Structural and thermodynamic investigations of lanthanide halide species in metal halide discharge lamps
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CHAPTER

1

General introduction
1.1 Introduction

While modern means of transportation and the ever increasing possibilities of information and communication technology are generally accredited the transformation of the society as we experience it today, the revolution that took place when man invented electric lighting seems to be completely forgotten. Electric illumination is everywhere; its existence is taken for granted. Nevertheless, electric lighting is since the days of Edison, now well over 100 years ago, still under continuous development. Longer lifetimes, better color properties, lower energy consumption and environmental responsibility are key words in lighting industry (see e.g. refs. 1-3).

The past century has brought forth a wide variety of lamp types either based on incandescence or luminescence. In incandescent light sources, electrical energy is converted into thermal radiation by passage of an electrical current through a solid conducting material. As a result this material is heated to a high temperature until it glows. For the commonly used incandescent lamp with a tungsten filament, the maximum applied temperature is in the range of 2500–3000 K. Most of the radiation emitted by the heated wire falls in the infrared region of the spectrum, but a small part is visible radiation, thus making it a light source. The incandescent lamp has dominated domestic lighting applications for the largest part of the twentieth century. This was mostly the merit of its pleasant warm white color in combination with a low cost of ownership. Its low energy efficiency and rather disappointing life span of about 1000 hours for the latest type of conventional incandescent lamps were apparently regarded as less important. The efficiency of electric lighting is usually expressed as the amount of light produced (in Lumens) divided by the amount of energy consumed (in Watt) and is referred to as luminous efficacy. Figure 1.1 shows a comparison of the luminous efficacy of different lamp types and it is obvious that the incandescent lamp has the lowest efficiency (10–15 lm/W) of all lamp types considered.

The halogen lamp, which also belongs to the group of incandescent lamps, has a slightly better luminous efficacy (15–33 lm/W) and improved lifespan (2000–6000 hours) with respect to the conventional incandescent lamp. The improvement of the efficiency is the result of an increase of the filament temperature up to 3300 K. Without any counter measures, the temperature raise of the filament would result in an increased evaporation of tungsten and consequently shorter lifetime of the lamp. However, a significantly higher inert gas pressure results in a slower evaporation rate of tungsten compared to the normal incandescent lamp, while halogens are added in order to keep the vessel free from the tungsten that does evaporate from the filament (by a regenerative halogen cycle).

Significant better luminous efficacies are found for lamps based on luminescence. In the Light Emitting Diode (LED), the application of a low-voltage direct current to a suitable doped crystal containing a p-n junction produces light. This phenomenon is called
electroluminescence. The emission of a specific type of LED is not a continuous spectrum as is the case in an incandescent lamp, but it falls within a small wavelength range, with its color depending on the semiconductor material used for the diode. There are several ways to produce white light from LEDs, two of them practically applied in commercially available white LEDs (see e.g. ref. 6). One of the methods is to combine the light of three individual LEDs, emitting the three primary colors, red, green, and blue. Their combination results in white light. The other method is to convert the emission of a blue or UV LED with a fluorescent material to a broad spectrum white emission.

The luminous efficacy of the currently available white LEDs (up to 55 lm/Watt)\textsuperscript{3} is already more than a factor 3 better compared to that of incandescent lamps. Under laboratory conditions several prototypes have demonstrated luminous efficacies of over 200 lm/W, showing the enormous potential of this type of electric lighting (see e.g. ref. 7).

![Luminous efficacy of currently available white light sources.](image-url)
All other efficient lamp types from Figure 1.1 belong to the group of discharge lamps. A discharge lamp converts electrical energy into radiation by passage of an electrical current through an ionized gas, which is often referred to as plasma. The emission of a gaseous discharge is also not a continuous spectrum, but consists mainly of discrete spectral lines, the amount and their spectral positions depending on the discharge medium.

In case of the two types of fluorescent lamps mentioned in Figure 1.1, a discharge through low pressure mercury vapor results in a strong UV emission. This emission is converted into visible light by a fluorescent coating in the lamp, which is often referred to as the phosphor. The luminous efficacies of up to 80 lm/W for the compact fluorescent lamp and up to 100 lm/W for the linear fluorescent lamp are an enormous improvement of the efficiency with respect to the incandescent lamp. In particular the compact type is gradually replacing incandescent lamps in the domestic setting.

