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Plasma is often called the fourth state of matter. The first state is the solid state. If energy is added to matter in the solid state, eventually it will melt and become liquid: the second state. If even more energy is fed to the now liquid matter, it will evaporate and reach the third state of matter: gas. On earth these three states of matter are by far the most common. There is however a fourth state of matter, called the plasma state. Plasmas are formed when even more energy is added to the already gaseous matter. In a plasma, (a part of) the atoms and molecules are ionized, leading to the presence of free electrons and ions, but in total it will be quasi neutral, meaning that the total net charge is zero.

Plasmas are often produced by an electrical discharge in a gas, but not always. On the contrary: In the universe, one could argue that the majority of all plasmas is not created in this way: e.g. the sun is a plasma which is not produced by an electrical discharge, just like all stars. On earth however, most of the plasmas are created by an electrical discharge. Nowadays, man-made electrical gas-discharges are very common, but electrical discharges also occur in nature, where they have fascinated people for thousands of years. In the distant past, naturally occurring gas discharges such as the Aurora Borealis and Australis (the Northern and Southern lights), lightning and St. Elmo’s fire were ascribed to a divine source.

In the 18th century, advances in physics, especially the discovery and understanding of electricity, provided a scientific explanation for these impressive phenomena. Isaac Newton (1643–1727) was one of the first to report that light
Chapter 1. Introduction

is emitted by electrical discharges created by charging due to friction. The understanding of electricity however, remained very poor until Benjamin Franklin developed his theory of a self-repulsive electric fluid after extensive experimental observations in 1747. Later research, by Michael Faraday and John Townsend, shed more and more light on this matter. Nowadays, many of the physical concepts of atmospheric gas discharges are well understood. Nevertheless, the beauty of these natural gas discharges never ceased to impress and inspire humans. Besides providing humility and inspiration, plasmas are often used for practical purposes, such as the treatment of surfaces, cleaning of polluted exhaust fumes and perhaps most of all, lighting.

1.1 Lighting

Light is essential to life. Not only is life very impractical in the absence of light, but light is in fact needed for many of the biochemical processes that are part of life. In the modern world, the presence of light is taken for granted. Only very rarely are we confronted with the absence of light, leading to all kinds of issues, some of which are more problematic than others. Among a few other things, such as the use of tools and capability of speech, the ability to make light is what sets us apart from the animal world. The presence of human life is (almost) always accompanied by the presence of light as is illustrated in figure 1.1. 99% of the outdoor lighting is produced by plasmas, of which roughly 35% by Philips lamps.

![Figure 1.1: The earth during the night as seen from space.](image)
1.1 Lighting

The shape of our world is dominated by the fact that we can make light. Almost no office building is illuminated adequately (yet) by daylight alone. Metro systems would be nearly suicidal and cinemas wouldn’t make any sense at all.

In the distant past, the most common and perhaps only way to make light, was by lighting a fire. Fires were used for other things as well of course, but it brought light into our—until then—dark nights. Humans have been making fires for a very long time. The oldest campfire known today was lit around 790,000 years ago on the banks of the river Jordan [1].

Fires remained in use as the main source of light until relatively recently, though not in the form of campfires. The technology progressed to the candle and the oil lamps, which may have been with us for 3000 years or more. A later improvement was the advent of gas lighting in the late 1700s.

The biggest improvement in lighting occurred around 1876 when Thomas Alva Edison produced his first electric incandescent lamp. Incandescence had been shown before by Warren de la Rue, but Edison was the first to make it into a practical product. For the first time since the beginning of lighting, a lamp was produced that did not use a fire to produce light. It is based on a carbon filament that acts as a resistor for electricity. If enough power is supplied, it heats up and radiates light. Today’s incandescent lamp is still based on this principle, even though the filament is now commonly made of tungsten. It is still widely used and even today it is the most common light source in domestic applications.

The efficiency of these lights was still very low: 10–20 lm/W for incandescent lamps. In theory an ideal white light source with good color rendering ($R_a \geq 80$) could produce up to 400 lm/W.

In the 1930s, discharge lamps became available. There were several kinds of discharge lamps that became available more or less at the same time: the low pressure fluorescent lamp, the low pressure sodium lamp and the high pressure mercury lamps. They were more efficient than the incandescent lamps, however their color rendering was not as good. The efficiency of the fluorescent lamp is in the range of 50–110 lm/W. The low pressure sodium lamps reach 60–200 lm/W. Discharge lamps had been developed even before the incandescent lamp: e.g. Francis Hauksbee showed as early as 1705 that he could make a lamp bright enough to read by using an evacuated glass sphere filled with a small amount of mercury, however no widespread application occurred using this technology before the 1930s.
A few decades later, in the 1960s a new class of discharge lamps was introduced: the metal halide lamps. They were also lamps with a higher efficiency and much better color rendering properties. Their efficiency is 60–130 lm/W. Also the high pressure Sodium lamp was introduced, which we now commonly see as road lighting. Since then there have been gradual improvements of our lighting systems.

In the future, LEDs (Light Emitting Diodes) may play a major role in general lighting. The potential efficiency of LEDs in practical applications is \( \sim 160 \text{ lm/W} \) [2]. Although LEDs hold great promises for the future of lighting, for the foreseeable future one of their major issues will remain the high cost of purchase per unit, whereas the purchase price of a plasma light source is and will remain relatively low. In the past, the purchase price has proved to be an important factor in the acceptance of new lighting systems. Besides the price, LEDs at present have not reached the level of color rendering currently available in discharge lamps and suffer from cooling problems. LEDs are now appearing in a variety of special applications where the above mentioned disadvantages are not a concern.

All this lighting however, comes at a cost. Lighting consumes large amounts of energy: in fact around 20% of all electricity is used for lighting [3]. For this reason alone, efficient lamps are important [4], not only for financial reasons, but also for preserving the environment and our natural resources.

### 1.2 Discharge Lamps

Discharge lamps can be classified in three distinctly different groups: low pressure discharge lamps, high pressure discharge lamps and intermediate pressure lamps. Their methods of producing radiation differ significantly.

#### 1.2.1 Low Pressure Lamps

As was mentioned before, the discovery of the low pressure lamp actually predates the invention of the incandescent lamps. Only much later, in the 1920s, it was discovered that in a mixture of mercury vapor and a noble gas electric energy could be converted into UV radiation very efficiently. As we now know, efficiencies of 75% are possible in practical configurations. As John Waymouth said at the Gaseous Electronic Conference in Norfolk, VA, in 1999:
„Mother Nature had a fluorescent lamp in mind when she designed Argon and Mercury.”

The electric energy is converted into UV radiation with most of the energy in photons with a wavelength of 254 nm and 185 nm [5]. This radiation is invisible to the human eye, so in order to use this discharge as a practical light source, this issue had to be resolved. An efficient phosphor had to be found to convert the UV radiation of the discharge into the visible part of the spectrum (380–780 nm). In the late 1930s such a phosphor class was found, i.e. the halophosphates.

To this day, fluorescent lamps remain the most frequently used energy efficient lamps. As such it is probably the most produced man-made plasma. The traditional standard fluorescent lamp has a cylindrical geometry with a diameter of about 26 mm. It contains 300–600 Pa of argon buffer gas, and mercury with a vapor pressure of about 1 Pa. The typical current through such a lamp is a few hundred mA. A schematic view of a fluorescent lamp is shown in figure 1.2.

Since the pressures are so low, the interaction between various particles in the lamp is relatively infrequent. This leads to the electrons having a much higher temperature than the heavy particles (such as the mercury atoms), because the electrons are accelerated much more efficiently in the electric field inside such a lamp. The thermal equilibration mechanism —i.e. elastic collision between the two— is relatively weak due to the low density of the background gas. This non-equilibrium quality of the low pressure fluorescence lamp is an important contributor to the efficiency of the lamp: after all, it is no use heating the mercury atoms. The energy should be used as exclusively as possible
for the excitation of the mercury, through electron impact excitation from the
ground state. After a UV photon is emitted by an excited mercury atom, it will
eventually hit the phosphor on the wall of the lamp, where it will be converted
into a visible photon. Unfortunately, in this conversion, about half the photon
energy is lost. The losses incurred in this process are called the Stokes losses.

Low pressure sodium lamps have a slightly lower efficiency, but the sodium
resonant line at 590 nm is near the maximum sensitivity of the eye-sensitivity
curve. Therefore no phosphors are needed, yielding a very efficient lamp, which
unfortunately is monochromatic and thus of limited use. The application of the
low pressure sodium lamp is restricted to road lighting, where color distinction
is considered to be less important [6].

**Stokes Losses**

The Stokes losses are the dominant energy loss process in fluorescent lamps.
They occur when a UV photon with a high energy is converted to a visible
photon with a low energy. This is illustrated in figure 1.3. The UV photon
carries more energy than a visible photon. In the phosphor, this excess energy
is effectively removed. The phosphor absorbs a high energy UV photon and
later emits a low energy visible photon. The difference is appears as heat.

In theory, the stokes losses could be avoided by „quantum-cutting“ phos-
phors [7]. Although there has been substantial research on quantum-cutting or
„quantum-splitting” phosphors, no practical phosphor of this type is in widespread
use. In addition to a quantum efficiency above unity with appropriate absorp-
tion and emission wavelengths, a quantum-cutting phosphor must have long
term stability in a high UV lamp environment.

1.2.2 High Pressure Lamps

High pressure gas discharge lamps generally have a small volume (a few mm$^3$
or cm$^3$), high pressure (more than 1 bar), high luminance, and a large variety
in power settings (10 W to 18 kW). The plasma in these lamps is usually close
to local thermodynamic equilibrium (LTE). At a pressure higher than 1 bar
the energy transformation process is different than for low pressure discharges.
The mean free path of electrons decreases with increasing pressure, which also
increases the number of collisions. Although the electron passes only a small
percentage of its kinetic energy to heavy particles during elastic collisions, the
1.2 Discharge Lamps

A huge number of collisions ensures a considerable energy transfer from electrons to heavy particles. This results in an increasing heavy-particle temperature with a simultaneously decreasing electron-temperature.

In high pressure discharge lamps, the electrons and heavy particles have temperatures between 1400 K and 8000 K depending on local position and lamp type. At these temperatures, the excitation of atoms is high, resulting in radiative transitions from excited states to the ground state and from excited states to other excited states [5]. The resulting spectral power distribution of high-pressure discharge lamps consists therefore not only of resonance lines but also of spectral lines due to transitions between excited states. High pressure discharge lamps typically contain at least mercury and/or sodium. Sodium is often chosen for the convenient wavelength of the resonance radiation (589 nm) and mercury for its high vapor pressure as well as some electrical benefits (high cross-section for elastic electron collisions).

Since the 1960s metal halides have been added to the mix of components in the lamp to increase the efficiency of the lamp as well as to improve the color properties. By choosing the additive, one can tune the spectrum to the desired distributions. The metals are beneficial because they are efficient radiators in the visible part of the spectrum; they are added as halides to increase their vapor pressure in the discharge.

Metals generally have a very low vapor pressure at the relevant cold spot temperatures (~1000 K). Typically, metal halides have a much higher vapor pressure, so the metals can enter the gas phase as metal halide molecules. Some
of these molecules migrate to the hottest part of the plasma where the metal halide molecules are dissociated, delivering the metal atoms and ions right where they are wanted. A typical example of a metal halide lamp is shown in figure 1.4.

![Figure 1.4: A typical example of a metal halide lamp. This one is a Philips MHN-TD 150W/842 (150 watts, 4200 K) linear/tubular metal halide lamp.](image)

In contrast with the fluorescent lamps discussed earlier, these lamps do not require any radiation conversion in a phosphor. This is a huge advantage for attaining higher efficiencies. However, these lamps also have an extra disadvantage: because of their operating conditions, they are in LTE, leading to a lot of heating of the heavy particles, which results in significant thermal conduction and convection losses to the lamp walls. This is energy that is not converted to light and thus decreases the efficiency of the lamp.

### 1.2.3 Intermediate Pressure Lamps

After discussing the presently available lamp types, the question arises if there are any lamps possible that do not have the drawbacks that the ones described above do. The answer to that question is: there are. Of course, these lamps will not be perfect either.

The idea(1) would be to make a plasma that produces visible radiation directly —*i.e.* without the need for a conversion in a phosphor— without the
operating losses of the high pressure lamp. To do this, the pressure is lowered to a level where the heavy particles are not heated anymore. If the particles are not heated anymore, they will remain cold, causing the traditional metal halides to condensate and essentially depart from the discharge chemistry. To deal with this, another chemical mixture had to be found: a molecule that has a vapor pressure that is high enough at low temperatures to operate it and that has a spectrum that is good for lighting purposes.

Basically, the goal is a lighting system that has the best of both worlds: no conversion losses and no heat losses. In reality though, such a lamp will have a bit of both worlds. The discharge will probably produce radiation with a more desirable spectrum than a low pressure mercury discharge, though probably not quite as good as the discharge in a high pressure lamp. Therefore it may well need some limited conversion of the spectrum in phosphors, but the hope is that the Stokes losses can at least be significantly reduced. The same holds for the heat losses of such a lamp: much better than for a high pressure discharge, but probably not quite as good as for a low pressure discharge. All in all though, this approach can open up possibilities for a more efficient discharge lamp [6], [8], [9], [10], [11].

A potential problem of using other species as the prime radiators in a lamp is that electrodes similar to those in the more traditional plasma lamps may not survive in such a plasma. The chemistry in these plasmas will likely quickly erode the electrodes. So it will be necessary to mount the electrodes outside of the plasma, i.e. external electrodes. This is possible and it also greatly reduces the likelihood of lamp failure due to electrode erosion, which is one of the causes of failure in lamps that have internal electrodes.

Another benefit of intermediate pressure lamps is: it will not contain mercury. Reducing the dose of mercury in lamps has been an important theme for the lighting industry over the last decade. The amount of mercury in fluorescent lamps has been decreasing for years, but to completely eradicate its use altogether, novel lamp types have to be developed. These lamps have to be efficient too, not only for financial or energy reasons, but also to achieve the goal of reducing mercury pollution. Mercury is released to the environment in the production of electricity from fossil fuels —coal in particular—. During the life of a modern lamp, more mercury is released into the environment from the power it consumes, than is present in the lamp itself. So in order to reduce the total amount of mercury released into the environment, it doesn’t suffice to take it out of the lamp if that reduces the efficiency of the lamp. A mercury free
lamp that is equally or more efficient would be a huge step forward.

A typical example of a molecular lamp can be seen in figure 1.5. It is a lamp that does not contain any mercury. Instead it contains argon as a buffer gas and indium bromide as the primary radiating species. The lamp is capacitively driven with two electrodes placed on the outside of the lamp.

![Figure 1.5: A drawing of a typical example of a molecular lamp.](image)

### 1.3 Atomic vs Molecular Radiation

In the more traditional lamp types, the main radiators have always been atoms in the plasma. Atomic radiation works relatively simply. An atom undergoes a transition from one higher electronic energy level to another lower electronic energy level. During this process, a photon is produced. The energy difference between the two levels corresponds to the energy of the photon. During this process an electron moves to another (lower) orbit. The energy of the various levels is discrete, so the possible energy differences between the various electronic levels is relatively limited compared to the energy differences possible in a molecular system. This gives rise to a line spectrum.

As was mentioned before, another discharge chemistry has to be considered for this new lamp type. Moreover, the operating conditions may also be different from the traditional lamps, with more of the radiation production being done by molecules. Molecular radiation is, however, very different in nature, because molecules —by definition— consist of not just one single atom, but at least two. This creates some additional energy storage possibilities. Whereas atoms can only store internal energy in the orbits of their electrons, molecules can also store energy in the relative motion of their constituent atoms. The atoms of a molecule can rotate around each other and they can also vibrate. This gives rise to a much richer and more complex set of energy differences, because molecules
1.4 Laser Induced Fluorescence Spectroscopy

The set of spectral lines that is emitted by an excited atomic or molecular species can be used as a fingerprint of that particular species. It can be used to identify the species, but also to determine various aspects about that species, e.g., its density, temperature or even its speed. The science of these phenomena is spectroscopy.

Many different kinds of spectra exist, usually defined by the way they are measured. Their respective names are usually self-explanatory: emission spectra, absorption spectra and laser induced fluorescence (LIF) spectra among others.

In LIF spectroscopy, the spectrum of the fluorescence of a sample is studied after the sample is first excited by laser irradiation. Many aspects of these spectra can be studied, e.g., the position of the various lines, their (relative) intensities or their temporal behavior. To study fluorescence though, it first has to be produced. In LIF, this is done by exciting a species using a laser. It is of paramount importance then that the energy of the laser photons matches exactly that of the energy difference between the targeted levels: the transition energy, sometimes referred to as the transition wavelength.

By defining the wavelength of the laser, the excitation transition of the species is determined. This is helpful, because, since the supplied photons determine what transition(s) a molecule can undergo, they also determine—to a large extent—what level it will end up in. Very rarely does one transition energy correspond to more than one specific lower level and one specific upper level.

For atoms, LIF spectra are still fairly simple because of the relatively small number of possible electronic transitions in most species. For molecules on the other hand, the LIF spectra become somewhat more complicated, because for every electronic transition possible, there is a multitude of vibrational transitions that can (and will) occur, along with an even greater number of rotational transitions.

typically do all these things at once.
1.5 This Thesis

This introduction to plasmas, lighting and measurement techniques has given a flavor of what will be the subjects of the following chapters. To find out if Indium Bromide (InBr) is a suitable candidate as the prime radiator for a novel efficient lamp type, several experiments were carried out.

One part of the work presented in this thesis consists of the determination of the fundamental constants of InBr. This part will be presented in chapter 4. This includes work on the Franck-Condon factors for certain transitions, wavelengths of certain transitions and the determination of several spectroscopic constants, such as rotational constants and their anharmonicities. To accomplish this, a new method was developed. This method helped in the unravelling of the recorded spectra. The setup that was built to perform these measurements is discussed in chapter 3.

Time resolved measurements were carried out to determine the variation of the decay time as a function of the rotational quantum number. These measurements are presented in chapter 5. Also, a model was developed to calculate a rotational temperature from a LIF spectrum. Details on this model will be given and results obtained with it will be presented in chapter 6. Finally the temperature dependence of the LIF signal was investigated. This is discussed in chapter 7.

References


In this chapter an overview of the theory underlying this thesis will be given. First the relationship between atomic structure and atomic radiation is discussed. This serves as a stepping stone to help introduce the theoretical foundation for this thesis. After discussing atomic structure and radiation, the focus will be extended to molecules and their structure. The main emphasis of the discussion will be on diatomic molecules —specifically Indium Bromide. Besides an electronic structure that is analogous to the electronic structure of atoms, a molecule can vibrate and rotate. For vibrations and rotations, discrete energy levels exist rather like for electronic states, as will be shown later in this chapter. The intensity of transitions in molecular spectra will be discussed. More details on the theory discussed in this chapter can be found in [1], [2], [3] and [4].

2.1 Atomic Structure and Radiation

An atom consists of a positively charged nucleus surrounded by electrons with a negative charge. Electrons are bound to the nucleus by the (electrostatic) Coulomb forces. Depending on the way the electrons are distributed and moving around the nucleus, an atom can have different internal energies.

In the Rutherford-Bohr model, electrons can only move around the nucleus in certain stationary orbits, resulting in discrete internal energy states for the atom. These orbits are characterized by the principal quantum number \( n \) and the azimuthal quantum number \( l \). The quantum number \( n \) can have any positive
integer value and $l$ can have an integer value between 0 and $n-1$. It is common practise to refer to $n$ and $l$ with letters instead of numbers; for $n = 0, 1, 2, 3, \ldots$ the upper case letters $K, L, M, N, \ldots$ are used, and for $l = 0, 1, 2, 3, \ldots$ the lower case letters $s, p, d, f, g, \ldots$ are used.

According to the Rutherford-Bohr theory, the quantum numbers $n$ and $l$ are related to the orbits such that the major axis of the orbit is proportional to the square of $n$, and the minor axis is proportional to the product of $n$ and $l$. This is illustrated in figure 2.1. The orbit in which the electron moves—and therefore the internal energy of the atom—is determined by the quantum numbers $n$ and $l$.

![Figure 2.1: Illustration of how the principal quantum number $n$ and the azimuthal quantum number $l$ determine the orbit of the electrons.](image)

When an electron changes from a quantum orbit with energy $E_1$ to another orbit with a lower energy $E_2$, the energy difference can be released in the form of a photon, as illustrated in figure 2.2. This photon will have an energy $hc\nu = E_1 - E_2$. In this equation $\nu$ is the wave number in cm$^{-1}$. For consistency, the speed of light $c$ is taken in cm s$^{-1}$. The discrete energies of the atom determine the possible energy differences and therefore the energies of the emitted photons.

An electron can also transfer from one quantum orbit with energy $E_2$ to another orbit with a higher energy $E_1$ by absorbing a photon. The same formula applies for the energy of the absorbed photon. These transitions can not take
place for arbitrary combinations of orbitals. Only when the azimuthal quantum number $l$ changes by exactly $\pm 1$, a transition is allowed.

![Figure 2.2: Illustration of how an electron changes from an orbit with a higher energy to an orbit with a lower energy. The energy difference is released in the form of a photon.](image)

For hydrogen-like atoms\(^1\), the theory provided by Bohr, based on discrete stationary states and calculated from the classical laws of motion, agrees with experiments. For non-hydrogen-like molecules, Bohr’s theory does not. To calculate the energy levels of such atoms, a wave mechanical approach is required. This approach will be discussed in the following section.

### 2.1.1 Wave Mechanics

Wave mechanics is also based on the idea of discrete stationary states, but in the wave mechanical approach, these stationary states are solutions to Schrödinger’s equation (equation 2.4). To determine the states of an atom according to the wave mechanical approach, one has to determine a Hamiltonian for the system and subsequently solve Schrödinger’s equation:

$$H\Psi = E\Psi.$$ \hspace{1cm} (2.1)

First hydrogen-like atoms are discussed, later atoms with more electrons will be discussed. The Hamiltonian for a particle moving under the influence of a potential energy is \([2]\):

$$H = -\frac{\hbar^2}{2m}\Delta + V.$$ \hspace{1cm} (2.2)

In this function, $\hbar$ is Planck’s constant divided by $2\pi$, $m$ is the mass of the moving particle, $V$ is the potential energy, $\Delta = \nabla^2$ is the Laplace operator\(^2\), which

---

\(^1\)a hydrogen-like atom is a one-electron atom or ion, such as H, He\(^+\), Li\(^2+\).

\(^2\)This symbol ($\Delta$) can also mean „the difference“. The context of the symbol should make clear which of the meanings is intended.
is the second-order partial derivative to all directions \( e.g \) for three dimensions in a cartesian coordinate system\(^3\) \( \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \).

Generally, when calculating wave functions for atoms or molecules, the motion of the center of mass is separated from the equations. The interactions between the nucleus and the electron are calculated in a center-of-mass system. For the motion of an electron relative to the nucleus the reduced mass (\( \mu \)) is used. The potential \( V \) is the potential energy of the Coulomb attraction between the nucleus and the electron(s) and is chosen such that the energy of the system is zero when the distance between the electron and the nucleus is infinity. For hydrogen-like atoms, the Hamiltonian is:

\[
H = -\frac{\hbar^2}{2\mu} \Delta - \frac{Ze^2}{4\pi\varepsilon_0 r}.
\] (2.3)

In this equation \( Z \) is the atomic number of the nucleus, which represents the number of protons in it, \( e \) is the elementary charge, \( \varepsilon_0 \) is the permittivity of vacuum, and \( r \) is the distance between the nucleus and the electron.

The Schrödinger equation is solved in spherical coordinates. The Schrödinger equation is:

\[
-\frac{\hbar^2}{2\mu} \Delta \Psi - \frac{Ze^2}{4\pi\varepsilon_0 r} \Psi = E \Psi.
\] (2.4)

First the wavefunction \( \Psi \) is separated into a radial and angular component:

\[
\Psi(r, \theta, \phi) = R(r)Y(\theta, \phi).
\] (2.5)

The equations to be solved now are:

\[
\Lambda^2 Y(\theta, \phi) = -l(l+1)Y(\theta, \phi)
\] (2.6)

and

\[
-\frac{\hbar^2}{2\mu} \left( \frac{d^2R(r)}{dr^2} + \frac{2}{r} \frac{dR(r)}{dr} \right) + V_{\text{eff}}(r)R(r) = ER(r),
\] (2.7)

\[
\text{with } V_{\text{eff}}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{l(l+1)\hbar^2}{2\mu r^2}.
\] (2.8)

The first equation describes the angular part of the wave function. In this equation the \( \Lambda^2 \) operator is the angular part of the Laplace operator in spherical coordinates\(^4\). The second equation describes the radial part.

---

\(^3\)for a spherical coordinates system \( \Delta = \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \)

\(^4\)\( \Lambda^2 = \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \)
Solving these separated equations yields the allowed discrete energies and their respective wave functions. The wave functions can be used to determine what transitions are allowed. This will be done in the following subsection. For the radial component, solutions can only be found for integer values of the quantum number $n$. The energies and wave functions are:

$$E_n = -\frac{Z^2 \mu e^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2}.$$  \hspace{1cm} (2.9)

$$R_{n,l}(r) = N_{n,l} \left( \frac{\rho}{n} \right)^l L_{n,l}(\rho) e^{-\rho/2n}$$ \hspace{1cm} (2.10)

with: \hspace{0.5cm} $\rho = \frac{2Ze^2 rm_e}{4\pi\epsilon_0\hbar^2}$ \hspace{1cm} (2.11)

In this equation, $N_{n,l}$ is a normalization constant that depends on $n$ and $l$. $L_{n,l}$ denotes the associated Laguerre polynomials.

The angular part of the wave functions are spherical harmonics \cite{2}, which depend on the orbital angular momentum quantum number $l$, and the magnetic quantum number $m_l$. The energies are:

$$E_l = -l(l+1)\frac{\hbar^2}{2I}.$$ \hspace{1cm} (2.12)

In this equation, $I$ is the moment of inertia of the atom. The total energy of the state is the sum of the energies as given by equations (2.9) and (2.12) and therefore depends on quantum numbers $n$ and $l$.

When an electric or magnetic field is present, the quantum number $m_l$ influences the energy of the state. When such a field is present, $m_l$ is the component of $l$ in the direction of the field. This is illustrated in figure 2.3

$m_l$ can have values $-l, -l+1, \ldots, l-1, l$. When there is no external field, states with different $m_l$ have the same energy, those states are called degenerate states, and have a multiplicity of $2l + 1$.

To completely describe the state of the electron in the hydrogen-like atom, it is necessary also to take the intrinsic spin angular momentum of the electron into account. Electrons have a spin of $\frac{1}{2}$. The quantum number for spin is called $s$. In an external field the electron spin can be aligned with or against the magnetic field direction. Analogous to the relation $l$ and $m_l$ there is a quantum number $m_s$ which determines the component of the spin in the direction of the field. In case of a single electron atom, $m_s$ can be $\pm\frac{1}{2}$.
Figure 2.3: Illustration of what directions $l$ can have in the presence of a field for different values of $m_l$. The example shown here is for $l = 3$.

The interpretation of the quantum numbers $n$ and $l$ is very similar to the interpretation in the Rutherford-Bohr model. The numbers $n$ and $l$ determine certain orbitals. An electron in an orbital with a higher $n$ is more likely to be found further away from the nucleus. The orbitals are classified in shells according to the quantum number $n$ and subshells according to the quantum number $l$. When discussing shells and subshells, $n$ and $l$ are often referred to with letters according to their definitions in the Rutherford-Bohr model. In each subshell, the number of possible different $m_l$s determines the amount of orbitals possible. Each orbital can be filled by a maximum of two electrons, which will then have opposite spins ($m_s = \pm \frac{1}{2}$). E.g. for $n = 2$, $l = 1$ (state 2p), there are three different orbitals possible ($m_l = -1, 0, +1$), each of which can contain an electron with spin up or down, so a total of 6 electrons can fill this subshell.

**Atomic Transition Selection Rules: Hydrogen-like Atoms**

Transitions between states with different energies may occur by emitting or absorbing a photon. Not every transition is allowed; certain selection rules apply. The selection rule for atomic transitions follows from the conservation of angular momentum. A photon has an intrinsic spin (angular momentum) of unity: $s = 1$. The change in angular momentum of the electrons that undergo the transition, must be unity as well, resulting in the selection rule: $\Delta l = \pm 1$ and $\Delta m_l = 0, \pm 1$.

The quantum number $n$ is not related to the angular momentum. For that reason, it can change freely, unless the change in $l$ imposes restrictions on the
value of $n^5$. Next a more mathematical approach to finding atomic selection rules is shown.

To determine selection rules, the transition moment ($R$) is evaluated. If the transition moment is zero, a transition is not allowed, if the transition moment is nonzero, the transition probability is proportional to the *square* of the transition moment.

Radiation can be emitted by electric dipoles, magnetic dipoles, electric quadrupoles etc. Electric dipole interaction is stronger than magnetic dipole interaction and so on. Therefore, it can be said that the interaction between an atom and a photon, is in first approximation determined by the electric dipole interaction. The dipole moment ($\vec{M}$) of two opposite charges $q$ is defined as

$$\vec{M} = q \vec{r}.$$  \hspace{1cm} (2.13)

with $\vec{r}$ the displacement vector from the negative to the positive charge.

The following calculations will be based on a Hydrogen atom: a nucleus with charge $+e$ at the origin, and an electron with charge $-e$ at a distance $r$ from each other. The dipole moment of a Hydrogen atom follows from 2.13 and is $\vec{M} = e \vec{r}$, with $\vec{r}$ the displacement vector from the electron to the nucleus.

The interaction between dipoles depends on their orientations, so it is useful to define the dipole moment in three directions, depending on the orientation. The dipole moment can be written as $\vec{M} = (M_x, M_y, M_z)$. However, since the wave functions are in spherical coordinates, it is useful to state the dipole moment in spherical coordinates as well $M_x = e |r| \sin \theta \cos \varphi$, $M_y = e |r| \sin \theta \sin \varphi$, $M_z = e |r| \cos \theta$.

