Structural and thermodynamic investigations of lanthanide halide species in metal halide discharge lamps
Groen, C.P.

Citation for published version (APA):
Groen, C. P. (2012). Structural and thermodynamic investigations of lanthanide halide species in metal halide discharge lamps

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Summary

The metal halide lamp combines great color characteristics with energy efficient operation, a strong power output and a long product life span. Besides the tremendous recent developments in solid state lighting, metal halide lamps also represent a great potential for fulfilling future demands in light generation, in particular for applications where a high power output is essential. Typical applications of metal halide lamps are street lighting, large area lighting, automotive headlights, projector systems and shop lighting.

In Chapter 1 the history, the working principles and possible failure mechanisms of metal halide discharge lamps are outlined. Important design directives for future generations of metal halide lamps, in particular the concentration and composition of the metal halide fill, the maximum allowable vessel temperature, and the allowable level of impurities, can be obtained by modeling the life-limiting processes in these lamps. The computer codes used for this purpose follow the approach of a Gibbs free energy minimization, assuming local thermodynamic equilibrium. The quality of the results obtained by using these programs strongly depends on the reliability of the thermodynamic input data. The present status of the thermodynamic characterization of the pure lanthanide halide lamp additives and their vapor complexes with alkali halides was addressed in Chapter 1 as well. It was concluded that the experimental basis for the thermodynamic functions used for the solid lanthanide tribromides and triiodides is very limited. A significant improvement of the thermodynamic models involving these systems can be accomplished by performing additional low- as well as high-temperature heat capacity measurements. Another conclusion following from Chapter 1 is that an extension of the knowledge on the molecular parameters necessary to calculate the gas-phase thermodynamic functions of both the monomers and the dimers of the lanthanide halides and of their vapor complexes with alkali halogenides would certainly contribute in refining the thermodynamic description of these systems.

The results of low-temperature calorimetric measurements and high-temperature enthalpy increment measurements on DyBr₃(s) and on DyI₃(s) are described in Chapter 2. The data reveal enhanced heat capacities below $T = 10$ K, consisting of a magnetic and an electronic contribution. From the results obtained and enthalpies of formation from the literature, the thermodynamic functions for DyBr₃(s) and DyI₃(s) have been calculated from $T \to 0$ K to their melting temperatures at 1151.0 K and 1251.5 K, respectively. Besides the direct applicability to the improvement of models for metal halide lamps containing the bromide or iodide of dysprosium as additive, the results described in chapter 2 can also be used in the future for improving the existing estimates of the solid state thermodynamic functions of experimentally undetermined lanthanide bromides and iodides.

For the gaseous lanthanide tribromides and triiodides, the thermodynamic functions are derived in the harmonic-oscillator rigid-rotator approximation by use of statistical
thermodynamic methods. Essential input parameters for the derivation of the thermodynamic functions are the molecular structure and the vibrational frequencies. In the work described in chapter 3, the molecular geometry and vibrational frequencies of monomeric and dimeric dysprosium tribromide, DyBr$_3$ and Dy$_2$Br$_6$, together with the electronic structure of their ground and first few excited states were determined by high-level computations, electron diffraction, gas-phase infrared, and matrix isolation infrared and Raman spectroscopy. The effect of partially filled 4f orbitals and spin–orbit coupling on their structure was studied by computations. While the geometry of the monomer does not depend on the 4f orbital occupation, the bond angles of the dimer are noticeably influenced by it. The monomer is found to be planar with all methods; however, it forms a complex with the matrix molecules in the matrix-isolation spectroscopic experiments, leading to the pyramidalization of the DyBr$_3$ unit. The model calculations in this regard also explain the often conflicting results of computations and different experiments about the shape of lanthanide trihalides.

In chapter 4, the combination of experimental and theoretical methods which was demonstrated to be successful for DyBr$_3$ and its dimer in chapter 3, was subsequently applied to determine the molecular and electronic structure and the vibrational frequencies of dysprosium triiodide, DyI$_3$, and its dimer, Dy$_2$I$_6$. The free monomeric molecule is planar according to all methods, but similar to the behaviour of DyBr$_3$, the molecule forms complexes in the matrix-isolation experiments causing pyramidalization of planar monomeric molecules. The likelihood of having both pyramidal and planar DyI$_3$ molecules in the matrix was discussed in order to explain certain features of the spectra. In analogy with the results obtained for Dy$_2$Br$_6$ in chapter 3, the computations suggest also that the Dy$_2$I$_6$ dimer geometry depends on the occupation of the partially filled 4f orbitals.