The mercury vapor lamp, the high pressure sodium lamp and the metal halide lamp are three examples of high intensity discharge (HID) lamps. These lamps are all characterized by a large luminous flux and are therefore very well suited for large area lighting and street lighting applications. Considering the efficiency alone, the high pressure sodium lamp would be the best choice with a luminous efficacy of up to 120 lm/W. The low-pressure variant of the sodium discharge lamp (not indicated in Figure 1.1) is showing an even better efficiency, with reported luminous efficacies of up to 200 lm/W. The light produced by the low-pressure sodium discharge is however bichromatic, consisting only of two very near emission lines at 589.0 nm and 589.6 nm. Light of this wavelength is strongly yellow colored, which makes it impossible to distinguish the colors of different objects, when illuminated by this type of light. Therefore, the low-pressure sodium discharge lamp is less suitable as a light source for general lighting applications.

This illustrates that besides the efficiency and expected lifespan of the light sources, the quality of light is just as much an important factor which determines the adoption of a specific type of lamp. Color temperature is one of the characteristics of the light emitted by a lamp and corresponds to the temperature (in Kelvin) of a blackbody radiator that radiates light of comparable chromaticity to that of the light source. Lamps with a color temperature below 3500 K have a warm white appearance, while a color temperature above 4000 K corresponds to a cool appearance. Light with a color temperature in between these values is experienced as neutral white. In order to have a daylight appearance, a light source needs to be rated with a color temperature of 5500 K or higher. The Color Rendering Index (CRI) is another important characteristic of a light source. It is a mathematical comparison of how well a certain set of standard colors are reproduced when illuminated by this source as compared to a reference source of the same color temperature. With a perfect match, the light source will have the maximum CRI value of 100, while lamps with a very poor color rendition will have a very low CRI.
The CRI values for the high pressure mercury lamp (max. 49 CRI) and the high pressure sodium lamp (24 CRI) are significantly worse compared to the CRI of metal halide lamps (up to 96 CRI).\(^5\) The metal halide lamp represents the best combination of the color characteristics of incandescent lamps with the general advantages of discharge lamps like giving a strong power output and retaining a long lifetime of up to 20000 hours. With a luminous efficacy of up to 105 lm/W\(^5\), they are the most energy efficient commercially available light source with a good color rendition. Together with white LEDs, they represent the greatest potential for fulfilling future demands in light generation. Beside the aforementioned applications of street lighting and large area lighting other applications of metal halide lamps are for example automotive headlights, projector systems and shop lighting.

The fundamental research described in this thesis provides essential information for improving the understanding of the chemical processes taking place in current and future metal halide discharge lamps. In the remainder of this chapter a short overview of the history and working principles of metal halide lamps will be presented and the current status of knowledge on important fundamental data necessary for the understanding of the chemical processes in metal halide lamps will be evaluated.

### 1.2 History of Metal Halide Lamps

The origin of the metal halide lamp can be traced back to a series of discoveries and inventions that started in the year 1675. In this year, the French astronomer Jean-Felix Picard observed that while he was carrying a mercury barometer, the empty space started to glow as the mercury joggled.\(^8\) In the following years, this phenomenon was studied in more detail by several researchers, amongst them the English scientist Francis Hauksbee. In 1705 he placed a small amount of mercury in a glass bulb and evacuated most of the air from it. By charging the bulb with static electricity he demonstrated the appearance of a discharge. The glow of this discharge was bright enough to enable reading.\(^9,10\)

In the beginning of the nineteenth century, almost one century after the work of Hauksbee, the Russian scientist Vasily V. Petrov\(^11\) and Sir Humphry Davy\(^11\) independently demonstrated the principle of an electric arc powered by a pile of Volta, which was invented several years before, in the year 1800. In the demonstration of Humphry Davy for the Royal Institution, an arc of brilliant light between two pieces of carbon could be observed when they were connected to a high voltage electricity supply and brought at a short distance. Since the elaborate battery needed for the experiment was at that time an expensive laboratory curiosity, which suffered from rapid internal destruction of the plates, his discovery was at that time not used as a source of illumination. Nevertheless, in the following decennia, after the invention
of steam powered generators, several engineers were stimulated by the work of Humphry Davy to develop practical lamps based on the carbon arc principle. Most of the light emitted by the carbon arc lamp originated from incandescence of the carbon electrodes, while only a minor fraction came from the electrical arc in air. Due to its harsh and brilliant light output, the carbon arc lamp was found most suitable for lighting large public places such as for example squares, parks and railway stations. One of the first applications was in a theatre.