The calculation of the transition moment ($R$) can now be performed. It is the expectation value of the dipole moment operator $M$ acting on the wave equations $\Psi_i$ and $\Psi_f$ of the initial and final state with quantum numbers $n_i, l_i, m_l$ and $n_f, l_f, m_{lf}$. As an example, the operations on $M_z$ are shown.

$$R = \langle \Psi_f | \mu_z | \Psi_i \rangle = e \langle R_{n_f, l_f} | r | R_{n_i, n_f} \rangle \langle Y_{l_f, m_{lf}} | \cos \theta | Y_{l_i, m_l} \rangle$$  \hspace{1cm} (2.14)

To determine the selection rules, the second part of this equation is evaluated. The spherical harmonic $Y_{l, m_l}$ with $l = 1$, $m_l = 0$ is proportional to $^6 \cos \theta$. This

\footnote{for example when $l$ changes from 3 to 4, $n$ has to be at least 5.}

\footnote{It is $(\frac{3}{4\pi})^{\frac{1}{2}} \cos \theta$.}
part can now be rewritten as:

$$\langle Y_{l_f,m_{l_f}} | \cos \theta | Y_{l_i,m_{l_i}} \rangle = \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} Y_{l_f,-m_{l_f}}^* Y_{1,0} Y_{1,m_{l_i}} \sin \theta d\theta d\varphi$$  \hspace{1cm} (2.15)$$

To calculate this integral, a standard triple integral for spherical harmonic wave functions is used. This triple integral is

$$\int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} Y_{l_a,-m_{l_a}}^* Y_{l_b,m_{l_b}} Y_{l_c,m_{l_c}} \sin \theta d\theta d\varphi$$  \hspace{1cm} (2.16)$$

In this integral the subscripts $a,b$ and $c$ are used to distinguish different input variables for the spherical harmonics. This triple integral is nonzero only if:

- $m_{l_a} = m_{l_b} + m_{l_c}$
- the triangle rule for $l$ is satisfied
- $l_a + l_b + l_c$ is even.

In this example $l_b = 1$ and $m_{l_b} = 0$, so this triple integral is nonzero if $m_{l_a} = m_{l_c}$, resulting in $\Delta m_l = m_{l_a} - m_{l_c} = 0$. The triangle rule for $l$ is satisfied if: $|l_a - (l_b = 1)| \leq l_c \leq l_a + (l_b = 1)$. This can be summarized as $\Delta l = l_a - l_c = \pm 1, 0$, however $\Delta l = 0$ is not allowed because for $\Delta l = 0$ the sum $l_a + (l_b = 1) + l_c$ is odd.

The elements $M_x$ and $M_y$ can be written in terms of $Y_{1,1}$ and $Y_{1,-1}$ and can be evaluated analogously to find the complete set of selection rules. The selection rules obtained this way are:

- $\Delta l = \pm 1$.
- $\Delta m_l = 0, \pm 1$.

The $r$-dependent part of (2.14) has both $n$ and $l$ in it. This part does not yield more restrictive selection rules.

---

7Even though this integral only integrates over two variables, it is called a triple integral because the integrand consists of three spherical harmonics.
2.1 Atomic Structure and Radiation

2.1.2 Atoms with Multiple Electrons

For a system with $i$ electrons, the following Schrödinger’s equation needs to be solved:

$$\frac{1}{m_e} \sum_i (\Delta \Psi) + \frac{1}{M} \Delta \Psi + \frac{2}{\hbar^2} (E - V) \Psi = 0$$  \hspace{1cm} (2.17)

In this equation $m_e$ is the electron mass, $M$ is the mass of the nucleus, and $V$ is the resulting potential energy from all interactions between all particles. This potential $V$ is dependent on the coordinates of all particles involved. It is not (yet) possible to find an exact solution for this equation. The approximation used to find solutions is the orbital approximation. In this approximation each electron is assumed to occupy its own orbital. The combinations of orbitals with lower total energies are occupied first. Then the Schrödinger equation for each electron is solved as if the system was a hydrogen-like atom, with the potential modified by the presence of the other electrons. For an atom with several electrons, quantum numbers and angular momenta can be found by adding the contributions of the electrons present [1].

The resultant angular momentum $L$ of the atom consisting of $i$ electrons is given by:

$$L = \sum_i l_i.$$  \hspace{1cm} (2.18)

Since all $l_i$ are integers, the resultant $L$ is also an integer. The resultant total electron spin $S$ is given by:

$$S = \sum_i s_i.$$  \hspace{1cm} (2.19)

Since all $s_i$ are half-integers, the resultant $S$ is an integer if $i$ is even, and a half-integer if $i$ is odd.

The angular momentum $L$ and spin $S$ are assumed to be coupled, and together give the total angular momentum of the electrons of the atom. This total angular momentum is labeled $J$ and can have values $J = L + S, L + S - 1, \ldots, |L - S|$. In the presence of an external magnetic field, there is a component $M_J$ of $J$ that is aligned in the field direction. The quantum number $M_J$ is defined analogous to the previous definition of $m_l$. $M_J$ can have values $0, \pm 1, \ldots, \pm J$. For an atom with several electrons, selection rules for transitions can also be determined. For dipole radiation, the selection rules are [1], [3]:

- $\Delta J = 0, \pm 1$.
- $\Delta J = 0$ is not allowed if $J = 0$. 

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In the presence of a magnetic field, the additional selection rules are:

- $\Delta M_J = 0, \pm 1$.
- $\Delta M_J = 0$ is not allowed if $J = 0$.

### 2.2 Molecular Structure and Radiation

In this thesis, radiation from the diatomic molecule Indium Bromide is studied. Rather like atoms, molecules consist of nuclei, with electrons around them, and the interaction between them is governed by coulomb forces. In addition to this, the nuclei can move with respect to each other. The internuclear distance can vary —movements of this kind are called *vibrations*— and the the nuclei can rotate, causing movements called *rotations*. For molecules, just as for atoms, different states of discrete energies can be defined. When a molecule in a state with a high energy, transitions to a state with lower energy, the excess energy can be released in the form of a photon. To identify the energy levels possible in the molecule, Schrödinger’s equation has to be solved for this system. For a system consisting of $i$ electrons moving around $k$ nuclei, the equation is as follows:

$$\frac{1}{m_e} \sum_i \Delta \Psi + \sum_k \frac{1}{M_k} \Delta \Psi + \frac{2}{\hbar^2} (E - V) \Psi = 0$$  \hspace{1cm} (2.20)

In this equation $m_e$ is the mass of an electron, an $M_k$ are the masses of the nuclei. The difficulty in solving this equation is due to the potential $V$ which includes all interactions between all particles.

As is the case for the multiple electron atom, an exact solution to Schrödinger’s equation is not possible. To find an approximate solution, the Born-Oppenheimer approximation can be used. The essence of this approximation is to assume that the electrons move so much faster than nuclei that the electrons can adjust themselves to the motion of the nuclei instantly.

This allows the separation of the electronic part in the Schrödinger equation. For calculations regarding the electronic part, the nuclei are assumed to be stationary. It is now possible to calculate the electronic energies, and electronic wave functions for different internuclear separations. This gives the molecular potential energy curve as a function of internuclear distance. A typical molecular potential energy curve looks like the curve drawn in figure (2.4). This molecular potential energy curve is then used to solve Schrödinger’s equation.
2.2 Molecular Structure and Radiation

Figure 2.4: A typical molecular potential energy curve, on the vertical axis the energy, on the horizontal axis the internuclear distance. The distance at the minimal value is called the equilibrium distance $r_e$.

for the vibrations and rotations of the molecule. When the molecular potential energy curve varies sufficiently slow with the change of internuclear distance during vibration or rotation this approximation is justified [1].

Using the Born-Oppenheimer approximation the wave function and the internal energy of the molecule can be split into an electronic, vibrational and rotational contribution:

$$\Psi = \Psi_e \frac{1}{r} \Psi_v \Psi_r$$  \hspace{1cm} (2.21)

$$E = E_e + E_v + E_r$$  \hspace{1cm} (2.22)

In these equations the subscripts $e, v, r$ indicate the electronic, vibrational and rotational part respectively. In order to avoid confusion between the $r$ for rotation and the $r$ for radius, the latter is in bold typeface in this formula.

In spectroscopy it is common practice to use wave numbers ($\nu = E/\hbar c$) and the unit of cm$^{-1}$ to describe energies of levels and transitions. In terms of wave numbers, the expression for the energy is generally given as follows.

$$T = T_e + G + F.$$  \hspace{1cm} (2.23)
Chapter 2. Theory

In this equation $T$ is the total energy of the state, $T_e$, $G$ and $F$ are the electronic, vibrational and rotational contribution respectively. When a molecule undergoes a transition from a state with high energy $T'$ to a state with lower energy $T''$, the excess energy may be released in the form of a photon. This photon will be emitted with wave number:

$$\nu = \Delta T = (T'_e - T''_e) + (G' - G'') + (F' - F'').$$

(2.24)

The description of energy levels and transitions will now first focus on vibrational energy and transitions. Then the focus will be on rotational energy and transitions of the molecule. After these are discussed, some properties of the electronic functions will be discussed. Finally, rovibronic transitions will be described and the properties of the rovibrational structure of the electronic transition will be discussed.

2.2.1 Vibrations

In this section the vibrational properties of a diatomic molecule are discussed. When a molecule vibrates, the distance between the nuclei changes periodically in time. When the variations with respect to the equilibrium distance are small, the potential energy curve can be approximated by a parabolic function near the equilibrium bond length ($R_e$). This approximation can be justified by investigating the Taylor expansion of the potential energy curve around $R_e$. The molecular potential energy curve $V(x)$, with $x = R - R_e$, can be written in a Taylor series around $x = 0$ as follows:

$$V(x) = V(0) + \left( \frac{dV}{dx} \right)_0 x + \frac{1}{2} \left( \frac{d^2V}{dx^2} \right)_0 x^2 + \frac{1}{3!} \left( \frac{d^3V}{dx^3} \right)_0 x^3 + \ldots$$

(2.25)

Adding a constant to a potential can be done without consequences, so $V(0)$ can be set to zero. By definition, the first derivative is zero at the minimum of the potential curve, so the second derivative is the first nonzero term in this formula. In the model of the harmonic oscillator, higher order terms can be neglected. The resulting potential can be written as $V(x) = \frac{1}{2} k x^2$, the potential

---

8Generally, the quantity related to the upper level receives a single prime (') and the quantity relating to the lower level receives a double prime (“”).

9A transition involving rotations vibrations that accompany an electronic transition.

10rotational-vibrational
of the harmonic oscillator, with \( k \) a force constant depending on the steepness of the potential curve.

With this potential, Schrödinger’s equation becomes:

\[
\frac{d^2 \Psi}{dx^2} + \frac{2\mu}{\hbar^2} \left( E - \frac{1}{2} k x^2 \right) \Psi = 0, \tag{2.26}
\]

with \( \mu \) the reduced mass \((\mu = \frac{m_A m_B}{m_A + m_B})\). The solutions to the equation for the harmonic oscillator are:

\[
E(v) = \hbar \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right), \tag{2.27}
\]

or, in terms of wave numbers:

\[
G(v) = \omega_e (v + 1/2). \tag{2.28}
\]

In these equations \( v \) is the vibrational quantum number. A state with a higher vibrational quantum number (and other quantum numbers the same) has a higher energy. Here \( \omega_e \) is the vibrational frequency in units of \( \text{cm}^{-1} \).

The wave functions that are solutions for Schrödinger’s equation for the harmonic oscillator, are the Hermite orthogonal functions [1].

\[
\Psi_v = N_v e^{-\frac{1}{2} \alpha x^2} H_v(\sqrt{\alpha} x) \tag{2.29}
\]

Here \( N_v \) is a normalization constant, \( H_v \) are the Hermite polynomials, and \( \alpha = 4\pi^2 \mu \omega_e^2 \) is a constant depending on the reduced mass and the vibrational frequency. The wave functions are important when considering selection rules and transition probabilities. This will be done at the end of this section.

Further away from the equilibrium bond length, the approximation of the harmonic oscillator potential is no longer valid. Here the model of the anharmonic oscillator is more appropriate. For the anharmonic oscillator, terms of a higher order than quadratic are also taken into account when determining the potential. When this is done, the energy of the vibration (in wave numbers) is:

\[
G(v) = \omega_e (v + 1/2) + \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3 + \ldots \tag{2.30}
\]

Here the terms \( \omega_e x_e \) and \( \omega_e y_e \) are the higher order correction terms. \( \omega_e x_e \) is nearly always positive, because a negative value here would easily lead to an unrealistic potential.
Selection Rules Vibrational Transition

In this section the selection rules that govern transitions in which only the vibrational quantum number changes are discussed. As mentioned before, when a molecule changes state, the excess energy can be released in the form of a photon, or a molecule can absorb a photon of a certain energy to make a transition to a state with a higher energy. When we consider a state with a lower energy having vibration number \( v'' \) and a state with a higher energy having vibration number \( v' \), the energy of the photon which can be emitted or absorbed is:

\[
\nu = \frac{E(v')}{hc} - \frac{E(v'')}{hc} = G(v') - G(v'').
\]

(2.31)

With \( G \) defined by the equations in the previous section.

Radiation can be emitted by electric dipoles, magnetic dipoles, electric quadrupoles and so on. Electric dipole interaction is stronger than magnetic dipole interaction and so on. The interaction between a molecule and a photon can in first approximation be described by evaluating the electric dipole of the molecule. The dipole moment \( \vec{M} \) of two opposite charges \( q \) is defined as \( \vec{M} = q \vec{r} \), with \( \vec{r} \) the displacement vector.

It is assumed that in a (heteronuclear) diatomic molecule, the electrons are concentrated somewhat around one nuclei with respect to the other, since their electronegativity will differ. Therefore there is a net charge of \(+\delta q\) on one side of the molecule, and a net charge of \(-\delta q\) on the other side. The distance between the nuclei will be written as \( R = R_e + x \), with \( R_e \) the equilibrium bond length, and \( x \) a deviation from this. A vibration can then be described by varying \( x \) periodically. The vibrations take place in the same direction as the direction of the dipole moment. The dipole moment of the molecule can now be written as:

\[
M = \delta q R = R_e \delta q + x \delta q.
\]

(2.32)

The first term is a constant, and the second term varies with the bond length. This leads to \( M = M_0 + M_1 x \), with \( M_0 \) the constant contribution to the dipole moment, and \( M_1 \) a contribution that is linearly variable with the bond length.

The calculation of the transition moment \( \langle R \rangle \) can now be completed, as the mathematical expectation of the dipole moment \( M \) acting on the wave functions \( \Psi_i \) and \( \Psi_f \) of the initial and final state having vibration number \( v' \) and \( v'' \) respectively. Since only vibrations are considered, here the orientation of the
molecule is not taken into account. The calculation then is as follows:

\[ R = \langle \Psi_f | M | \Psi_i \rangle = \langle \Psi_f | M_0 | \Psi_i \rangle + \langle \Psi_f | M_1 x | \Psi_i \rangle \]

or, written in integral form:

\[ R = M_0 \int \Psi_f^* \Psi_i \, dx + M_1 \int \Psi_f^* x \Psi_i \, dx. \]

For the Harmonic oscillator, the wave functions are Hermite polynomials. A property of Hermite polynomials is that they are orthogonal, this means that the product of two Hermite polynomials \( H_v(x) \) with different \( v \)'s, is zero. As a consequence, the first integral in equation (2.34) is zero. Now, from the second integral it can be concluded that there is a transition only if \( M_1 \neq 0 \), this means that the following selection rule for transitions involving radiation can be formulated:

The electric dipole moment of the molecule must change when the atoms are displaced relative to one another in order for a transition to be allowed.

Evaluation of the integral \( \int \Psi_f x^* \Psi_i \, dx \) leads to a more specific selection rule for vibrational transitions. This is done by writing the integral in terms of the Hermite polynomials as follows:

\[ R \propto N_{v',v''} \int x H_{v'}(x) H_{v''}(x) \, e^{-x^2} \, dx. \]

In this formula \( N_{v',v''} \) is a normalization constant that depends on the vibration number of upper and lower level. The recursive formula for Hermite polynomials is used to rewrite this equation. The recursion formula is:

\[ xH_n(x) = \frac{1}{2}H_{n+1}(x) + nH_{n-1}(x) \]

This leads to the following equation:

\[ R \propto N_{v',v''} \left[ \frac{1}{2} \int H_{v'}(x) H_{v'+1}(x) \, e^{-x^2} \, dx 
+ v'' \int H_{v'}(x) H_{v'-1}(x) \, e^{-x^2} \, dx \right] \]
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Like before, the orthogonality of the Hermite polynomials is used to evaluate the results. It follows that $R \neq 0$ only if $v' = v'' + 1$ or if $v' = v'' - 1$. This leads to the selection rule for vibrational transitions:

$$\Delta v = \pm 1$$

(2.38)

If also magnetic dipole, electric quadrupole transitions or higher order are considered, transitions with other $\Delta v$’s also give rise to a non-zero transition moment. However, just like for atoms, these probabilities are much smaller than the electronic dipole transition probability.

This derivation was carried out for wave functions based on the model of the harmonic oscillator. This is a sensible, mathematically attractive approximation. For the anharmonic oscillator, the same selection rule results. However in addition to the transitions allowed in this rule, transitions with other $\Delta v$ are also weakly allowed.

This derivation has been made for pure vibrational transitions. When an electronic transition takes place, a change in the vibrational quantum number can accompany this transition. For vibrational transitions accompanying an electronic transition other selection rules apply. It will be shown that for vibrational transitions accompanying an electronic transition, all $\Delta v$’s are allowed. This will be discussed in section 2.2.4. The ratios between the intensities of these transitions are called the Franck-Condon factors.

2.2.2 Rotations

In this section the rotation of a diatomic molecule is discussed. For the rotational motion certain simplifications are made as well. The first model discussed is the rigid rotator, where the two nuclei are at a fixed distance, and after this, the model will be extended by allowing the rotator to be nonrigid\footnote{Somewhat elastic that is.}. A diatomic rigid rotator, consists of two atoms, one with mass $m_A$ and one with mass $m_B$ at a fixed distance $r$. Since the nuclei are at a fixed distance, the potential energy is constant; $V = 0$. The Schrödinger equation that needs to be solved to find the energy levels is:

$$\Delta \Psi + \frac{2\mu}{\hbar^2} E \Psi = 0,$$

(2.39)

with the reduced mass. For this equation, again, only for certain discrete eigenvalues a solution can be found. The solutions of this equation can be found for
the following eigenvalues:

\[ E = \frac{\hbar^2 J(J + 1)}{2\mu r^2}, \quad (2.40) \]

with \( J \) the rotational quantum number.

A rigid rotator consisting of two atoms with mass \( m_A \) and \( m_B \), has a moment of inertia \( I = \mu r^2 \), with \( \mu \) the reduced mass and \( r \) the distance between the two nuclei. Its angular momentum is \( \vec{P} = I\vec{\omega} \), with \( \vec{\omega} \) the angular frequency of the rotation. Its energy is

\[ E = \frac{1}{2}I\omega^2 = \frac{P^2}{2I}. \quad (2.41) \]

Comparing this result with equation 2.40 gives:

\[ P = \hbar \sqrt{J(J + 1)} \approx \hbar J, \quad (2.42) \]

which justifies the use of \( J \) as a quantum number of angular momentum.

The energy of a rigid rotator can also be written in terms of wave numbers:

\[ F(J) = \frac{\hbar}{4\pi c I} J(J + 1) = BJ(J + 1), \quad (2.43) \]

with \( B \) the rotational constant. For the Schrödinger equation of the rigid rotator, the eigenfunctions can be determined. The eigenfunctions of the rigid rotator are the spherical harmonics. They are as follows, the subscript \( r \) standing for rotation, not radius:

\[ \Psi_r = N_r P_J^{|M|}(\cos \theta) \ e^{M\varphi}. \quad (2.44) \]

In this formula \( M \) is a quantum number representing the component of the angular momentum \( J \) in the direction of a \( z \)-axis. Like the atomic quantum number \( m_l \), \( M \) only affects the energy when a \( z \)-axis can be determined, \( e.g. \) in the presence of a magnetic field.

The quantum number \( M \) can take the values: \( J, J-1, \ldots, -J \). In the formula above, \( N_r \) is a normalization constant and \( P_J^{|M|}(\cos \theta) \) is the associated Legendre function. The combinations \( P_J^{|M|}(\cos \theta) \ e^{M\varphi} \) are the spherical harmonics, which are also the solutions for the angular component of the Schrödinger equation for an electron orbiting a nucleus. The wave functions are important when selection rules and transition probabilities are discussed, which will be done at the end of this section.

When the distance between the nuclei changes, the moment of inertia changes as well: \( e.g. \) when the molecule is stretched under influence of the centrifugal
force, the moment of inertia increases with increasing rotation. This leads to a
correction term in the energy levels. The new energy levels, in terms of wave
numbers are:

\[ F(J) = B[1 - uJ(J + 1) \pm \ldots ]J(J + 1), \quad (2.45) \]

where \( u \) is a correction factor. This is often written as:

\[ F(J) = BJ(J + 1) - DJ^2(J + 1)^2 \pm \ldots \quad (2.46) \]

The factor \( D \) in this formula is called the centrifugal distortion constant or the
anharmonicity. The vibration of an (an)harmonic oscillator causes the average
distance between the nuclei to be greater for a higher vibrational level. This
leads to a correction term in the energies of the rotation that depends on the
vibrational state \( v \) the molecules are in. This can be accounted for by making
the constants \( B \) and \( D \) dependent on \( v \):

\[ B_v = B_e - \alpha_e(v + 1/2) + \ldots \quad (2.47) \]
\[ D_v = D_e + \beta_e(v + 1/2) + \ldots \quad (2.48) \]

In this equation, the \( B_e \) and \( D_e \) are the values \( B \) and \( D \) would have at the
equilibrium bond length and \( \alpha_e \) and \( \beta_e \) are (small) correction constants.

Another simplification which has been made is that there is no moment of
inertia about the line connecting the nuclei. However, the electrons rotating
around the molecule cause a moment of inertia for this axis. Although the
electrons have a much smaller mass than the nuclei, they move much faster,
resulting in a moment of inertia that can not be neglected. This has an influence
on the energy levels. The model which takes these effects into account is called
the symmetric top [1]. The result of this model is that a correction term has to
be taken into account. This term is:

\[ (A - B_v)\Lambda^2, \quad (2.49) \]

with:

\[ A = \frac{\hbar}{4\pi c I_A}, \quad (2.50) \]

where \( I_A \) is the moment of inertia of the electrons. Since in this correction
term\(^{12} A\Lambda^2 \) only varies for different electronic levels, it is taken into account

\(^{12} \Lambda \) will be defined a little further on in this chapter in section 2.2.3.
when determining the electronic energy. Since in this correction term $B_v\Lambda^2$ only varies for different vibrations within an electronic level, it is taken into account when determining the vibrational energy. Thus, for the calculation of the rotational energy levels this correction term can be ignored.

Selection Rules Rotational Transition

In this section the selection rules for pure rotational spectra are briefly discussed, the discussion is based on the model of the rigid rotator. Determining selection rules for the rotations starts by determining the dipole of the rotating molecule; analogous to the discussion of the dipole moment of an electron rotating around the nucleus as discussed from page 20. This dipole moment is $\overrightarrow{M} = er$. The operation to be performed is:

$$R_r = \langle \Psi_r | M_z | \Psi_r \rangle. \quad (2.51)$$

Here, the wave functions $\Psi_r$ are spherical harmonics. The same type of functions which are used in the discussion of the transition moment of electronic (atomic) transitions, but then with $J$ and $M$ instead of $l$ and $m_l$. The evaluation of the overlap integrals of the wave functions of the rotation is analogous to the discussion of the transition moment of atomic transitions. This results in the following selection rules:

- In order for a molecule to have a purely rotational spectrum it must have a permanent dipole moment,
- $\Delta J = \pm 1$,
- $\Delta M = 0, \pm 1$.

When a pure rotational spectrum is considered, the energy levels of the upper and lower state are given by equation (2.43). The energy of the emitted or absorbed photon is as follows.

$$\nu = F(J') - F(J'') = F(J'' + 1) - F(J'') = 2B(J'' + 1). \quad (2.52)$$

In this equation a single prime designates the upper state, a double prime designates the lower state.

As will be shown later, when a rotational transition accompanies an electronic and/or a vibrational transition, the same selection rules apply. Since for different
electronic or vibrational states the $B$ value of the rotations will be different, the following formula apply for the rotation contribution to the wave number of the photons that may be emitted or absorbed.

$$\Delta J = +1: \quad \nu = \nu_0 + 2B' + (3B' - B'')J + (B' - B'')J^2$$

$$\Delta J = -1: \quad \nu = \nu_0 - (B' + B'')J + (B' - B'')J^2.$$ (2.53)

In this equation $\nu_0$ is the contribution to the wave number by the electronic and/or vibrational transition(s).

The progression of rotational transitions with $\Delta J = +1$ is called the $R$-branch, the rotational transitions with $\Delta J = -1$ are called the $P$-branch.

If $B' < B''$, the quadratic term $(B' - B'')J^2$ is negative. For the $R$-branch this means that the linear term in $J$, and the quadratic term in $J$ are of the opposite sign. This means that the wave number of the transition first increases with $J$, but as $J$ gets higher, the spacing between the different transitions decreases, and even changes sign, so the wave number decreases with increasing $J$. Near the turning point, the rotational transitions lay close together and form a band head. If $B' > B''$ there is a band head in the $P$-branch. The latter is the case for InBr. This is confirmed by the experiments in chapter 4.

When the model of the nonrigid rotator is used, higher order correction terms—such as $D$—have to be taken into account. When the model of the symmetric top is used to determine the selection rules, the following selection rule is added: $\Delta J = 0$ is allowed if $\Lambda \neq 0^{13}$. The progression of rotational transitions with $\Delta J = 0$ is called the Q-branch. The meaning of $\Lambda$ is explained in more detail the next section.

### 2.2.3 Electronic States and Transitions

In this thesis, mainly one electronic transition is studied. Therefore the discussion has been focused on the vibration and rotation of the molecule. Here only some properties of the electronic functions are mentioned, for a thorough discussion see [1].

One of the essential differences between an atom and a diatomic molecule is that, since there are two nuclei present, the electrons no longer move in a spherically symmetric field, but in a cylindrically symmetric field. The $z$-axis of the cylindrical symmetry is defined as the line connecting the nuclei. As a

---

$^{13}\Lambda = |M_L|$
result of this symmetry, not only the electronic orbital angular momentum \((L)\) is a constant of motion, but the component of this angular momentum along the \(z\)-axis is a constant of motion as well. This constant is named \(M_L\).

The orbital angular momentum (with quantum number \(L\)), and its \(z\)-component \(M_L\) are defined analogous to \(l\) and \(m_l\) in the atomic case; \(M_L\) is in the range of \(-L, -L + 1, \ldots, L - 1, L\). For diatomic molecules the energy of the state is invariant under a change of sign in \(M_L\), therefore a state with \(M_L\) and one with \(-M_L\) have the same energy. The quantum number associated with \(M_L\) is called \(\Lambda\), with \(\Lambda = |M_L|\). States with \(\Lambda \neq 0\) thus have a multiplicity of 2. According to convention and analogous to the atom, the electronic states of diatomic molecules are classified to \(\Lambda\), using the notation \(\Sigma, \Pi, \Delta, \Phi, \ldots\) for \(\Lambda = 0, 1, 2, 3, \ldots\).

Like for the atoms, for molecules a spin \(S\) can be determined. Due to the cylindrical symmetry, \(S\) also has a component along the \(z\)-axis \(M_S\). \(M_S\) can have values \(M_S = -S, -S + 1, \ldots, S\). The quantum number associated with \(M_S\) is called \(\Sigma\). For each value \(S\) there are \(2S + 1\) different values possible for \(\Sigma\). A state determined by \(M_L, S, M_L \neq 0\) is split into \(2(2S + 1)\) different components.

The quantum numbers \(\Lambda\) and \(\Sigma\) can be added together to obtain the resultant electronic angular momentum in the direction of the internuclear axis \((\Omega)\). The quantum number \(\Omega\) is the diatomic molecular analogon of \(J\) for the atom.

Another property of the electronic states is the reflection symmetry. An electronic state of a heteronuclear diatomic molecule has a + symmetry if the wavefunction does not change sign under reflection in a plane through the centers of both nuclei, and has a − symmetry if it does change sign. The notation used to specify electronic states is as follows:

\[
2S+1\Lambda_{\Omega}^\pm
\]  

(2.55)

In a molecule, the different angular momenta are coupled. The electronic spin, electronic orbital angular momentum and the angular momentum of rotation constitute a resultant total angular momentum. Depending on which interactions are stronger, several types of coupling —called \(\text{Hund’s cases}\)— can be distinguished. The type of coupling determines the selection rules that apply. According to [5] Indium Bromide follows the rules for \(\text{Hund’s case c}\). Selection rules in \(\text{Hund’s case c}\) are:

- \(\Delta \Omega = 0, \pm 1\).
- The + or − symmetry of the level may not change during transition.
• If upper and lower state have $\Omega = 0$ then the transition $\Delta J = 0$ is not allowed.

For InBr, the ground state, referred to as X is a $1\Sigma^+_0$ state, so $S = 0$, $\Lambda = 0$ and $\Omega = 0$ and the symmetry is +.

The first exited state, referred to as A is a $3\Pi^+_0$ state, so $S = 1$, $\Lambda = 1$, $\Omega = 0$ and the symmetry is + as well.

From $\Omega = \Lambda + \Sigma$ it is concluded that $\Sigma$ has the value $-1$. According to the selection rules of Hund’s case c, the transition to the ground state is allowed.