Lamp fillings do not only contain rare earth halides, but usually mixtures consisting of rare earth halides and alkali halides are applied. The gas phase complexes formed between the lanthanide halides and alkali halides are very important for the lamp characteristics. Therefore, a systematic theoretical study has been performed on the structure, bonding and thermodynamics of these mixed MLnX$_4$ (M = alkali metal; Ln = rare earth metal; X = halogen) complexes from which the results are covered in two parts in chapter 5.

The structural, bonding and vibrational results obtained for LiLnX$_4$ (Ln = La, Dy; X = F, Cl, Br, I) complexes in part A of chapter 5 were obtained using various quantum chemical methods (HF, MP2 and the Becke3-Lee-Yang-Parr hybrid density functional) in conjunction with polarized triple-ζ valence basis sets and quasi-relativistic effective core potentials for the heavy atoms. Our comparative study indicated the superiority of MP2 theory while the HF and B3LYP methods as well as less sophisticated basis sets failed for the correct energetic relations. In particular, f polarization functions on Li and X proved to be important for the Li···X interaction in the complexes. In part B of chapter 5, the study of the structure, bonding, and vibrational properties of the mixed MLaX$_4$ (M = Na, K, Cs; X = F, Cl, Br, I) rare
earth/alkali metal halide complexes is reported, using the MP2 method in conjunction with polarized triple-\(\zeta\) valence basis sets and quasi-relativistic effective core potentials for the heavy atoms.

From the results in chapter 5, 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. From the three characteristic structures, possessing 1- \((C_{3v})\), 2- \((C_{2v})\), or 3-fold coordination \((C_{3v})\) between the alkali metal and the bridging halide atoms, the bi- and tridentate forms are stable isomers with similar dissociation energies. In general, for the complexes existing of lighter alkali metals and halogens, the bidentate structure corresponds to the global minimum of the potential energy surface, while the heavier analogues favour the tridentate structure. At experimentally relevant temperatures \((T > 800 \text{ K})\), however, the isomerisation entropy leads to a domination of the bidentate structures over the tridentate forms for all complexes.

Variation of the geometrical and bonding characteristics between the lanthanum and dysprosium complexes reflect the effect of “lanthanide contraction”. An important effect of the size of the alkali metal is manifested in the larger stabilities of the K and Cs complexes. The natural atomic charges are in agreement with strong electrostatic interactions in the MLnX\(_4\) complexes. The marginal covalent contributions show a slight increasing trend in the heavier analogues. The calculated vibrational spectra indicate that infrared spectroscopy may be an effective tool for the experimental investigation and characterization of MLnX\(_4\) molecules.

This conclusion is utilized in chapter 6, where the computed structures, energetic, and vibrational properties of MDyX\(_4\) \((M = \text{Li, Na, K, Rb, Cs}; X = \text{F, Cl, Br, I})\) mixed alkali halide/dysprosium halide complexes have been benchmarked by matrix-isolation Fourier-transform infrared spectroscopic experiments on three complexes, which have relevance for currently available metal halide lamps: NaDyBr\(_4\), CsDyBr\(_4\) and CsDyI\(_4\). In accordance with the MP2 results of chapter 5 on the MLnX\(_4\) molecules, the DFT computations reported in chapter 6 result in a tridentate ground state for the complexes with heavier halides and alkali metals, while at high temperatures the bidentate structural isomer dominates. The survey of various dissociation processes revealed the preference of the dissociation to neutral MX and DyX\(_3\) fragments over ionic and radical dissociation products. Cationic complexes are considerably less stable at 1000 K than the neutral complexes, and they prefer to dissociate to \(M^+ + \text{DyX}_4^-\) fragments.

The vapor species of selected mixtures of NaBr and CsBr with DyBr\(_3\) and of CsI with DyI\(_3\) in the temperature range 900–1000 K have been isolated in krypton and xenon matrices and investigated by infrared spectroscopy. Besides the characteristic vibrational frequencies of the monomeric and dimeric alkali halide species and of the dysprosium trihalide molecules, certain signals indicated the formation of MDyX\(_4\) \((M = \text{Na, Cs}; X = \text{Br, I})\) mixed complexes.
Comparison with the computed vibrational and thermodynamic characteristics of the relevant species leads to the conclusion that these complexes appear in the vapor predominantly as the $C_{2v}$-symmetry bidentate isomer. This is the first time that this structure was identified in an experimental vibrational spectroscopic study. The signals appearing upon performing a thermal anneal cycle were tentatively assigned to the double complex $\text{M}_2\text{DyX}_5$ ($\text{M} = \text{Na, Cs}$; $\text{X} = \text{Br, I}$). A structure in which one alkali atom is bound to dysprosium by three and the other by two bridges is proposed for these double complexes.