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Novel Molecular Discharge Light Sources

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Abstract. A systematic investigation into transition metal halides and -oxides showed the high potential of transition metal oxides as visible radiators for highly efficient gas discharge light sources. Zirconium monoxide (ZrO) has been identified as most promising candidate combining highly attractive green and red emission band systems with very high dissociation energy (8.2eV) which assures that the molecule is stable even in the hot plasma centre. Thus far, however, it has been impossible to keep ZrO in the gas phase of a closed discharge vessel, because at wall temperature usually compounds are formed which have negligible vapour pressures. We succeeded in establishing a regenerative chemical cycle by filling ZrX_4 (X=Cl, Br, I) together with a stable, but volatile oxygen compound (like MoO_2X_2) and realized thus highly attractive, novel gas discharge light sources.

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1. Introduction

The aim of any lamp engineer is to develop a white light source with good colour rendering properties ($Ra_8 > 80$) and highest luminous efficacy η . Current discharge lamps – emitting mainly *atomic* radiation – are reaching only about *half* of the theoretical efficacy limit of 200-230 lm/W. The possible efficacy rise by increasing atomic radiation is limited by self-absorption of the atomic lines (= radiation trapping). This limitation does not apply for *molecular* radiation, since the molecular emission is distributed over a huge number of molecular transitions which is several orders of magnitude higher than the corresponding number of atomic lines.

As a matter of fact, *various* molecular radiators have been investigated in gas discharges for lighting applications in the course of the last century [1-15]. Nevertheless there still is no large-scale commercially applied discharge lamp type on the market whose radiation output is dominated by molecular emission. Molecular discharge light sources investigated in the past suffered from serious drawbacks: Severe chemical attack of the wall material, corrosion of the tungsten electrodes and – in most cases – poor plasma efficacy.

Therefore, we strive for a breakthrough efficacy improvement by introducing *novel molecular* radiators for discharge lamps.

2. Transition Metal Atoms and Molecules

Transition metal (TM) *atoms* are known to have strong p-s transitions leading to radiation in the *near UV* or *blue* spectral range. Therefore, we need additional, highly efficient *molecular* radiators in the *green* and *red* spectral range to realize a discharge lamp emitting white light with good colour rendering properties.

It is well-known that certain *transition metal oxides* (e.g. NbO) emit interesting red or near IR band systems [15]. For a systematic overview we simulated visible emission spectra of all Group IVb-VIb transition metal oxides using spectroscopic constants from literature [16][17]. Figure 1 is showing these spectra in the spectral range from 300nm to 900nm. The chosen colours of the individual molecular band systems are approximately representing the colours of the corresponding light emission.

Figure 1. Predicted Spectra of Transition Metal Oxides

This overview taught us that the spectrum of *zirconium oxide* (ZrO) is most promising, since it has broad, strong band systems in the green ($e^3\Pi-a^3\Delta$) ($A_{ik} \approx 2 \cdot 10^7 s^{-1}$ [18]) and red ($d^3\Phi-a^3\Delta$) ($A_{ik} \approx 1 \cdot 10^7 s^{-1}$ [18]) spectral region, but almost no emission in the IR [19]. These strong transition probabilities A_{ik} imply that ZrO molecules at 1mbar partial pressure and an excitation temperature of 4500K would emit $25 W/cm^3$ in each of those triplet band systems. Such low partial pressures of ZrO will thus be high enough to realize efficient molecular discharge light sources.

TM oxides also show very *high dissociation energies* (8.2eV for ZrO), because they have a *double bond* between the metal and oxygen. This gives a huge efficacy advantage compared to TM *halides*, because TM *oxides* will remain *undissociated* in the hot centre ($\approx 4500\text{K}$) of our novel molecular discharge. (Our novel molecular discharge is not a common HID discharge, because the total pressure will be below 1bar with the buffer gas (Xe) as dominating species (see Figure 10). As explained later we are aiming at a high centre gas temperature to realize a regenerative chemical cycle. Therefore, we have to raise the buffer gas pressure considerably above the values ($\approx 1\text{bar}$) usually applied in low-pressure lamps to increase the electron collision frequency and thereby to guarantee sufficient heating of the discharge gas).