Analyzing a $1\Sigma^+_0 \leftrightarrow 3\Pi^+_0$-transition with coupling according to Hund’s case c, can be done analogous to a $1\Sigma \leftrightarrow 1\Sigma$-transition with coupling according to Hund’s case a [1], with the considerations for $\Lambda$ replaced by $\Omega$.

When an electronic transition takes place, a vibrational and rotational transition can take place as well. In the following section the selection rules for vibrational and rotational transitions accompanying an electronic transition are discussed.

**Selection Rules for Rovibrational Transitions Accompanying an Electronic Transition**

Now the transition moment $R$ of a complete transition is evaluated. This transition is a transition between an upper state with electronic quantum number $e'$, vibrational quantum number $v'$ and rotational quantum number $r'$, and the lower state has quantum numbers $e''$, $v''$ and $r''$. The integral to be calculated is:

$$R = \int \Psi^{*}_{e',v',r'} M \Psi_{e'',v'',r''} \, d\tau.$$  \hspace{1cm} (2.56)

In this equation the integral over $\tau$ is the integral taken over the contribution dependent on the electronic configuration $\tau_e$ and the nuclear configuration, $\tau_n$. The latter can be split into $\int \Psi^{*}_{e',v',r'} M \Psi_{e'',v'',r''} \, d\tau_e \int \Psi^{*}_{r'} \cos \theta \Psi_{r''} \sin \theta \, d\theta d\varphi$. Using this, the $x, y$ and $z$ components of $M$ can be evaluated separately.

Equation (2.21) is used to separate the electronic, vibrational and rotational part of the wavefunction. For e.g. the z component ($M_z = M \cos \theta$), this yields:

$$R_z = \int \Psi^{*}_{e',v',r'} M_z \Psi_{e'',v'',r''} \, d\tau_e \int \Psi^{*}_{r'} \cos \theta \Psi_{r''} \sin \theta \, d\theta d\varphi.$$  \hspace{1cm} (2.57)

\[\text{14}\] The internuclear distance ($r$) is printed in bold letters to avoid confusion with rotation ($r$).
The integral on the right, is the same integral as has to be evaluated for pure rotational transitions. The selection rules for the rotational transitions accompanying an electronic transition are therefore the same as for the pure rotational case. The same conclusions are drawn for the $x$ and $y$ contribution to the dipole moment.

The rotational contribution to the transition moment is named $R_r$. The integral to be considered is reduced to:

$$R = R_r \int \Psi_{v'}^{\ast} \Psi_{v''} M \Psi_{v'} \Psi_{v''} d\tau_e dr.$$  \hfill (2.58)

Now the assumption is used that the dipole moment operator consists of a part that depends on the positions of the electrons ($M_e$), and a part that depends on the nuclei ($M_n$). Then equation (2.21) is used (again) to separate the electronic and vibrational part of the wave function. This allows us to split this equation as follows:

$$R = R_r \int M_e \Psi_{v'}^{\ast} \Psi_{v''} \Psi_{v'} \Psi_{v''} d\tau_e dr + R_r \int M_n \Psi_{v'}^{\ast} \Psi_{v''} \Psi_{v'} \Psi_{v''} d\tau_e dr.$$  \hfill (2.59)

Next, the assumption is made, that the electronic wave functions do not depend on the positions of the nuclei, and that the rotational and vibrational wave functions do not depend on the positions of the electrons. This allows further splitting of the previous equation:

$$R = R_r \int M_e \Psi_{v'}^{\ast} \Psi_{v''} d\tau_e \int \Psi_{v'}^{\ast} \Psi_{v''} dr + R_r \int \Psi_{v'}^{\ast} \Psi_{v''} d\tau_e \int M_n \Psi_{v'}^{\ast} \Psi_{v''} dr.$$  \hfill (2.60)

First, the electronic wave functions are evaluated. In the bottom part of equation 2.60, the integral $\int \Psi_{v'}^{\ast} \Psi_{v''} d\tau_e$ appears. There is only an electronic transition when $v' \neq v''$. Due to the orthogonality of these wave functions, this integral is zero.

In the top part of equation 2.60, the integral $\int M_e \Psi_{v'}^{\ast} \Psi_{v''} d\tau_e$ appears. This integral is nonzero only for the electronic transitions for which the electronic selection rules are met (see section 2.2.3). For these transitions, the integral can be evaluated and is replaced with the electronic transition moment $R_e$. For this derivation, it is assumed that $R_e$ can be approximated with a constant, while
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—in practice— the transition moment $R_e$ is often dependent on the internuclear distance. The equation that is now further evaluated is:

$$R = R_e R_r \int \Psi_v^* \Psi_{v'} \Psi'' d\mathbf{r}.$$    \hfill (2.61)

This integral represents the part depending on the vibrations.

When intensities in spectra are considered, it is not only important to know which transitions have a non-zero probability, but also the value of the transition moment squared is important, because this is proportional to the transition probability, which in turn determines the intensity of the transition. Since we can separate the transition moment into a contribution depending on only the electronic part, only the vibrational part and only the rotational part, the transition probability ($|R|^2$) can be separated as well. For the transition probability the following equation can be constructed:

$$|R|^2 = |R_e|^2 |R_v|^2 |R_r|^2.$$    \hfill (2.62)

The part of the transition probability that depends on the vibrations is called the Franck-Condon factor. The Franck-Condon factor will be evaluated next. The part of the transition probability that depends on the rotations is called H"{o}nl-London factor. The H"{o}nl-London factor will be discussed after the Franck-Condon factor.

2.2.4 Franck-Condon Factor

For a lower level introduction to Franck-Condon factors, see chapter 4 section 4.2.2. In this section, the part of the transition moment that depends on the vibrations is investigated. To determine this quantity, it is assumed that the potential energy curves of the upper and lower electronic level can be approximated by the harmonic oscillator model, and that the shapes of the potential energy curves are the same, such that the force constant $k$ is the same for the upper and lower level, however, the equilibrium internuclear distance of the two levels is not the same. The following integral must be evaluated:

$$R_v = \int \Psi_{v'}(x') \Psi''_{v''}(x'') dx'.$$    \hfill (2.63)

In this equation $\Psi_{v'}(x')$ is the wave function for the vibration of the upper level, as described by equation (2.29), and $\Psi''_{v''}(x'')$ is the wave function for the
vibration of the lower level, also described by equation (2.29). In this equation, 
\( x' \) and \( x'' \) are used, because the wave functions for the vibration, as described in

equation (2.29) are based on a small deviation \( x \) from the equilibrium distance \( R_e \). Since \( x' \) and \( x'' \) are deviations from different equilibrium distances \( R'_e \) and \( R''_e \) respectively, the integral has to be rewritten before it can be calculated. The

following relations are used:

\[
\begin{align*}
    x' &= r - R'_e, \\
    x'' &= r - R''_e, \\
    x'' &= x' + (R'_e - R''_e) = x' + y \quad \text{and} \\
    dr &= dx' = dx''.
\end{align*}
\]

This allows one to rewrite \( \Psi''_{v'}(x'') \) as a function of \( x' \). Resulting in the integral:

\[
\int \Psi'_{v'}(x')\Psi''_{v'}(x' + y)dx'.
\]

To continue evaluating this integral, \( \Psi_v \) is written out using equation (2.29),

resulting in:

\[
R = \int N_{v'} e^{-\frac{1}{2}ax'^2} H_{v'}(\sqrt{ax'})
\]

\[
N_{v''} e^{-\frac{1}{2}a(x'+y)^2} H_{v''}(\sqrt{a(x'+y)})dx'
\]

\[
= N_{v'} N_{v''} e^{-ay^2} 
\int e^{-\alpha(x'^2-xy')} H_{v'}(\sqrt{\alpha x'})H_{v''}(\sqrt{\alpha(x'+y)})dx'.
\]

To continue the evaluation, the following property of the Hermite polynomials

is used:

\[
H_n(x + y) = \sum_{k=0}^{n} \binom{n}{k} H_k(x)(2y)^{n-k}.
\]

This leads to the integral:

\[
R_v = N_{v'} N_{v''} e^{-\alpha y^2} \int e^{-\alpha(x'^2-xy')}
\]

\[
H_{v'}(\sqrt{\alpha x'}) \sum_{k=0}^{v''} \binom{v''}{k} H_k(\sqrt{\alpha x'})(2\sqrt{\alpha y})^{v''-k} dx'.
\]
Because the Hermite polynomials have been rewritten such that they now have the same argument, the orthogonality of the Hermite polynomials can be used to simplify this equation. From the orthogonality, it follows that integrals of $H_v' H_k \neq 0$ only if $k = v'$. For the following result it is assumed that $v'' > v'$. If $v'' < v'$ the integrals have to be written as a function of $x''$ instead of $x'$ to give a nonzero result. The new form of the equation is:

$$R_v = N_v N_{v''} \ e^{-\alpha y^2} \left( \frac{v''}{v'} \right)^{v''-v'} \int e^{-\alpha (x'^2-yx')} H_{v'}(\sqrt{\alpha x'}) H_{v'}(\sqrt{\alpha x'}) dx'. \quad (2.72)$$

The difference between the equilibrium distances of the upper and lower level ($y = R_{v'} - R_{v''}$) is small, it is much smaller than the internuclear distance itself. The integral limits are $x' = \pm \infty$. To complete the evaluation of the Franck-Condon factors, the following approximation is applicable:

$$e^{-\alpha (x'^2-yx')} = e^{-\alpha (x'-y)x')} \approx e^{-\alpha (x'^2)} \quad (2.73)$$

With this approximation the following standard integral for Hermite polynomials is used:

$$R_v = \int e^{-\alpha (x'^2)} H_m(x) dx = n! 2^n \sqrt{\pi} \delta_{nm}. \quad (2.74)$$

The transition moment for vibrational transitions within an electronic transition is thus:

$$R_v = \left| N_v N_{v''} \ e^{-\alpha y^2} \left( \frac{v''}{v'} \right)^{v''-v'} \frac{1}{\sqrt{\alpha}} \left( \frac{v'}{\sqrt{\alpha}} \right)^{v'} \frac{1}{\sqrt{\alpha}} \right| \quad (2.75)$$

which can in principle give a nonzero result for any combination of $v''$ and $v'$. If the wave functions are properly normalized, the sum of the Franck-Condon factors from a specific upper level $v'$ to any lower level is unity. Also, the sum of the Franck-Condon factors to a lower level $v''$ from any upper level equals unity as well. This is called the sum rule.

The approximation of identical force constants for the upper and lower level used to obtain this result can now be relaxed. If the potential energy curves, of the upper and lower level are not the same, the force constant $k$ is different for the upper and lower level. The result is that the factor $\alpha$ is different for the
upper and lower level. This means that the two Hermite polynomials in equation (2.71) do not have the same argument. Now the approximation \( \alpha_{up} = \alpha_{low} + \beta \) can be made, and by using (2.70) the equations can again be written in terms of Hermite polynomials with the same argument, and a solution can be found.

If the model of the harmonic oscillator is not sufficiently accurate to describe the wave functions, the model of the anharmonic oscillator can be used. This results in different wave functions which further complicates the calculation of the Franck-Condon factors. For InBr, calculated Franck-Condon factors have been published in [6].

### 2.2.5 Hönl-London Factor

For vibrations, the Franck-Condon factor describes the relative intensities of the different vibrational transitions within an electronic transition. For rotational transitions the factor that determines the relative intensities of the different rotational transitions is called the Hönl-London factor. The derivation of the Hönl-London factor will not be performed. For detailed information, please see [7] and the references therein.

As can be obtained from evaluating equations (III,169) and (III,173) in [1], the rotational transition probability \( \Sigma |R^{n_im_k}|^2 \) is equal to \( 2S_J \), the Hönl-London factor. Two remarks are made regarding this equality.

The first one is that these equations are for a transition with \( \Lambda = 0 \) for both upper and lower electronic level. This is not always the case. It is possible that \( \Lambda \neq 0 \) for the upper or lower level. In that case, \( \Sigma |R^{n_im_k}|^2 \) is equal to \( S_J \). For InBr, in the case of the \( \Lambda \leftrightarrow X \) transition, \( \Lambda = 1 \) and \( \Omega = 0 \) for the upper level. Because Hund’s coupling case c is relevant, the criterion \( \Lambda = 0 \) may be applied for \( \Omega = 0 \). Therefore the equations discussed here are valid for this transition.

The second remark refers to the sum rule for the Hönl-London factor. Like for the Franck-Condon factors, for the Hönl-London factors there is a sum rule. For transitions from an upper or lower level \( J \) the Hönl-London factors sum to \( 2J + 1 \). If \( 2S_J \) is used for the Hönl-London factor, the Hönl-London factors sum to \( 2(2J+1) \), not to \( 2J + 1 \). Whether the sum should be \( 2J + 1 \) or a constant multiple of \( 2J + 1 \) is a matter of definition involving division of constants into the electronic part of the transition probability, and into the Hönl-London factors. According to [8]:

In many cases factor-of-2 errors have been made because of confusion with regard to the sum rules for rotational line intensity factors and
Chapter 2. Theory

the definitions of published electronic transition moments.

For the InBr A ↔ X transition studied in this thesis, the Hönl-London factors are given below. The Hönl-London factors according to the theory in Herzberg [1] have been used. The Hönl-London factors for absorption are:

\[
\begin{align*}
R - \text{branch:} & \quad S_J = J'' + 1 \\
P - \text{branch:} & \quad S_J = J''
\end{align*}
\] (2.76) (2.77)

and for emission:

\[
\begin{align*}
R - \text{branch:} & \quad S_J = J' \\
P - \text{branch:} & \quad S_J = J' + 1
\end{align*}
\] (2.78) (2.79)

2.3 Population

To determine the relative population of levels, the contributions of the electronic, vibrational and rotational parts are taken into account separately. The electronic part of the population of a level is the relative number of molecules that are in certain electronic state with respect to the total number of molecules.

The vibrational part is the relative number of the molecules that are in a certain vibration level with respect to the total number of molecules in the same electronic state.

The rotational part is the relative number of molecules in a certain rotational state with respect to the total number of molecules that are in the same vibration level in the same electronic state.

If only relative populations are considered, and only one electronic transition is evaluated, then the electronic contribution to the population of the level is the same for all transitions that are evaluated. The electronic contribution to the population of the level is not discussed here.

2.3.1 Vibrations

First, the vibrational population is discussed assuming thermal equilibrium of the vibrational levels. According to the Maxwell-Boltzmann distribution law, the number of molecules in a certain state is proportional to the Boltzmann factor. The Boltzmann factor is: \( e^{-E/kT} \). The relative number of molecules in a
2.3 Population

Figure 2.5: Population of vibrational levels as a function of their energy. The vibrational levels 0–4 are indicated in the figure.

vibrational state \( v \) with respect to the number of molecules in vibrational state 0 normalized to a population of 1 for vibrational level \( v = 0 \), is as follows:

\[
\frac{N_v}{N_0} = e^{-\frac{(G(v)-G(0))hc}{kT}}.
\]  

(2.80)

This relation is illustrated in figure 2.5.

The constant \( G(v) \) is the vibrational energy of the level, as given by equation (2.30). Instead of scaling all transitions to the population of \( v = 0 \), the population of an individual state can also be scaled to the total population in all vibration levels via the state sum \( (Q_v) \). The state sum, also called the partition function, is the sum of the Boltzmann factors of the energy levels.

\[
Q_v = \sum_v e^{-G(v) \frac{hc}{kT}}.
\]  

(2.81)

The relative population of a vibrational level is thus:

\[
N_v = \frac{1}{Q_v} e^{-G(v) \frac{hc}{kT}}.
\]  

(2.82)

2.3.2 Rotations

For the rotational populations, an analogous reasoning is used. Again, the number of molecules in a certain state is proportional to the Boltzmann factor.
Chapter 2. Theory

Relative Population

\[ \text{Figure 2.6: Illustration of the population of rotational levels as a function of the rotational quantum number } J. \]

In this case the Boltzmann factor is: \( e^{-F(J) \frac{\hbar c}{kT}} \). Each state has a multiplicity of \( 2J + 1 \), therefore, the population of a state is proportional to:

\[ (2J + 1)e^{-F(J) \frac{\hbar c}{kT}}. \]  
(2.83)

This is illustrated in figure 2.6.

The relative population of one rotational level with respect to the total population of all the rotational levels in the same vibration is as follows:

\[ N_{J} = N_{v} \frac{1}{Q_r} (2J + 1)e^{-F(J) \frac{\hbar c}{kT}}. \]  
(2.84)

In this equation \( N_{J} \) is the number of molecules in rotational state \( J \), \( F(J) \) is the rotational energy of the level, as given by equation (2.46), \( N_{v} \) is the total (relative) number of molecules in the vibrational level and \( Q_r \) is the rotational partition function, the summation over the Boltzmann factors times the multiplicity of all possible rotation levels:

\[ Q_r = \sum_{J=0}^{\infty} (2J + 1)e^{-F(J) \frac{\hbar c}{kT}}. \]  
(2.85)

The rotational partition function can be approximated by replacing the summation with an integration yielding the approximate value:

\[ Q_r = \frac{kT}{\hbar c B_v}. \]  
(2.86)
However, for the different vibrational levels $B_v$ is different. Therefore the state sum changes for different vibrational levels. Within an electronic transition, the population of an energy level with vibrational quantum number $v$ and rotational quantum number $J$ is:

$$N_{v,J} = N_e \frac{1}{Q_v} e^{-G(v) \frac{\hbar c B_v}{kT}} \frac{\hbar c B_v}{kT} (2J + 1) e^{-F(v,J) \frac{\hbar c}{kT}}. \quad (2.87)$$

In this equation $N_e$ is the total population of the considered electronic level. In this section, the population distribution based on thermal equilibrium has been determined. In a discharge environment non-equilibrium distributions may exist.

### 2.4 Intensities in Spectra

The allowed energy levels and the allowed transition between them, which have been discussed in the previous sections determine the wave numbers of the photons that can be emitted or absorbed.

When studying spectra, not only the location of the emission or absorption in the spectrum is interesting, but also the intensity of the line is. The intensity of a line in emission is defined as the energy emitted by the source per second per unit solid angle. Therefore, the intensity of a line is the number of photons that is emitted per unit time per unit solid angle, multiplied by the energy of the photon. In this thesis however, to comply with the measurements that are discussed later, intensity is taken in counts. Actually a radiant power is measured, for a certain solid angle. The measured data must be divided by the solid angle to obtain the intensity. For all measurements the solid angle is the same and only relative data is compared, therefore —although relative radiant powers are measured— they can be called relative intensities.

For the intensity of an emission line, two parameters are important. The first one is the number of molecules ($N_n$) in the upper state ($n$), the second is the decay rate of the molecules in the upper state to the lower state ($m$). In a
Chapter 2. Theory

formula this is:

\[ I_{em}^{nm} = N_n A_{nm}, \text{ with} \]

\[ A_{nm} = \frac{64\pi^4 \nu_{nm}^3 \Sigma |R_{nm}|^2}{3h g_n}. \]  

(2.89)

In this equation \( A_{nm} \) is the Einstein transition probability of spontaneous emission. The Einstein transition probability of spontaneous emission is the chance that atoms in the initial state \( n \) carry out a transition to \( m \). The sum \( \Sigma |R_{nm}|^2 \) is over the transition probabilities of the transitions between the upper state(s) \( n_i \) and the possible lower states \( m_k \).

The factor \( g_n \) is the multiplicity of the upper level. The Einstein transition probability of spontaneous emission \( A \) depends on the transition matrix element \( |R|^2 \). The transition probability follows from the discussion of the selection rules and transition moment in the previous sections, however now it is not only interesting to know which transitions have a nonzero probability, but also the transition probability itself.

Ab-initio evaluation of transition probabilities is beyond the scope of this work. The transition probability depends on the Franck-Condon factors and on the Hönl-London factors that were discussed in sections 2.2.4 and 2.2.5 respectively. For absorption the intensity of the incident radiation has to be taken into account too:

\[ I_{abs}^{nm} = \rho_{nm} \Delta x N_m B_{nm} \]  

(2.90)

\[ B_{nm} = \frac{8\pi^3 \Sigma |R_{nm}|^2}{3h^2 c g_m} \]  

(2.91)

In this equation, \( \rho_{nm} \) is the density of the radiation, \( \Delta x \) is the thickness of the absorbing layer. The number of specimen in the lower state \( m \) is designated \( N_m \). The \( B_{nm} \) is the Einstein transition probability of absorption, which is related to the transition probability \( |R|^2 \). The sum \( \Sigma |R_{nm}|^2 \) is over the states of the lower level(s) \( m_k \) and the upper level \( n_i \). The factor \( g_m \) is the degeneracy of the lower level.

To determine the number of molecules in a certain state, thermal equilibrium is assumed, so that the equations of the Maxwell-Boltzmann distribution can be used.

\[^{16} i.e. \text{the multiplicities: the same level, but a different state}\]
2.5 Determining Rotational Temperature

All these considerations are now combined into equation (2.92), with \( N_{v,J} \) from equation (2.87) for \( N_m \), the population of the lower state. The Einstein transition probability of absorption \( (B) \) as given by equation (2.91). The equation that is obtained is:

\[
I_{nm}^{\text{abs}} = \rho_{nm} \Delta x N_e \frac{1}{Q_v} e^{\frac{-G(v)hc}{kT}} \frac{1}{Q_r} (2J + 1) e^{\frac{-F(J)hc}{kT}} \frac{8\pi^3}{3h^2c} \frac{\Sigma |R_{nm}^{mk}|^2}{g_m}. \tag{2.92}
\]

To obtain a relative intensity spectrum, the constants of equation (2.92), are put together into a constant \( C_{abs} \). The equation is rearranged to obtain the following equation for the relative intensities of a rovibrational absorption spectrum of an electronic transition:

\[
I_{nm}^{\text{abs}} = C_{abs} \frac{1}{Q_v} F C e^{\frac{-G(v)hc}{kT}} \frac{hcB_v}{kT} 2S_J e^{\frac{-F(J)hc}{kT}}. \tag{2.93}
\]

In this equation \( FC \) is the Franck-Condon factor, \( S_J \) is the Hönly-London factor.

2.5 Determining Rotational Temperature

The rotational temperature is often accepted as being equal to the heavy particle temperature. Therefore if one is interested in the heavy particle temperature, it can be determined via the rotational temperature. Here two methods that can be used to determine the rotational temperature are discussed, the first is based on finding the rotation number where the intensity of a single line is maximal, the other is based on the variation of intensity with rotational quantum number.

2.5.1 \( J_{\text{max}} \) Method

First, equation (2.84) is considered. The intensity of a line is proportional to the population of the level. In equation (2.84), for lower rotational quantum numbers \( J \) the part linear factor \( 2J + 1 \) is dominant, resulting in an increase in the population and therefore an increase in the intensity with increasing \( J \). For higher \( J \) the exponential term is dominant, resulting in a decrease in the population and therefore a decrease in intensity with increasing \( J \). The \( J \) with maximum intensity can be found by solving

\[
\frac{d}{dJ} N_J = 0. \tag{2.94}
\]
The solution to this equation is $J_{\text{max}} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$. This value has to be rounded off because $J$ can only have discrete values. This equation can be rewritten to find an equation for the temperature:

$$T = \frac{2Bhc}{k} \left( J_{\text{max}} + \frac{1}{2} \right)^2. \quad (2.95)$$

In this equation $B$ is the rotational constant of the lower level when an absorption spectrum is considered, and the rotational constant of the upper level when an emission spectrum is considered. Since $J$ can only take integer values, the temperature is subject to the round off error in $J$.

Two points should be mentioned: first, it must be possible to find the resolved rotational line with maximum intensity. Second, it must be possible to determine the rotational quantum number $J$ of the peak. This may seem trivial, but it is not. In a rovibrational spectrum of an electronic transition, the rotation branches of different vibrations may overlap, resulting in overlap of rotational lines for different vibrational levels. Also, band heads can be formed, resulting in overlap between lines with different $J$ within a branch. Due to these effects, different lines overlap each other. Therefore it is not always possible to determine which rotational quantum number $J$ has maximum intensity. This method, therefore, is most feasible in pure rotational spectra, or in other spectra where the spacing between the rotational lines is big.

### 2.5.2 Intensity Method

Another method to determine rotational temperature is based on evaluation of the intensities of multiple peaks. The discussion here will be based on evaluating an absorption spectrum, however for an emission spectrum an analogous procedure can be performed. For this procedure, equation (2.93) is evaluated. The logarithm of this equation can be rewritten as follows\(^\text{17}\):

$$\log \left( \frac{I_{\text{abs}}}{2S_J} \right) = \log (C_{\text{abs}}) - F(J) \frac{hc}{kT}. \quad (2.96)$$

When the R-branch of a $\Sigma - \Sigma$ or equivalent transition is studied, $S_J = J + 1$. For the model of the rigid rotator, $F(J) = BJ(J + 1)$. From these equations

\(^{17}\)In the general case the logarithm of $I_{\text{abs}}/S_J$ should be taken. However the factor two can be separated of, and taken into account within $C_{\text{abs}}$, a constant whose value does not influence the slope.
it can be concluded that if \( \log \frac{I_{abs}}{J+2} \) is plotted against \( J(J+1) \), the rotational temperature can be found from the slope; \( T = \frac{\hbar c B}{k} \) divided by the slope.

Again, there are two important points to consider: first, it must be possible to identify the rotational quantum number \( J \) of each line. Secondly, the lines must be resolved.

This procedure has been applied in this work to determine the rotational temperature of an InBr gas. Because there is an overlap of different vibrational bands, as well as an overlap between the P- and the R-branch, this procedure can only be applied to a few peaks in a small range. To find the rotational temperature, a fitting procedure has been developed in this work. This procedure will be discussed in a subsequent section.

### 2.6 Laser-Induced Fluorescence

The type of measurements that are performed and discussed in this work are mostly laser-induced fluorescence (LIF) measurements. In a LIF experiment, two processes are important. First, there is the absorption of photons emitted by the laser. This produces a number of exited molecules. Secondly, there is emission of light by the excited molecules relaxing back to the ground (or any other) state. The light emitted by the relaxing molecules is studied. A schematic drawing of these processes is shown in figure (2.7).

In this thesis, three different methods of studying a LIF signal are discussed. The emitted light is studied spectrally resolved and time integrated (sr-LIF), time resolved and spectrally integrated (tr-LIF), or temporally and spectrally integrated (i-LIF).

For sr-LIF studies, the wave number at which light is emitted contains information about the energy levels of the studied species. For tr-LIF studies, the time dependence of the signal gives information about decay times, which are related to the transition probabilities. For the tr-LIF measurements, to be able to couple measured values to specific upper levels, the redistribution over different upper levels must be negligible within the time frame of the measurements. The i-LIF signal is a measure of the absorption. Performing a LIF measurement at different wave numbers \( e.g. \) with a tunable dye laser yields information about different levels.

---

\(^{18}\)The wave number of the laser has to match the wave number of a transition, of course.
Chapter 2. Theory

Figure 2.7: A schematic drawing of laser-induced fluorescence, the laser wavenumber matches the transition (a) from a lower to an upper level. The emission (e) from the upper level is studied.

References


Experimental Setup

3.1 Introduction

A setup was built to perform LIF experiments [1] to determine various fundamental properties of Indium Bromide as well as some operating properties of the lamps under investigation. The gas temperature of these plasmas was one of the most important properties to be measured, as it carries a lot of information about the state of the discharge.

Furthermore, the Franck Condon factors of various vibrational transitions and the corresponding transition energies were determined. Also the transition energies of some rotational transitions were measured.

3.2 General

In this section we will give a general description of the setup. A schematic drawing is shown in figure 7.4. The setup is built around an oven with inside it a quartz tube containing Indium Bromide. The tube containing the InBr is heated to the desired temperature to evaporate the InBr. A laser system is used to excite the molecules. An elaborate detection system containing an iCCD camera and photon counting equipment is used to detect the fluorescence.
Figure 3.1: A schematic drawing of the setup. The setup is built around an oven with inside it a quartz tube containing Indium Bromide. The top of the figure shows the laser system for excitation. On the right hand side is the detection system. The excitation system consists of a tunable dye laser pumped by a high repetition rate, frequency tripled Nd:Yag laser. In the detection system, light emitted by the excited InBr is collected and directed to either a photomultiplier tube (PMT), or an intensified CCD camera (iCCD). To select the detection range, either a UG11 filter (which will be discussed in section 3.6), or a monochromator is used to select different bands.

3.3 Oven

For the experiment on InBr vapor, the quartz tube with InBr vapor is placed in an oven. In this oven the sample can be heated up to approximately 633 K.
However, most of the measurements were done at a temperature of about 513 K. Figure 3.2 shows a detailed view of this part of the setup.

![Figure 3.2: A picture of the oven, rendered by Autodesk Inventor.](image)

The oven is mounted on two rails that allow for horizontal movement, perpendicular to the axis of the quartz tube inside it. The position is adjusted by moving the micrometer adjuster screw (1 in figure 3.3). To prevent turbulence in the optical path accessing the oven, two 20 cm long tubes (2 in figure 3.3) are mounted on both ends of the oven.

Around the oven a heat shield is mounted (3 in figure 3.3). It also serves as a radiation shield, since the discharge inside can produce UV-radiation. The oven is suspended from 3 rods (4 in figure 3.3) that connect it to the baseframe. The rods are connected to the quartz part of the oven. The purpose of this construction is to reduce heat conduction losses to the base and optical table.

The oven is heated by six infrared radiators (5 in figure 3.3): three mounted above the quartz tube and three mounted below the quartz tube. Each group of three heaters is controlled by a separate 2132 Eurotherm PID controller. Each controller is fed with temperature data from a K-thermocouple strategically placed above or below the quartz tube.

The front and back ends of the oven are also heated to create a temperature...
profile that is as homogeneous as possible. The edge heaters are controlled by one Eurotherm 2116 PID controller. This controller receives temperature data from 2 K-thermocouples attached to the ends of the oven.

