PHOTOEXCITATION OF RARE EARTH AND METAL-HALIDE MOLECULES IN THE ULTRAVIOLET

BY

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THESIS

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ABSTRACT

In the search for new sources of light and gain media for lasers, lanthanide fluoride powders and rare earth tri-iodide salts in vapor phase have been studied spectroscopically by photopumping in the ultraviolet. Knowing the spectral response of these molecules with respect to incident light and understanding the energy level structure entailed would be useful to establish their suitability for lighting or lasing. This thesis describes the spectroscopic experiments performed, reports the measured data and analyzes them.
To my parents, for their love and support
I would like to thank all of the people who have helped me out along the way to fulfill what I have done. First, I would like to address my thanks to my adviser Professor J. Gary Eden for his guidance, encouragement, and the enthusiasm he has transmitted to me. Thanks to Darby Hewitt for his practical advice and experimental suggestions, to “Gamma Tom” Galvin for his theoretical supervision and precious Matlab programming tips, and to “Scruffy Tom” Houlahan for his software and hardware troubleshooting expertise. I do not forget all my other colleagues at the Laboratory for Optical Physics and Engineering for their assistance, good mood and friendship.

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Last but not least, special thanks goes to my family, especially Maman, Papa and Coco for their endless support, the love they have given me and without which I would not have been able to pursue such ambitious studies in a foreign country. Finally I have a thought of gratitude to all of my grandparents, uncles, aunts, and cousins for their trust and encouragement, as well as all my friends that made my stay in the USA a wonderful experience.
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CHAPTER 1

MOTIVATION AND BACKGROUND

The overarching goal of the research in this thesis is to study the optical properties of selected atoms and molecules and, more broadly, to search for new laser gain media. To reach this target, several different types of materials have been investigated. This document focuses on the study of several molecules, most of which are diatomic monohalides, in the form of powders and salts in the vapor phase.

Understanding how a material absorbs and emits photons is a key to inferring molecular energy structures [1]. Once these structures are understood, efficient approaches to producing light at desired wavelengths may then be deduced, by optimizing the excitation process to populate an energy level of interest. Thus, the main process under scrutiny is the interaction of matter with light radiation, in terms of absorption or optical emission. In the latter case, fluorescence spectra are recorded following excitation in the ultraviolet (UV) that is provided by an argon-fluoride (ArF) or a krypton-fluoride (KrF) excimer laser that produces a powerful laser beam at peak wavelengths of 193 nm and 248 nm, respectively.

On the one hand, interest in this thesis research has been focused on the topic of random lasers and the study of various molecules in powder form. This type of laser employs a disordered gain medium and no optical cavity. The produced light generally contains many wavelengths emitted over a large solid angle. Such lasing has been observed in a wide variety of media, including laser dye solutions containing microparticles [2], semiconductor powders [3], thin films, and ceramics. An attractive aspect of random lasers is that they do not require precisely designed mirrors or a carefully aligned optical cavity that are required for conventional lasers. Rather, the light scatters multiple times before escaping the medium, thus making random lasers potentially less expensive and more robust than conventional laser sources. After considering the generation of light in the interstellar medium, Letokhov
et al. reported in 1966 a laser with nonresonant feedback using scattering reflectors [4]. Later in the 1980s, Markushev et al. observed lasing in Nd-doped laser crystal powder [5]. Eventually, lasing was first demonstrated from zinc oxide (ZnO) powder by R. K. Thareja and A. Mitra in 2000 [6].

The second emphasis of this thesis is the optical properties of several metal-halide diatomic molecules in the vapor phase. Such salts are a component of virtually all metal-halide arc lamps that were developed in the 1960s and have been in use worldwide ever since. This type of high-intensity gas discharge lamp produces light by an electric arc in a mixture of mercury and metal-halide vapors. The tube is filled with a low background pressure of a rare gas (such as argon) that facilitates the initial strike of the arc. As the lamp heats, the metal-halide and mercury (Hg) evaporate, producing a high-temperature (roughly 8000 K) arc in the vapors. These salts have quite literally revolutionized lighting by increasing the intensity of light produced by the arc while reducing its power consumption, thus improving efficiency, and generating an output spectrum having a color rendering index (CRI) well above 90 (for a CRI value of 100, the maximum value, the colors of objects are seen as they would appear under an incandescent or daylight spectrum of the same correlated color temperature). Also, high-intensity discharge lamps emit a greater fraction of their radiation in the visible domain than do fluorescence and incandescent lamps. Moreover, its spectrum more closely matches that of a 6000 K blackbody which represents approximately the solar spectrum.