2.1. Molecular Orbital Theory: Why Transition Metal **Oxides** are so well-suited

When browsing through the literature on radiative properties of transition metal molecules we came across figure 16 of [20]. We recognized that a modified version of this figure (figure 2) could be the key to understand the radiative properties of transition metal atoms, positive ions and halide molecules.

Figure 2. Atomic Orbital Energies of 5th Row Transition Metals (based on figure 16 of [20]).

The following conclusions can be immediately drawn from this graph:

- The strongest *atomic* radiation contributions will come from the 5p-5s transitions.
- Those transitions will basically be located in the UV and blue spectral region.
- The 5s-4d transitions would be highly attractive, because they would cover the whole visible spectrum and the wavelength could be “tuned” by selecting the proper transition metal.
- Unfortunately, these transitions are *electric dipole forbidden* in the atoms and positive ions.

The crucial question is thus: How can these promising 5s-4d transitions be enabled?

A possible option is “to break the symmetry”. In our case this would mean that we could place our atoms or ions into a strong, inhomogeneous electric field, which would split-up the 4d orbital into three sub-levels of different energies, which are characterized by the absolute value of the angular momentum M_L along the direction of the field and designated as σ , π and δ for $M_L = 0, 1$ and 2 , respectively. Due to the interaction energy of the permanent electric quadrupole moment Q of the atomic orbital with the inhomogeneous electric field the energetic ordering will always be in that way that δ will be pushed towards lower energies and σ and π will be pushed upwards in energy as sketched in figure 3:

Figure 3. Sublevels of the 4d orbital in an inhomogeneous electric field.

The important point is that electric dipole transitions with $\Delta\Lambda = 0, \pm 1$, i.e. transitions between $5s\text{-}\sigma$ and $4d\text{-}\sigma$ and between $5s\text{-}\sigma$ and $4d\text{-}\pi$, are now allowed. From figure 3 it is apparent that those 4d sublevels with allowed transitions to 5s will be pushed upwards in energy with respect to the 4d orbital.

The easiest way to realize such a “strong, inhomogeneous electric field” is, of course, to combine a positively charged *transition metal ion* and a negatively charged *halogen ion* into a transition metal halide *molecule*. Since the transition metals have quite low first ionisation potentials (especially towards the left side of the period) and the halogens have quite high electron affinities, these molecules can indeed very well be approximated as *ionic* molecules. This simplifies the spectroscopic discussion a lot, because the halogen ion has a rare-gas configuration – which means it will only have very high-lying excited states and not take part in any observed transitions – and the observed molecular transitions are basically transitions between the states of the *transition metal ion*, which are somewhat shifted in energy due to the electrostatic interactions between both ions of the molecule. This would mean that the spectroscopic properties of transition metal halide molecules – and especially the $5s\text{-}\sigma$ to $4d\text{-}\sigma$ transitions – could be discussed by using a modified version of figure 2. Figure 4 plots this dependence for the 5th row transition metals:

Figure 4. Energies of TM^+ ions in TM-halides

From figure 4 it is now apparent, where we should look for new, ionic red radiators: They should be located about midway between the crossing point of the $4d\sigma$ and $5s\sigma$ orbitals (near zirconium and niobium) and the right hand side (near silver) of the diagram. To find these “new” radiators we would have to look for $4d\text{-}5s$ excitations of the positive transition metal ions, which should have slightly higher energy differences than the desired molecular emission, i.e. be in the range $17000 - 20000\text{cm}^{-1}$. Performing a corresponding systematic investigation of *all* transition metal ions we indeed find only *one* promising candidate, Ru^+ , which is exactly located at that predicted point in figure 4. The Ru^+ ground state is a $4d^7\ ^4F_{9/2}$ term and the first excited quartet state with $4d^6(^3D)\ 5s$ configuration is a $^4D_{7/2}$ term at 19378.7cm^{-1} [21]. This energy difference in Ru^+ would thus correspond to a wavelength of 516nm , which should be shifted towards higher wavelengths in the ruthenium halide molecules. Unfortunately, to our knowledge there is no information in literature about the emission spectra of the ruthenium halides. Therefore, we filled 2mg RuCl_3 into a 32mm diameter spherical HID quartz microwave vessel and

measured the emission spectrum [22]. Indeed the measured spectrum showed – beside the emission lines of Ru-atoms – additional, probably molecular contributions in the green-orange and (infra)red spectral range. However, the efficacy of this first lamp was not high (about 6lm/W), because the wall blackened quickly (presumably by ruthenium metal deposits). There are two other drawbacks associated with most group VIIIB halide molecules as lamp filling constituents:

1. The dissociation energies of the diatomic molecules are quite low (e.g. 3.7eV for RuCl).
2. The vapour pressures are very low.