After enough stabilization time, the temperature of the oven is within 1 K of the requested temperature. The homogeneity of the temperature is illustrated in figure 3.4.

6 steel rings (6 in figure 3.3) hold the quartz tube (7 in figure 3.3), that will be described in the following section, in place by clamping it firmly. They are flexible, to allow for variation of the tube diameter.

### 3.4 Quartz Tube

The quartz tube used in this experiment is depicted in figure 3.5. It is mounted inside the oven described in section 3.3 as can be seen in figure 3.3. The tube is about 30 cm long and has a diameter of 3 cm. A small protrusion can be seen at about $\frac{1}{4}$ of the length. This is the pipe that was used to fill the tube with
the desired dose and seal it. On the ends of the tube, Tantalum electrodes are used to increase the RF coupling efficiency.

![Figure 3.5: A picture of quartz tube.](image)

**Figure 3.5:** A picture of quartz tube.

### 3.5 Excitation

The excitation in this setup is performed by a tunable dye laser pumped by a high repetition rate, frequency tripled Nd:Yag laser, built by EdgeWave GmbH. A picture of the pump laser can be seen in figure 3.6.

The dye laser used in these experiments is a Cobra Stretch high repetition
rate laser, manufactured by Sirah GmbH, a picture of which can be seen in figure 3.7.

The laser dye used in the experiments is Exalite 376, which can emit in the 370—380 nm wavelength range ($\approx 27.0 \cdot 10^3$ cm$^{-1} - 26.3 \cdot 10^3$ cm$^{-1}$). The tuning curve of this dye is shown in figure 3.8. The laser is used to excite the InBr at various wave numbers. In table (3.1) the specifications of the Nd:Yag laser and of the dye laser are summarized.

The absolute wavelength error of $\leq 0.03$ nm at 570 nm scales to an absolute error of about 1.5 cm$^{-1}$ at 26600 cm$^{-1}$. The reproducibility of $\leq 0.005$ nm at 570 nm scales to an error of about 0.2 cm$^{-1}$ at 26600 cm$^{-1}$. These specifications indicate the direct tuning to a specific wave number will likely not be very accurate. This is why a laser scan is used. The starting wave number has an offset, but from a starting wave number, the subsequent steps of a scan are reproducible. The shape of the spectrum can be used to calibrate the wave number axis.

The high repetition rate is vital for these experiments, due to the easily saturated transitions in this study. To prevent saturation, only very small amounts of energy per shot can be used to induce the fluorescence. This yields a very small amounts of fluorescence. In order to detect these signals, the experiment
3.5 Excitation

Figure 3.7: A photograph of the Sirah dye laser.

Figure 3.8: The tuning curve of Exalite 376 when excited by the third harmonic of a Nd:YAG laser.
Table 3.1: Properties of the Nd:Yag laser which is used to seed the dye laser

<table>
<thead>
<tr>
<th>Nd:Yag laser</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>wavelength</td>
<td>355 nm</td>
</tr>
<tr>
<td>operating current</td>
<td>20 - 40 A</td>
</tr>
<tr>
<td>output power</td>
<td>0 - 4 W</td>
</tr>
<tr>
<td>pulse duration</td>
<td>5 - 7 ns</td>
</tr>
<tr>
<td>repetition rate</td>
<td>1 kHz</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>dye laser</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>grating</td>
<td>3600 lines/mm 90mm</td>
</tr>
<tr>
<td>resolution</td>
<td>$3 \cdot 10^6$</td>
</tr>
<tr>
<td>absolute wavelength error</td>
<td>$\leq 0.03$ nm @ 570 nm</td>
</tr>
<tr>
<td>wavelength reproducibility</td>
<td>$\leq 0.005$ nm @ 570 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>laser dye</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>dye</td>
<td>Exalite 376</td>
</tr>
<tr>
<td>range</td>
<td>370-380 nm</td>
</tr>
<tr>
<td>dye peak efficiency</td>
<td>13%</td>
</tr>
</tbody>
</table>

has to be repeated many times. To do this in a reasonable amount of time, a high repetition rate is needed.

The physics of the saturation is explained in the following section.
3.5 Excitation

3.5.1 Saturation

To describe the saturation of a transition, the physics of absorption and emission must be considered. Saturation is dependent on the properties of the molecules that are under investigation and on the properties of the laser used to provide excitation.

The Einstein $A$ coefficient describes the chance that a spontaneous optical transition occurs from one state to another. In figure 3.9 this is depicted schematically. The Einstein $A$ coefficient is defined as the total rate of spontaneous emission $W_{21}^s$ from an upper level 2 to a lower level 1 for a system of $N_2$ atoms in the upper level [2]:

$$W_{21}^s = A_{21} \cdot N_2. \quad (3.1)$$

The $A$ value is related to the spontaneous radiative decay time of level 2 in the following way:

$$\frac{1}{\tau_2} = \sum_i A_{2i}, \quad (3.2)$$

so the dimension of $A$ is $s^{-1}$.

The $B$ coefficients are used to describe the absorption and stimulated emission for atomic or molecular transitions. The coefficient for (induced) absorption is defined in:

$$W_{12}^i = B_{12}^\omega \cdot \rho^\omega \cdot N_1, \quad (3.3)$$

where $W_{12}^i$ denotes the absorption rate$^1$ $B_{12}^\omega$ the Einstein coefficient for absorption and $N_1$ is the density of molecules in the lower level. This is graphically shown in figure 3.10.

$^1$The number of absorptions per second.
\[ \rho \omega \] stands for the energy density per unit angular frequency interval in the absorbing region. \( \rho \omega \) has the dimension of \( \text{energy} \times \text{volume}^{-1} \times (\text{angular frequency})^{-1} \). For the whole angular frequency interval where absorption can take place, \( \rho \omega \) is assumed to be a constant, both spectrally and spatially. \( B \) then has the dimensions of \( \text{volume} \times \text{angular frequency} \times \text{energy}^{-1} \times \text{time}^{-1} \).

The \( B \) coefficient for stimulated emission is defined in:

\[
W^i_{21} = B^\omega_{21} \cdot \rho \omega \cdot N_2, \tag{3.4}
\]

where \( W^i_{21} \) is the total rate of stimulated (induced) emission. This is depicted graphically in figure 3.11.

![Figure 3.10: Schematic diagram of absorption.](image)

The \( A \) and \( B \) coefficient can be converted into each other using:

\[
B^\omega_{21} = \frac{\pi^2 c^3}{\hbar \omega^3_{21}} A_{21}, \tag{3.5}
\]

and

\[
B^\omega_{12} = \frac{g_2}{g_1} B^\omega_{21}, \tag{3.6}
\]

where \( g_1 \) and \( g_2 \) denote the multiplicity factors of the two levels.
3.5 Excitation

To estimate \( \rho_\omega \), we need to know the energy per pulse, the volume in which the energy of the pulse is distributed and the spectral width of the pulse.

The time averaged power of the laser is 10 mW. Since the repetition frequency of the laser is 1 kHz, that leads to an average pulse energy of 10 \( \mu \)J.

The volume of the laser pulse can be estimated using:

\[
V_{\text{pulse}} = O \cdot c \cdot \Delta t, \tag{3.7}
\]

where \( O \) is the cross-section of the laser pulse and \( c \cdot \Delta t \) the spatial length of the pulse.

The pulse length of the laser is of the order of 10 ns and the cross-section is of the order of 1 cm\(^2\) leading to a volume of \( 3 \cdot 10^{-4} \) m\(^3\).

Then using the differential of equation \( \omega = \frac{2\pi c}{\lambda} \) we find that:

\[
\Delta \omega = -\frac{2\pi c}{\lambda^2} \cdot \Delta \lambda. \tag{3.8}
\]

Now, using \( \Delta \lambda = 2 \cdot 10^{-12} \) m (the width of the lines as observed, due to the spectral width of the laser beam) we find that \( \Delta \omega = 27 \cdot 10^9 \approx 30 \cdot 10^9 \) rad s\(^{-1}\).

This leads to:

\[
\rho_\omega = 10^{-5} \cdot \frac{1}{3 \cdot 10^{-4}} \cdot \frac{1}{30 \cdot 10^9} \approx 10^{-12} \text{ J m}^{-3} \text{ (rad s}^{-1})^{-1}. \tag{3.9}
\]

So then estimating \( A = 1 \cdot 10^6 \) s\(^{-1}\), based on measurements described later in this chapter, using equations 3.6 and 3.5 with all multiplicities set to 1, we can calculate that \( \rho_\omega \cdot B_{12}^\omega = 10^{-12} \cdot 10^{19} = 1 \cdot 10^7 \) s\(^{-1}\). That means that with this laser power, all the molecules in the ground state would be excited \( \sim 10^7 \) times every second.

\[
\frac{W_{12}^i}{N_1} = 10^7 \text{ s}^{-1}
\]

Fortunately, the laser is on only for a short period of time, so the fraction of molecules that gets excited stays small enough, \( \text{i.e.} \frac{W_{12}^i}{N_1} \cdot \Delta t < 0.1 \).

To calculate the level of saturation one has to solve the differential equations:

\[
\begin{align*}
\frac{dn_2(t)}{dt} &= \rho_\omega B_{12}^\omega n_1(t) - A_{21} n_2(t) - \rho_\omega B_{12}^\omega n_2(t) \tag{3.10} \\
\frac{dn_1(t)}{dt} &= -\rho_\omega B_{12}^\omega n_1(t) + A_{21} n_2(t) + \rho_\omega B_{12}^\omega n_1(t) \tag{3.11}
\end{align*}
\]
where \( n_1 \) is the population of level 1 and \( n_2 \) the population of level 2 and with \( n_2(0) = 0 \) and \( n_1(0) = N_1 \).

Initially we discuss a situation where the laser is on continuously. The solution to equations 3.10 and 3.11 indicates that the total population of the lower level \( n_1 \) does not change very much even if the laser is on continuously. This is shown in figure 3.12.

![Figure 3.12: Graph showing the change in the normalized population of \( n_1 \) as a function of time.](image)

If we now look at the population of \( n_2 \) in this case we see that this population is much smaller than that of \( n_1 \). In figure 3.13 we see that after the laser has been on for around 2 ns the difference between a purely linear steady state regime and the calculated population level is about 1%.

Finally a graph showing the relative deviation from linearity is presented in figure 3.14.

As a last remark, it is worth mentioning that the assumption for the multiplicities does not hold for real situations. In reality, at virtually all wavelengths, many transitions overlap, dividing the power of the laser over various transitions. Nearly all of these transitions have very large multiplicities, especially the ones with large rotational quantum numbers. All these factors contribute to decrease the saturation. But even in a worst case scenario as was shown above, saturation is of limited concern. In our experiments the risk is negligible.

To verify this, tests were done to confirm the absence of saturation. The typical modus operandi of these tests was to repeat a measurement with only half the laser power as in the first measurement. Without exception, all these tests showed that the signal scaled linearly with the laser power, confirming the
3.6 Detection

The fluorescence emitted by the excited InBr-molecules is collected with a lens and directed to either a photomultiplier tube (PMT) or an intensified CCD camera (iCCD). A monochromator is used to select the bands for study. Alternatively, a UG11 filter, for which a transmission curve is shown in figure 3.15, is used to allow light from all A→X and B→X transitions to reach the PMT.
Chapter 3. Experimental Setup

at once. Using this filter, light from all possible decay paths of the excited level can be detected. The PMT is used to perform the time resolved (tr)-LIF measurements. The iCCD camera is used to perform the spectrally resolved (sr)-LIF measurements.

Figure 3.15: Transmission curve of a UG11 filter for a thickness of 1 mm.

3.6.1 Monochromator

The monochromator used in this experiment is a Jobin-Yvon HR1000. One of the issues that we encountered with the monochromator was due to temporal stability. The wavelength calibration of the monochromator varied with ambient temperature. This caused undesirable intensity fluctuations in measurements with the PMT resulting in unreliable intensity profiles. To illustrate this, a graph of the correlation between the ambient temperature and the monochromator offset is shown in figure 3.16.

The monochromator offset is determined by measuring the position of the image of a Helium-Neon laser beam (632.8 nm) on a CCD. The initial pixel number is set to zero and any further deviation is shown in the graph as the monochromator drift.

A clear correlation can be seen between the ambient temperature and the monochromator offset. In fact, hysteresis also appears in the graph. To suppress this offset, a system was built to isolate the monochromator from ambient temperature fluctuations. The system was made of an insulating box, a heating device and a feedback control system. This system stabilized the temperature of the monochromator at 40 °C. With this system in place the fluctuations are reduced to an acceptable level of ±1 pixel, as can be seen in figure 3.17. 1 pixel
3.6 Detection

Figure 3.16: Graph showing the monochromator offset as a function of the ambient temperature. The arrow in the graph shows the direction of time.

roughly corresponds to 15 pm. Fluctuations up to about 75 pm are acceptable, but anything beyond that creates serious intensity fluctuations in measurements with the PMT.

Figure 3.17: Graph showing the progression of the monochromator offset in time. The red line is a guide to the eye. It is clear that —after sufficient stabilization time— the stability of the monochromator is now of the same order as the digital resolution i.e. 1 pixel.

3.6.2 iCCD Camera

Observing the LIF signal is not easy because of the low intensity of the light. An iCCD camera was used because it is much more sensitive than a classic CCD camera. The camera used in these experiments is a 4 QuickE iCCD camera made by Stanford Computer Optics. The 4 Quick E camera is fast: it can
switch the intensifier on or off in 1.2 ns, making short gating times possible. This is combined with a very high repetition rate (3.3 MHz in burst mode). The spatial resolution of the CCD is $768 \times 494$ pixels.

The background level increased significantly during long measurements. This was caused by the increasing temperature of the lab during these measurements. The time evolution of the background level can be seen in figure 3.18. The measurement shown in this graph was started at 5h30 PM and finished at 9h30 AM. The effect of temperature on the background noise level of the iCCD is clearly visible. The temperature in the laboratory rises much more quickly after sunrise at around 850 minutes into the experiment, because at that time, the sun is shining directly onto the windows of the lab.

![Figure 3.18: Time evolution of the background level of the iCCD camera. Sunrise occurs at around 850 minutes into the experiment, causing a significant temperature rise in the lab.](image)

To decrease the influence of ambient air temperature fluctuations, a Peltier element is used. It is attached to a heat sink that is directly attached to the CCD matrix. A water cooling system is mounted on top of the Peltier element to cool it. The camera is placed in a dry atmosphere to avoid condensation of moisture in undesirable places. Figure 3.19 is a picture of the water cooling system placed on the camera. Figure 3.20 illustrates the improvement after installation of the cooling system.

With this cooling system, a constant temperature of $-3 \, ^\circ\text{C}$ is maintained in the iCCD camera. In this way, the background is reduced by a factor $\sim 6$, which is essential to make the LIF signal detectable against the background.
3.6 Detection

Figure 3.19: Photo of the cooling system for the iCCD camera. On the top is the copper water cooling system, which is mounted directly onto the peltier element which is on top of the metal heatsink that is in contact with the CCD of the camera.

Figure 3.20: Illustration of the improvement after the installation of the cooling system. The noise level with cooling drops quickly after starting the cooling system.

3.6.3 Photon Counting

The light from the spectrometer is detected with a photomultiplier (PMT) (Hamamatsu H6780) tube to capture single photons of one distinct wavelength with good time resolution.

The PMT is connected via an amplifier (Ortec 9306) to an Ortec 9353 multichannel scaler (MCS) to obtain time resolved signals. The MCS has a burst sampling rate of 1 GHz.

A multichannel scaler reacts to a start and a signal pulse. The start pulse starts an internal clock of the MCS that runs from 0 to a preset end time for the experiment. In our experiments, the preset end time is typically of the order of 10 µs: the time after which the LIF signal has decayed below the noise level.
Chapter 3. Experimental Setup

The detection interval is divided into smaller intervals called bins. The binwidth in our case is typically 1.2 ns.

The signal pulse —sometimes called stop pulse in the instrument jargon— is in our case an amplified pulse from a PMT. If the voltage on the signal port of the MCS increases above an adjustable discriminator level, the MCS detects a pulse. It responds to that by increasing the counter of the appropriate bin by 1. After detecting a pulse, an MCS typically is unable to respond to pulses for some time: the dead time.

By repeating an experiment multiple times, a time evolution of a signal can be gradually acquired this way.

3.7 Plasma

In a number of experiments, a plasma is ignited in the tubes for these experiments. To do this, various RF amplifiers have been used, such as the KALMUS 122C, the Amplifier Research 75A250 and the Electronics & Innovation AB-250. To measure the power going into the plasma, a system of directional couplers was used, made by Amplifier Research. To read out the data from the couplers, the Amplifier Research PM2002 was used. A block diagram of the plasma power supply and power measurement is shown in figure 3.21.

![Block diagram of the plasma power supply and power measurement system.](image)

Figure 3.21: Block diagram of the plasma power supply and power measurement system.
3.8 Timing

To control this experiment, a number of timing signals are produced. To explain the measurement sequence, a block diagram of the sequence is shown in figure 3.22. When the experiment is started, first the dye laser wavelength is set to the right position. Following that, the camera is primed to be ready for gate pulses. Subsequently the acquisition phase is started in which the Nd:YAG laser is pulsed repeatedly, gate pulses are produced to activate the iCCD camera and the digitizer is triggered. When a preset number of pulses is fired, the next phase is started, which is exactly the same as the acquisition phase, only this time, the laser is not fired and a background measurement is performed. When this background is complete, the dye laser is triggered and moves to the next preset wavelength etc. etc. When the dye laser reaches the end of a preset scan range, it no longer responds to triggers and the experiment is terminated.

The timing diagram is shown in figure 3.23. The experiment is started by generating the first pulse to the DYE laser ”trigger IN” port. This triggers the dye laser to move to the desired wavelength. As the dye laser accepts the initial pulse, it lowers the voltage on the DYE laser ”trigger OUT” port until it is at the correct wavelength. When the voltage is increased, the measurement session begins. The iCCD camera is triggered to accept external gate pulses which control the intensifier. Triggers for either the digitizer or the delay generator that generates the gate pulses are produced. During this time a "busy" signal is set. When the measurement is complete, this signal is unset, triggering a pulse on the DYE laser ”trigger IN” port, telling the dye laser to move to the next wavelength.

This way, a wavelength scan can be performed. When the end of the scan is reached, the dye laser will not respond to the DYE laser trigger IN signal, stopping the sequence.

References


Figure 3.22: Block diagram of this experiment.
Figure 3.23: Timing diagram of this experiment.
4

Spectrally Resolved LIF

4.1 Introduction

In this work, InBr is studied because it is an interesting candidate for plasma lighting applications. InBr is interesting because of its high vapor pressure at low temperature, and because a significant part of the light is emitted in the (near) visible part of the spectrum. In this section, the physics behind the spectrally resolved measurements on indium bromide will be discussed. First we will discuss the theoretical aspects, such as the general properties of the InBr spectrum and the Franck-Condon factors. Then we will describe the method used to carry out the measurements presented later in this chapter. Finally we will show the results and draw conclusions.

4.2 Theory

4.2.1 Indium Bromide Spectrum

In this section, features of the Indium-Bromide spectrum will be discussed [1], [2]. The ground state of InBr is a $^1\Sigma_0^+$ state. The first exited state, (A) is a $^3\Pi_0^+$ state. There is also a B-state, this is a $^3\Pi_1$ state. Together with the metastable $^3\Pi_0^-$ and $^3\Pi_2$ states, they form a triplet state\(^1\) which is split due

\(^1\)On first sight, it is strange that this triplet state consist of four states, however the A ($^3\Pi_0^+$) state and the metastable $^3\Pi_0^-$ are split. Together they are one of the three states that form the triplet state.
to spin-orbit coupling. The C state is a $^1\Pi$ state. A schematic drawing (not to scale) of the energy levels is shown in figure (4.1). The wavelength of the

$$C^1\Pi(1) \quad \text{with rotational structure}$$

$$^3\Pi_2$$

$$B^3\Pi_1(1) \quad \text{with rotational structure}$$

$$A^3\Pi_0(0^+)$$

$$^3\Pi_0(0^-)$$

$$X^1\Sigma^+$$

with vibrational structure

electronic level $v = 0$

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Figure 4.1: A schematic view of the energy levels of InBr freely after [3]. The electronic states of InBr are shown with three vibration levels each. For the electronic ground state X (vibrational state 0) a schematic drawing of the rotational structure is shown in an inset. All vibrational states of all electronic states of InBr have a rotational structure similar to this one. The dotted lines represent metastable states. The arrows indicate vibrational transitions between the ground state (X) and the A-state with $\Delta v = 0$.

Photons that can be emitted or absorbed is determined by the difference in energy between the upper and the lower state involved in the transition. In the InBr spectrum, the wave number difference between transitions that have the same $\Delta v$ is small$^2$. Therefore, they are grouped together in so called $\Delta v$ bands.

Three of the vibrational transitions that belong to the $\Delta v = 0$ band are shown in figure (4.1).

$^2$Difference in vibrational quantum number ($\Delta v = v' - v''$)
4.2 Theory

An example of an InBr-Argon plasma spectrum is given in figure (4.2). In this spectrum, the rovibrational structure of the transitions between the electronic A-state and the ground state (X), alongside transitions between the electronic B-state and the ground state (X) can be seen.

![Spectrum of an InBr-Argon plasma](image)

**Figure 4.2:** The emission spectrum of an InBr-Argon plasma. The various $\Delta v$ bands of the electronic A-state and of the electronic B-state are indicated in the figure.

In this thesis, mainly transitions between the ground state and the electronic A-state are studied. This work focusses on the rotational structure of vibrational transitions in the $\Delta v = 0$ band. However, measurements on the $\Delta v = +1$ and $\Delta v = -1$ bands have also been performed. The rotational structure consists of a P-branch, and an R-branch. The P-branch forms a band head\(^3\). An example of an i-LIF spectrum of the $\Delta v = 0$ band is given in figures (4.3) and (4.4). In figure (4.3) the band heads of the P-branch of the 0-0 and the 1-1 level are indicated. A more detailed view, with the rotational quantum numbers of the levels indicated is shown in figure (4.4).

Two different stable isotopes of Bromine exist, which are approximately equally naturally abundant: \(^{79}\)Br and \(^{81}\)Br. Therefore, different isotopes of the InBr molecule exist. They are indicated as InBr\(^{79}\) and InBr\(^{81}\). For different

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\(^3\)A band head is a point in the series of rotational transition energies where the energy difference between 2 consecutive elements of the series changes sign. In other words, the graph of energy versus rotational quantum number has a minimum in the band head.
Figure 4.3: An absorption spectrum of the $\Delta v = 0$ band of the electronic transition between the A-state and the ground state. The band head of the 0-0 and the 1-1 transition are visible on the left. Rotational transitions with higher $J$ are visible to the right.

Isotopes, the same general formulae hold, however, the spectroscopic constants such as $B_v$ are different.

4.2.2 Franck-Condon Factors & Branching Ratios

The vibrational structure of an electronic transition is explained by the Franck-Condon [4] [5] principle as paraphrased by [6]:

Because the nuclei are so much more massive than the electrons, an electronic transition takes place very much faster than the nuclei can respond.

During a transition, e.g. from the ground state, the electronic configuration of the molecule is rapidly changed. The nuclei are subjected to a new force field due to the new constellation of electrons around them. They respond by starting to vibrate from their original positions, which was so far unchanged during the rapid electronic transition. As can be seen in figure 4.5, the stationary equilibrium separation of the nuclei in the initial (ground) state becomes the stationary turning point in the final electronic state. According to the Franck-
Figure 4.4: A closer view of the spectrum of figure (4.3). The big peaks are rotation transitions of the R-branch. In this wave number range the peaks of the P-branch are much less intense. The numbers indicate the rotational quantum number of the ground state of the InBr$^{79}$. To obtain the rotational quantum number of the exited A-state add one, since for the R-branch $J' = J'' + 1$ holds. In this region of the spectrum the rotational quantum number of the R-branch peaks of InBr$^{81}$ is one higher than that of InBr$^{79}$, these peaks coincide.

Condon principle, the transition from (or to) the vibrational ground state (in the electronic ground state) to (or from) the vibrational state (in the electronically excited state) located vertically above it in the energy diagram, is much more likely than vibronic transitions to other vibrational levels. Vertically above in this context means that the potential energy curve is located vertically above the ground state in the molecular energy diagram.

The Franck-Condon principle also dictates that the nuclear framework remains constant during the excitation, so the transition occurs in a vertical line as is shown in figure 4.5. Such a transition is called a vertical transition \textit{i.e.} an electronic transition that happens without a change of nuclear geometry. In the quantum mechanical formulation of the Franck-Condon principle, the molecule undergoes a transition to the upper vibrational level that most closely resembles the vibrational wave function of the lower vibrational level of the electronic ground state. The two wave functions of the levels shown in figure 4.6 have the greatest overlap integral of all the vibrational levels of the upper electronic
Figure 4.5: Scheme explaining that the most intense vibronic transition is from the ground vibrational state to the vibrational state lying vertically above it [6].

The intensity of a vibronic transition is proportional to the square of the overlap integral between the vibrational wave functions of the two states that are involved in the transition. This is known as the Franck-Condon factor for the transition. It follows that, the greater the overlap of the wave function of the vibrational level in the upper electronic state with the vibrational wave function in the lower electronic state, the greater the absorption or emission intensity of that particular vibronic transition. The Franck-Condon factor determines the probability for vibronic transitions, and thus determines the intensity of spectral lines in the InBr spectrum. For details about this, please read section 2.2.4 on page 38 of this thesis.

4.2.3 Rotational Redistribution Broadening

When the InBr molecules collide with the Argon atoms, the rotational quantum number can change. It has been observed that for the typical Argon pressures in our experiments, this process can be as fast as the optical decay. The rotational redistribution process becomes faster at higher temperatures, due to the
increased collision frequency.

Evidence for the redistribution can be found in the measurements presented further on in this chapter. The spectra with Argon as a background gas look distinctly broader than the spectra without background gas. The various aspects of these measurements will be discussed in more detail in section 6.2.

4.3 Method: DETEX Plots

The spectrally resolved LIF (sr-LIF) measurements have been performed using the iCCD camera (as described in the experimental setup) to collect the emitted light. Also for these measurements, the dye laser (as described in the experimental setup) is scanned over a preset wave number range. Typically 1000 laser shots are accumulated to produce a camera image. The sr-LIF measurements are time integrated. The time integration frame is 1 \( \mu \)s. This means that the first 1 \( \mu \)s of the fluorescence emission is collected on the iCCD. For each step of the scan, an iCCD image is obtained. The spectral range of one iCCD
image is typically about $700 \text{ cm}^{-1}$.

![Figure 4.7: Schematic representation of step 1 in constructing a DETEX plot. For each scan, the energy collected by the camera is plotted as is shown on the bottom of this figure; the detection wave number is put on the horizontal axis. The intensity of the signal is color coded in this frame.](image)

The camera images from all steps in the dye laser scan are combined into a detection-excitation plot (DETEx plot). This portmanteau was introduced to abbreviate this word, but also because this is a completely new type of diagram. In these DETEx plots, the excitation wave number is put on the vertical axis. The detection wave number is put on the horizontal axis. The intensity of the detected signal is plotted color coded in this frame, so the color at an x-y coordinate gives the intensity of the emission at the detection wave number (on the horizontal axis) after absorption at the excitation wave number (displayed on the vertical axis). In figure 4.7 the color coding process is schematically shown. Figure 4.8 shows a complete DETEx plot.

### 4.4 Results

In this section the results of the measurements will be shown and discussed. First results for the InBr vapor without bugger gas will be shown, followed by results for the vapor with the buffer gas. Finally results for the plasma will be shown, both for the capacitively coupled plasma and the inductively coupled plasma.
4.4 Results

Figure 4.8: Example of a DETEX plot. The intensity of the measured spectrum is color coded for each x-y-coördinate.

4.4.1 InBr Vapor DETEX Plots

The DETEX measurements on the InBr vapor will be presented in this section. Figure 4.9 shows the DETEX plot of the measurement carried out in InBr vapor without background gas. In these plots, the sr-LIF signal is shown with the detection wavenumber on the horizontal axis, for different laser wave numbers (vertical axis). The vertical bands are the various $\Delta v$ bands. For the InBr measurement, each of them consists of three smaller branches. For these measurements, the laser excitation was in the $\Delta v = 0$ band.

The vibration bands of the DETEX plots of the InBr measurement show three branches. When the branches are studied carefully, one can see a spot in the central branch for every spot in the left branch, as well as one for every spot in the right branch. This is shown in figure 4.10.

This phenomenon is explained as follows. When the laser is tuned to a wave number that matches absorption in the P-branch ($\Delta J = -1$) — e.g. between the ground state vibration level 0, $J=130$ to the exited A-state, vibration level 0, $J=129$ —, there are two possibilities to go back to the electronic ground
Figure 4.9: The DETEX plot of the sr-LIF measurement on InBr. Excitation was in the $\Delta v = 0$ band. From left to right the bands $\Delta v = -3$ through $\Delta v = +2$ are shown. Each vibration band consists of three different branches that are explained by the different combinations of rotational transitions in the P-branch and R-branch for excitation and detection.

state vibrational level 0: to $J=130$, P-branch emission and to $J=128$, R-branch ($\Delta J = +1$) emission. Because the energy difference between $(A,0,129)^4$ and $(X,0,130)$ is smaller than the energy difference between $(A,0,129)$ and $(X,0,128)$, this emission appears at the high wave number side.

Near these lines, there is also excitation via the R-branch, e.g., from electronic ground state vibrational level 0, $J=86$ to the exited A-state, vibration level 0 $J=87$. Also for this exited level, there are two possibilities to go back to the electronic ground state vibrational level 0: to $J=86$, R-branch emission and to $J=88$, P-branch emission. Because the energy difference between $(A,0,87)$ and $(X,0,86)$ is bigger than the energy difference between $(A,0,87)$ and $(X,0,88)$, this emission appears at the low wave number side.