However, electrical ballast is required to regulate the arc current (to cope with the negative resistance of electric arcs) and supply the proper voltage to the arc. Finally, metal-halide arc lamps are widely used in public areas, athletic facilities, professional lighting fixtures and projectors, as well as by the film and entertainment industry. In fact, the metal-halide arc lamp currently bears much of the worldwide load in total visible output power, providing more than a GW continuously. However, the mixture of metal and metal-halide vapors currently used in commercial lamps was determined through a largely empirical process and little is known regarding the spectroscopic properties and structure of the diatomics and triatomics that are produced in the lamp by the dissociation of the triatomic “parent” molecules such as scandium tri-iodide.
CHAPTER 2

EXPERIMENTS

The laser used in the following spectroscopic measurements is an LPX 105 NT excimer laser manufactured in Germany by Lambda Physik. It is capable of producing laser pulses from both argon fluoride (ArF) at 193 nm and krypton fluoride (KrF) at 248 nm. The pulse energy is about 50 mJ with ArF and up to 200 mJ with KrF; the typical repetition rate used for the experiments is typically 10 Hz.

2.1 Fluorescence of Powder Samples

As indicated in the diagram of the experiment in Figure 2.1, the laser beam is directed onto the sample with mirrors. The incident beam photoexcites the molecules and induces fluorescence from the sample which is dispersed into $4\pi$ steradians. A fiber picks up a fraction of the emitted light and directs it into a spectrometer connected to a computer that records the data. The behavior of the samples has been studied both at room temperature and 77 Kelvin. The latter is achieved by placing samples in a small, UV grade quartz cell and cooling the cell with liquid nitrogen.

The powder samples examined in the experiments include ZnO (since random lasing has already been obtained from ZnO powder and nanostructures), as well as several lanthanide halide molecules such as LaF$_3$, PrF$_3$, and PrCl$_3$. Several of these molecules have lased previously when in the form of a single crystal [7].

Fluorescence spectra recorded from photoexcited zinc oxide (ZnO) powder are shown in Figure 2.2. Notice that as the sample is cooled, peak fluorescence shifts from 394 nm to 372 nm, and the spectral width of this dominant peak narrows from 22 to 7 nm Full Width at Half Maximum (FWHM). Random lasers involving ZnO material have been achieved in the form of thin
films deposited on a silicon substrate. S. F. Yu et al. have obtained emission spectra similar to those in the present experiment, but with 355 nm optical excitation [8]. In the present experiments, a single, broad spontaneous emission peak centered on 384 nm with a FWHM of about 15 nm is observed in the emission spectra of the sample at low pump intensities. Above a certain threshold of the excitation intensity (approximately 0.42 MW/cm²), Yu et al. observed the emergence of lasing modes having linewidths less than 0.4 nm. These modes emerged from the background continuum as sharp peaks lying around 390 nm. Dried ZnO powder has also been spectroscopically studied using 360 nm wavelength excitation [9]. The relatively intense emission peak at 388 nm was attributed to near band-edge emission and corresponds to the band-gap energy of the material, which is 3.3 eV (i.e. 376 nm) at room temperature. Thus, it is understandable that cooling will narrow the thermal energy distribution dictated by the Boltzmann distribution, resulting in a narrower exciton emission line [10].