Let us thus go back to figure 4 and have a look at the *left hand side* of the transition metals, i.e. at the group IVB, where the dissociation energies and vapour pressures of these halides are both very high. Unfortunately, these transition metals are located near the intersection point of the $5s\sigma$ and $4d\sigma$ orbital energy curves. This means that we would expect mainly *infrared* radiation emission from the corresponding transitions. This assumption is confirmed when looking into literature. Figure 4 in [23], for example, depicts an energy diagram of the group IVB chlorides showing that most of the transitions in the doublet and quartet systems – these transitions correspond to $5s\sigma$ - $4d\sigma$ transitions – have energies below 10000 cm^{-1} , i.e. wavelengths above 1000 nm.

Finally, we have to conclude that the strongest molecular emissions from the stable and volatile group IVB to group VIB transition metal halides are again located in the near UV / blue spectral region, because they are correlated to the well-known $5p$ - $5s$ transitions in the metal ions (see figure 4). The interesting $5s\sigma$ - $4d\sigma$ transitions are mainly located in the IR – with the hafnium halides as one notable exception –, but it would be very desirable to have the $4d\sigma$ orbital “pushed up” towards higher energies in order to shift these transitions from the IR into the red or even green region of the spectrum.

First, there is apparently no possibility to further push up the $4d$ s orbital by electrostatic forces generated within an ionic molecule, because there are no other elements having higher electron affinities than the halogens. Consequently, we have to look for another type of interaction: *covalent bonds*. To realize strong covalent bonds we just have to step one column left from the halogens and use *oxygen* as molecular partner for the transition metals. We then might use molecular orbital theory to qualitatively describe these transition metal oxides by the so-called interaction diagram of figure 5.

At the left border of this diagram we find the $5s$ and $4d$ atomic valence orbitals of the transition metal and at the right the $2p$ atomic valence orbital of oxygen. There is still a (small) positive charge on the metal and a (small) negative charge on the oxygen, so the metal’s $4d$ and the oxygen’s $2p$ orbitals are split up into $4d\sigma$, $4d\pi$ and $4d\delta$ and $2p\pi$ and $2p\sigma$ terms, respectively (illustrated at the inner left and right parts of the diagram). But these σ and π terms are modified further due to the overlap interaction between the metal and the oxygen orbitals and are thus resulting in the bonding 11σ and 5π molecular orbitals, which are pushed lower down in energy than the corresponding oxygen orbitals and the antibonding $13\sigma^*$ and $6\pi^*$ molecular orbitals – which are, of course, *pushed higher up in energy than the corresponding metal orbitals*. The $4d\delta$ ($=2\delta$) and $5s$ ($=12\sigma$) orbitals remain largely metal-based nonbonding orbitals that are very close in energy.

Filling the molecular orbitals with the $2p^4$ valence electrons of oxygen (blue) and, as an example, the $4d^4 5s^1$ valence electrons of niobium (brown) we obtain the following configuration for the $^4\Sigma^-$ ground state of niobium oxide (figure 5):

Figure 5. Schematic molecular orbital diagram and electron configuration of NbO.

From figure 5 it is apparent that TM oxides are stable “*radicals par excellence*”:

- They have a double bond (5π and 11σ), i.e. high dissociation energies (~ 8 eV).
- They have unpaired electrons for bonds to other atoms.

It’s then the transitions from the 13σ* and 6π* antibonding orbitals to the 2δ and 12σ nonbonding orbitals, which offer us the possibility to directly generate visible radiation from the group IVB to group VIB transition metal oxides! This is illustrated in figure 6.