The central branch consists of emissions from relaxation transitions from upper to lower level that take place through the same path as the excitation.

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4This is an ad hoc abbreviation for electronic A-state, vibrational level 0, rotational level 129.
Figure 4.10: A zoomed in part of the DETEX plot of the sr-LIF measurement on InBr. On closer inspection of the dots visible in this plot, one can see that the left and right dots do not coincide completely, although they do overlap largely.

The left branch is emission in the R-branch after absorption in the P-branch. The right branch is emission in the P-branch after absorption in the R-branch. In figure (4.11) an energy level diagram is shown to illustrate this process. In terms similar to the terminology used for selection rules, $\Delta J'' = +2, 0, -2$ can be used to indicate the left (lower detection wave number) central and right (higher detection wave number) branch respectively.

From this explanation it can be concluded that the distance between the left branch and the central branch can be calculated from $F(J''+2) - F(J'')$. The distance between the right branch and the central branch follows from $F(J'') - F(J''-2)$. Also, the other way around, if the rotational constants of the lower level are known e.g. from microwave studies, the distance between the branches can be used to determine the rotational quantum number of the level, though this would require a greater resolution than what is available in our setup.

When the rotational quantum numbers of the upper level and their peak positions are known, the rotational constants of the upper level can be determined.
Figure 4.11: A schematic drawing to assist in explaining the three branches. The lengths of the arrows represent the wave number of the transition, a longer arrow means a higher wave number. Left: Excitation via the R-branch. Relaxation is possible through two paths, in the R-branch, with the same wave number as the excitation, and in the P-branch, with a lower wave number than the excitation. Right: Excitation via the P-branch. Relaxation is possible through two paths, in the P-branch, with the same wave number as the excitation and in the R-branch, with a higher wave number. The letter A stands for absorption, the letters L, C, R indicate that the emitted light is detected in the left, center or right branch of the detex plot resulting from the sr-LIF measurements.

from the distance between them. This is done as follows; two peaks with the same lower level are searched, the distance between them is now determined by the rotational constants of the upper level by a formula analogous to the previously mentioned ones.

Determining wave numbers of rotational transitions of the P-branch $\Delta v = 0$

The sr-LIF measurements can be used to determine the rotational quantum number and the wave number of the transitions. For the electronic A-state
vibration 0 to the electronic X-state vibration 0 a list of the wave numbers at which different rotations of the P and R-branch appear have been produced by [7]. For high wave numbers, the rotational quantum number of a P-branch transition is approximately 40 higher than the rotational quantum number of an R-branch transition that appears near the same wave number. This is due to fact that the P-branch forms a band head. Because the rotational quantum number of the R-branch is lower, the transitions are more intense. It is therefore difficult to determine the locations of the P-branch transitions for high wave numbers.

From the discussion in the previous section it is concluded that in the DETEX plots, the left rotation branch is light that is emitted in the R-branch after absorption in the P-branch. In this branch, there is no emission from absorption in the R-branch. Therefore, the left rotation branch can be used to determine the wave number of transitions of the P-branch.

To do this, the range of data corresponding to the P-branch under investigation has to be identified and isolated. This is done by carefully selecting the part of the DETEX plot (generally 9 data points wide) and creating a graph of the fluorescence emission of the $v = 0$ P-branch emission of the electronic A-state versus the excitation wavelength. Typically, such a graph looks like an absorption spectrum such as in figure 4.3, but it exclusively contains emission from the P-branch. After this, the tedious job of identifying peaks and noting their wave number begins (see figure 4.4). This procedure, produces a list of wave numbers of a sequence of peaks. To find the corresponding rotation quantum number $J$, it has to be matched with the list produced by [7] —in this case—and for any additional lines, the numbering is continued.

In this thesis the wave numbers of P-branch transitions have been determined up to $J=174$, which extends the list produced by [7] that goes up to $J=140$. The results are listed in table 4.1.

Table 4.1: Identification of the P-branch rotational transitions of the transition between the electronic A-state vibration 0 and the ground state vibration 0 for InBr$^{79}$ and InBr$^{81}$

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In the $\Delta v = 0$ band, the rotational transitions of the electronic A-state vibration 1 to the electronic X-state vibration 1 appear. Because the transition probability of this transition is smaller [8] (see also table 4.2), and because the population of vibration level 1 is smaller than that of vibration level 0, the intensity of this transition is lower than the intensity of the 0–0 transition. It is difficult to identify the wave numbers of the 1-1 transition in the $\Delta v = 0$ band. However, after excitation in the $\Delta v = 0$ band, the fluorescence signal in the $\Delta v = 1$ band can be evaluated to determine the wave numbers of the rotations of the 1–1 vibrational transition as a function of the rotational quantum number. These values can then be used to determine the rotational constants of vibration 1 of the electronic A-state. At $T = 500$ K, the expected relative intensities of emission in the $\Delta v = 1$ band after excitation in the $\Delta v = 0$ band for a LIF measurement are displayed in table 4.2 for the different upper levels.

To determine the rotational constants of vibrational state 1 of the electronic A-state from a normal absorption or emission spectrum, the $\Delta v = 1$ band is evaluated. At $T = 500$ K, the expected relative intensities of emission in the $\Delta v = 1$ band are displayed in table (4.3).

By comparing tables 4.2 and 4.3, it can be concluded that in a DETEX plot with excitation in the $\Delta v = 0$ band, the fluorescence signal in the $\Delta v = 1$
Table 4.2: The relative intensities calculated from the data in [8] in the $\Delta v = 1$ band in a detex plot, after excitation in the $\Delta v = 0$ band at $T = 500$ K, scaled to an intensity of 1 for $v' = 1$.

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Table 4.3: The relative intensities of emission in the $\Delta v = 1$ at $T = 500$ K for a regular emission or absorption spectrum, scaled to an intensity of 1 for $v' = 1$, based on [8].

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</table>

band will have less interference from rotations of other upper levels than in an ordinary absorption or emission spectrum of the $\Delta v = 1$ band. Therefore, it will be easier to determine the wave numbers of the transitions from such a LIF experiment.

This same procedure can be used to isolate rotational spectra from different upper levels by choosing the right combination of excitation and detection band. It can be concluded that detex plots resulting from LIF measurements are an accurate method to determine the wave numbers of rotational transitions of various upper levels. This is particularly helpful in dense spectra such as the InBr spectrum.

Determining $B_{A0}$ from the R-branch data of the $\Delta v = 0$ transition

In the same way as described in the previous section, the wave numbers of transitions in the R-branch of the transition from the A-state, vibrational level
0 to the ground state, vibrational level 0, have been determined. The results are listed in table 4.4.
Table 4.4: Wave numbers of the R-branch rotational transitions of the transition between the electronic A-state vibration 0 and the ground state vibration 0 for InBr\textsuperscript{79} according to the measurement in this report and according to [7]

<table>
<thead>
<tr>
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<th>InBr\textsuperscript{79} (cm\textsuperscript{-1})</th>
<th>[7] (cm\textsuperscript{-1})</th>
<th>$J$, R-branch</th>
<th>InBr\textsuperscript{79} (cm\textsuperscript{-1})</th>
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</table>
4.4 Results

Using this information, one can make a graph of $J$ versus wave number for this specific transition. It can then be fitted with a formula describing the relationship between $J$ and the wave number for the R-branch:

\[
\nu(J) = \nu_0 + J^4(D'' - D') + J^3(2D'' - 6D') + J^2(-B'' + B' - D'' - 13D') + J(-B'' + 3B' - 12D') + 2B' - 4D'.
\]

In this equation, $\nu(J)$ denotes the wave number of the R-branch transition for that particular rotational quantum number $J$. $\nu_0$ is the wave number of the vibronic transition (incorporating the electronic and vibrational transition energy). $B$ is the rotational constant where a single prime denotes the upper state and a double prime the lower state.

This aforementioned graph for the most comprehensive data set we have, which is from [7] up to $J = 76$ and data from our own measurement up to $J = 130$, is presented in figure 4.12. The R-branch data is fitted with equation 4.1. From microwave measurements [7] it is known that the ground state rotational constant $B'' = 0.0557099$ cm$^{-1}$ and the ground state anharmonicity $D'' = 1.42 \cdot 10^{-8}$ cm$^{-1}$. From the fit various constants were determined: the rotational constant of the lowest vibrational level of the A-state $B' = B_{A0} = 0.058410 \pm 0.000002$ cm$^{-1}$ and the anharmonicity $D' = D_{A0} = 1.59 \cdot 10^{-8} \pm 1 \cdot 10^{-10}$ cm$^{-1}$.

To check the consistency, also the P-branch data was fitted. The values found were $B' = B_{A0} = 0.05842 \pm 0.00001$ cm$^{-1}$ and $D' = D_{A0} = 1.55 \cdot 10^{-8} \pm 5 \cdot 10^{-10}$ cm$^{-1}$. These results are consistent with the data presented above, however less accurate, due to the smaller and noisier data set.

Determining $B_{A1}$ from the R-branch data of the $\Delta v = 1$ transition

To determine the rotational constant of the first vibrational level of the A-state (and its anharmonicity), the DETEX plot acquired by exciting in the $\Delta v = +1$ band has to be examined. It is shown in figure 4.13.

After isolating the R-branch of the $\Delta v = +1$ in the data set, a graph of the relative intensity of the R-branch signal versus the wavelength is obtained, as is shown in figure 4.14.

From this graph, the wave numbers of the peaks were obtained, resulting in a sequence of identified peaks which are listed in table 4.5.
Figure 4.12: Graph of wave number versus rotational quantum number for the R-branch of the 0-0 transition from the A-state to the ground state. The red line running through the data points is a fit based on 4.1.
**Figure 4.13:** The DETEX plot of the sr-LIF measurement on InBr. Excitation was in the $\Delta v = +1$ band. From left to right the bands $\Delta v = -3$ through $\Delta v = +2$ are shown. Each vibration band consists of three different branches that are explained by the different combinations of rotational transitions in the P-branch and R-branch for excitation and detection.
Figure 4.14: Graph of the intensity of the R-branch of the $\Delta v = +1$ vibrational transition versus the wave number versus at which it occurred.
Table 4.5: Wave numbers of the R-branch rotational transitions of the transition between the electronic A-state vibration 1 and the ground state vibration 0 for InBr, for both isotopes. Since the assignment of these levels is unknown, they are simply numbered with index $i$. Note that in the first entry in the table the wave number of the band start is stated. Due to the noise levels, it can be quite difficult to identify and follow sequences of peaks and in this case the confidence in the accuracy of the first column of peaks is bigger.

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4.4 Results

Due to the noise levels, it can be quite difficult to identify and follow sequences of peaks and in this case the confidence in the accuracy of the first column (Isotope 1) of peaks is higher. Therefore, this column will be used to calculate $B_{A1}$ and $D_{A1}$. Of course a major obstacle in achieving this goal is the assignment of the rotational quantum number (or lack thereof). To make a best guess — because that is what it will be — the fit with formula 4.1 is performed for various values of $i$. The various fitted parameters are evaluated and compared to the values that are expected. This is shown for the wave number of $\nu(0)$, as is shown in figure 4.15.

![Figure 4.15](image)

**Figure 4.15:** Graph of the wave number of $\nu(0)$ as determined from the fit based on 4.1 versus various values for $J-i$. The red line running through the data points is the actual $\nu(0)$ as directly measured from the data. The position of the bandhead suggests that $J = i + 38$ provided the best fit.

The same is done for the rotational constant $B_{A1}$ as is shown in figure 4.16 and for $D_{A1}$ as is shown in figure 4.17.

The best value for $J - i$ is determined by assuming that the value found for the fitted $\nu(0)$ should be close to the measured value. For the values of $B_{A1}$ and $D_{A1}$ it is assumed that they are probably close to the values found for $B_{A0}$ and $D_{A0}$.

The best fit (for $J = i + 38$) is shown in figure 4.18. It leads to $B_{A1} = 0.05809 \pm 0.00005$ cm$^{-1}$ and $D_{A1} = 1.8 \cdot 10^{-8} \pm 0.2 \cdot 10^{-8}$ cm$^{-1}$. In this case the assignment for $J$ is $J = i + 38$. The uncertainty band of these numbers is
determined by the change as a consequence of a mis-assignment of $J$ of $\pm 1$. This would lead to a relatively small change in $B_{A1}$, but it would lead to a significant change in $D_{A1}$ of the order of 10%.

**Determining $B_{X1}$ from the R-branch data of the $\Delta v = -1$ transition**

To determine $B_{X1}$, the first method to be tried was by looking at the DETEX plot obtained by exciting via the $\Delta v = -1$ transition. This plot is shown in figure 4.19. The problem with this approach is that there are simply too many different vibrational transitions with a high intensity in this particular $\Delta v$-branch. This fact makes it virtually impossible to distinguish the individual rotational transitions on close inspection, because there are simply too many sets of lines that are mixed together. What would have been nice about this method is that it couples the $v = 1$ level of the electronic ground state with the $v = 0$ level of the A-state, of which the rotational constants are known to a high degree of accuracy.

Another option to obtain $B_{X1}$ is to use the $\Delta v = 0$ DETEX plot as was shown in figure 4.9. Since $B_{A1}$ was already determined in the previous section, we can
4.4 Results

Figure 4.17: Graph of the value of $D_{A1}$ as determined from the fit based on 4.1 versus various values for $J-i$. The red line running through the data points is $D_{A0}$ as determined in the previous section.

Figure 4.18: Graph of wavenumber versus rotational quantum number for the R-branch of the transition from the A-state vibrational level 1 to the ground state vibrational level 0. The red line running through the data points is a fit based on equation 4.1.
Figure 4.19: The detex plot of the sr-LIF measurement on InBr. Excitation was in the $\Delta v = -1$ band. From left to right the bands $\Delta v = -3$ through $\Delta v = +2$ are shown. Each vibration band consists of three different branches that are explained by the different combinations of rotational transitions in the P-branch and R-branch for excitation and detection.

use this plot to couple the $v = 1$ level of the ground state with the $v = 1$ level of the A-state.

Just like in the previous section, the applicable set of data is isolated. A graph of the relative intensity of the R-branch signal versus the wavelength is obtained, as is shown in figure 4.20.

From this graph, the peaks were identified, resulting in a sequence of identified peaks which are tabulated in table 4.6.
Figure 4.20: Graph of the intensity of the R-branch of the $\Delta v = +1$ vibrational transition versus the wave number of the fluorescence.
Table 4.6: Wave numbers of the R-branch rotational transitions of the transition between the electronic A-state vibration 1 and the ground state vibration 1 for InBr, for both isotopes. Since the assignment of these levels is unknown, they are simply numbered with index $i$. Note that in the first entry of the table is the wave number of the band start. Due to the noise levels, it can be quite difficult to identify and follow sequences of peaks and in this case the confidence in the accuracy of the first column of peaks is better.

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</tr>
<tr>
<td>42</td>
<td>30.9727</td>
<td>53.2332</td>
<td>99</td>
<td>63.5859</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>31.4258</td>
<td>53.7391</td>
<td>100</td>
<td>64.2284</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>31.8379</td>
<td>54.2879</td>
<td>101</td>
<td>65.0137</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>32.2910</td>
<td>54.7742</td>
<td>102</td>
<td>65.7598</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>32.7461</td>
<td>55.3875</td>
<td>103</td>
<td>66.4844</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>---</td>
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<td>-----</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>33.1777</td>
<td>55.9363</td>
<td>104</td>
<td>67.1465</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>33.6113</td>
<td>56.4656</td>
<td>105</td>
<td>67.8711</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>34.1484</td>
<td>57.0144</td>
<td>106</td>
<td>68.6563</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>34.5820</td>
<td>57.5223</td>
<td>107</td>
<td>69.4238</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>35.0547</td>
<td>58.0281</td>
<td>108</td>
<td>70.1484</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>35.5098</td>
<td>58.5789</td>
<td>109</td>
<td>70.9551</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>35.9844</td>
<td>59.2977</td>
<td>110</td>
<td>71.6798</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>36.5000</td>
<td>59.8250</td>
<td>111</td>
<td>72.4453</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>36.9941</td>
<td>60.4598</td>
<td>112</td>
<td>73.2949</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>37.4492</td>
<td>61.0301</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To make a best guess the fit with formula 4.1 is performed for various values of $i$. The various fitted parameters are evaluated and compared to the values that are expected for them. This is done for the wave number of $\nu(0)$, as is shown in figure 4.21.

![Figure 4.21](image)

**Figure 4.21:** Graph of the wave number of $\nu(0)$ as determined from the fit based on equation 4.1 versus various values for $J - i$. The red line running through the data points is the actual $\nu(0)$ as directly measured from the data.

The same is done for the rotational constant $B_{X1}$ as is shown in figure 4.22 and for $D_{X1}$ as is shown in figure 4.23.

The best value for $J - i$ is determined by assuming that the value found for the fitted $\nu(0)$ should be close to the measured value. For the values of $B_{X1}$ and $D_{X1}$ it is assumed that they are probably close to the values found for $B_{X0}$ and $D_{X0}$.

The best fit (for $J = i + 56$) is shown in figure 4.24. It leads to $B_{X1} = 0.056677 \pm 0.00002$ cm$^{-1}$ and $D_{X1} = 2.83 \cdot 10^{-8} \pm 0.01 \cdot 10^{-8}$ cm$^{-1}$. In this case the assignment for $J$ is $J = i + 56$. The uncertainty band of these numbers is determined by the change as a consequence of a mis-assignment of $J$ of $\pm 1$. This would lead to a relatively small change in $B_{X1}$ and in $D_{X1}$. The value of $D_{X1}$ is surprising, because it differs significantly from $D_{X0}$.
Chapter 4. Spectrally Resolved LIF

Figure 4.22: Graph of the value of $B_{A1}$ as determined from the fit based on equation 4.1 versus various values for $J - i$. The red line running through the data points is $B_{A0}$ as determined in the previous section.

Franck-Condon Factors

Closer inspection of the DETEX plots reveals the data necessary to determine the Franck-Condon factors of various transitions, because for every excitation wave number, a fluorescence spectrum was recorded as was explained earlier. The intensity ratios of the various $\Delta v$-bands are a manifestation of the Franck-Condon factors and the population of the (vibrational) level from which the excitation took place.

By looking for an excitation wave number that only excites from a single vibrational level of the ground state and therefore to a single vibrational level of the A-state, it is possible to find a very direct representation of the Franck-Condon factors in the DETEX plots.

For the $v' = 0$ vibrational level of the A-state this was done by looking at the fluorescence spectrum after excitation at $26600 \text{ cm}^{-1}$. At this energy, only excitation from $v'' = 0$ in the ground state to $v = 0$ in the A-state is possible, so all excited molecules are in the $v' = 0$ level of the A-state. By evaluating the fluorescence spectrum taken from the $\Delta v = 0$ DETEX plot (figure 4.9) as shown in figure 4.25, it is possible to determine the relative intensities of the different

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4.4 Results

Figure 4.23: Graph of the value of $D_{X1}$ as determined from the fit based on equation 4.1 versus various values for $J - i$. The red line running through the data points is $D_{X0}$ as determined in the previous section.

decay paths, which correspond directly to the probability of that specific decay path. This probability is the Franck-Condon factor.

The relative intensities are determined from figure 4.25 by calculating the total fluorescence emission for each $\Delta v$-band by integrating the area under each emission peak and dividing it by the total emission from all $\Delta v$-bands. The Franck-Condon factors found this way are listed in table 4.7.

Table 4.7: Franck-Condon factors determined from the detex plots with excitation via $\Delta v = 0$. Theoretical values from Singh [8] are given for comparison.

<table>
<thead>
<tr>
<th>Franck-Condon factor</th>
<th>[8]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A(v = 0) \rightarrow X(v = 0)$</td>
<td>0.602</td>
</tr>
<tr>
<td>$A(v = 0) \rightarrow X(v = 1)$</td>
<td>0.289</td>
</tr>
<tr>
<td>$A(v = 0) \rightarrow X(v = 2)$</td>
<td>0.088</td>
</tr>
<tr>
<td>$A(v = 0) \rightarrow X(v = 3)$</td>
<td>0.018</td>
</tr>
<tr>
<td>$A(v = 0) \rightarrow X(v = 4)$</td>
<td>0.0046</td>
</tr>
</tbody>
</table>

The error in these values is estimated to be 2%. That brings the measured values very close to—but not exactly in—agreement with the values found
Figure 4.24: Graph of wave number versus rotational quantum number for the R-branch of the transition from the A-state vibrational level 1 to the ground state vibrational level 1. The red line running through the data points is a fit based on equation 4.1.

The same procedure was followed for the $v' = 1$ level of the A-state. The resulting graph taken at 26825 cm$^{-1}$ from the $\Delta v = 1$ excitation DETEX plot is shown in figure 4.26.

The integrated intensities of these peaks are listed in table 4.9.

Table 4.8: Relative intensities of each $\Delta v$-band as determined from 4.26.

<table>
<thead>
<tr>
<th>Fluorescence band</th>
<th>Relative emission</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta v = +2$</td>
<td>0.056</td>
</tr>
<tr>
<td>$\Delta v = 0$</td>
<td>0.118</td>
</tr>
<tr>
<td>$\Delta v = -1$</td>
<td>0.244</td>
</tr>
<tr>
<td>$\Delta v = -2$</td>
<td>0.150</td>
</tr>
<tr>
<td>$\Delta v = -3$</td>
<td>0.057</td>
</tr>
</tbody>
</table>

An interesting observation is the fact that there is emission visible in the $\Delta v = +2$-band, since photons emitted in that band can not originate from molecules in the $v' = 1$ level of the A-state. This is caused by higher vibrational
4.4 Results

Figure 4.25: Graph of the fluorescence recorded after excitation at 26600 cm$^{-1}$. At this wave number, all excited molecules are at $v' = 0$ in the A-state.

transitions, such as the 3-4 and 4-5 transition. This means that a small part of the emission recorded in figure 4.26 does not originate from the desired $v' = 1$ level. This has consequences for the accuracy of the Franck-Condon factors determined from this data. Since about 5.6% of the emission is visible in the $\Delta v = +2$-band, the margin of error for the Franck-Condon factors found is estimated at 10%. The Franck-Condon factors determined from this data are listed in table 4.9. Again, the values found in these experiments are close to, but not in exact agreement with the values found in [8].

Table 4.9: Franck-Condon factors determined from the DETEX plots with excitation via $\Delta v = +1$. Theoretical values from Singh [8] are given for comparison.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Franck-Condon factor</th>
<th>[8]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A(v = 1) \rightarrow X(v = 0)$</td>
<td>0.375</td>
<td>0.3273</td>
</tr>
<tr>
<td>$A(v = 1) \rightarrow X(v = 1)$</td>
<td>0.118</td>
<td>0.1538</td>
</tr>
<tr>
<td>$A(v = 1) \rightarrow X(v = 2)$</td>
<td>0.244</td>
<td>0.2863</td>
</tr>
<tr>
<td>$A(v = 1) \rightarrow X(v = 3)$</td>
<td>0.150</td>
<td>0.1562</td>
</tr>
<tr>
<td>$A(v = 1) \rightarrow X(v = 4)$</td>
<td>0.057</td>
<td>0.0555</td>
</tr>
</tbody>
</table>
Figure 4.26: Graph of the fluorescence recorded after excitation at 26825 cm$^{-1}$. At this wave number, most excited molecules are at $v' = 1$ in the A-state.

Determination of Band Head Wave Numbers

In most measurements various band heads are superimposed on each other. This makes it difficult to accurately determine their respective wave numbers. This problem makes it more difficult to accurately simulate spectra. In DETEX plots, more band heads are separately visible because of the resolution of both the excitation and detection wave number. One can simply choose the most suitable $\Delta v$-band to determine its wave number.

Different detection bands can be used to determine wave numbers of band heads with low intensity that are super positioned on the rotational structure of a transition with high intensity. In this section the wave numbers of the 4-4, 5-5 and 6-6 band heads will be determined. Often, absorption or emission spectra are evaluated to determine the wave number of transitions. In these spectra the rotation band heads of the different vibrational levels may overlap. This is the case for InBr. In [8] the locations of the band heads of vibrational transitions have been determined. From these evaluations it follows that in the $\Delta v = 0$ band, the 4-4, 5-5 and 6-6 transitions are superimposed on other strong transitions such as the 0-0 transition. Therefore it is difficult to determine the exact
locations of these band heads. For the determination of band heads involved in superpositions, an sr-LIF experiment can be analyzed to more accurately determine the location of the band heads.

The procedure is based on evaluating the DETEX plots. The band head identification will be based on the following two factors. One is the wave number where the band head is expected according to literature. The other is the relative theoretical intensity of the emission in different $\Delta v$ bands. This last aspect is used to determine in which $\Delta v$ band to search. In the case of examining the 4-4, 5-5 and 6-6 transition of InBr this is the $\Delta v = 2$ band. The relative intensity of the different bands is also used to identify peaks. The intensity detected in $\Delta v$ band depends on the population of the upper level and the Franck-Condon factor of the transition. The population of the upper level is created by absorption. The population of the upper level therefore depends on the Franck-Condon factor for the excitation and on the population of the lower level. An illustration of the basic principles behind the method is presented in figure (4.27).

Vibrational level 0 as well as vibrational level 1 of the excited A-state have no emission in the $\Delta v = 2$ band. Therefore, after excitation in $\Delta v = 0$, the emission in the $\Delta v = 2$ band is evaluated. Upper level 4 has emission in this band; the 4-2 transition does emit in this band. Vibration levels 2 and 3 of the A-state may also have emission in the $\Delta v = 2$ band, however the Franck-Condon factors of the 2-2 and 3-3 transitions are very small. This means that the vibration levels 2 and 3 of the A-state will have a very small population, therefore the 2-0 and 3-1 transition in the $\Delta v = 2$ band are not expected to be strong.

Although on the detection axis, the wave number of the 4-2 transition is shown, the wave number on the excitation axis is the wave number at which the 4-4 excitation has taken place, hence the band head of the 4-4 transition can be determined without being troubled by light from the 0 and 1 upper vibration level. The 4-2 transition can also be determined form a normal absorption or emission experiment, but in normal absorption or emission experiments it does not yield information about the 4-4 transition. Also for the 5-5 and the 6-6 transition, the $\Delta v = 2$ band can be evaluated.

In table (4.10), the predicted relative intensities of the peaks detected in the $\Delta v = 2$ band are listed. Although all the information on intensities is

\footnote{scaled to an intensity of 1 for the emission of upper level 0 in the $\Delta v = 0$ band}
Figure 4.27: The intensity detected in \( \Delta v \) band depends on the population of the upper level and the Franck-Condon factor of the transition. The population of the upper level is created by absorption. The population of the upper level therefore depends on the Franck-Condon factor in the excitation and the population of the lower level. In the figure the thickness of arrow pointing up symbolizes the intensity of the absorption. It determines the population of the upper level, and it is determined by the population of the lower level and the Franck-Condon factor of the excitation. The thickness of the arrows pointing down symbolizes the detected intensity of the transition in the specified \( \Delta v \) band. The arrow pointing from upper level vibration 0 to lower level vibration 0 is thicker than the arrow pointing from upper level 1 to lower level 1. In the spectrum, these transitions are superimposed in the \( \Delta v = 0 \) band, and therefore it is difficult to identify the properties of the 1-1 transition. In the \( \Delta v = 1 \) band, there is no emission from the upper level vibration 0, therefore it is easier to identify emission from upper level vibration 1 in this band.

available from the DETEX plots, it is difficult to visualize the intensity profile from them. Therefore, the part of the DETEX plot that shows the \( \Delta v = 2 \) band is spectrally integrated. The resulting partial spectrum shows the intensity of emission in the \( \Delta v = 2 \) band after absorption in the \( \Delta v = 0 \) band as a function of the wave number of absorption. The result is shown in figure 4.28. In table 4.11 the wave number of the identified band heads is displayed.

When sr-LIF measurements are partially integrated, they give spectra like
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**Table 4.10:** The relative intensities of emission in the $\Delta v = 2$ band depending on the upper level $v'$, after excitation in the $\Delta v = 0$ band. The data is scaled to a value of 1 for the emission of upper level 0 in the $\Delta v = 0$ band.

<table>
<thead>
<tr>
<th>transition</th>
<th>relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v' = 0 \rightarrow v'' = -2$</td>
<td>-</td>
</tr>
<tr>
<td>$v' = 1 \rightarrow v'' = -1$</td>
<td>-</td>
</tr>
<tr>
<td>$v' = 2 \rightarrow v'' = 0$</td>
<td>0.001</td>
</tr>
<tr>
<td>$v' = 3 \rightarrow v'' = 1$</td>
<td>0.001</td>
</tr>
<tr>
<td>$v' = 4 \rightarrow v'' = 2$</td>
<td>0.007</td>
</tr>
<tr>
<td>$v' = 5 \rightarrow v'' = 3$</td>
<td>0.014</td>
</tr>
<tr>
<td>$v' = 6 \rightarrow v'' = 4$</td>
<td>0.016</td>
</tr>
<tr>
<td>$v' = 7 \rightarrow v'' = 5$</td>
<td>0.014</td>
</tr>
<tr>
<td>$v' = 8 \rightarrow v'' = 6$</td>
<td>0.011</td>
</tr>
</tbody>
</table>

**Table 4.11:** The wave number of the band heads of the $\Delta v = 0$ absorption spectrum. A systematic error resulting from a shift of the excitation axis as a whole should be taken into account on top of the error indicated in the table.

| $v'$ | wavenumber (cm$^{-1}$) | $|S|$ (cm$^{-1}$) | difference (cm$^{-1}$) |
|------|-------------------------|------------------|------------------------|
| 4    | 26605.77 ± 0.07          | 26605.47         | 0.30                   |
| 5    | 26603.59 ± 0.06          | 26603.78         | -0.19                  |
| 6    | 26599.70 ± 0.04          | 26599.66         | 0.04                   |
| 7    | 26593.65 ± 0.06          | 26593.61         | 0.04                   |
| 0    | 26599.00 ± 0.04          | 26599.00         | 0.00                   |

the ones in figure (4.28). This type of spectra can be made for detection in different $\Delta v$ bands.