The spectra of irradiated Praseodymium Fluoride (PrF₃) in Figure 2.3 shows a narrow double line at 271 and 274 nm that appears only when the pump beam is at 193 nm (blue and black line). Intense violet emission around 400 nm with a FWHM of 10 nm is also observed when the powder
Figure 2.2: Emission spectrum in the near-UV and visible domain produced by ZnO powder photoexcited at 193 nm (black and blue curves) and 248 nm (grey and red curves) for different temperatures, that is, room temperature (black and grey curves) and 77 K (blue and red curves).
Figure 2.3: Emission spectrum of photoexcited PrF$_3$ powder in the visible and UV region.
is illuminated with the ArF laser. Conversely, KrF laser excitation of the powder produces strong continua in the mid-UV, peaking at 287 nm and 302 nm, but the violet and 270 fluorescence have vanished. This suggests that some molecular levels are accessed only with the energy afforded by an ArF photon (6.4 eV).

Figure 2.4: Emission spectrum in the UV and visible domain of photoexcited LaF\textsubscript{3} powders.

Figure 2.4 illustrates the photoluminescence spectrum of lanthanum tri-fluoride (LaF\textsubscript{3}) powder. Besides a large double-band peaking at 400 and 500 nm, it depicts a peculiar hump around 300 nm that only appears under the 248 nm excitation at room temperature.

PrCl\textsubscript{3} powders exhibit a significantly different behavior under ArF or KrF laser excitation. As can be seen in Figure 2.5, PrCl\textsubscript{3} pumped by a 193 nm radiation generates a multi-peak fluorescence band between 230 nm and 300 nm. When cooled, the bluer component separates more clearly into two
White Crystal

Hydrated PrCl$_3$7H$_2$O at 300 K

Cooled at 77 K with liquid N$_2$

Raw powder at room temperature

PrCl$_3$ λ$_p$ = 193 nm

Relative Intensity of PrCl$_3$ Fluorescence

Wavelength (nm)

Figure 2.5: Emission spectrum in the UV and visible region resulting from 193 nm photoexcitation of PrCl$_3$ powders and by-product. The 1000 intensity shifts have been introduced between the various curves for clarity and readability of the graph.
secondary peaks at 237 and 248 nm. Moreover, small crystals up to 1 mm$^3$ in volume were found within the raw green powder and they contrast with the bulk powder because they emit bright white fluorescence when illuminated by the laser. Green fluorescence was measured from these particles isolated from the rest of the sample. After letting the sample sit in the laboratory for a few days, a change is noticeable as it absorbs humidity and becomes puffy. At this point, a new emission feature appears at 405 nm.

![Emission spectrum in the UV and visible domain resulting from 248 nm photoexcitation of PrCl$_3$ powders. Intensity offsets of 0.1 have been introduced between the various curves for legibility of the graph.](image)

Figure 2.6: Emission spectrum in the UV and visible domain resulting from 248 nm photoexcitation of PrCl$_3$ powders. Intensity offsets of 0.1 have been introduced between the various curves for legibility of the graph.

When excited at 248 nm, fluorescence spectra consist of a large hump in the near-UV between 300 and 400 nm as it can be viewed in Figure 2.6. Three weak features at 730, 731 and 733 nm, as well as narrow, intense lines at 616 and 619 nm, emerge as the sample is cooled, and the 646 nm spike distinguishable at room temperature becomes the dominant line of the
spectrum. With regard to the spectra produced by the small crystals, a second hump appears between 650 and 700 nm.

2.2 Fluorescence of Vapor Phase Samples

The experimental layout illustrated in Figure 2.7 is similar to that shown previously in Figure 2.1 but, in this case, the sample is contained in a cell under vacuum in the form of small solid grains at room temperature. These are heated to about 800 °C in order to obtain a significant vapor pressure inside the cell, above a tenth of a Torr. Laser pulses from a KrF excimer laser (photon energies of 5 eV) are directed into the cell from the side, and fluorescence from the sample is then measured along the axis of the cell, which greatly reduces the detection of scattered photons from the pump beam during the measurements.

Figure 2.7: Experimental arrangement for recording emission spectra of several metal-halides in the form of a vapor.

DyI₃, PrI₃ and ScI₃ are rare earth tri-iodide salts often used in high pressure arc lamps in order to produce visible light with the proper spectral
properties. The sample is contained inside a cell under vacuum and comprises solid grains at room temperature. As the temperature of the sample in the cell initially under vacuum increases, the salt produced vapor within the cell and the pressure corresponding to a given temperature can be determined from the vapor pressure curves (for a thermodynamic equilibrium of the vapor with its condensed phases and the pressure depends only on the temperature). Formulas have been derived and can be found in the literature for the compound related to the present thesis (Dy$_3$ [11], Pr$_3$ [12] and Sc$_3$ [13]).