Figure 6. Orbital Energies of TM-oxides

Figure 1 – showing simulated spectra of the Group IVb to Group VIb TM oxides – is confirming this prediction of strong molecular emission band systems in the green to red visible region. It also teaches us that B⁴Π – X⁴Σ⁺ band system of the Group V oxide NbO is located in the far red region, where the eye sensitivity is low. Therefore, the neighbouring Group IVb oxide ZrO – where the corresponding molecular emission band systems are shifted towards higher energy differences (=lower wavelengths) – is the ideal candidate for a highly stable, green and red molecular radiator.

3. Regenerative Chemical Cycle

The volatility of TM oxides is generally extremely low. For TM with valences ≥ 5 the corresponding *TM oxide halides* (like e.g. NbOBr₃ or WO₂I₂) have reasonably high vapour pressures and can be used to bring *both* the TM *and* the oxygen into the vapour phase. Group IVb oxide halides (ZrOX₂), however, *cannot be*

evaporated at reasonable coldest spot temperatures ($\leq 1500\text{K}$), because their vapour pressures are below 1Pa. These limitations have thus far *excluded* the use of Group IVb oxides (e.g. ZrO) as gas phase radiators in closed systems like a discharge lamp.

We succeeded in bringing Group IVb oxides into the hot region of the gas discharge by filling certain “precursor molecules” into the discharge vessel. A sketch of the working principle is given in figure 7 for the example of ZrO formation.

We use *two different* “precursors” to bring the Group IVb metal and the oxygen into the vapour phase. By dosing the very volatile Group IVb tetra-halides (like ZrX_4) together with a volatile oxygen compound (like MoO_2X_2 [24] or P_2O_5 [25]) we succeeded in obtaining a regenerative chemical cycle. In this cycle the “precursor” molecules are dominating at low temperatures near the vessel wall (thereby excluding the formation of non-volatile TM oxides or TM oxide halides), but the Group IVb monoxide dominates at the high temperatures of the plasma centre (thereby generating the desired radiation). Amazingly, this “two precursor” trick works so well that the necessary cold spot temperatures may become extremely low (500-700K). The stability of this regenerative cycle is proven by the fact that the spectral output of the discharge does not change over hours.

Figure 7. Regenerative cycle using 2 different “precursors” [24].

3.1. Electric multipole moments: Which Molecules are volatile ?

Transition metal (oxy)halides are rather *polar* molecules with a positive excess charge at the transition metal and negative excess charges at the other atoms. If the charge distribution of the molecule has a *non-vanishing electric dipole or quadrupole moment*, the molecules will “stick” together by electrostatic forces yielding larger entities with *very low vapour pressure*. This will especially be the case for “*planar*” configurations (see figure 8).

This statement can be proven as follows: Assume that the transition metal atom is at the origin. The Cartesian electric quadrupole moment Q_{33} is then [26]

$$Q_{33} = \int (3z^2 - r^2) \cdot \rho(\vec{x}) d^3x \quad (1)$$

If the molecule is planar, then $z=0$ can be chosen for all atoms and Q_{33} will become:

$$Q_{33} = \sum_i (-r_i^2 \cdot q_i) \quad (2)$$

The transition metal atom doesn't contribute (since it has $r=0$) and Q_{33} will be *non-zero and positive* due to the contributions of the negative excess charges. Therefore, a planar molecule will have a non-zero quadrupole moment Q_{33} and there will be at least a quadrupole contribution W_q to the interaction energy due to the electric field gradient $\frac{\partial E_z}{\partial z}$ in the neighbourhood of a second, planar molecule:

$$W_q = -\frac{1}{6} \sum_i \sum_j Q_{ij} \frac{\partial E_j}{\partial x_i}(0) \quad (3)$$

Figure 8. Transition metal compounds in planar configuration (=not volatile).

In contrast to the situation sketched above, it is possible to form molecules with vanishing dipole *and* quadrupole moments, if the transition metal atom is surrounded by ≥ 4 halogen or oxygen atoms (see figure 9Figure):

Figure 9. Transition metal compounds with high vapour pressure (=TM atom screened by ≥ 4 halogen or oxygen atoms).