In the second half of the nineteenth century the electrical discharge through gases and vapors was investigated by several researchers, using evacuated glass tubes provided with two electrodes and a filling of the respective gas or vapor. These studies were made possible by the work of the German physicist and inventor Heinrich Geissler, who designed the first glass tubes with electrodes (so-called Geissler tubes) and a mercury vacuum pump, which enabled the application of a superior vacuum to these tubes. The work of Geissler, together with Julius Plücker and the subsequent experiments from Johann Wilhelm Hittorf, William Crookes and Eugen Goldstein revealed that the spectrum of the light emitted by a discharge through low pressure gases and vapors is characteristic of the gas filling in these tubes.\textsuperscript{14,15}

Already in 1860 John Thomas Way adapted a carbon arc lamp to operate in a mixture of air and mercury vapor at atmospheric pressure.\textsuperscript{14} In this invention it was the arc itself giving most of the light and not the incandescence of the carbon electrodes. This improvement of the carbon arc resulted in a significant increased output of light, but never came to a widespread use.

A low-pressure mercury lamp was first investigated in 1892 by the German physicist Martin Leo Arons.\textsuperscript{16} These mercury vapor lamps used a mercury cathode and an anode of either mercury or another material which does not form an amalgam with mercury. Peter Cooper-Hewitt patented in 1900 his version of the low-pressure mercury arc lamp.\textsuperscript{17} He introduced an improved form of his lamp in 1903 which found widespread use for industrial lighting. The commercial success of his lamps makes that he is often accredited the invention of the low-pressure mercury discharge lamp. In 1906, R. Küch and T. Retschinsky introduced an atmospheric pressure variant using a quartz discharge tube.\textsuperscript{18} Although the efficiency and color rendition of the atmospheric pressure variant was slightly better, the short life expectation due to the absence of a reliable method to seal the metal conductors through the quartz, and dangerous amounts of UV emission resulted in only a limited success.

Both the lamps of Cooper-Hewitt and Küch and Retschinsky emitted a greenish blue light, deficient in red. This light was not flattering to human skin color and was therefore experienced as highly unpleasant. Their use was limited to streets, warehouses and industries. Cooper-Hewitt already experimented with fluorescent materials on reflectors around the lamp to improve the color characteristics. It took however until the late 1930s that fluorescent lamps were introduced resembling the working principles of the ones still marketed today. An important breakthrough in the 1920s was the discovery that the mercury emission was
influenced by the mercury pressure inside the discharge tube. A proper mixture of mercury at low pressure and a rare gas at a somewhat higher pressure proved to be very efficient in converting electrical energy into the 253.7 nm and 184.9 nm UV lines of mercury.\textsuperscript{15} Other important milestones before the introduction of fluorescent lamps turned into reality were the development of a suitable fluorescent phosphor for converting this UV light into visible radiation and proper electrodes to supply electrons to the discharge.\textsuperscript{14,15}

Several researchers also worked on improving the color characteristics of the atmospheric pressure mercury lamp of Küch and Retschinsky. The addition of red emitting metals was suggested by Guercke in 1906\textsuperscript{14} and this method was practiced by M. Wolke in 1912, using the metals cadmium and zinc.\textsuperscript{14} His experiments were however not successful as the wall temperature was too low for achieving appreciable vapor pressures of these metals. Moreover, the metals reacted with the quartz envelope.

In a patent filed in 1902, Charles P. Steinmetz describes for the first time the application of metal halides instead of metals for the improvement of the color rendition of mercury lamps.\textsuperscript{19} He experimented with metal iodide additives, but because of the liquid mercury cathode material he was limited to metal iodides with a vapor pressure sufficiently high to evaporate below the boiling point of mercury. Only lamps based on the relatively volatile iodides of indium and thallium gave off strong spectra of both metals. The work of Steinmetz did at that time not lead to the introduction of practical metal halide lamps, it seems his ideas were too much ahead of his time.

It took until the 1930s before proper electrodes and quartz to metal seals were developed allowing the introduction of mercury discharge lamps with operating pressures above atmospheric pressure. These high pressures could only be reached by a high wall temperature of the quartz arc tube. The use of a larger glass bulb around the arc tube provided the necessary thermal insulation and protection from UV radiation. The high-pressure mercury lamps showed an enhanced emission in the visible part of the spectrum, while the mercury UV emissions were much weaker compared to the early low-pressure lamps. Since the mercury spectrum does not contain emission lines of wavelength longer than 579 nm, these high-pressure mercury discharges were still lacking emission in the red. In the following two decades research activities were focused on color-corrected mercury lamps. In these lamps a phosphor coating on the inside of the outer bulb resulted in additional red emission, thereby improving the color rendition of the lamp (see \textit{e.g.} ref. 20 and 21).