By making the right choice of excitation and detection bands, the signal from the desired upper level can be found with as little as possible interference from other transitions. Therefore the wave numbers of the transitions involved in superposition in a normal absorption or emission experiment, can be more accurately determined from a sr-LIF experiment.

In this section a calculation has been made to calculate the intensities emitted by the different upper levels in the different $\Delta v$ bands based on the Franck-Condon factors. The other way around, this principle can be used to calculate Franck-Condon factors based on the relative intensities of the different upper
levels in integrated spectra of the different $\Delta v$ bands. This is because by comparing the shape of the different integrated spectra insight can be gained on the contributions of other upper levels and the effect of redistribution.

4.4.2 InBr Vapor with Background Gas

Spectrally resolved measurements were also performed for the $\Delta v = 0$ excitation transition in InBr vapor with 2.5 mbar as a background gas. Figure 4.29 shows the DETEX plot obtained from measurements.

Comparing this DETEX plot with the DETEX plot of the tube without the background gas, it is observed that the vibrational bands look very different when the background gas is present. The rotational branches are not visible anymore; each vibrational band is now represented by a very wide, unresolved
Figure 4.29: The DETEX plot of the sr-LIF measurement on InBr with 2.5 mbar of Argon as a background gas. Excitation was in the $\Delta v = 0$ band. From left to right the bands $\Delta v = -3$ through $\Delta v = +2$ are shown. The vibrational bands do not show a separation into rotational branches as opposed to the DETEX plot obtained without the background gas.

From this it is concluded that the rotational redistribution processes\(^6\) are much faster than the optical decay processes. The overall species density in the tube is higher due to the presence of the Argon. The rotational redistribution visible in figure 4.29 is caused by the collisions with Argon.

Rotational branches are not visible anymore, but vibrational bands are still clearly visible. The intensity ratios of these vibrational bands appear about the same as in the DETEX plot of the tube without the background gas. To confirm this, the relative intensities of the different vibrational bands were determined, in exactly the same way as in the previous section and they confirm that no vibrational redistribution has occurred.

\(^6\)i.e. the processes that redistribute the excited molecules over all the rotational levels in the excitation space of InBr. In other words, the processes that thermalize the distribution over all rotational states.
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The relative intensities of the various $\Delta v$-bands at 26600 cm$^{-1}$ for the determination of the Franck-Condon factors are listed in table 4.12.

Table 4.12: Franck-Condon factors determined from the DETEX plots compared with the relative intensities in the presence of a buffer gas.

<table>
<thead>
<tr>
<th>$\Delta v$</th>
<th>InBr vapor</th>
<th>InBr vapor + Argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta v = +2$</td>
<td>0.001</td>
<td>0.000</td>
</tr>
<tr>
<td>$\Delta v = +1$</td>
<td>0.003</td>
<td>0.009</td>
</tr>
<tr>
<td>$\Delta v = 0$</td>
<td>0.602</td>
<td>0.621</td>
</tr>
<tr>
<td>$\Delta v = -1$</td>
<td>0.289</td>
<td>0.267</td>
</tr>
<tr>
<td>$\Delta v = -2$</td>
<td>0.088</td>
<td>0.084</td>
</tr>
<tr>
<td>$\Delta v = -3$</td>
<td>0.018</td>
<td>0.019</td>
</tr>
</tbody>
</table>

4.4.3 Capacitively Coupled Plasma

The measurements discussed in this section were performed with the same tube as in the previous section, containing InBr powder and Argon at a pressure of 2.5 mbar. To make a plasma, the RF amplifier discussed in chapter 3 was used at 13.56 MHz. It was connected to the tube via an L-type matching network. The measurements were performed with the RF power set to 15 W.

To allow the plasma to, measurements were started at least 1 hour after the start of the plasma. All other settings of the trigger system, the laser and the camera used to perform these experiments were identical to the experiment in the previous section.

The DETEX plot obtained from a burning plasma is shown in figure 4.30.

Comparing figure 4.30 and figure 4.29 reveals no significant differences. From this it is concluded that for these conditions, the impact of the plasma on the fluorescence processes is very small, i.e. below the detection limit of our setup.

4.4.4 Inductively Coupled Plasma

For studies of the InBr plasma lamp, the first step was to find out at what locations in the lamp LIF-experiments are possible.

The most suitable location was picked and a DETEX plot was made for this location. No LIF-signal could be observed in the center of the lamp, but in other sections of the lamp the LIF-signal could be observed. These sections
were just outside the bright center of the lamp, at the point where the white color faded to blue. Figure 4.31 illustrates the approximate location of the LIF measurements in this lamp.

This fact that no LIF signal could be observed in the center of the lamp leads to the question whether the LIF-signal was actually not there, or just not visible because the lamp masked the fluorescence by its own emissions. To gain insight in this matter, the intensity fluctuations of the plasma emission in the center of the lamp was compared to the intensity of the fluorescence signal at the sections where it could be observed. This comparison gave rise to the conclusion that the LIF signal is in fact not present at the center of the lamp. If it were there, it would have been observed, since the fluorescence signal elsewhere in the lamp exceeds the fluctuations of the plasma by a factor $\sim 5$.

From this the conclusion is drawn that all the InBr in the center of the lamp is completely dissociated, so all molecular contributions to the spectrum
 originating from the edge of the plasma, where (3-particle) association processes can compete with the dissociation process, due to the lower plasma density. This also explains the strong atomic character of an inductive InBr lamp.

A DETEX plot was created for the section of the lamp where the LIF signal could be observed. Figure 4.32 shows this plot.

The uninterrupted diagonal line in the DETEX plot is an interesting artefact. It is caused by scattered light from the laser and therefore this line indicates the position where the detection wave number is equal to the excitation wave number.
Another important observation is that all transitions, both A-X and B-X transitions, start at the same excitation wave number. This is different from what was observed in all other measurements. It indicates that in this situation, vibrational redistribution plays an important role. Furthermore, it is noted that the A-X emission at $\Delta v = +1$ is more intense than the emission at $\Delta v = 0$. This is an unexpected result as well, because the excitation of the laser produces population in $v' = 0$. Somehow, more fluorescence appears at photon energies higher than the energy of the photons supplied for excitation by the laser.

Similar to the measurements with the background gas, the rotational splitting
is no longer visible, which is unsurprising.

The most important observation though, is that emission from the B-state occurs when excitation is to the A-state. This means that somehow, molecules are transferred from the A-state to the B-state. The emission seen in the B-bands is not just plasma emission, as it is not present when the laser energy is lower than $\sim 26600 \text{ cm}^{-1}$—and thus no laser excitation of the A-state takes place—but it is also clear that just the presence of the laser beam itself is not enough to create the emission from the B-state from the same observation.

It cannot be determined exactly how population is transferred to the B-state. Direct collisional transfer cannot be ruled out and neither can increased plasma emission due to increased population of the A-state. Some collisional process could populate a higher excited level of InBr from the A-state which in turn decays to the B-state.

### 4.5 Conclusions

For the correct assignment and interpretation of rovibronic spectra, sr-LIF measurements have a great advantage compared to normal emission or absorption spectra. This advantage is that there is a wave number axis for both the emission wave number as well as for the absorption wave number in the resulting detex plot. Normal emission or absorption spectra only have one of the two. The newly introduced detex plot is a very insightful way of representing the data found with this measuring technique. It also enables exploration of finer details of molecular spectra.

In a detex plot, transitions that interfere with each other in a normal absorption or emission spectrum can be separated. This splitting may occur for rotational transitions as well as for vibration transitions. Due to this splitting, in a detex plot, transitions with a low intensity can be studied with less interference from other transitions with higher intensity.

In this thesis, the splitting of rotational branches has been used to extend a list produced by [7], containing the wave numbers at which the rotational transition of the electronic A-state vibrational level 0 to the ground state vibrational level 0 of InBr occurs. Almost 30 extra P-branch transitions have been identified.

The list of wave numbers of rotational transitions that was found to expand the list in [7] has been used to determine the rotational constant of $v = 0$ of the
A-state and its anharmonicity, \( B_{A0} \).

For the transition from \( v = 1 \) of the A-state to \( v = 0 \) of the ground state, a list of wave numbers of rotational transitions was also produced by looking at the DETEX plot for excitation via the \( \Delta v = +1 \) band. This list is incomplete, i.e. the beginning is missing. To still assign the correct rotational quantum number \( J \) to the transitions found, comparisons to the known values of such as \( B_{A0} \) were made. After this assignment, the value of the rotational constant \( B_{A1} \) of the \( v = 1 \) level of the A-state and its anharmonicity were determined. Similarly, \( B_{X1} \) and its anharmonicity were determined. The constants determined from all these experiments are listed in table 4.13. The values found and the branch that has the band head are in agreement with the fact that \( B' > B'' \) as was expected in chapter 2.

### Table 4.13: Rotational constants and anharmonicities determined in this work.

<table>
<thead>
<tr>
<th>constant</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B_{A0} )</td>
<td>( 0.058410 \pm 0.000002 \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>( D_{A0} )</td>
<td>( 1.59 \cdot 10^{-8} \pm 0.01 \cdot 10^{-8} \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>( B_{A1} )</td>
<td>( 0.05809 \pm 0.00005 \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>( D_{A1} )</td>
<td>( 1.8 \cdot 10^{-8} \pm 0.2 \cdot 10^{-8} \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>( B_{X1} )</td>
<td>( 0.056677 \pm 0.00002 \text{ cm}^{-1} )</td>
</tr>
<tr>
<td>( D_{X1} )</td>
<td>( 2.83 \cdot 10^{-8} \pm 0.01 \cdot 10^{-8} \text{ cm}^{-1} )</td>
</tr>
</tbody>
</table>

Franck-Condon factors for vibrational transitions from \( v = 0 \) and \( v = 1 \) of the A-state of InBr to the ground state were determined by comparing the intensities of the various vibrational bands in the appropriate DETEX plots.

In this work, the splitting of vibrational transitions has been used to determine the wave number at which the band heads of the 4-4, 5-5 and 6-6 vibrational transition between the electronic A-state and the ground state of InBr occur. In a normal absorption or emission spectrum the much stronger 0-0 transition is located in the same wave number range. This makes the determination of the location of the 4-4, 5-5 and 6-6 band head nearly impossible or inaccurate at best without the DETEX plots.

In the DETEX plot, the \( \Delta v = +2 \) band emission has been used to determine at which wave number emission from vibrational levels 4, 5 and 6 of the electronic A-state occur. Since the excitation of InBr has been in the \( \Delta v = 0 \) band, the wave number on the excitation axis can be used to determine the band heads.
Chapter 4. Spectrally Resolved LIF

of the 4-4, 5-5 and 6-6 vibrational transitions.

Also, DETEX plots were made of not just the InBr vapor, but vapor in combination with a background gas, of 2.5 mbar of Argon. In this situation, rotational redistribution due to the increased collision rate was shown to be significant compared to optical relaxation. This redistribution obscured the rotational branches, transforming each $\Delta v$ band into a single smeared out shape.

Additionally, a capacitively coupled plasma was produced in the tube with InBr and Argon at a power of $\sim$10 W. The capacitively coupled plasma yielded similar data in a DETEX plot.

When a LIF experiment was attempted for an inductively coupled plasma, no LIF signal was visible in the center of the discharge. From this observation, the conclusion is that all the InBr in the center of the lamp is completely dissociated. All molecular contributions to the spectrum originate from the edge of the plasma, where association processes can compete with the dissociation process, due to the lower plasma density. The high degree of dissociation also explains the strong atomic character of an inductive InBr lamp.

However, when a DETEX plot was produced of the edge of an inductively coupled plasma at $\sim$100 W, some striking differences were noticed. Not only could we observe rotational redistribution as in the low power plasma, but also a significant amount of vibrational redistribution was visible, as well as some electronic redistribution, i.e. from the A- to the B-state.

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5

Time Resolved LIF

5.1 Introduction

The measurements presented in this chapter were performed by the setup described in chapter 3 on page 53. The time resolved decay data was detected by the photomultiplier tube and recorded by the multichannel scaler.

Generally —for rovibronic transitions— it is assumed that the decay time is independent of the rovibrational state and thus only determined by the electronic transition involved. To determine the validity of this assumption for InBr, an experiment was done, in which decay time as a function of the rovibrational state of the molecule was recorded.

5.2 Theory

In a time resolved LIF (tr-LIF) experiment, the time dependence of the LIF signal from the upper level is studied. To be able to assign the measured time dependence to a specific upper level, it is important that there is no redistribution. If rotational and/or vibrational redistribution does occur, the upper level is no longer uniquely determined.

A time-resolved(tr)-LIF experiment is described as follows. First there is absorption of laser light by the studied species; in this case InBr. For an optically
Chapter 5. Time Resolved LIF

thin medium, the absorption is described by the equation 5.1 [1]:

$$\frac{dN_n}{dt} = I_\nu \frac{\lambda^2}{8\pi} A_{nm} \frac{g_n}{g_m} g(\nu - \nu_0) N_m,$$

(5.1)

where $I_\nu$ is the number of photons of frequency $\nu$ per unit area per unit time, $\lambda$ is the wavelength, $A_{nm}$ is the Einstein A-coefficient. The number of specimen in the lower state $m$ is designated $N_m$ and $g_n$ and $g_m$ denote the degeneracy of the upper and lower level respectively and $g(\nu - \nu_0)$ is a normalized line shape.

For the intensity of an emission line, two aspects are important. The first one is the number of molecules ($N_n$) in the upper state ($n$), the second is how likely it is that they will undergo a transition to a lower state ($m$). In a formula this is:

$$I_{em}^{nm} = N_n A_{nm}, \text{ with}$$

(5.2)

$$A_{nm} = \frac{64\pi^4 \nu_{nm}^3}{3h} \frac{\sum |R_{nm}|^2}{g_n}.$$  

(5.3)

In this equation, $A_{nm}$ is the Einstein transition probability of spontaneous emission. The Einstein transition probability of spontaneous emission is the chance that atoms in the initial state $n$ carry out a transition to $m$. The summation $\sum |R_{nm}|^2$ is the sum of the transition probabilities ($|R|^2$) of the transitions between the upper states $n_i$ and the possible lower states $m_k$, where the indices are simply used to enumerate the respective multiplicities of the level under investigation. The factor $g_n$ is the degeneracy of the upper level. The Einstein transition probability of spontaneous emission $A$ depends on the transition probability $|R|^2$.

Typically the laser pulse that causes the absorption is short with respect to the decay time of the studied species\(^1\), and the absorption may be considered as instantaneous. After the laser pulse has stopped, the molecules in the upper level have a probability to make a transition to a lower level, emitting a photon in the process. It is assumed that the studied gas is optically thin, which means that the light emitted within the gas is not significantly reabsorbed in the gas. The population of a level decreases in time according to equation (I,58) in [1] as follows:

$$N_n(t) = N_n(0)e^{-(\sum_m A_{nm})t}.$$  

(5.4)

\(^1\text{LIF measurements with long laser pulses can also be performed. For these experiments other equations should be used [1]. In this case the duration of the laser pulse ($\tau \ll \frac{1}{\lambda}$).} \)
In this equation, the upper level is designated by \( N_n \) and \( A_{nm} \) indicates the Einstein \( A \) value for a transition from state \( n \) to state \( m \).

If it is assumed that for all transitions from the upper level \( n \) a photon is emitted, then the signal emitted in a time interval \( \Delta t \) is \((N_{\text{begin}} - N_{\text{end}})\). The detected signal as a function of time is as follows:

\[
I_n = \frac{d}{dt} N_n = N_n^0 \sum_m A_{nm} e^{-(\sum_m A_{nm})t}. \tag{5.5}
\]

Another way to derive this formula is by taking equation (5.2) and putting in the time dependent population \( N_n \) from equation (5.4). The summation is over the Einstein transition probabilities \( A_{nm} \) of all possible transitions to lower levels \( m \) from upper level \( n \).

According to equation (5.3) this summation is proportional to \( \Sigma |R_{nm,k}|^2 \): the transition probabilities of the levels. The factor \( \frac{\Sigma |R_{nm,k}|^2}{d_n} \) can be expressed as a product of the transition probabilities of the electronic transition \(|R_{e,m}^n|^2\), the vibrational transitions (Franck-Condon factor: \( FC_{n,m_i} \)) and the rotational transitions (Hönl-London factor: \( HL_{n,m_i} \)):

\[
\frac{\Sigma |R_{nm,k}|^2}{d_n} = \frac{\Sigma |R_{e,m}^n|^2 FC_{n,m_i} HL_{n,m_i}}{d_n}. \tag{5.6}
\]

The multiplicity \( g_n \) is an aggregate of the multiplicity of the electronic, vibrational and rotational states:

\[
g_n = g_{ne} g_{nv} g_{nr}. \tag{5.7}
\]

However, \( g_{ne} \) is the same for all rovibrational transitions within an electronic band and can therefore be accounted for by a constant. The degeneracy of the vibrational levels \( (g_{nv}) \) is unity. The degeneracy of the rotational transition \( g_{nr} \) of the level is \( 2J + 1 \) and is equal to the multiplicity that results from the Boltzmann distribution.

Since all possible transitions from the upper level to all allowed lower levels are considered, the sum rule can be applied to the Franck-Condon factors as well as the Hönl-London factors. This results in the following equation:

\[
\sum_m A_{nm} \propto \frac{|R_{e,m}^n|^2}{g_{ne}}. \tag{5.8}
\]
In this equation $|R_{em}^2|$ denotes the transition probability of the electronic transition, with $g_{ne}$ the multiplicity of the considered electronic transition. The former factor is assumed to be constant, following the Born-Oppenheimer approximation. However, in practice, this factor can depend on the internuclear distance. With increasing rotational quantum number $J$ and/or increasing vibration number $v$, the internuclear distance changes (increases).

For equation 5.8 to be valid, the approximation has been made that the wave number $\nu$ does not change too much over the various possible transitions, so that the dependency of $A$ on $\nu$ in equation 5.3 can be approximated by replacing $\nu$ with an average $\bar{\nu}$. If this is not the case, the $\nu$ dependency has to be taken into account in the summation.

For this experiment it is assumed that the dependence on the wave number of $A$ is small enough to use an averaged $\bar{\nu}$. Also it is assumed that the change of this average wavelength over the excitation range of the tr-LIF measurements is negligible. Because the value of this averaged $\bar{\nu}$ is not determined, no absolute value for electronic transition probabilities can be determined. Also, if a change in $A$ is measured, one has to be careful about conclusions drawn from this change, because they can be partially due to a change in $\bar{\nu}$ with changing excitation wave number.

5.3 Results and Conclusions

For the time resolved LIF (tr-LIF), the detected signal is expected to follow the temporal behavior of equation 5.5. An example of a tr-LIF measurement is shown in figure 5.1. Since this figure is on a logarithmic scale, the decay time can be found by fitting a straight line.

The decay time is a property of the upper level, therefore the tr-LIF measurements have been performed for the InBr gas only, and not for the InBr-Argon mix because in that situation there is rotational redistribution due to collisions. When there is redistribution, the upper level is no longer uniquely determined, and an averaged decay time$^2$ will be measured$^3$.

To obtain the decay time for different wave numbers (i.e. different rotational

---

$^2$An average over the decay times of the populated levels weighted by their relative populations.

$^3$When there is no redistribution there will still be 2 levels contributing to the decay since excitation can occur via a P- and an R-branch transition. For this experiment this can be considered a relatively uniquely determined upper level.
quantum numbers $J$), a laser scan has been performed. For a range of excitation wave numbers the decay time has been determined. The output of these scans was stored in a large file. A program to fit the decay time from this data has been written based on the NAG\textsuperscript{4} [2] routines [3] and used to determine the decay times. The decay time as a function of wave number has been plotted in figure (5.2).

As can be seen in figure 5.2 there is substantial variation. This variation is related to the intensity of the spectrum. If the intensity is too high, the PMT might have been saturated. If the intensity is low, influence from e.g. background noise has an influence on the fitted decay time, giving a higher decay time as a result. This is illustrated in figure 5.3. Based on these criteria, some points were dropped from figure 5.2 where the measured decay times are shown.

It can be seen that the decay time decreases gradually with increasing wave number. The decay time and the Einstein coefficient of spontaneous emission are related as follows $\tau = \frac{1}{\Sigma A}$, with $\Sigma A$ the summation of the probabilities over all possible paths. For the rotations and the vibrations, their respective sum

\textsuperscript{4}The Numerical Algorithms Group Ltd
rules are used. So \( \Sigma A \) can be taken equal to \( A \).

Near the band head of the 0-0 transition the decay time is: 0.66 \( \mu s \) and the corresponding \( A \)-value is: \( 1.5 \times 10^6 \) \( s^{-1} \). Over a range of 80 \( cm^{-1} \) the decay time decreases to 0.62 \( \mu s \), which is about 94% of the value in the band head.

The changes in decay time measured here are small and the noise level in these measurements is significant. However the trend visible in this data is consistent with expectations. As shown in chapter 7, collisional relaxation processes play a role at this temperature. At higher wave numbers, and therefore higher rotational quantum numbers, the internuclear distance increases. Higher internuclear distance signifies a higher transition probability in general but it also leads to a geometrically larger molecule. In other words, the collisional cross section for an InBr molecule in a highly excited rotational state, may be larger than for a ground state InBr molecule. As we have seen in chapter 7 the collisional processes are important for this molecule, so a geometrically larger molecule may well lead to a shorter decay time. In this case, the cross section for collisions would have to increase by 6% over an excitation range of 80 \( cm^{-1} \). That would mean an increase in the internuclear distance of 3%. This is not

\[ \text{Figure 5.2: The measured decay times as a function of wave number. A linear fit through the data is shown as well. The decay times measured here are a consequence of spontaneous emission as well as collisional relaxation processes.} \]
5.3 Results and Conclusions

Figure 5.3: Graph showing the correlation between the fitted decay time and the amplitude of the signal. The left hand side of the curve shows that measurements with a very small signal tend to produce a very high fitted decay time, due to the relative importance of noise. The right hand side of the curve shows that measurements with a very large signal also tend to result in a very high fitted decay time, due to saturation of the PMT.

unheard of for the stretching of a molecule [4].

On the other hand, if the effect visible in these measurements is not caused by an increased collisional de-excitation rate due to an expanding molecule, then it is most likely caused by a higher rate of spontaneous decay since a higher rotational quantum number generally leads to a higher likelihood of spontaneous emission [1], because as the molecules rotate at a higher level in the potential curve of the vibronic level, the difference in internuclear distance between the upper and lower level will naturally decrease. To explain the observations, the rate of spontaneous decay must be substantially higher than the rate for the rotational ground state as found in chapter 7, since it is now able to compete with the rate of collisional decay as discussed in chapter 7.
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References


6

Rotational Temperature Determination

6.1 Introduction

In this chapter the results of measurements discussed in previous chapters will be used to determine the rotational temperature of the plasma or vapor inside the vessel. One method used to do this—the intensity method—finds the rotational temperature from the slope of a logarithmic plot of the intensities of the rotational lines in the spectrum. Another method used to determine the rotational temperature—the fitting method—involves a fitting procedure that uses these measurements as input to determine the rotational temperature. The computer programs used to simulate and fit the spectra are discussed first.

6.1.1 Simulations

To interpret the results of our experiments and compare them to theory, a computer model was developed. When measuring rovibrational spectra, the number of calculations needed to predict the features of the spectra based on theory is quite large. For every combination of \( v' \) (the upper vibrational level) and \( v'' \) (the lower vibrational level), a P-branch and an R-branch occur; each typically consists of a few hundred transitions. For all these transitions, a spectral position as well as a (relative) intensity must be determined. In the case of InBr, groups of vibrational transitions also overlap, so line broadening effects have to be taken into account as well. Typically a few thousand calculations have to be made for each \( \Delta v \) band. To perform all these calculations efficiently, two
computer programs have been written. Both programs use spectroscopic data such as rotational constants as input parameters.

One program also takes temperature and resolution as input parameters. This program produces an absorption spectrum which can be used to predict the outcome of LIF measurements. Also, this program keeps track of the position of the transitions. It produces a list of the vibrational and rotational quantum number of the transitions that take place at each wave number. This list can be used to link properties—such as decay times—that are measured for various wave numbers to the energy levels they belong to.

The other program that has been written needs a measured spectrum as input, and determines various parameters from a non-linear least squares fit. In this thesis, this program has been used to determine the rotational temperature of the InBr vapor. The fitting method used is the Levenberg-Marquardt procedure [1].

### 6.1.2 Formulae

The formulae used for these programs are discussed in detail in the theory section. They are summarized here. The wave number of a transition is calculated as follows:

\[
\nu = T'_e - T''_e + G(v') - G(v'') + F(v', J') - F(v'', J'').
\]  

(6.1)

In this equation the single prime denotes the upper level, the double prime denotes the lower level. The component \(T_e\), the electronic energy, is given in the literature. The components \(G\) and \(F\) are calculated using [2]:

\[
G(v) = \omega_e(v + 1/2) + \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3,
\]

(6.2)

\[
F(J) = B_v J(J + 1) - D_v J^2 (J + 1)^2,
\]

(6.3)

\[
B_v = B_e - \alpha_e (v + 1/2) \quad \text{and}
\]

(6.4)

\[
D_v = D_e + \beta_e (v + 1/2).
\]

(6.5)

In these equations \(v\) is the vibrational quantum number and \(J\) is the rotational quantum number. The constants that are used can be found in literature [3] and [4]. The intensity of a transition is calculated using the following equation:

\[
I = FC'(v', v'') e^{-(G(v'') - G(v'))} e^{\frac{\hbar c}{k \nu_{\text{vib}}}} \frac{B_{v''}}{T_{\text{rot}}} S_{J'} e^{-F(v'', J'')} e^{\frac{\hbar c}{k \nu_{\text{rot}}}}.
\]

(6.6)
In this equation $F_C(v', v'')$ is the Franck-Condon factor, $S_J$ is the Hönl-London factor. The spectrum is convoluted with a Gaussian function to correct for the detection resolution, determined by the monochromator.

### 6.1.3 Simulation Procedure

The simulation procedure is used to predict the outcome of the LIF measurements. Because the shape of the spectrum changes with temperature, and also with the resolution of the monochromator, these are input parameters in the program. For the simulations, the calculation of the wave numbers and intensities is performed in a loop that runs for different vibrational quantum numbers of the upper and lower level. This loop is called the vibration loop. In the vibration loop, the value of the vibrational contribution to the wave number and the intensity are calculated. Inside each vibration loop, a rotation loop is run, doing the same for the contribution of the rotational quantum number. The vibrational contribution is calculated outside of the rotation loop, to save computing time.

Basically, the simulation program calculates a spectrum by going over all possible quantum mechanical permutations — possible within the range specified and respecting the $\Delta J = \pm 1$ selection rule — and calculating their contribution to a specific wave number.

In the rotation loop, an array containing wave numbers, intensities and a label is created for the P-branch and for the R-branch. The array index indicates the rotational quantum number of the transition. This array is called the rotation array.

The spectrum is saved in an array, called the spectrum array. As is illustrated in figure 6.1, specifying the starting wave number of the simulation ($\nu_{start}$), the bin width ($\nu_{bin}$) and the array index ($i$) defines the wave number by:

$$\nu = \nu_{start} + i \cdot \nu_{bin}. \quad (6.7)$$

The spectrum array contains two items, the intensity and a label, containing identifiers for the rotational and vibrational transition that produced the peak.

After each rotation loop, the rotation array is merged with the spectrum array. The wave number item is used to decide to which bin of the spectrum array the contents of the intensity item and the label of the rotation array have to be added.
Chapter 6. Rotational Temperature Determination

Figure 6.1: Illustration of how the simulated spectrum is stored in the spectrum array following equation 6.7. The wave number is defined by the starting wave number $\nu_{\text{start}}$, the bin width $\nu_{\text{bin}}$ and the array index $i$.

After all vibrational transitions and rotational transitions have been calculated and sorted in the spectrum array, the spectrum array is convoluted with a Gaussian function to obtain a spectrum with a detector resolution corresponding to the experiment.

The size of the bins in the spectrum array depend on the desired resolution of the spectrum. A bin size that is too large with respect to the resolution will result in unacceptably large rounding errors. If the bin size is too small, the spectrum array will be too large and this slows down the calculations significantly.

The shape of the resolution is a normal distribution. The correct bin size is calculated by the program. The criterion used is that the value of a continuous normal distribution will change less than 1% over the total width of the bin. In a formula for a standard deviation around $x_0 = 0$, this requirement is posed as
follows:
\[
\frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(x+dx)^2}{2\sigma^2}} \geq 0.99 \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{(x)^2}{2\sigma^2}}.
\] (6.8)

In this equation \(\sigma\) is the standard deviation, \(x\) is the left edge of the bin and \(dx\) is the width of the bin. The multiplication by 0.99 can be combined with the exponential:
\[
e^{-\frac{(x)^2}{2\sigma^2} - 0.01}.
\] (6.9)

The equation that has to be solved to find the bin width is:
\[
(x + dx)^2 = x^2 + 0.02\sigma^2.
\] (6.10)

Solving this equation gives \(dx \leq 0.01\sigma^2/x\). It follows that if \(x\) (the deviation from the center of the distribution) is bigger, the bin width must be smaller to meet this demand. In this simulation, only contributions within \(\pm 3\sigma\) are evaluated. It follows then, that the maximum allowed bin width is \(dx = 0.003\sigma\). The value used for \(\sigma\) in this thesis was \(0.1\ cm^{-1}\) (about the same as the spectral resolution of the monochromator), thus \(dx = 3 \cdot 10^{-4}\ cm^{-1}\).