As an example the tetrahedral configuration of $ZrCl_4$ would yield zero monopole, dipole and quadrupole moments with the first non-zero spherical multipole moment being $q_{30} = 0.067 q_e a^3$, where q_e = Zr excess charge and a = nearest distance of Cl-atoms. The interaction energy W_o of this octopole moment with the second derivative of the electric field of a neighbouring $ZrCl_4$ molecule is much weaker than the quadrupole contribution W_q of Eq. (3); therefore, those non-planar molecules don't "stick" together and show thus vapour pressures which are many orders of magnitude higher.

From the preceding discussion it is clear (see figure 8) that it is impossible to evaporate Group IVB oxyhalides at reasonable temperatures. Therefore, it is necessary to evaporate *two different*, volatile compounds (Group IVB tetrahalide *and* a volatile, oxygen-containing molecule) in order to form a (radiating) Group IVB oxide in the gas phase.

3.2. Chemical Equilibrium Calculations: How to dose Novel Molecular Discharge Lamps?

As an example we will consider the Zr / Mo / O / Cl system in a quartz glass (SiO_2) vessel at a coldest spot temperature of, say, 600 K. At this temperature the vapour pressure of $ZrCl_4$ would be 0.74 bar. Part of the dosed $ZrCl_4$ will, however, react with SiO_2 to form solid zircon ($ZrSiO_4$) and gaseous $SiCl_4$. The corresponding equilibrium reaction equation is

This equilibrium equation implies that the partial pressures of $\text{ZrCl}_4(g)$ and $\text{SiCl}_4(g)$ are just proportional (with a temperature-dependent ratio $\text{ZrCl}_4 / \text{SiCl}_4$ which is about 40 at 600K). The SiCl_4 pressure, however, should not be too high (say, $< 1.E-4$ bar) to avoid excessive quartz transport. This condition is thus limiting the ZrCl_4 partial pressure (in our example to < 4 mbar) which may be present in our lamp.

When adding molybdenum (oxy)chloride to this system we have to take notice of the fact that the two dominating *gaseous* molybdenum compounds in this system (MoOCl_4 and MoO_2Cl_2) contain Mo in its 6 valence state. On the other hand, the Mo compounds (MoCl_3 , MoO_2 , MoOCl_2 , MoOCl_3) containing Mo in lower valence states (i.e. 3-5) are all *solid*, or – speaking the other way round – the solid Mo compounds we will dose into a lamp are containing Mo in lower valence states than 6. This implies that we have to add an *excess* of chlorine to guarantee the formation of the desired volatile molybdenum oxychlorides. A simple possibility for dosing well-defined amounts of chlorine in the form of a solid is to use gold chloride (AuCl_3), which is a commercially available, but *metastable* compound [27]. AuCl_3 will decompose at first operation of the lamp, release all of this chlorine into the gas phase and form a tiny deposit of inert, solid gold at the coldest spot.

With these strategies we designed our sample lamp dosed with 0.222 mg ZrCl_4 , 0.134 mg MoCl_3 , 0.065 mg AuCl_3 and 50 mbar (at room temperature) Xe into a tubular quartz envelope with 24mm inner diameter and about 30mm inner length. At an (estimated) coldest spot temperature of 500-600 K this lamp will have *summed elemental pressures* of approximately 0.31 bar Xe, 49 mbar Cl, 5.5 mbar Zr, 1.1 mbar O and 1.0 mbar Mo. The partial pressures of the most important gaseous constituents of the plasma are plotted versus temperature in figure 10:

Figure 10. Most important constituents of a $\text{ZrCl}_4 / \text{MoCl}_3 / \text{AuCl}_3 / \text{Xe}$ plasma in a quartz vessel.

4. Sample Result

The lamp dimensions and filling are described at the end of the previous chapter. An excitation coil was directly wound onto the quartz vessel and used to couple 269W of 14.0MHz RF power into an inductive

discharge torus within the lamp. Photos of the lamp / coil system are given in figure 11 for the idle, cold lamp (figure 11(a)) and the operating lamp (figure 11(b)).

Figure 11. Photographs of the ZrCl_4 / MoCl_3 / AuCl_3 / Xe lamp before (figure 11(a)) and during (figure 11(b)) operation.

Under these conditions the lamp emitted the spectrum shown in black in figure 1 below. This figure also shows spectral simulations of the contributions of the various radiation emitters present at the plasma centre.