In the late 1950s and early 1960s the application of Steinmetz’s ideas for color modification of mercury lamps was investigated for the high-pressure mercury discharge lamps. This led in 1961 to the first patent for this type of lamp by Gilbert Reiling from General Electric.\textsuperscript{22} Shortly after its market introduction in 1964, most major manufacturers launched similar lamps. It was recognized already in these years, that a change of the material
of the arc tube from quartz to a translucent ceramic material, would allow higher wall temperatures of up to 1200 K, leading to a better efficiency and better color properties. A ceramic arc tube would also be more resistant to the corrosive nature of the metal halide salts. Suitable solutions for electrical feed troughs were, however, not available at that time. It took until 1993 for Philips to invent a complex solution which enabled them to introduce the first viable metal halide lamp with a sintered alumina ceramic discharge tube. This type of metal halide lamp is still marketed today.

1.3 Metal Halide Lamps: Physics and Chemistry

Metal halide lamps are currently produced in a large variety of power ratings, and spectral distributions. Each application has its own specific design characteristics. Besides differences in size and power output, also differences exist in applied wall materials and filling substances. A recent example of a compact metal-halide lamp is shown in Figure 1.2.
This typical example contains a polycrystalline alumina (PCA) discharge vessel (also referred to as arc tube), while quartz glass is also still in use as construction material. Figure 1.2 also contains a schematic representation of the discharge vessel. In the arc tube two tungsten electrodes are positioned opposite of each other. The light generating electric discharge occurs between the tips of these electrodes. The arc tube furthermore contains a mixture of metal halide compounds, a dose of mercury and a certain amount of noble gas (e.g. argon or xenon). The metal halide salts have a negligible vapor pressure at room temperature, therefore the noble gas and the mercury are needed for the startup of the electric arc. The noble gas is also supporting a stable arc. In the startup phase of the lamp, the mercury discharge warms up the arc tube to temperatures where the metal halide mixture melts and starts to evaporate. As metal halide molecules evaporate, they are transported by diffusion and convection to the discharge area, where they dissociate to atoms and ions. Thermal and electronic excitation results in additional emissions to the mercury emission lines, which are characteristic for the metals used in the metal halide salt mixture. When the atoms and ions leave the emitting arc, they recombine again to metal halide molecules in the cooler parts of the arc tube. These molecules either condense on the coldest spot or are transported back to the discharge region. This cyclic process maintains a constant amount of metal species in the arc and thus results in a stable emission spectrum of the lamp. Depending on the added metals, the appearance of the emitted white light can be tuned. Using sodium iodide in combination with rare-earth iodides or with tin, thallium and indium halides results in a warm or neutral white color. A daylight white color is obtained by the combination of cesium halides with rare-earth bromides. The use of mixtures of Lanthanide bromides and iodides (LnX₃, Ln = lanthanide atom; X = Br, I) and the bromides and iodides of the alkali metals Na and Cs (MX, M = Na, Cs; X = Br, I) results in much higher lanthanide concentrations in the arc than expected on the basis of the vapor pressure of the lanthanide bromide or iodide alone. The formation of MLnX₄-type mixed complexes in the vapor phase is responsible for this vapor pressure enhancement (see refs. 25-27 and references cited herein).

The rated lifetime of the various available types of metal halide lamps differs from 6000 to over 20000 Hrs. The operating lifetime is limited by the reactions of the lamp filling with the quartz or PCA of the wall or reactions between the lamp filling and the tungsten electrodes. Typical temperatures for these reactions to take place are 1100–1400 K for the wall and 2850–3100 K for the electrode. Three mechanisms have been identified:

- Transportation of tungsten from the electrode to the wall by interaction with iodine in the gas phase originating from the metal halide salts (e.g. NaI or DyI₃). Wall blackening is the result, translating itself in loss of light and automatically in loss of efficiency.
• Reaction of the metal halide lamp filling with the wall of the arc tube. This results in transportation of wall material from hotter places to the cooler regions by a gas phase process. Complex gaseous molecules like SiO$_2$ are involved in this process. The light emitted from the arc is scattered by the corroded wall surface, and as a result the reflector cannot generate an effective bundle. Besides, corrosion products like SiI$_4$ can react with the electrode material.

• Part of the aluminium oxide arc tube wall of the latest generation of metal halide discharge lamps can dissolve in the metal halide salt pool. This enables transportation of wall material by way of the salt pool.