### 6.1.4 Fitting Procedure

In this section the fitting procedure is discussed. The fitting procedure that is used in this work is built around the Levenberg-Marquardt procedure explained in Numerical Recipes [1]. Some small changes in the procedure have been made to allow for easier selection of parameters that should be kept constant or variable during the procedure.

The Levenberg-Marquardt procedure is a nonlinear least-squares fitting routine. In this procedure, a \(\chi^2\) function is calculated. This \(\chi^2\) is a measure for the discrepancy between the data and the fit:
\[
\chi^2 = \sum_{i=1}^{n} \left( \frac{x - \mu}{\sigma} \right)^2,
\] (6.11)

where \(x\) denotes the measured value and \(\mu\) the fitted value. Based on the gradients of the function this procedure finds a minimum value of \(\chi^2\). The strength of the Levenberg-Marquardt procedure is in avoiding so called zero-pivots\(^1\).

\(^1\)points for which solving of the solution-matrix is not possible.
Starting values for the fit parameters have to be estimated based on other sources, such as the measured temperature of the oven for the rotational temperature and values found in literature for the rotational constants. The key to using the Levenberg-Marquardt procedure is in providing these values. If the $\chi^2$ is not smooth enough, it is not guaranteed that the procedure will find the global minimum. Rather, it will find a local minimum. This problem can be mitigated by not fitting all variables simultaneously. This makes the $\chi^2$ function a simpler function that is hopefully smoother as well. Normally first individual parameters are fitted, followed by various subsets. Finally all parameters are freed to be fitted simultaneously.

In the fitting procedure the wave number at which the intensity is calculated depends on the evaluated dataset. The faster procedure based on binning— that is used for the simulations— cannot be used here. Therefore, for each wave number in the dataset, the complete spectrum has to be calculated and convoluted with the resolution. To save calculation time here, the spectral location of the transition is calculated first, and transitions with a wave number more than $3\sigma$ from the considered wave number are not evaluated. This reduces the part of the spectrum that has to be evaluated.

To investigate the capability of the fitting procedure to find solutions, spectra generated by the simulation procedure itself were fitted.

The fitting infrastructure has been built to use the procedure to fit the rotational temperature and the rotational constants. To be able to use this fitting procedure for different measurements, the resolution of the spectrum, a baseline correction and a multiplication factor are also implemented as fitting parameters.

To be able to verify the parameters calculated by the fitting procedure, a spectrum is calculated with the simulation procedure, based on the results of the fitting procedure. This calculated spectrum is compared to the measured spectrum visually.

### 6.1.5 Correctness Test by Fitting Simulated Spectra

The fitting procedure is tested by fitting a simulated spectrum. In the previous section it was mentioned that the outcome of the fitting procedure may depend on the initial value of the fitting parameters if the $\chi^2$-function is not smooth. In fact it always finds a local minimum. By optimizing the procedure, one can significantly increase the chance that the local minimum found is indeed the global minimum.
6.1 Introduction

enough. The capability of the fitting procedure to retrieve the correct parameters depending on the initial guess is investigated. This is done by fitting to a spectrum created with the simulation program itself. The fitted parameters are compared to the known input parameters of the simulation.

This investigation has been split in two parts. First, all parameters except one of them are fixed at the correct value and the remaining parameter is fitted for various initial guesses. Second, more than one parameter is fitted at once for various initial values.

In this investigation it is found that the result of the fitting procedure does not depend on the initial estimation\(^3\) for the rotational temperature, the resolution, the baseline correction and the multiplication factor. For the rotational constants, this fitting procedure is indeed sensitive to the value of the initial estimates. It is concluded that for the rotational temperature, the resolution, the baseline correction and the multiplication factor the \(\chi^2\)-function is smooth enough and the program can be used to fit these parameters. It is however also concluded that for the rotational constants, the \(\chi^2\)-function is not smooth enough. The programs can not be used to fit the rotational constants. The consequence is that fixed rotational constants from literature or obtained from a different experiment (see chapter 4) must be used.

Although the fitted resolution does not change with various input parameters, the result in \(T_{rot}\) is up to 2\% different from the value used in the simulation. This is possibly due to rounding errors that occur because the simulation procedure uses a discrete Gaussian function for the resolution, and the fitting procedure uses a continuous Gaussian function. Another possibility is that the peaks of the spectrum are close together and often overlap, therefore they may appear slightly wider than they should appear.

The preceding test of the fitting procedure were focussed on finding various fitting parameters while the fixed parameters have the same value as the value used producing the spectrum in the simulation. When a measured spectrum is fitted, there is no guarantee that the fixed parameters of the programs are fixed at the correct value. There is always some uncertainty in the fixed parameters. Therefore, the next step in the investigation is to test the effect of errors in the fixed parameters. Since the goal of this model is to fit the rotational temperature, the focus of this investigation has been on finding the error in the rotational temperature due to errors in the values of the fixed parameters.

\(^3\)As long as the initial estimate is of the same order of magnitude as the correct value.
Using a fixed resolution, that is up to 20% different from the value used in the simulation, leads to a rotational temperature that is up to 1% different from the input value in the simulation. When the scaling factor and the baseline are fixed up to 20% different from the value used in the simulation, this leads to a rotational temperature that is up to 5% different from the value used in the simulation. The scaling factor and the baseline are values that will be free to vary when the fitting procedure is used.

There are two parameters that are not free to vary in this model. They do influence the rotational temperature determined by the model. The complete spectrum can be shifted, due to e.g. a monochromator offset. If the spectrum is shifted up to ± 0.1 cm$^{-1}$, the rotational temperature is up to 5% different from the value used in the simulation. The other parameters are the rotational constants used in the model. They may differ from the true rotational constants. The fitted value of the rotational temperature depends strongly on the rotational constants. When the rotational constants are up to 0.1% different from the value used in the simulation, errors in the fitted rotational temperature of up to 17% can result. The relative uncertainty for the rotational constant found in literature is of the order of 10$^{-6}$. The sensitivity of this error is larger if the difference between the fitted and measured rotational peak position increases.

The fact that the fitted rotational temperature is dependent on the rotational constants is bothersome because previously it was concluded that the fitting procedure can not be used to fit these rotational constants. Because of this influence on the rotational temperature, it is important to carefully examine the various and different rotational constants that can be obtained from different sources in literature. To decrease the influence of non-overlap in peaks due to errors in the rotational constants the spectrum can be smoothed. When this operation is performed, the error in the fitted rotational temperature decreases, but the amount of decrease varied with the error in the vibrational constants and other errors.

The influence of random noise on the dataset has been investigated as well. Random noise of up to 5% of the maximum value has an influence on the fitted rotational temperature of less than ± 0.5%.

In conclusion, errors of up to 25% in the rotational temperature can be expected for worst case scenarios, but, using correct rotational constants, an error margin of 10% or less should be possible.
6.2 Results

In this chapter the i-LIF measurements will be used to determine the rotational temperature. First the intensity method will be applied, this is used to find the rotational temperature from the slope of a logarithm plot of the intensities. Then these measurements will be used as input for a fitting procedure that determines the rotational temperature.

6.2.1 Intensity Method

In this section, the rotational temperature will be determined using the intensity method. This method has been discussed in section 2.5.2. The following formula is used:

\[
\log \frac{I_{abs}}{2S_J} = \log C_{abs} - F(J) \frac{hc}{kT}.
\]  

(6.12)

In this equation, \(B_v J(J+1)\) is used for \(F(J)\). When \(\log \frac{I_{abs}}{2S_J}\) is plotted versus \(J(J+1)\). The rotational temperature is \(\frac{B_v hc}{k}\) divided by the slope.

In this section, this method will be applied to determine the rotational temperature of the InBr vapor sample, with the oven at 513 K. The measurement is performed on an absorption spectrum of the \(\Delta v = 0\) band. The spectrum of the \(\Delta v = 0\) band of InBr consists mainly of overlap between the 0-0 and the 1-1 transitions. At 500 K they occur at a ratio of approximately 7:1 respectively\(^4\). This method is best applied to single, distinguishable peaks. If these do not exist in the evaluated spectrum, a choice has to be made for peaks that best meet this demand.

The vibrational transitions consist of a P-branch and an R-branch. The P-branch first progresses to lower wave numbers, forms a band head and then returns to higher wave numbers. The R-branch consistently progresses to the higher wave numbers. Therefore, it is expected that near a rotational line of the R-branch, a rotational line of the P-branch can also be found. From the list generated by the spectral simulation it can be found that there is a rotation number difference of about 40. From this difference it can be concluded that further in the spectrum, the relative contribution of the P-branch is smaller than that of the R-branch. In order to determine the intensities of single peaks, it is therefore best to look at R-branch peaks, at high \(J\).

\(^4\)This is a result of the product of the Franck-Condon factors and the relative population of the vibration levels 0 and 1 of the ground state.
When determining the intensity of the peak, a choice has to be made between integrating a wave number region wide enough to include the total intensity of the peak, but also narrow enough to be able to neglect the influence of neighboring peaks. The width of the integrated wave number range is fixed. Determination of the background correction is another challenge. In the measurements there is influence from scattered light, which is assumed to be constant over the spectrum and should be subtracted from the intensity. There also is influence from other rotational transitions, which are different over the spectrum and should only be subtracted when they coincide with the R-branch.

Besides different vibration bands and the P- and R-rotational branch, another complication is that InBr consists of two isotopes. Both isotopes have their own rotational constants, and therefore for each of them the rotations appear at different wave numbers. At the part of the spectrum where the R-branch peaks of the isotopes can be distinguished, the influence of the P-branch is too strong. At the part of the spectrum where the influence of the P-branch is minimal, the rotational lines of the two isotopes lie closely together. Even further in the spectrum, the R-branch peaks of the isotopes separate again, however in this part of the spectrum intensities are low and the signal to noise ratio is not good enough to get reliable results.

In order to use this method, the rotational quantum numbers $J$ of the considered peaks have to be determined. This is done using the list generated in the simulation.

The part of the spectrum that meets all mentioned requirements best is evaluated. This is the part from 26642 cm$^{-1}$ to 26654 cm$^{-1}$. Here the R-branch rotation lines $J=106$ to 121 of the InBr$^{79}$ isotope and rotation lines $J=107$ to 122 of InBr$^{81}$ are situated and coincide. Two absorption spectra have been evaluated. In figure 6.2 the evaluated part of the spectrum is shown; the result of a simulated spectrum in this region is also shown, as well as the peaks’ rotational quantum numbers. The numbers indicate the rotational quantum number of the ground state of the InBr$^{79}$ isotope. In this region, the InBr$^{81}$ isotope’s rotational number is one higher than the InBr$^{79}$ isotope’s rotational number.

In figure 6.3 the resulting intensity versus rotation number plot is shown for the measured spectrum of figure 6.2.

This fitting procedure has been applied for two different measurements. Since the lines of the two isotopes are on top of each other in this region, the rotational temperature is determined two times, once using the $J$-numbering and
6.2 Results

**Figure 6.2:** The solid line is the measured spectrum, the dotted line is a simulated spectrum. The numbers indicate the rotational quantum number of the R-branch of the InBr\textsuperscript{79} ground state.

**Figure 6.3:** The plot of log \( \frac{I_{abs}}{S_J} \) versus \( J(J+1) \) from the data in figure 6.2. The dotted line is a fit of the datapoints. The fit has a slope of $21 \cdot 10^{-5}$, resulting in a temperature of 370 K.
Table 6.1: Calculated rotational temperatures for two measurements, using \( J \) numbering of InBr\(^{79} \) and InBr\(^{81} \).

<table>
<thead>
<tr>
<th>Measurement</th>
<th>InBr(^{79} )</th>
<th>InBr(^{81} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( 3.7 \times 10^2 ) K</td>
<td>( 3.9 \times 10^2 ) K</td>
</tr>
<tr>
<td>2</td>
<td>( 3.2 \times 10^2 ) K</td>
<td>( 3.2 \times 10^2 ) K</td>
</tr>
</tbody>
</table>

Table 6.2: Calculated rotational temperatures for InBr plus Argon in the gas phase as well as in the plasma phase. The term PMT is used to indicate that the measurement has been made with the PMT, the term iCCD indicates that the measurement has been made with the iCCD camera.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>InBr(^{79} )</th>
<th>InBr(^{81} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>InBr plus Argon, gas</td>
<td>PMT</td>
<td>( 3.8 \times 10^2 ) K</td>
</tr>
<tr>
<td>InBr plus Argon, gas</td>
<td>iCCD</td>
<td>( 5.3 \times 10^2 ) K</td>
</tr>
<tr>
<td>InBr plus Argon, plasma</td>
<td>iCCD</td>
<td>( 6.6 \times 10^2 ) K</td>
</tr>
</tbody>
</table>

\( B_v \) value of one isotope, and once using the \( J \)-numbering and \( B_v \) value of the other isotope. The result is shown in table 6.1. As can be seen in table 6.1, the difference between the known temperature of 513 K and the calculated temperature is quite large. It can be seen from the figures that the statistical scatter of the data is quite large as well.

This procedure has also been applied to an i-LIF measurement performed on InBr with Argon as a buffer gas. This measurement was performed with the PMT. The sr-LIF measurements that have been made with the iCCD are spectrally integrated to obtain an i-LIF spectrum. The iCCD measurements have been performed on InBr with Argon as a buffer gas and on an InBr Argon plasma. The rotational temperatures are calculated for these situations as well. The results are displayed in table 6.2. The temperatures that result from the PMT measurements typically have a lower value than the oven temperature. The temperatures that result from the iCCD measurements typically have a higher value than the oven temperature. The PMT measurements are performed at low laser power, the iCCD measurements are performed at high laser power. The tuning curve for the laser dye may be different at low laser power than at high laser power. However, it is not sure that this effect is present. No explanation for the difference in temperatures between the PMT and the iCCD measurements has been found.
6.2 Results

Table 6.3: Rotational temperatures resulting from the fitting procedure. The term PMT is used to indicate that the measurement has been made with the PMT, the term iCCD indicates that the measurement has been made with the iCCD camera.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>$T_{\text{rot}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>InBr m1 PMT</td>
<td>$4.3 \cdot 10^2$ K</td>
</tr>
<tr>
<td>InBr m2 PMT</td>
<td>$4.0 \cdot 10^2$ K</td>
</tr>
<tr>
<td>InBr plus Argon, gas PMT</td>
<td>$4.6 \cdot 10^2$ K</td>
</tr>
<tr>
<td>InBr plus Argon, gas iCCD</td>
<td>$5.6 \cdot 10^2$ K</td>
</tr>
<tr>
<td>InBr plus Argon, plasma iCCD</td>
<td>$5.3 \cdot 10^2$ K</td>
</tr>
</tbody>
</table>

6.2.2 Fitting the Rotational Temperature

A model was designed to fit the rotational temperatures. The fitting procedure is discussed in chapter 6.1.3. This fitting procedure is used to determine rotational temperatures from the same measurements as those used in the previous section. The results of both methods are compared.

The fitting procedure starts by determining the baseline of the spectrum and by determining the multiplication factor for a fixed rotational temperature of 300 K. The goal of this part of the procedure is to find input parameters for the baseline and multiplication factor that will be used in the next step of the procedure. After these values have been determined, the rotational temperature is fitted. At the same time the baseline and the multiplication factor are free to vary. The resolution of the fit has been fixed at 0.07 cm$^{-1}$ for the PMT measurements, and at 0.10 cm$^{-1}$ for the iCCD measurements. This is in agreement with the known resolution of the experiments. The rotational temperatures resulting from the fitting procedure are displayed in table 6.3.

When comparing the rotational temperatures determined with the fitting procedure to the rotational temperatures determined with the intensity method, one can conclude that the values resulting from the fitting procedure are closer to the oven temperature than the values resulting from the intensity method.

As was mentioned in section 6.1.4 where the fitting procedure is discussed, the error in the rotational temperature can decrease when smoothing the data. This has been done and rotational temperatures have been fitted for the smoothed measurements. The results are displayed in table 6.4.

The difference between the fits of InBr m1 and InBr m2, two measurements performed under the same conditions, has decreased. In general it can be con-
Table 6.4: Rotational temperatures resulting from the smoothed fitting procedure. The data has been convoluted with a gaussian function with a resolution of 0.3 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>$T_{rot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>InBr m1</td>
<td>PMT</td>
</tr>
<tr>
<td>InBr m2</td>
<td>PMT</td>
</tr>
<tr>
<td>InBr plus Argon, gas</td>
<td>PMT</td>
</tr>
<tr>
<td>InBr plus Argon, gas</td>
<td>iCCD</td>
</tr>
<tr>
<td>InBr plus Argon, plasma</td>
<td>iCCD</td>
</tr>
</tbody>
</table>

cluded that the resulting rotational temperatures from the smoothed measurements are not a significant improvement with respect to the rotational temperatures resulting from the unsmoothed measurements. The rotational temperatures that result from these fitting procedures are an improvement with respect to the rotational temperatures found using the intensity method. The fitting procedure reproduces data from the simulations very well.

To verify the results, a spectrum based on the results of the fitting procedure is produced. Because the general shape of the spectrum is most useful for verifying the rotational temperature, the results of the smoothed spectra are displayed in figures 6.4 and 6.4. The fitted spectrum is shown with the measured spectrum for two situations; for InBr measurement 1, performed with the PMT in figure 6.4 and for the InBr plus Argon plasma measurement performed with the iCCD camera in figure 6.5. It can be seen that the measured and the fitted spectra agree. It can also be seen that there are more variations in the spectrum for the PMT measurement than for the iCCD measurement. This supports a suggestion that the tuning curve of the laser dye might have been different for the measurement performed with the PMT than the tuning curve for the measurement performed with the iCCD, however it does not confirm the suggestion that the difference in the dye laser tuning curve may have been the cause for the difference in the determined rotational temperatures.

References

Figure 6.4: The measured and the fitted spectrum of measurement InBr m1. The solid line is the measured spectrum, the dotted line is the calculated spectrum with the parameters resulting from the fitting procedure.

Figure 6.5: The measured and the fitted spectrum of measurement InBr plus Argon plasma, performed with the iCCD. The solid line is the measured spectrum, the dotted line is the calculated spectrum with the parameters resulting from the fitting procedure.
Chapter 6. Rotational Temperature Determination


7

Spectral Response of Indium Bromide to 266 nm Pulsed Laser Irradiation

7.1 Introduction

Indium halides have recently received a lot of attention from researchers, for their fundamental properties as well as their potential applications [1]. Their chemical and physical properties play an important role in the development of semiconductor devices for high frequency and opto-electronic applications [2]. They are also used in the lighting industry [3], [4], e.g. as an additive to mercury discharge lamps [5] and are being investigated as potential future light sources based on low pressure Hg-free discharges [6],[7],[8].

Possible future discharge lamps based on an InBr low pressure discharge (as discussed in [7],[8]) could be based on a discharge that produces a spectrum similar to the one shown in figure 7.1. The strong emission of the Indium lines and also the InBr molecular bands can be converted into visible light by a phosphor. Since the radiation produced by such a discharge is much closer to the visible part of the spectrum than for a mercury discharge, the Stokes losses (the losses associated to the fluorescent conversion) for such a lamp are much smaller. Reducing these losses could result in more efficient lamps. All these potential applications emphasize the need for fundamental data on Indium halides.

The present paper will discuss laser induced fluorescence (LIF) measurements done on an InBr vapor and on an InBr plasma. The focus will be on the dynamics
Chapter 7. Spectral Response of Indium Bromide to 266 nm Pulsed Laser Irradiation

of the spectral response of Indium Bromide to 266 nm laser irradiation.

\[ \text{Intensity [a.u.]} \]

\[ \text{Wavelength [nm]} \]

**Figure 7.1:** Emission spectrum of an InBr-plasma measured at 240 °C in a capacitive discharge with 2.5 mBar argon as a buffer gas (see figure 7.4). The InBr vapor pressure is around 2 Pa.

The emission spectrum of InBr in a discharge (figure 7.1) shows strong atomic Indium lines as well as molecular radiation. The electronic spectrum of Indium Bromide consists mainly of three band systems in the ultraviolet region of the spectrum. These systems are attributed to \(A \left( ^3\Pi_{0^+} \right) - X \left( ^1\Sigma^+ \right)\), \(B \left( ^3\Pi_1 \right) - X \left( ^1\Sigma^+ \right)\), \(C \left( ^1\Pi \right) - X \left( ^1\Sigma^+ \right)\) transitions. In this article we will focus on spectroscopy of the \(A \rightarrow X\) and \(B \rightarrow X\) transitions. Data of the laser induced fluorescence (LIF) performed on both an InBr vapor as well as an InBr gas discharge will be presented. In this experiment we used the fourth harmonic of a Nd:YAG laser (266 nm) to excite InBr to a high electronic state (figure 7.2). This state is designated D-state after [2]. From this D-state the A-, B- and C-state are subsequently populated.

The fluorescence signal from the A- and B- state is detected and analysed with a spectral resolution of \(\sim 2 \text{ cm}^{-1}\) which is an improvement with respect to the results presented in the past by Yang et.al. [2]. In addition we have performed time resolved measurements.

In our experiments, radiation from the Indium atoms was also detected. As it is not certain what the dissociation energy of InBr is, [2], [1], the energy diagram is shown separately in figure 7.3 instead of integrated with the energy
Figure 7.2: LIF scheme used in our experiment. The InBr molecules are excited from the ground state (X) to the excited state (D). They then relax either through a radiative transition from the D-state directly to the ground state or through a collisional transition to the A-, B- or C-state. After [2].

diagram of InBr.

Figure 7.3: Energy diagram of Indium showing the 3 levels that are responsible for the atomic radiation detected in our measurements. Just slightly above the ground state is a metastable state. From the 6s $^2S_{1/2}$ level, two decay paths are possible: one to the ground state ($5p^2P_{1/2}$), one to the metastable ($5p^2P_{3/2}$). Their wavelengths are given in the line connecting the two levels.
7.2 Experimental Setup

A schematic drawing of the setup is shown in figure 7.4.

InBr vapor is generated inside a cylindrical quartz tube (30 cm long, 3 cm inner diameter) filled with InBr salt. To create a sufficiently high vapor pressure, the quartz tube is situated inside a furnace that heats the tube to a uniform wall temperature of maximum 640 K. The measurements are carried out for a tube without any background gas, and for a tube containing 2.5 mbar of Argon as a buffer gas. In most measurements presented in this paper, the wall temperature is fixed at 513 ± 1 K. At this temperature the vapor pressure of InBr is 2.6 Pa [9]. The ends of the tube, where the light from the laser enters the lamp, are kept at a temperature 5 K higher than the bulk of the tube to prevent condensation of InBr on the entrance and exit windows.

Most experiments are carried out with InBr in the gas phase without a discharge. However, inside the tube a discharge can be ignited. The discharge is capacitively driven by a Radio Frequency (RF) electric field at 13.56 MHz. The RF power is produced by an oscillator and amplified (Amplifier Research 75A250) to about 5 W. A home-made L-type matching network is used to couple the power to a 1 cm wide Tantalum electrode which is mounted on the outside of the sealed quartz tube. This dielectric coupling prevents a direct contact between the InBr salt and the metal electrodes.

To excite the InBr molecules to the D-state, the fourth harmonic of a Nd:YAG laser (266 nm) is used. The YAG laser employed is a Quantel, type Ultra. The pulse energy is 4 mJ, the repetition rate is 20 Hz and the pulse length is 6–8 ns. The beam diameter is 2.8 mm. To prevent jitter in the time domain of the detected signals, the q-switch of the laser is triggered by an external delay generator. The q-switch is generally triggered 135 µs after the ignition of the flash lamp.

The laser light is directed along the center of the quartz cylinder, i.e. in the axial direction. The fluorescence is detected at an angle of 90° in the lateral direction. First it is collected using a positive lens (f=300 mm). Then the horizontal LIF image is rotated 90° and focused onto the vertical entrance slit of a 1 m spectrometer (Jobin Yvon) with a 2400 lines/mm grating. The light from the spectrometer is detected in two different ways: with a photomultiplier (PM) (Hamamatsu H6780) tube to capture single photons of one distinct wavelength with a high time resolution or with a Stanford Computer Optics 4quickE iCCD camera. This camera provides an image of a part of the spectrum in one frame.
7.3 Results: InBr Vapor

Figure 7.4: Schematic drawing of the setup, showing the quartz tube in the oven, the excitation laser and the detection scheme.

(10 nm per image). The integration time of this camera can be varied between 1 ns and 100 ms. The PM is connected to an Ortec 9353 multichannel scaler (MCS) to obtain time resolved signals. The MCS has a burst sampling rate of 1 GHz.

7.3 Results: InBr Vapor

This section deals with the results obtained from LIF measurements on an InBr vapor. The temporal behavior of the fluorescence of InBr-molecules in the gas
phase without plasma excitation will be discussed. This will be done for both
the A-state and the B-state. We start the discussion with the analysis of the
spectrum after which the temporal behavior is presented.

These measurements were first done with 2.5 mbar of Argon as a buffer gas.
Later, the pressure was varied. Also measurements without any buffer gas, i.e.
pure InBr vapor, were carried out. The presence of the buffer gas did not affect
the results of these measurements. Since the pressure of the buffer gas seemed
to have no effect on these measurements, the focus was on the interaction of
InBr with itself, i.e. the pure InBr case.

In Figure 7.5 the LIF spectrum of InBr in the gas phase (no plasma but with
2.5 mBar argon present) is shown. This spectrum was recorded using a PMT.
While the laser was producing pulses at 20 Hz, the wavelength setting of the
spectrometer was slowly increased to scan the whole spectrum.

The peaks visible in the spectrum correspond to different vibrational pro-
gressions that are assigned in the graph, e.g. B\textsubscript{−4} corresponds to a transition
from the electronic B-state to the electronic ground state where the vibrational
quantum number increases by 4 (so e.g. from \(v = 0\) in the upper state to \(v = 4\)
in the ground state). This notation convention was developed originally for
absorption spectrometry [9].

In our measurement, the progressions between \(\Delta v = +2\) to \(\Delta v = -4\) are
visible for the electronic A\(\rightarrow\)X as well as the electronic B\(\rightarrow\)X transition. This
LIF spectrum has a higher spectral resolution \(\sim 2\text{cm}^{-1}\) than the LIF spectrum
that was presented by [2], and as a result the fluorescence bands of the A- and
B-state are separately visible. The relative intensities of the spectrum are in
rough agreement with [2]: the \(\Delta v = +1\) is more intense than the \(\Delta v = 0\) for
both the A\(\rightarrow\)X and the B\(\rightarrow\)X transitions. Furthermore, the B\(\rightarrow\)X transitions
appear to be more intense than the A\(\rightarrow\)X, albeit somewhat less significantly
than what is reported in [2].

Figure 7.6 and figure 7.7 show the time resolved LIF signal for the \(\Delta v = 0\)
progression of the B\(\rightarrow\)X transition at 364.9 nm and for the \(\Delta v = 1\) of the A\(\rightarrow\)X
transition at 372.5 nm. The graphs show an instantaneous increase of the signal
once the laser is fired. After that, the signal decays exponentially. The decay
time of the signal, for both the A- and B-state is 1.65 \(\pm 0.1\) \(\mu\)s.

In both cases, the decay is followed by a tail with a much larger decay time in
the order of 6 \(\mu\)s. Note that the signal is significantly lower for photons detected
at the B\(\rightarrow\)X than at the A\(\rightarrow\)X transition. This is probably caused by instability
of the wave length setting of the spectrometer and must therefore be assumed
to be an artefact.

The second decay time visible in these graphs may be a consequence of different levels populating each other. This phenomenon is not investigated further in our study.

The measured decay time is independent of the energy of the laser pulse whereas intensities of the signals scale linearly with the laser power. This means that we are in the linear regime for LIF; no saturation effects are occurring. Also, no instrumental saturation effects are occurring.

In this setting, fluorescence of Indium atoms was also recorded. The intensity of this fluorescence showed a quadratic dependence of the applied laser power. This suggests that a 2-photon process is at play, which is consistent with our expectations since the energy of a single 266 nm photon is not enough to dissociate the molecule and then excite the Indium atom. The decay times seen for this atomic fluorescence were 23 ns for the 410 nm line and 14 ns for the 451 nm line. They are consistent with the Einstein A-coefficients found in literature.
Chapter 7. Spectral Response of Indium Bromide to 266 nm Pulsed Laser Irradiation

**Figure 7.6:** Time resolved LIF signal at 364.9 nm (B→X, Δν = 0, no plasma). The temperature for this measurement was 513 K. The decay time –measured directly after the laser pulse occurred at 134 µs– for this signal was around 1.65 µs.

**Figure 7.7:** Time resolved LIF signal at 372.5 nm (A→X, Δν = 1, no plasma). The temperature for this measurement was 513 K. The decay time –measured directly after the laser pulse occurred at 134 µs– for this signal was around 1.65 µs.
(1.02 \cdot 10^8 \text{ s}^{-1} \text{ for the } 451 \text{ nm line and } 5.6 \cdot 10^7 \text{ s}^{-1} \text{ for the } 410 \text{ nm line [10]}).

### 7.4 Results: Molecules in a Plasma

Next, a plasma was ignited in the tube. The effects of the plasma on the properties of the LIF signals were studied. First an emission spectrum was taken. In figure 7.8 the $A \rightarrow X$ and $B \rightarrow X$ band of the emission spectrum between 358 and 390 nm of an InBr discharge is presented. In this figure the various vibrational progressions of the $A \rightarrow X$ and $B \rightarrow X$ transitions are visible.

![Emission spectrum of InBr, at 510 K, with Ar as a buffer gas, with the peaks from the A-state mostly on the right side of the spectrum and the peaks of the B-state mostly on the left side of the spectrum.](image)

**Figure 7.8:** Emission spectrum of InBr, at 510 K, with Ar as a buffer gas, with the peaks from the A-state mostly on the right side of the spectrum and the peaks of the B-state mostly on the left side of the spectrum.