Figure 2.8: Emission spectrum in the near-UV, visible and near-IR resulting from 248 nm photoexcitation of DyI$_3$. Each of the curves shown has been intentionally offset for the sake of clarity.

Figure 2.8 shows the spectrum of Dy$_3$ vapor. A continuum may be observed in the yellow to red region (550 to 700 nm) along with many narrow lines between 300 and 800 nm. Several of them match well with known lines
of atomic dysprosium, or the singly charged ion. Emission at 479.129 nm and 608.826 nm, for example, are attributed to neutral Dy, whereas lines at 756.296 nm and 766.678 nm originate from the ionized species Dy\(^+\).

![Emission spectrum](image)

Figure 2.9: Emission spectrum in the near-UV, visible and near-IR region resulting from 248 nm photoexcitation of ScI\(_3\). The individual spectrum have again been offset vertically for the sake of the clarity.

Figure 2.9 presents several spectra in the ultraviolet, visible and infrared that were recorded when ScI\(_3\) vapor was photopumped with a KrF (248 nm) laser. The spectrum comprises a broad continuum between 500 and 900 nm together with several lines lying between 300 and 800 nm. The components matching with atomic lines of Scandium (atomic number Z = 21) are listed in Table 2.1 where the levels concerned are indicated with their energy, electronic configuration and term symbol. The broad feature with a FWHM of about 50 nm appearing around 900 nm has the appearance of a bound→free molecular transition, and is tentatively attributed to emission.
from the diatomic molecule ScI. Further details and analysis of this unusual spectrum are discussed in Section 3.3. The breadth and asymmetry of the two peaks around 800 nm suggest that these features are also associated with molecular transitions.

Table 2.1: Summary of neutral atomic scandium transitions matching with lines observed experimentally in this work (from [14]). Energy, electronic configuration and term symbol are cited for each level involved.

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>Lower level</th>
<th>Upper level</th>
</tr>
</thead>
<tbody>
<tr>
<td>570.864</td>
<td>11677.38</td>
<td>29189.84</td>
</tr>
<tr>
<td></td>
<td>3d²(3F)4s</td>
<td>3d²(3F)4p</td>
</tr>
<tr>
<td>589.456</td>
<td>18711.02</td>
<td>35671.04</td>
</tr>
<tr>
<td></td>
<td>4s²4p</td>
<td>3d4s(3D)5s</td>
</tr>
<tr>
<td>621.066</td>
<td>0.00</td>
<td>16096.90</td>
</tr>
<tr>
<td></td>
<td>3d4s²</td>
<td>3d4s(1D)4p</td>
</tr>
<tr>
<td>624.455</td>
<td>0.00</td>
<td>16009.77</td>
</tr>
<tr>
<td></td>
<td>3d4s²</td>
<td>3d4s(3D)4p</td>
</tr>
<tr>
<td>628.474</td>
<td>18515.69</td>
<td>34422.83</td>
</tr>
<tr>
<td></td>
<td>3d4s(3D)4p</td>
<td>3d4s(3D)5s</td>
</tr>
<tr>
<td>641.334</td>
<td>168.34</td>
<td>15756.57</td>
</tr>
<tr>
<td></td>
<td>3d4s²</td>
<td>3d4s(3D)4p</td>
</tr>
<tr>
<td>769.776</td>
<td>20719.86</td>
<td>33707.06</td>
</tr>
<tr>
<td></td>
<td>3d²(3P)4s</td>
<td>3d²(3F)4p</td>
</tr>
</tbody>
</table>

If the spectra generated by the tri-iodides of Sc and Dy are compared as in Figure 2.10, several common emission lines are immediately observable. Several of them have been attributed to Iodine (atomic number Z = 53) as they match closely with transitions between well-known energy levels of this atom or its singly charged ion. The latter are summarized in Table 2.2 in which the energy and spectroscopic designations (electronic configuration and term symbol) of the levels concerned are indicated.