The modeling of corrosion processes in metal halide lamps can result in important design directives for optimizing the expected operating lifetime (e.g., maximum allowable temperature, concentration and composition of metal halide salt, allowable level of impurities). The available computer codes for modeling these processes are based on the assumption of local thermodynamic equilibrium (LTE) and follow the approach of a Gibbs free energy minimization. The quality of the results obtained by using these programs strongly depends on the reliability of the thermodynamic input data of all possible species that might be present under the conditions in the lamp. The present status of the thermodynamic characterization of the pure lanthanide halide additives and their vapor complexes with alkali halides will be covered in the following two paragraphs.

1.4 Thermochemical Characterisation of the Pure Lanthanide Tribromide and Triiodide Additives

The required input for species to be taken into account in thermodynamic equilibrium calculations is the Gibbs free energy as a function of temperature. Essential parameters for the derivation of the Gibbs free energy function of the species under consideration are the heat capacity as a function of temperature, the enthalpy of formation and the standard entropy.

The enthalpy of formation of the solid lanthanide tribromides and triiodides is generally obtained from solution calorimetry. Cordfunke and Konings have evaluated all relevant literature up to the year 2000 containing experimental results on the enthalpy of formation of lanthanide trichlorides, tribromides and triiodides. Recommended values for the enthalpy of formation of all lanthanide bromides and iodides can be found in their review.

The heat capacity function from several degrees above absolute zero to room temperature can be measured by adiabatic low-temperature calorimetry and the standard molar entropy at $T = 298.15$ K can be derived from these measurements. Unfortunately, only
two low-temperature heat capacity measurements have been reported for the lanthanide tribromides and triiodides, namely for EuBr$_3$ and LuI$_3$. Based on this very limited set of experimental data, Konings and Kovács have derived a best possible estimate for the standard molar entropy at $T = 298.15$ K for the experimentally undetermined tribromides and triiodides. Earlier estimates for the standard molar entropies for the lanthanide bromides and iodides in the solid state by Myers and Graves were only based on the measurement for EuBr$_3$ and the experimental results available for the lanthanide trichlorides. These estimates are superseded by the assessment of Konings and Kovács and should not be used in thermodynamic equilibrium calculations.

From $T = 298.15$ K up to above their melting temperatures, the heat capacity functions for the lanthanide tribromides CeBr$_3$, NdBr$_3$, GdBr$_3$ and HoBr$_3$ and the lanthanide triiodides LaI$_3$, NdI$_3$, GdI$_3$ and TbI$_3$ have been derived from the enthalpy increments measured by drop calorimetry. In addition, differential scanning calorimetry (DSC) was used to determine the heat capacity functions of the tribromides LaBr$_3$, CeBr$_3$, PrBr$_3$, NdBr$_3$, TbBr$_3$, DyBr$_3$, and the triiodides LaI$_3$, CeI$_3$, NdI$_3$, and TmI$_3$. The DSC and drop calorimetry measurements have also resulted for several of the above mentioned systems in enthalpies and entropies of fusion and heat capacities for the liquid phase. For all other tribromides and triiodides where experimental information regarding the heat capacity function for $T > 298.15$ K or about the phase transitions is lacking, Konings and Kovács have published estimates.

It is obvious that thermodynamic models involving lanthanide tribromides and triiodides can significantly be improved by performing additional low- as well as high-temperature heat capacity measurements, thereby extending the experimental basis for recommended heat capacities and standard entropies.

The thermodynamic description of gas-phase species also requires knowledge of the heat capacity function, the enthalpy of formation and the standard entropy. In general, the enthalpy of formation is obtained by the summation of the sublimation enthalpy and the enthalpy of formation of the solid. For high-temperature gaseous species, the heat capacity function is not obtained by measurements, but the ideal-gas thermodynamic functions are derived in the harmonic-oscillator rigid-rotator approximation by use of statistical thermodynamic methods. The corresponding equations relate the heat capacity, and as a consequence also the entropy and enthalpy, to the molecular partition function $Q$. This function consists of a translational, an electronic, a vibrational and a rotational contribution, which are all treated individually.

Knowledge of several molecular properties is essential for evaluating $Q$. For the translational partition function, only the molecular weight is needed. Necessary for the calculation of the electronic partition function are the electronic energy levels of the gaseous
molecules. Experimental information regarding the electronic energy levels of the lanthanide tribromides and triiodides in the gas phase is absent in literature. Therefore, as an approximate, the energy levels of Ln$^{3+}$ ions determined in crystals with a local symmetry resembling the lanthanide coordination in the respective LnX$_3$ (X = Br, I) molecules are used. The vibrational partition function requires knowledge of all vibrational fundamentals and the input for the rotational partition function are the molecular symmetry and the moments of inertia of the gaseous molecules.