Figure 12. Spectrum of a lamp dosed with ZrCl_4 , MoCl_3 , AuCl_3 and Xe. Measurement (black) plus simulations for ZrO (red), ZrCl (magenta), Zr atom (light blue), Mo atom (dark blue) and Zr^+ ion (green) radiation [28].

The total radiation output of this lamp is 182W – thus corresponding to a plasma radiation efficiency of 68%. The visible radiation output (400-780nm range) is 128W (~48%) corresponding to a plasma efficacy of 102lm/W, a correlated colour temperature of 5436K (21SDCM below the black-body locus) and a colour rendering index $\text{Ra}_8 = 87.8$. If the UV radiation below 400nm is converted by suited commercially available fluorescent powders into white light a theoretical efficacy of about **160lm/W** is derived.

5. Classification of discharge lamp types

Gas discharges can roughly be classified by the *power density* coupled into the gas and by the *total operating pressure*. If the power density is low, the translational temperature of the gas atoms and molecules will stay near room temperature (“cold gas”). At high power density, however, the working gas is heated to values of several thousand Kelvin due to some inevitable heat losses within the conversion process of electric power to electromagnetic radiation.

When considering the pressure scale we see that a high pressure (in the order of an atmosphere) will lead to high collision rates of all particles involved and thus bring a continuously operated discharge into “Local Thermodynamic Equilibrium” (LTE). At low pressure (in the order of mbar), however, not all processes will reach equilibrium. Especially the populations of excited (radiating) levels and the charge carrier densities may deviate substantially from their equilibrium values calculated using the translational gas temperature.

Up to now there was no efficient light generating discharge with high power density and operating pressure considerably below one atmosphere. The exciting message of the present contribution is that we filled this gap: Our new molecular discharges can be operated efficiently at high power densities – yielding translational temperatures of about 4000 K – and at such low pressures (or collision rates) that a certain degree of over-equilibrium population of the radiating levels is maintained. This is the reason for stating that we indeed revealed a “novel promising type of light source” which has the potential to overcome the traditional limits of efficacy and colour rendering known from the “common” lamp types.

6. Conclusions

Transition metal (TM) atoms and ions mainly emit near UV or blue radiation. For white light generation additional (molecular) contributions in the green or red range are desired.

A systematic investigation into TM halides and ~oxides shows the high potential of TM oxides. Zirconium oxide (ZrO) is identified as the most attractive radiator.

The evaporation of ZrO from a single filling substance is found to be impossible. We succeed in establishing a regenerative chemical cycle by dosing two volatile “precursors”: a zirconium (tetra) halide (ZrX_4) and a volatile oxygen compound (like e.g. MoO_2X_2 or P_2O_5).

A corresponding inductively coupled, Hg-free discharge lamp yields excellent light technical properties demonstrating the high potential of these novel radiators.

Spectroscopic diagnostics and energy balance modelling indicate that these new molecular discharges form a novel class of discharge lamps combining the advantages of both HID and LP lamps:

High power density, i.e. a hot gas ($T_{max} \approx 4000K$) showing low heat conduction losses ($\leq 25\%$) – just as in HID lamps.

Low operating pressure ($p_{tot} \leq 0.5bar$), i.e. non-LTE effects ($T_{excit}-T_{gas} \approx 1000K$) leading to high radiation efficiencies – just as LP lamps.

References

- [1] McFarlan Moore D 1895 Method of Electrical Illumination *Patent* US 0548129
- [2] Schirmer H and Seehawer J 1967 Al-Cl-Discharges of high luminance efficiency *8th ICPIG (Vienna)* 229
- [3] Speros D M, Caldwell R M and Smyser 1972 W E Thermodynamic and Kinetic Considerations Pertaining to Molecular Arcs *High Temp. Sci.* **4** 99-127
- [4] Chalmers A G, Wharmby D O and Whittaker F L 1975 Comparison of high-pressure discharges in mercury and the halides of aluminium, tin and lead *Lighting Res. and Technol.* **7** 11-18