2.3 Absorption of Vapor Phase Samples

Absorption measurements have also been carried out on the metal salts, using a broadband light source. Figure 2.11 presents spectra that are the result
Figure 2.10: Comparative emission spectrum in the near-UV, visible and near-infrared (IR) region of Dy$_3$ and Sc$_3$ photoexcited at 248 nm. A 1000 vertical offset have been introduced on the Sc$_3$ curve for legibility of the graph.
Table 2.2: Summary of atomic and singly ionized iodine transitions (from [15, 16]) corresponding with transitions observed in the photodissociation of both DyI$_3$ and ScI$_3$.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength</th>
<th>Lower level</th>
<th>Upper level</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$^+$</td>
<td>534.51 nm</td>
<td>56 650.55 cm$^{-1}$</td>
<td>115 353.94 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5s$^2$5p$^3$(2D$^o$)6s$^3$D$_3$</td>
<td>5s$^2$5p$^3$(2D$^o$)6p$^3$F$_4$</td>
</tr>
<tr>
<td>I</td>
<td>589.40 nm</td>
<td>56 092.88 cm$^{-1}$</td>
<td>73 054.598 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5s$^2$5p$^4$(3P$_2$)6s$^2[2]_3/2$</td>
<td>5s$^2$5p$^4$(3P$^1$)6p$^2[1]_{3/2}$</td>
</tr>
<tr>
<td>I$^+$</td>
<td>671.88 nm</td>
<td>87 734.06 cm$^{-1}$</td>
<td>102 613.52 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5s$^2$5p$^3$(4S$^o$)5d$^5$D$_1$</td>
<td>5s$^2$5p$^3$(4S$^o$)6p$^3$P$_2$</td>
</tr>
<tr>
<td>I</td>
<td>770.02 nm</td>
<td>66 020.47 cm$^{-1}$</td>
<td>79 003.596 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5s$^2$5p$^4$(3P$<em>2$)5d$^2[3]</em>{5/2}$</td>
<td>5s$^2$5p$^4$(1D$^2$)6p$^2[3]_{7/2}$</td>
</tr>
</tbody>
</table>

of detecting light that is transmitted by the DyI$_3$ sample heated at several temperatures.

To get a better picture of the light absorbed by the sample, it is relevant to plot the absorbance, as in Figure 2.12. Absorbance is given by the following Beer-Lambert expression: $\alpha(T) = \ln(I(T)/I_0)$. Most of the absorption is concentrated in the ultraviolet region between 225 and 400 nm. The peculiar shape of the graph may also be dependent on the spectrum of the light source, especially below 300 nm where the incident intensity is low and the semi-log scale could emphasize the details. This could explain the peak and null lying between 300 and 350 nm, and the resemblance with Figure 2.13 associated with PrI$_3$.

Interesting features are observed in the ScI$_3$ absorption spectra (see Figures 2.14 and 2.15). If the absorbance spectrum of ScI$_3$ up to 330 nm is similar to the previous molecules described, the 350 to 550 nm range demonstrates a rising level of absorption as the temperature and partial pressure of the vapor increases, while absorption of higher frequencies remains at a steady level. This means that the blue component of ScI$_3$ emitted by molecules located in the center of the active medium of a metal-halide arc lamp would be partially absorbed before reaching the outside environment,
Figure 2.11: Light transmitted through the DyI$_3$ sample heated to different temperatures. The top black curve represents the measurement performed at room temperature and it reflects the spectrum of the incident light from the source.
Figure 2.12: Absorbance spectrum of DyI$_3$ vapor at several pressures.

Figure 2.13: Absorbance spectrum of PrI$_3$ vapor at different pressures.
Figure 2.14: Light transmitted by ScI$_3$ vapor at several temperatures.

probably hindering the lighting potential of the lamp.