Lanthanide tribromides and triiodides have a low volatility; the temperatures where the compounds have a sufficiently high vapor pressure to be studied are well over 800 K. The experimental methods which can be used to determine the vibrational properties and the molecular structure – information essential for the evaluation of the vibrational and rotational partition function, respectively – are gas-phase infrared (gas-IR) and gas-phase Raman spectroscopy (gas-R) and gas-phase electron diffraction (GED). These experimental methods suffer from limitations, inherently connected with the high temperature conditions necessary to perform the experiments. Besides technical difficulties, the thermal average geometry determined by the electron diffraction experiment may be quite different from the equilibrium geometry of the molecules. Moreover, the high experimental temperature leads to the excitation of vibrational states and, accordingly, results in broad band contours in the infrared and Raman spectra. This makes unambiguous symmetry assignments on the basis of infrared and Raman selection rules impossible (see e.g. ref. 53 and 54).

Alternatively, matrix-isolation infrared and Raman techniques are used to determine the vibrational properties and molecular symmetry of high-temperature species. By applying the matrix-isolation technique, where the evaporated molecules are “captured” inside cavities in an excess of frozen inert gas (e.g. argon, krypton or xenon), the problems associated with the high temperatures are circumvented, while alike the gaseous state, the molecules can be considered as isolated from each other. However, due to matrix site effects, and possible complex formation between the studied molecule and the matrix host, vibrational frequencies might shift in the matrix compared to their gas-phase values, or even new signals might appear. In addition to the above mentioned experimental techniques, quantum chemical computations have become an increasingly important tool in the study of the molecular properties of rare earth compounds. Several effective core potentials are available for the lanthanide atoms that make these computations feasible. The results of quantum chemical computations create a bridge between the results obtained by various experimental techniques and moreover can be used to predict the properties of species which have not been the subject of an experimental study.

Numerous experimental and theoretical studies have been performed in order to elucidate the molecular geometry and vibrational properties of the lanthanide tribromides and
triiodides in the past decades, the results most recently being summarized in a review by Kovács and Konings. A set of recommended parameters for the calculation of thermodynamic functions is included in their review, the vibrational parameters partially based on preliminary results from the study reported in this thesis. An earlier summary of the vibrational properties can be found in the review of Boghosian and Papatheodorou, while structural results were previously included in a review of Hargittai about the molecular structure of metal halides. As a result of the rather confusing results in literature, a controversy regarding the molecular symmetry of the lanthanide halides existed for over 30 years. Amongst the more recent experimental and theoretical results there finally seems to be consensus about assigning a planar molecular structure to the tribromides and triiodides of the heavier lanthanides. The tribromides and triiodides of the light lanthanides are assigned a planar or quasiplanar structure.

Nevertheless, comparing the results of the computations and the experimental data reveals also significant discrepancies, in particular with respect to the equilibrium bond length and the value of the out-of-plane deformation vibration. A recent investigation of a lanthanide chloride (DyCl₃) has shown the synergy of using a broad range of experimental data in combination with state-of-art high level computations. It proved even possible to derive theoretical corrections to the high-temperature spectroscopic values. Similar studies for lanthanide bromide and iodide systems could serve as a benchmark for future adjustments of the recommended values for the equilibrium structures and vibrational frequencies of these systems.

A profound knowledge of the influence of the theoretical level on the reliability of the predicted structural and energetic properties would also enable to select the appropriate level of theory for the computation of the molecular properties of several oligomers, such as the dimer and trimer. Before 1975 it was assumed that the vapor of the rare earth trihalides was monomeric. Mass spectrometric measurements performed since then have shown that appreciable amounts of dimer, of up to 10%, might occur in the vapor (see e.g. ref. 31 and references cited herein). The amount of dimer is too low to allow for a thorough analysis of its structural, vibrational and energetic properties from experimental data. The experimental information of the vibrational fundamentals of lanthanide bromide and iodide dimer molecules is limited to the observation of one single band (of altogether 18 fundamentals) in the matrix isolation spectra of dysprosium bromide and dysprosium iodide. Structural data from GED experiments are thus far rather limited as well. The low dimer content in combination with a strong correlation between the monomer and dimer structural parameters make the introduction of constraints taken from quantum chemical calculations mandatory in order to get proper results for the monomer. It has been shown that for ignoring each percent of dimer, the determined monomer bond length will contain an error of about 0.01Å.
Not only the bond length from GED will suffer, but also the enthalpy of sublimation derived from vapor pressure studies is influenced by ignoring the presence of dimers. Konings and Kovács estimated the influence to be an underestimation of the sublimation enthalpy by 2–3 kJ·mol\(^{-1}\) for a dimer content of 10\%.\(^{31}\) This corresponds to a relative error of about 1\%, which was lower than the variation between studies on the same molecule performed in different laboratories. Therefore, they have neglected the dimers in their analysis of literature vapor pressure data which ultimately resulted in recommended values for the enthalpies of sublimation of the lanthanide tribromides and triiodides.\(^{31}\) By a summation with the enthalpy of formation of the condensed state, the formation enthalpies of the gaseous tribromides and triiodides of the lanthanides were derived. Recently, the group of Kudin and Butman have investigated the evaporation of a variety of lanthanide tribromide systems and PrI\(_3\), in which the dimers were included in the analysis.\(^{40,90-97}\)