- [5] Dolan J T, Ury M G and Wood C H 1992 A novel high efficacy microwave powered light source 6th *Int. Symp. on the Science and Technology of Light Sources (Budapest)*
- [6] Ukegawa S and Gallagher A 1999 A discharge lamp based on MgH radiation *J. Appl. Phys.* **86** 5365-71
- [7] Lapatovich W P 2004 Recent Advances in Lighting Science *AIP Conf. Proc.* **730** 255-64
- [8] Hilbig R, Koerber A, Baier J and Scholl R 2004 Molecular Discharges as Light Sources 10th *Int. Symp. on the Science and Technology of Light Sources (Toulouse)*
- [9] Baier J, Koerber A, Scholl R and Hilbig R 2004 Group IV-VI Compounds as Molecular Radiators in HID Plasmas 10th *Int. Symp. on the Science and Technology of Light Sources (Toulouse)*
- [10] Sosnin E A, Erofeev M V and Tarasenko V F 2005 Capacitive discharge exciplex lamps *J. Phys. D: Appl. Phys.* **38** 3194-201
- [11] Franke S, Methling R, Hess H, Schneidenbach H, Schoepp H, Hitzschke L, Kaening M and Schalk B 2007 Mercury-free high-intensity discharge with high luminous efficacy and good colour rendering index *J. Phys. D: Appl. Phys.* **40** 3836-41
- [12] Smith D J, Michael J D, Midha V, Cotzas G M and Sommerer T J 2007 Efficient radiation production in a weakly ionized, low-pressure, nonequilibrium gallium-iodide positive column discharge plasma *J. Phys. D: Appl. Phys.* **40** 3842-56
- [13] Kitsinelis S, Zissis G and Fokitis E 2009 A strategy towards the next generation of low pressure discharge lamps: lighting after mercury *J. Phys. D: Appl. Phys.* **42** 045209
- [14] Hayashi D, Hilbig R, Koerber A, Schwan S, Scholl R, Boerger M and Huppertz M 2010 Low-pressure indium-halide discharges for fluorescent illumination applications *Appl. Phys. Lett.* **96** 061503
- [15] Lapatovich W P, Keefe W M, Brates N, Liebermann R W and Maya J 1986 Metal oxide containing high intensity discharge lamp 4th *Int. Symp. on the Science and Technology of Light Sources (Karlsruhe)*
- [16] Huber K P and Herzberg G 1979 *Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules* (New York: Van Nostrand Reinhold)
- [17] Bernath P F and McLeod S 2001 DiRef, a database of references associated with the spectra of diatomic molecules *J. Mol. Spectrosc.* **207** 287 <http://diref.uwaterloo.ca>
- [18] Langhoff S R and Bauschlicher C 1990 Theoretical Study of the Spectroscopy of ZrO *Astrophys. J.* **349** 369-75
- [19] Davis S P and Hammer P D 1988 Energy levels of zirconium oxide *Astrophys. J.* **332** 1090-1
- [20] Hamrick Y M, Taylor S and Morse M D 1991 Optical spectroscopy of jet-cooled MoO *J. Mol. Spectrosc.* **146** 274-313
- [21] NIST atomic spectra database at: <http://physics.nist.gov/PhysRefData/ASD/index.html>
- [22] Koerber A, Hilbig R, Hayashi D and Schwan S 2008 *Int. Appl. Pub.* WO 2008/120172 A2
- [23] Ram R S, Adam A G, Sha W, Tsouli A, Liévin J and Bernath P F 2001 The electronic structure of ZrCl *J. Chem. Phys.* **114** 3977-87
- [24] Koerber A, Hilbig R, Hayashi D and Schwan S 2008 *Int. Appl. Pub.* WO 2008/126014 A2
- [25] Hilbig R, Koerber A, Schwan S and Hayashi D 2008 *Int. Appl. Pub.* WO 2008/126020 A2
- [26] Jackson J D 1975 *Classical Electrodynamics* 2nd edition (New York: John Wiley & Sons) chapter 4
- [27] Koerber A, Hilbig R, Hayashi D and Schwan S 2008 *Int. Appl. Pub.* WO 2008/120171A2
- [28] Hilbig R, Koerber A, Schwan S and Hayashi D in 2010 *LS-WLED* eds. Haverlag M, Kroesen G M W and Taguchi T (Sheffield: FAST-LS) 277-78