit for the pressure path length of 0.03 barm was introduced due to the large underprediction at short path lengths (figure 5.15).
- 3. The SNB model RADCAL had a maximum deviation of 24%. The total emissivity was overpredicted at very short path lengths (figure 5.7). A lower pressure path limit of 0.03 bar m limited the deviations to 14%.
- 4. The EWB model had the worst accuracy of the variable composition models with underpredictions of up to -57%. These high deviations were due to discontinuities in the used functions at short path length. A lower pressure path limit of 0.004 bar m lead to an improved accuracy of 20%. The model underpredicted the total emissivity at long path length (figure 5.3). Therefore, it should not be used for the validation of simpler spectral models.

The simplified WSGG models, which can be used with justifiable effort in largescale CFD simulations, showed large differences in accuracy.

1. The latest model from Johansson et al. [64] had the best accuracy with deviations up to 21 % at high temperatures. The accuracy was better for simulations of temperatures up to 800 °C with maximum values of 13 %. The bad accuracy at high temperatures was contributed to the missing of hot lines in its reference SNB model EM2C. Another negative point was the low pressure path length limit of 0.01 bar m which equals a path length of 4 cm in air blown combustion (figure 5.25). This limit is too high for the fine grids in the near burner zone. Lallemant et al. [72, p. 545] states that cell sizes as small as 0.5 mm are necessary for the correct simulation of a 2 MW natural gas flame.

- 2. The older models from Johansson et al. [63] had worse accuracy with maximum deviations of 26 % (four grey gases) and 30 % (three grey gases). The deviations were lower at temperatures of up to 1300 °C with 23 % and 26 %.
- 3. The next accurate model was the WSGG model with the parameters from Yin et al. [126]. It had deviations up to 37%, which could be reduced to 21% with an upper temperature limit of 800 °C. The model has a lot of parameter sets for different H_2O/CO_2 ratios. The flaws from its reference model EWB especially at high temperatures lead to the high deviations from the benchmark calculations with the HITEMP2010 LBL model.
- 4. The WSGG model with the parameters from Khare [67] had deviations up to 49%. This was due to the limited range of given H₂O/CO₂ parameter sets. The model should not be used for ratios far away from the given values. It is best suited for coal combustion atmospheres. The implementation of its reference EWB model in the work from Khare [67] was possibly incorrect as the WSGG model overpredicted the total emissivity compared to the EWB model implemented in this work substantially at long path length even at similar H₂O/CO₂ values as given by the author (figure 5.28). The overprediction evened out the missing hot lines from the EWB model but was not mentioned by Khare [67]. The model had its worst deviations at short path length and high temperatures. The accuracy was 13% at temperatures up to 800 °C, with a lower pressure path limit of 0.01 bar m and for atmospheres with a H₂O/CO₂ ratio close to the given values.
- 5. The Smith et al. [105] model showed an accuracy of 59% for all combustion cases in the validity range given by the authors. The highest deviations were for combustion cases far below the given composition ratios of 1 and 2. This was the case for most coal combustion atmospheres (table 2.7). The accuracy for given ratios was better with 23%. Especially the accuracy at short path length was very good (figure 5.18). The model was not valid for simulation of large-scale oxyfuel boilers as the total emissivity was strongly underpredicted outside of the upper pressure path length limit.
- 6. The model from Krishnamoorthy et al. [70] had large overpredictions of up to 131 % at short path length. The authors gave only parameters for composition



Figure 5.38: Relative deviation ranges for spectral models from HITEMP2010 total emissivity for all combustion atmospheres at various temperatures. The WSGG models are only considered within the ranges of validity given by the authors.

ratios of 0.111 and 0.5 and the model subsequently had bad accuracy for other compositions. With a lower pressure path length limit of 0.1 bar m and only in atmospheres close to the given parameters, maximum deviations of 30% were reached. The model is therefore only correct for coal combustion atmospheres.

The WSGG model from Johansson et al. [64] can be recommended as the most versatile and accurate model for all combustion calculations as it factors in variable compositions. It can be further improved with an increase of the lower validity limit to shorter pressure path length to be able to resolve very fine grids and with a regeneration of the parameter based on the HITEMP2010 LBL model to include more hot lines at higher temperatures.

	Original limits New		limits			
	Min.	Max.	Min.	Max.	Recommended limits for im-	
					proved accuracy	
EWB	-57%	17%	-20%	17%	Lower pressure path length limit	
					of $0.004 \mathrm{barm}$	
SNB (RADCAL)	-7%	24%	-7%	14%	Lower pressure path length limit	
					of $0.03 \mathrm{barm}$	
SNB (EM2C)	-12%	6%	-	-	No improvement found	
SLW	-19%	12%	-7%	12%	Lower pressure path length limit	
					of $0.03 \mathrm{barm}$	
WSGG (Smith 1982)	-32%	59%	-19%	23%	H_2O/CO_2 close to given ratios	
					$(\Delta \le 0.3)$	
WSGG (Johansson $2010/3$ GG)	-30%	14%	-25%	13%	Temperatures up to $1300^{\circ}\mathrm{C}$	
WSGG (Johansson 2010/4GG)	-26%	14%	-23%	12%	Temperatures up to $1300^{\circ}\mathrm{C}$	
WSGG (Johansson 2011)	-21%	4%	-13%	3%	Temperatures up to $800^{\circ}\mathrm{C}$	
WSGG (Khare 2008)	-28%	49%	-9%	13%	$\rm H_2O/CO_2$ close to given ratios	
					$(\Delta \leq 0.3)$, temperatures up	
					to $800 ^{\circ}\text{C}$, lower pressure path	
					length limit of $0.01\mathrm{barm}$	
WSGG (Yin 2010)	-30%	37%	-21%	20%	Temperatures up to $800^{\rm o}{\rm C}$	
WSGG (Krishnamoorthy 2010)	-32%	131%	-22%	30%	Lower pressure path length limit	
					of $0.1\mathrm{bar}\mathrm{m},~\mathrm{H_2O/CO_2}$ close to	
					given ratios ($\Delta \leq 0.3$)	

Table 5.4:Maximum and minimum deviation of total emissivity from theHITEMP2010 reference calculations for combustion atmospheres.