Knowledge of the thermodynamic functions of both the gas-phase species, monomer and dimer, and the condensed phase is mandatory in order to derive the enthalpy of sublimation from vapor pressure studies such as mass spectrometry, torsion effusion, and Knudsen effusion. Improving the experimentally determined thermodynamic functions of the condensed phase LnX\(_3\) (X= Br, I) and extending the knowledge on the molecular parameters necessary to calculate the gas-phase thermodynamic functions of both the monomers and the dimers would certainly contribute in refining the thermodynamic description of these systems. New research would ideally use the synergy of state-of-art computations with all possible spectroscopic techniques.

1.5 Complexes in the Gas-Phase between Lanthanide Halides and Alkali Halides

The importance of the formation of vapor complexes in quasi-binary systems of rare-earth halides (LnX\(_3\), Ln = rare earth) with alkali halides (MX) for the application in metal halide lamps has been addressed before. The existence of these complexes has been shown and thermodynamic characteristics of their dissociation to LnX\(_3\) and MX have been determined by numerous experimental studies, mostly by Knudsen-effusion mass spectrometry.\(^{26,27,62,98-104}\) Other techniques, such as gas-phase spectrophotometry,\(^{105}\) torsion-mass-effusion, chemical analysis of the condensed equilibrium vapors, vapor transpiration techniques and vapor pressure measurements have also been applied to a lesser extent (see ref. 62 and references therein).

It has been known for a long time\(^{106-109}\) that complex formation increases the partial pressure of the lanthanide trihalide in the vapor resulting in several practical applications of these complex halides. Besides the earlier mentioned application of a variety of bromide and
iodide complexes as important vapor species in high-intensity metal halide lamps (as they are responsible for the vapor transport of the lanthanide elements from the cooler regions in these lamps to the emitting arc (see section 1.3 and e.g. ref. 27)), the chloride complexes were suggested for high-temperature extraction and separation of the lanthanide metals.\textsuperscript{110,111}

The reliability of optimizing the conditions of these high-temperature applications by thermodynamic modeling depends on the availability of accurate thermodynamic functions of all chemical species involved. For this, knowledge of their molecular structure and vibrational frequencies is needed. Similar to the situation with the pure lanthanide trihalides, the experimental determination of the molecular structure and the vibrational properties of MLnX\textsubscript{4} complexes is hindered by the required high temperatures. In addition, the complex nature of the vapor composition seriously hampers the interpretation of the results: besides the MLnX\textsubscript{4} species the MX and LnX\textsubscript{3} monomers and M\textsubscript{2}X\textsubscript{2} dimer are always present and, with less probability, the Ln\textsubscript{2}X\textsubscript{6} dimer, the M\textsubscript{2}LnX\textsubscript{5} heterocomplex and their decomposition products can appear as well.\textsuperscript{103} As a consequence no experimentally determined structure of any MLnX\textsubscript{4} complex is available to date. Only one single vibrational spectroscopic (matrix isolation infrared) study has been reported on MCl–NdCl\textsubscript{3} (M = Li, Na, Cs) mixtures and the LiBr-DyBr\textsubscript{3} system.\textsuperscript{112} Just one IR-active stretching mode of the LnX\textsubscript{4} tetrahedron of MLnX\textsubscript{4} (from the altogether 12 fundamentals) was reported, but no conclusion regarding the molecular symmetry of the complexes could be made. Gas electron diffraction and gas-phase Raman spectroscopic studies on related light rare earth species KYCl\textsubscript{4},\textsuperscript{113} and CsScI\textsubscript{4},\textsuperscript{101} respectively, did not provide any unambiguous structural assignment either.

The need for accurate thermodynamic functions for the MLnX\textsubscript{4} complexes is also illustrated by the available experimental thermodynamic data on these systems reported thus far. Most studies report the enthalpy and entropy of the formation reaction of the respective complex at the average temperature of the experiments (see ref. 62 and references therein). This makes a comparison of the formation characteristics of the variations in the alkali, lanthanide and halogen series difficult. The extrapolation of the thermodynamic quantities to \( T = 298.15 \text{ K} \) can only be done when the thermodynamic functions of the respective species are known.