If figure 7.8 is compared to figure 7.5, it is clear that the intensities of the various $\Delta v$ bands have changed significantly. Typically, the $B \rightarrow X$ bands are relatively more intense in the LIF spectrum than in the emission spectrum. This can be explained qualitatively by the suggestion that in the LIF spectrum the population source for the $A$- and $B$-states is the D-state, which is located at a higher energy level. In the emission spectrum, the population source is electron impact excitation from the ground level. For higher destination level energies, higher electron energies are required. As higher electron energies are less likely in a Maxwell-Boltzmann regime, excitation of the B-state is less likely than excitation of the A-state in a plasma.
Figure 7.9 depicts the LIF signal at 364.9 nm (Δν = 0 progression of the B-state) that was measured under the same conditions as the measurements presented in figure 7.6, except that there was a plasma this time. It is striking that there is a substantially longer rise time of the LIF signal when the plasma is on. The signal reaches its maximum after roughly 1 µs.

After extensive attempts to model this phenomenon, no single model was able to show a unique ability to describe this effect. Therefore they are fitted with an empirical formula. Since the fluorescence signals have a more complicated shape when the plasma is on, they are fitted with a combination of 3 exponentials, unlike the measurements that were previously presented:

\[ S(t) = C_1 \cdot \left( e^{-\frac{(t-t_0)}{\tau_1}} - e^{-\frac{(t-t_0)}{\tau_2}} \right) + C_2 \cdot e^{-\frac{(t-t_0)}{\tau_3}} + C_0 \]  

(7.1)

where \( C_1 \) and \( C_2 \) are fitting constants, \( t_0 \) the time the laser pulse arrives, and \( \tau_1 \), \( \tau_2 \) and \( \tau_3 \) the time constants. \( C_0 \) describes the base level of the signal. The first 2 exponentials share the same constant, because they are both caused directly by the laser excitation. The third one describes an indirect effect. \( \tau_1 \) denotes the time constant for transfer from the D-state to the A- or B-state. \( \tau_2 \) is the time constant for transfer from the A- or B-state to the ground state.

The initial decay time of the signal \( \tau_2 \) (attributed to the B→X transition) is 1.9 µs ± 100 ns, which is essentially the same as in the measurements with the plasma off. It now also has a very slow tail with a decay time (\( \tau_3 \)) of 11.5 ± 0.5 µs. This is assumed to be associated with the increased power in-coupling, due to the presence of additional electrons. For the Δν = 0 progression of the A-state (372.5 nm) we see a similar behavior as is shown in figure 7.10, with an initial decay time of 1.6 µs ± 100 ns. The decay time of the slow tail is 9.7 ± 0.5 µs.

### 7.5 Results: Temperature Dependence

The initial decay time for both the A- and B-state shows a temperature dependent behavior. When the wall temperature is increased from 473 K to 633 K, a dramatic drop in the decay time is recorded. In order to establish what the influence of the collisions with Argon was, we performed the experiment for several Ar pressures. A measurement in pure InBr vapor was also performed. The temperature dependence is shown in figure 7.11. In order to explain this
drop in decay time with collisional de-excitation, one has to assume that the relevant collisions are between InBr molecules, since the effect also occurs equally strong in a situation without anything else present. The decay of an upper level can proceed in 2 different ways: via an optical transition and via a collisional transition. Each of these transitions has its own rate. The rate for the optical transition is the Einstein coefficient for spontaneous emission. The collisional frequency is the product of a density speed and cross section. This is summarized as:

\[
\frac{1}{\tau} = A + n(T) \cdot \bar{v}(T) \cdot \sigma.
\]  

(7.2)

The density is calculated as follows using constants from [11]:

\[
n(T) = \frac{p(T)}{kT}.
\]  

(7.3)

The average thermal speed is calculated using:

\[
\bar{v}(T) = \sqrt{\frac{3kT}{2m}}.
\]  

(7.4)
Figure 7.10: Time resolved signal at 372.5 nm ($A \rightarrow X$, $\Delta v = 1$, plasma on). The fluorescence first rises relatively slowly to a maximum at around 1 $\mu$s after the laser pulse. After the maximum the signal starts to decay. This graph is similar to that in figure 7.9.

Figure 7.11: Temperature dependent behavior of the decay time. The red line plots values corresponding to the model described in this section. The measurements presented in this graph were carried out without a buffer gas present. Measurements with Argon as a buffer gas in the tube gave identical results.
Equation 7.2 leads to a value for the collisional cross-section ($\sigma$) of the order of $10^{-18}$ m$^2$. It is much larger than the geometric cross-section of this molecule, indicating that it is an efficient process. The values used for the fit in figure 7.11 are $5.2 \cdot 10^{-18}$ m$^2$ for $\sigma$ and the value for $A$ was $5.75 \cdot 10^5$ s$^{-1}$.

It is remarkable that the collisions of InBr with itself are more important for this process than collisions with argon, which is $\sim 100\times$ more abundant.

A possible collisional process involved in this phenomenon is:

$$\text{InBr}_{A,B} + \text{InBr} \rightarrow \text{InBr}_m + \text{InBr},\quad (7.5)$$

where the metastable Indium Bromide ($\text{InBr}_m$) molecule has a very slow decay, so it essentially does not radiate during our acquisition period. The metastable levels are very close to the A- and B-state in terms of energy; the only difference is the parity of the quantum mechanical wave function of the state. The exact energy of the metastable is not known, but more information can be found in [1].

An interesting thing to note here is that this mechanism will limit the lamp efficiency, since the rate of non-radiative de-excitation goes up significantly when the temperature goes up. Lowering the temperature is not a solution to this problem, because then the vapor pressure of InBr drops quickly. Because of this, too much of the electric energy will be used to excite the buffer gas instead of the radiating species, i.e. InBr.

This efficiency limiting mechanism is quite different to the one in a mercury based fluorescent tube, where the effective radiative decay time of the upper state increases strongly when the temperature–and with it the mercury pressure– is increased, mainly due to multiple reabsorption of photons. This basically slows down the radiation production process, giving more opportunity for non-radiative decay, resulting in reduced efficiency. In an InBr lamp it is not an increase of the effective radiative decay time that causes reduced efficiency; it stays roughly the same. It is a decrease of the non-radiative decay time that ultimately leads to reduced efficiency as is proved by the faster decay times at higher temperatures in figure 7.11.

7.6 Conclusions

A LIF experiment was carried out on InBr. Time resolved and spectrally resolved measurements were performed.
The detection setup is appropriate for fast transient signals. Signals on a timescale of nanoseconds, such as the fluorescence of the Indium atoms, were recorded. The noise level in the photon counting setup is very low.

The spectrum of the laser induced fluorescence was recorded with a resolution of \( \sim 2 \text{cm}^{-1} \). The various \( \Delta v \) peaks were separately resolved. The general profile of the LIF spectrum agrees with [2]. The \( \Delta v = +1 \)-peaks were larger than the \( \Delta v = 0 \)-peaks in the LIF spectrum. The decay time measured for both the \( \text{A} \rightarrow \text{X} \) and the \( \text{B} \rightarrow \text{X} \) transition was 1.65 \( \mu \text{s} \) at 240 °C. An emission spectrum of an Indium Bromide plasma was also recorded.

A strong temperature dependence of the fluorescence signal was observed during this research. This is due to the fact that InBr can relax through 2 processes: a radiative process and a process that is induced by collisions with ground state InBr, probably producing a metastable InBr molecule. This was concluded because the phenomena also occur in a pure InBr vapor. The collisional cross section for this process is of the order of \( 10^{-18} \text{ m}^2 \).

A conclusion that can be drawn from this is that the efficiency of a lamp cannot be increased by increasing the cold spot temperature (and with it the vapor pressure of InBr), because the rate of collisional de-excitation will increase rapidly. On the other hand, lowering the temperature will not help either, because eventually, the vapor pressure of InBr will become too low to operate a lamp. Summarizing: there is an optimal temperature for maximizing the efficiency of such a lamp.

Another conclusion that can be drawn from this work is that additional experiment are necessary to shed light on the dynamic behavior of InBr. Many questions remain with respect to the mechanisms that produce phenomena, such as the temperature dependence of the decay time and the increased rise time in the plasma. Too many parameters that could explain these phenomena are not adequately defined in these experiments.

To resolve a number of the remaining questions, an experiment with a tunable dye laser is planned. This will enable us to excite specific rovibrational upper levels of the A- and B-states of the InBr molecule. This will reduce the number of unknown variables in the analysis and will be very helpful in understanding these processes.
References


Chapter 7. Spectral Response of Indium Bromide to 266 nm Pulsed Laser Irradiation


8

General Conclusions

8.1 Introduction

In this work, four different experiments have been described: the response of InBr gas to 266 nm laser irradiation, spectrally resolved LIF, time resolved LIF and temperature determination from LIF spectra. In this final chapter, the general conclusions from these experiments will be presented and summarized.

8.2 DETEX Plots

In spectrally resolved LIF measurements both the excitation wave number and the detection wave number cover a certain wave number range.

For the interpretation of the spectrally resolved LIF data, the so-called DETEX plots were introduced. These plots are very helpful for the interpretation of rovibronic spectra.

The unprecedented detail visible in the DETEX plots enables a better unraveling of spectra than previously possible. This yields spectroscopic constants with greater accuracy. The spectroscopic constants found in this work are summarized in table 8.1.

The DETEX plots helped produce lists of rotational transitions, however the beginning of these lists was generally missing. To be able to assign the correct rotational quantum number to the observed transition, a method was developed based on the assumption that the unknown rotational constant must be similar to the rotational constant of a nearby vibrational level. This method can be
Table 8.1: Rotational constants and anharmonicities determined in this work.

<table>
<thead>
<tr>
<th>constant</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{A0}$</td>
<td>$0.058410 \pm 0.000002 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>$D_{A0}$</td>
<td>$1.59 \cdot 10^{-8} \pm 0.01 \cdot 10^{-8} \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>$B_{A1}$</td>
<td>$0.05809 \pm 0.00005 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>$D_{A1}$</td>
<td>$1.8 \cdot 10^{-8} \pm 0.2 \cdot 10^{-8} \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>$B_{X1}$</td>
<td>$0.056677 \pm 0.00002 \text{ cm}^{-1}$</td>
</tr>
<tr>
<td>$D_{X1}$</td>
<td>$2.83 \cdot 10^{-8} \pm 0.01 \cdot 10^{-8} \text{ cm}^{-1}$</td>
</tr>
</tbody>
</table>

applied in the determination of rotational constants for other species.

8.3 Time Resolved LIF

It can be seen that the decay time decreases gradually with increasing wave number. Near the band head of the 0-0 transition the decay time is: $0.66 \mu s$ and the corresponding $A$-value is: $1.5 \cdot 10^6 \text{ s}^{-1}$. Over an excitation range of $80 \text{ cm}^{-1}$ the decay time decreases to $0.62 \mu s$, which is about 94% of the value in the band head.

At higher wave numbers, and therefore higher rotational quantum numbers, the internuclear distance increases due to stretching of the chemical bonds in the molecule. In general, higher internuclear distance is associated with a higher transition probability, but it also leads to a geometrically larger molecule. In other words, the collisional cross section for an InBr molecule in a highly excited rotational state, may be larger than for a ground state InBr molecule.

On the other hand, if the effect visible in these measurements is not caused by an increased collisional de-excitation rate due to an expanding molecule, then it is most likely caused by a higher rate of spontaneous decay since a higher wave number generally leads to a higher rate of spontaneous emission.

8.4 Temperature Determination

Two methods were used to determine the rotational temperature of a plasma: the intensity method, where the intensities of the rotational peaks are plotted and fitted with a modified Boltzmann distribution, and the fitting method, where the whole spectrum is fitted with a computer program based on the
known spectroscopic constants.

It has been demonstrated that both methods are able to determine the temperature in a gas, where the accuracy of the temperature found by the fitting method seemed to be (predictably) slightly better. The fitting method yielded results with an accuracy of $\sim$10 to 15\%, whereas the achieved accuracy for the intensity method was of the order of $\sim$25 to 30\%.

Using this method to determine the temperature in an inductive plasma proved to be impossible, due to the absence of InBr fluorescence in the region of interest.

8.5 InBr as a Light Source

As was seen in the experiments in chapter 7, collisions between InBr molecules contribute very significantly to the relaxation processes at temperatures typical for the operation of this lamp. This was confirmed by the measurements performed on the inductively coupled plasma (chapter 4), where molecular radiation was absent in the brightest part of the plasma. This leads to the conclusion that the molecular component in the radiation produced by an InBr discharge is (seriously) limited by collisional relaxation processes.

Indium itself is of course also a strongly radiating atom, so the use of Indium (perhaps in the form of InBr) as an additive to a chemical mix for a lamp is not precluded. However the molecule InBr can be discarded as a candidate to be the primary radiator in an intermediate pressure lamp.
Summary

Spectroscopic Investigation of Indium Bromide for Lighting Purposes

In the modern world, the presence of light is taken for granted, but it comes at a cost. A large portion of the energy that is consumed by all of us today is used for lighting: 20% of the total electricity consumption. In a world where energy is becoming increasingly scarce and expensive, efficient lighting becomes more and more important.

There are a few different lamp designs that are used to improve on the efficiency of the incandescent lamp: man’s first attempt at electric lighting. A new technology that is receiving a lot of attention currently is the light emitting diode (LED), and while this technology holds a great promise for the future, a major issue with this technology will be the purchase price per unit for the foreseeable future. Other commonly known technologies are the low pressure discharge lamp and the high pressure discharge lamp.

The low pressure discharge lamp is known in the form of the fluorescent tube. This lamp works via a low pressure mercury discharge that produces UV-photons very efficiently that it then converts to visible light somewhat less efficiently.

The high pressure discharge lamp is often seen in shop lighting. It works by the direct emission of visible light from a high pressure mercury discharge that has some (usually metal halides) additives in it. The high pressure discharge conditions make for a less efficient discharge. However, the light production efficiency of both these discharges is comparable (~ 100 lm/W).

Ideally, a discharge lamp would combine a high discharge efficiency, like the low
pressure discharge lamp has, with the direct production of visible light. To do this an intermediate pressure lamp is envisioned that produces light directly. The light producing species can not be the same as in the low or high pressure lamps.

Indium Bromide is suggested as a model species to study. The spectrum of Indium Bromide will be studied to find optimal operating conditions as well as fundamental properties of the molecule. To do this, a laser induced fluorescence experiment is designed and built.

A cylindrical tube with a diameter of 3 cm and a length of 30 cm is housed inside an oven that provides a homogenous temperature over the volume of the tube. Axially through the tube, a laser can be shone that provides excitation of the studied molecules. The laser used is either the 4\textsuperscript{th} harmonic of a YAG laser or a high repetition rate (1 kHz) tunable dye laser which is pumped by the 3\textsuperscript{rd} harmonic of a YAG pump laser. The high repetition frequency is necessary to prevent saturation effects, while still being able to measure meaningful fluorescence spectra.

The fluorescence is detected in a perpendicular direction. The fluorescence photons are guided through a monochromator and then detected by either an iCCD camera for spectral resolution or a photomultiplier tube connected to a multichannel scaler for time resolution.

In spectrally resolved LIF measurements both the excitation wave number and the detection wave number cover a certain wave number range.

For the interpretation of the spectrally resolved LIF data, the so-called DETEX plots were introduced. A DETEX plot shows the fluorescence emission color-coded in a graph with the detection wave number on the horizontal axis and the excitation wave number on the vertical axis. These plots are very helpful for the interpretation of rovibronic spectra.

The unprecedented detail visible in the DETEX plots enables a better unraveling of spectra than previously possible. This enabled the determination of various spectroscopic constants with greater accuracy.

The DETEX plots helped produce lists of rotational transitions, however the beginning of these lists was generally missing. To still be able to assign the correct rotational quantum number to the observed transition, a method was developed based on the assumption that the unknown rotational constant must be similar to the rotational constant of a level nearby. This method can be useful in the determination of rotational constants for other species too.
It can be seen that the decay time decreases gradually with increasing excitation wave number. At higher wave numbers, and therefore higher rotational quantum numbers, the internuclear distance increases due to *stretching* of the chemical bonds in the molecule. In general, a higher internuclear distance is associated with a higher transition probability, but it also leads to a geometrically larger molecule. In other words, the collisional cross section for an InBr molecule in a highly excited rotational state may be larger than for a ground state InBr molecule.

Two methods were used to determine the rotational temperature of a plasma: the intensity method, where the intensities of some rotational peaks are plotted and fitted with a modified Boltzmann distribution, and the fitting method, where the whole spectrum is fitted with a computer program based on the known spectroscopic constants.

Both methods have been shown to be able to determine the temperature in a gas, where the accuracy of the temperature found by the fitting method seemed to be (predictably) slightly better. The fitting method yielded results with an accuracy of $\sim 10 - 15\%$, whereas the achieved accuracy for the intensity method was of the order of $\sim 25 - 30\%$.

Using this method to determine the temperature in an inductive plasma proved to be impossible, due to the absence of InBr fluorescence in the region of interest.

The experiments with the 266 nm excitation showed that collisions between InBr molecules contribute very significantly to the relaxation processes at temperatures typical for the operation of the envisioned lamp. This was confirmed by the measurements performed on the inductively coupled plasma, where molecular radiation was absent in the brightest part of the plasma. This leads to the conclusion that the molecular component in the radiation produced by an InBr discharge is (strongly) limited by the collisional relaxation processes.

Indium itself is of course also a heavily radiating atom, so the use of Indium (perhaps in the form of InBr) as an additive to a chemical mix for a lamp is not categorically deemed as unwise. However the molecule InBr can be discarded as a candidate to be the primary radiator in an intermediate pressure lamp.
Samenvatting

Spectroscopisch Onderzoek van Indium Bromide voor Verlichtingstoepassingen

In de moderne wereld wordt de aanwezigheid van licht niet als iets bijzonders gezien, maar licht is niet gratis. Een groot deel van de mondiale energieconsumptie wordt gebruikt voor verlichting: 20% van het totaal. Tegen de achtergrond van steeds maar duurder en schaarser wordende energie, wordt efficiënte verlichting steeds belangrijker.

Er worden een paar verschillende lamptypen gebruikt om zuiniger met energie om te gaan dan de gloeilamp: het oudste type elektrische lamp. Momenteel is er veel aandacht voor de gelijkrichtlampen (LEDs) en, hoewel deze techniek veelbelovend is voor de verre toekomst, zal voor de nabije toekomst de prijs per eenheid van deze lampen een probleem blijven. Andere bekende technieken voor efficiënte verlichting zijn de lage en hoge druk gasontladingslampen.

Lage druk gasontladingen zijn bekend in de vorm van de TL-buis. Een dergelijke lamp werkt door met een lage druk kwikontlading heel efficiënt UV-fotonen te produceren, die vervolgens wat minder efficiënt worden omgezet in zichtbaar licht.

De hoge druk gasontladingslamp wordt veel toegepast in winkels. Deze lampen wekken direct zichtbaar licht op met een hoge druk kwikontlading waarin een aantal toevoegingen zitten (metaal halides in het algemeen). De omstandigheden in zo’n hoge druk kwikontlading zorgen voor een minder efficiënte ontlasting, maar het rendement van de lichtgeneratie is ongeveer hetzelfde in beide lamptypen (∼100 lm/W).

Een ideale ontladingslamp zou het hoge rendement van de ontlading van de lage
druk ontlading combineren met de directe productie van *zichtbaar* licht. Om dit te bereiken wordt het gebruik van een middeldruk ontladingslamp voorgesteld. Als licht genererend element kan niet hetzelfde element worden gebruikt als in de lage of hoge druk lampen.

Indium Bromide heeft model gestaan voor deze studie. Het spectrum van Indium Bromide is bestudeerd om optimale bedrijfsomstandigheden voor een dergelijke lamp te bepalen en om fundamentele eigenschappen van het molecuul te meten. Om dit te bereiken is een opstelling voor het produceren en meten van laser geïnduceerde fluorescentie (LIF) gebouwd.

Een cilindervormige buis met een diameter van 3 cm en een lengte van 30 cm bevindt zich in een oven die zorgt voor een homogene temperatuur over de hele buis. In axiale richting wordt een laser door de buis geschenen die zorgt voor de excitatie van de moleculen. De gebruikte laser is de 4e harmonische van een YAG laser of een verstembare kleurstoflaser met een hoge herhalingsfrequentie (1 kHz), die gepompt wordt met de 3e harmonische van een YAG pomplaser. De hoge herhalingsfrequentie is nodig om zinvolle fluorescentie spectra te kunnen meten zonder last te hebben van verzadigingseffecten.

De fluorescentie wordt via een monochromator, hetzij naar een iCCD camera voor spectrale resolutie, hetzij naar een snelle photomultiplier verbonden aan een multichannel scaler voor tijdsresolutie, geleid.

Bij spectraal opgeloste LIF metingen is er voor zowel de detectie als de excitatie een bepaald bereik aan golfgetallen.

Voor de interpretatie van de gegevens gevonden bij de spectraal opgeloste LIF metingen, zijn de DETEX plaatjes geïntroduceerd. Een DETEX plaatje laat de met kleur gecodeerde fluorescentie zien in een grafiek met op de horizontale as het detectie-golfgetal en op de verticale as het excitatie-golfgetal. Deze plaatjes zijn erg nuttig voor de interpretatie van rotationele vibrationele elektronische spectra.

Dankzij de DETEX plaatjes is voor het eerst zoveel detail zichtbaar. Dit maakt het mogelijk om de spectra verder uit te pluizen dan in het verleden mogelijk was. Hierdoor kunnen verschillende spectroscopische constanten bepaald worden met een grotere nauwkeurigheid.

Met behulp van de DETEX plaatjes werd een lijst van rotationele overgangen gemaakt, maar deze lijst was over het algemeen incompleet aan het begin. Om alsnog het juiste rotationele quantumgetal toe te wijzen aan de gemeten overgangen, is een methode ontwikkeld gebaseerd op de veronderstelling dat een
onbekende rotationele constante van een zeker niveau niet veel verschilt van die van een bekende rotationele constante van een ander nabij gelegen niveau. Deze methode kan ook toegepast worden om de rotationele constanten van andere moleculen te bepalen.

In de experimenten is waargenomen dat de vervaltijden geleidelijk afnemen bij toenemend excitatie golfgetal. Bij grotere golfgetallen (en daarmee ook grotere rotationele quantumgetallen), neemt de internucleaire afstand toe door het uitrekken van de chemische bindingen in het molecuul. In het algemeen geldt dat een grotere internucleaire afstand leidt tot een grotere overgangswaarschijnlijkheid, maar het molecuul zelf wordt ook groter. Met andere woorden, de botsingsdoorsnede van een InBr-molecuul in een rotationeel hoog aangeslagen toestand is groter dan van een InBr-molecuul in de grondtoestand.

Er zijn twee methoden gebruikt om de rotationele temperatuur van het plasma te bepalen: de intensiteitmethode, waarbij de intensiteit en van een aantal rotationele piekjes in een grafiek worden getekend en vervolgens gefit met een aangepaste Boltzmannverdeling, en de fitmethode, waarbij het hele spectrum wordt gefit met een computer programma gebaseerd op bekende spectroscopische constanten.

Met beide methoden is het mogelijk de temperatuur van een gas te bepalen, maar de temperatuur kon iets nauwkeuriger bepaald worden met de fitmethode. De fitmethode leverde resultaten op met een precisie van $\sim 10 - 15\%$, waar de nauwkeurigheid die behaald werd met de intensiteitmethode lag op $\sim 25 - 30\%$.

In een inductief plasma was het onmogelijk om de temperatuur te bepalen, vanwege de afwezigheid van InBr fluorescentie in het gedeelte van het plasma waar we geïnteresseerd waren.

De experimenten waarbij middels 266 nm straling excitatie plaatsvond, lieten zien dat botsingen tussen InBr-moleculen een dominante rol spelen bij de relaxatieprocessen bij temperaturen die relevant zijn voor dit type lamp. Dit werd bevestigd door de metingen aan het inductief gekoppelde plasma, waarbij geen moleculeaire straling werd waargenomen in het helderste deel van het plasma. Hierniet wordt de conclusie getrokken dat het moleculeaire deel van de straling, die geproduceerd wordt door een InBr ontlading, sterk begrensd is door botsingsrelaxatie.

Indium straalt natuurlijk zelf ook sterk, en daarom is het gebruik van Indium (wellicht in de vorm van InBr) als een toevoeging aan het chemische mengsel voor een lamp niet categorisch aan te merken als onverstandig. Als primaire
bron van straling echter, kan het molecuul InBr niet langer kandidaat zijn voor een middeldruk lamp.
Dankwoord

Er zijn heel veel goede mensen op de wereld. Zonder een heel aantal van die goede mensen zou mijn project niet mogelijk zijn geweest. Om die reden wil ik een poging wagen om mijn dank uit te spreken voor de mensen die belangrijk zijn geweest bij mijn promotie.

Iedereen die in het volgende stuk genoemd wordt ben ik dankbaar. Om het stuk aangenamer om te lezen te maken heb ik niet in elke zin het woord dankbaar of iets dergelijks gezet. In plaats daarvan vertel ik in het kort hoe het zo allemaal is gekomen.


Dit advies en het feit dat Gerrit Kroesen, met wie ik al veel langer samenwerk, mij een plek aanbood —waarbij ik experimenteel wetenschappelijk interessant werk kon doen in samenwerking met Philips— maakten de afweging wel of niet promoveren een makkelijke. Ik ben nog altijd blij met mijn keus van toen.

Mijn directe begeleider op de universiteit werd Winfred Stoffels, die gedurende de eerste 3 jaren van dit project mijn directe aanspreekpunt op de TU/e was. Hij stimuleerde mij om altijd betere en precieze experimenten te doen zonder te snel tevreden te zijn. Ik wens hem veel succes op zijn nieuwe carrièrepad, wat dat dan ook moge worden.

Ook Joost van der Mullen was erg intiem bij mijn project betrokken. Zijn hulp en ervaring bij het aanschaffen van de noodzakelijke lasersystemen was
van onschatbare waarde. Ook het elan waarmee hij zijn eigen AIO’s en mij als pleeg-AIO aanvuurde is onnavolgbaar. Ik heb dit als zeer motiverend ervaren.

Vanuit Philips had ik aanvankelijk contact met Ariël de Graaf, maar mijn aanspreekpunt bij Philips werd al snel Peter Vankan. De discussies die ik met hem heb gehad over zowel de wetenschappelijke als de niet-wetenschappelijke kanten van dit werk hebben mij geholpen om te komen tot dit proefschrift. Ook Daiyu Hayashi heeft vanuit Philips Aken bijgedragen aan dit project.

In de eerste jaren van mijn promotie volgden mijn promotoren Marco Haverlag en Gerrit Kroesen van enige afstand mijn verrichtingen. Toen er echter een behoefte aan intensievere begeleiding van hun kant ontstond, hebben zij zonder aarzeling de verantwoordelijkheid op zich genomen en mij op zeer constructieve wijze geholpen. Dit was zeer belangrijk voor mij. Het vertrouwen dat zij in mij toonden, gaf mij het zelfvertrouwen dat nodig is voor dit soort ondernemingen. De hoeveelheid suggesties en correcties die ze mij gegeven hebben op dit werk is fantastisch. Ik ben er erg trots op dat zij mijn promotoren zijn.

I would also like to take the opportunity to express my gratitude towards the other members of my PhD committee for taking the time to read my thesis, travel to the Netherlands and be part of the ceremony: the professors Jim Lawler from the USA and Georges Zissis from France. It is a real honor that you are here.

Ik ben ook erg blij dat Richard van de Sanden, Joost van der Mullen en Peter Vankan in mijn commissie zitten en alles hebben gedaan wat daar bij hoort, maar bij deze heren heb ik —wellicht onterecht— minder de neiging ze te bedanken voor het maken van de reis naar Eindhoven.

Tijdens de afgelopen 4 jaar heb ik ook met heel veel plezier samengewerkt met een heel aantal stagiairs en één afstudeerder. Het was voor mij een groot genoegen om met deze getalenteerde mensen samen te werken aan deze ontdekkingstocht.

De stagiairs waren: Lionel Hirschberg, Siebe Rossen, Maurice Fransen, Marie Guilleminier, Sjoerd Smit, Vincent Girault en Dirk Trienekens. Bij de stage van Siebe en Maurice heeft Jan van Dijk opgetreden als medebegeleider. Mijn afstudeerder was Arij Rijke, die inmiddels collega-AIO is geworden en die ook heeft toegezegd paraninfl te zullen zijn op mijn promotie.

Deze stagiairs en afstudeerder hebben een hands-on bijdrage geleverd aan veel van het werk dat in dit proefschrift gepresenteerd staat.
Zonder een prettige omgeving kan er niet goed gewerkt worden. Met een prettige omgeving bedoel ik hier een prettige groep mensen om je heen. (Nlaag is niet onaardig hoor, maar ik heb wel eens mooiere gebouwen gezien.) De prettige groep mensen werd gevormd door de vakgroep EPG. Met leden van deze groep heb ik heel veel prettige en interessante, relevante en irrelevante, natuurkundige en niet-natuurkundige gesprekken gevoerd bij de lunch of in de koffiepauze, zoals met Wouter Brok, Bart Broks, Michiel van den Donker, Kurt Gielissen, Job Beckers, Sander Nijdam, afijn het aantal mensen uit deze groep is veel te groot om allemaal op te noemen, maar jullie weten allemaal wie jullie zijn.

Verder was er altijd ondersteuning vanuit de groep of de technische dienst, zowel op technisch als administratief gebied. Loek Baede, Huib Schouten, Evert Ridderhof, Rina Boom en tegenwoordig ook Eddie van Veldhuizen hebben mij geholpen met 1001 zaken. Hun bijdrage kan niet genoeg benadrukt worden.

Verder wil ik familie en vrienden noemen met in het bijzonder mijn ouders, mijn broer, mijn zus en natuurlijk Wendy, die voor mij een stabiele, gezellige, spannende en ontspannende omgeving vormen, die zo belangrijk is om het werk goed te kunnen doen.

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