Figure 5.39: Relative deviation ranges for spectral models from HITEMP2010 total emissivity for all combustion atmospheres at various temperatures. The WSGG models are only considered within the new ranges of validity recommended in this work.

Chapter 6

Conclusions

The evaluation of the different detailed models in the controlled gas cell atmosphere at high temperatures lead to the observation, that the inclusion of the hot lines is essential for the correct prediction of the radiative behaviour. Both HITRAN editions deviated substantially from the values measured experimentally, as they are published for low temperature simulations and do not include the hot lines.

The first HITEMP edition from 1995 predicted the gas absorption to a satisfactory level to temperatures up to $727 \,^{\circ}C/1000 \,\text{K}$ as recommended by the authors [101]. For higher temperatures the extrapolated lines resulted in large deviations of the band transmissivity.

The SNB models RADCAL and EM2C showed a good agreement with the experimental spectra at all measured temperatures and concentrations. The band transmissivity deviations were at a maximum of 3%.

The EWB model predicted the band transmissivities of CO_2 with a maximum absolute error of 6%. The water band transmissivities were predicted better with a maximum absolute error of 2%. The model had a good accuracy for the reduced computational effort compared to the other models.

The model with the least deviations from the experimental measurements was the LBL model with the new HITEMP edition from 2010 [101]. It had absolute band transmissivity deviations of less than 2.2% in the observed spectral range at all measured temperatures from 727 - 1500 °C and concentrations. The spectra agreed better visually with the measured spectra as the other models. The model was therefore recommended as a reference model for validation of simplified spectral gas radiation models. The experiments with the turbulent natural gas flame proved the effect of increased gas radiation with higher concentrations of radiatively active gases in the flue gases of oxyfuel combustion. The temperature moderating effect of water could be clearly observed in the measurement results of the two oxyfuel cases with dry and wet recirculation. The results did not answer our question about the validity of spectral radiation models for oxyfuel combustion, though they pointed out the importance of accounting for turbulence-radiation-interaction in combustion simulations. The negligence of the effect of turbulence-radiation-interaction leads to large underprections of radiative energy transfer in turbulent flames with all accompanying effects on temperature field, flame structure and formation rate of hazardous emissions. A computationally efficient turbulence-radiation-interaction model is urgently needed.

The most valid variable composition model was the SNB model EM2C with a good validity in the whole pressure path length range (figure 5.38). Its only flaws were the slight underprediction of total emissivity at high temperatures and longer path length. This was most likely an effect of the missing of hot CO_2 lines. The other models had stronger deviations especially at short path length (SNB/RADCAL, SLW, EWB).

All variable composition models besides the SLW model underpredicted the CO_2 total emissivity at long path length and high temperatures. This was a consequence of the missing of hot lines. The hot lines become more important at longer path length, as lines, which are weak at short path length, begin to saturate, i.e. are opaque. The CDSD-HITEMP LBL database [101, 115], was the first database to include most of the hot lines. There were still some hot lines missing, but the database can be used without any corrections for the generation of parameters for simplified high temperature spectral model to yield a better accuracy as the existing parameters.

The most valid and most versatile simplified model was the WSGG model from Johansson et al. [64] with an accuracy in the range from -21% to 4%. It should not be used for smaller pressure path lengths as recommended, and it had the same underprediction of total emissivity at high temperatures and long path length as its reference SNB model EM2C. The other models had the drawback of not many sets for different H₂O/CO₂-ratios (Smith 1982, Johansson 2010, Khare 2008 and Krishanmoorthy 2010) or used a less accurate reference model (Khare 2008, Yin

2010, Krishnamoorthy 2010). The WSGG model from Johansson et al. [64] was therefore recommended for use in large scale CFD simulations for oxyfuel and air blown combustion.

The general methodology to start with an experimental model validation in a controlled environment, i.e. the hot gas cell, before validation on a full scale technical process, i.e. the turbulent natural gas flame, proved to be a good way to show strengths and weaknesses of the validated models.

The ability of the Fourier Transform Emission Spectroscopy to measure time resolved fluctuations of radiation in turbulent flames should be further developed to get a closer look at the complicated physical processes occuring in reacting flows. The method is able beside the timely fluctuations to give informations on gas temperature and gas composition profiles of the radiatively active species H_2O and CO_2 .

This thesis gave an overview of spectral modeling of gases in combustion. The research question "How valid are the existing spectral gas radiation models for oxyfuel combustion?" could be answered. The most valid existing detailed spectral model was accurate at temperatures as high as $1500 \,^{\circ}$ C with a maximum deviation of band transmissivities of 2%. The existing simplified models were not as accurate with an accuracy of 21%. The parameter for the simplified models need to be regenerated with the new LBL model HITEMP2010 to account for all hot lines, which are important for high temperatures and long path length to reach a satisfying accuracy of 10% for WSGG models. The spectral accuracy had to be seen in comparison to the effect of turbulence-radiation-interaction (TRI). TRI can intensify the radiative transfer from turbulent flames up to 75% compared to radiative transfer based on the mean scalar properties. There is not yet a simple modelling approach available. A TRI model is urgently necessary to correctly predict the wall heat transfer and the temperature field of turbulent combustion processes.

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