Due to the experimental difficulties with these complex halides, the importance of quantum chemical computations is obvious.\textsuperscript{52} Nonetheless, the number of papers reporting computed data on MLnX\textsubscript{4} complexes is quite small. Pioneering calculations at the Hartree-Fock level of theory were performed by Kapala et al. on NaCeCl\textsubscript{4} and NaNdCl\textsubscript{4}.\textsuperscript{114,115} Beside the simple theoretical level applied, another limitation of this study was that the authors considered only the bidentate structure, neglecting other possible isomers. A more detailed study using advanced theoretical levels has been performed on NaDyBr\textsubscript{4}.\textsuperscript{116,117} All three possible structures (mono-, bi- and tridentate, see Figure 1.3) have been evaluated and several properties of the ionized complex were investigated.\textsuperscript{116,117}
Introduction

Figure 1.3 Characteristic structures and labeling of the geometrical parameters of the $\text{MDyX}_4$ ($M = \text{Li, Na, K, Cs}; \ X = \text{F, Cl, Br, I}$) coordination complexes.

The tridentate complex was established as the ground-state structure, but the influence of entropy at the high temperature conditions in a metal halide lamp results in a larger stability of the bidentate structure under these conditions. It is obvious that these advanced theoretical methods offer a good alternative for the structural and vibrational analysis of the $\text{MLnX}_4$ vapour species. New calculations in combination with selected vibrational spectroscopic experiments are necessary which will allow to establish trends in the energetic, structural, bonding, and vibrational properties within the lanthanide series as well as in the alkali and halogen groups.
1.6 Scope of this Thesis

As described in the preceding paragraphs, metal halide lamps are complex high temperature systems. Important processes influencing product life span and light characteristics in these systems are difficult to fathom, due to a lack of knowledge on the interactions between the various components inside these lamps. Since future developments of these commercially important metal halide lamps depend on the availability of fundamental knowledge of the bonding, structure and thermodynamic stability of the basic filling components, the research project described in this thesis was initiated as a collaboration between the Science Technology Foundation STW, Philips Lighting B.V, the Netherlands Energy Research Foundation ECN and the University of Amsterdam.

The thermodynamic properties of the condensed phase of two examples of lanthanide halides applied as lamp fillings, the bromide and iodide of dysprosium, have been determined in Chapter 2. From the measurements in this chapter the thermodynamic functions for DyBr$_3$ (s) and DyI$_3$ (s) could be calculated to their melting temperatures.

Next to elucidate the chemical processes in the metal halide lamps under operating conditions, a systematic study of the structure, bonding and vibrational properties of the vapors of all compounds involved have to be performed. An essential start to come to a better understanding is the determination of the structure, bonding and vibrational properties of the vapors of the binary lanthanide halide systems. In Chapter 3 the molecular geometry and vibrational frequencies of the monomeric and dimeric dysprosium tribromide species have been determined by using a broad range of experimental techniques (gas-phase electron diffraction, gas-phase infrared and matrix-isolation infrared and Raman spectroscopy), in conjunction with high level molecular orbital calculations. In Chapter 4, the results of applying the same techniques for DyI$_3$ have been reported.

As described before, additives to the rare earth halides as lamp fillings have been used in the form of alkali halides. As expected, complexes are formed between the lanthanide halides and alkali halides. These complexes proved to be very important for the lamp characteristics. Therefore, systematic studies on the structure, bonding and thermodynamics of these complexes have been performed using advanced theoretical levels on LiLnX$_4$ complexes (Ln = La, Ce, Dy; X = F, Cl, Br, I), MLaX$_4$ complexes (M = Na, K, Cs; X = F, Cl, Br, I), and MDyX$_4$ complexes (M = Li, Na, K, Rb, Cs; X = F, Cl, Br, I). From these studies, trends in the energetic, structural, bonding, and vibrational properties have been established within the lanthanide series as well as in the alkali and halogen groups. The theoretical results have been benchmarked by measuring the matrix-isolation infrared spectra of three complexes, which have relevance for currently available metal halide lamps: NaDyBr$_4$, CsDyBr$_4$ and CsDyI$_4$. The theoretical study on LiLnX$_4$ and MLaX$_4$ complexes is
presented in Chapter 5, whereas the molecular structure and vibrational spectra in comparison with the theoretical outcomes are described in Chapter 6.

1.7 References

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Chapter 1