2.4 Comments

Photopumping of the vapors discussed in Section 2.2 has also been performed using the tripled frequency (355 nm) of a Nd:YAG laser emitting light with a wavelength of 1064 nm. Nevertheless, the one centimeter diameter beam with a pulse energy of 100 mJ did not lead to significant results above the background noise. A possible explanation of this result is that the beam size, being smaller than the rectangular excimer laser beam, does not excite a sufficiently large portion of the sample so that a significant fluorescence signal can be recorded. Another possibility is that the 355 nm radiation, representing a photon energy of 3.5 eV, is not sufficiently energetic to reach excited energy levels of the molecules, in contrast to the 5 eV of the 248 nm radiation generated by the KrF laser. A final possible cause for this result is a low absorption coefficient for the vapors at 355 nm.
Figure 2.15: Absorbance spectrum of \( \text{ScI}_3 \) vapor at different pressures.

The interesting features observed in the \( \text{ScI}_3 \) spectra raise the question of whether chemically similar molecules such as yttrium–tri-iodide and lanthanum–tri-iodide will yield similar behavior. It would, therefore, be judicious to conduct comparison experiments with new cells containing these species.

To validate this hypothesis and determine the origin of the bands and explain the measured spectra, the energy levels of the atoms and molecules involved in the observed transitions should be analyzed in order to determine which transitions are responsible for the observed spectral features. However, the lack of data in the literature over the wavelength range considered has made this task unrealizable in a more extensive way at the moment. Atomic spectral lines are well documented but limited molecular spectroscopic studies have been conducted. It is worth mentioning the thorough work of Effantin et al. [17] on the electronic states of scandium monoi-dide. Equilibrium vibrational and rotational constants were obtained from the analysis of fluorescence spectra of ScI excited by \( \text{Ar}^+ \) and \( \text{Kr}^+ \) laser lines. Nonetheless, no molecular state appears in their study between 21076 and 4393 cm\(^{-1}\) (474 - 2276 nm range) which is the spectral domain where peculiar features were
observed with the ScI$_3$ sample. Xia et al. also did spectroscopic studies on ScI but they were focused on the rotational analysis of the $D^1\Pi - X^1\Sigma^+$ system in the range 613 - 704 nm [18].
3.1 Photoexcitation Process

Plausible reactions occurring during the photoexcitation process of the rare earth tri-iodide salts are as follows. First, the molecule dissociated partially or totally after absorbing a photon $h\nu_1$ from the pump beam, resulting in the scission of one, two or three metal-iodine atom bonds. This hypothesis is justified by the observation of rare earth and iodine lines in the experimental emission spectra. Then, the product M resides in an excited state $M^{*2}$ or can reach one by absorbing another incident photon. After a short time, the product undergoes a transition to a lower energy level $M^{*1}$, ceding its energy by emitting a photon $h\nu_2$, which is detected and constitutes the fluorescence emanating from the sample. If the molecule has still not reached its ground state, it finally attains the latter by decay (see Figure 3.1).

Figure 3.1: Energy diagram representing the photoexcitation process.

The results of numerical modeling carried out by Beko et al. in Figure 3.2
shows which dysprosium compounds can be found as a function of temperature in a gas mixture at local thermodynamic equilibrium [19]. DyI$_3$ dominates by several orders of magnitude below 1000 K where a noticeable fraction of DyI$_2$ begins to appear and dominate above 1500 K. The temperature in the experiments performed never exceeded 847 °C or 1120 K and, therefore, the prevailing specie of the unexcited sample is presumed to be DyI$_3$.

Figure 3.2: Densities of selected species containing dysprosium, calculated for a mixture containing mercury, dysprosium and iodine. The elemental dysprosium pressure is 100 Pa, the elemental iodine pressure is 300 Pa and the total pressure is 2 MPa (from [19]).

3.2 Perspectives for Lighting with DyI$_3$

Curry et al. reported in 2012 that a strong enhancement in rare-earth vapor densities arises when Dy is placed in equilibrium with a DyI$_3$/InI condensate, as compared to vapors in equilibrium with the pure rare-earth metal-halides [20]. Moreover, the study was conducted for a temperature range and salt mixtures relevant to the operation of metal-halide high-intensity
discharge lamps (see Figure 3.3).

![Figure 3.3: Measured total vapor-phase densities of Dy over DyI₃/InI compared to that over pure DyI₃ (from [20]).](image)

This information can be used to increase the efficiency of metal-halide arc lamps, in this case especially if one wishes to use an arc lamp with an internal temperature less than 1200 K, where the partial pressure of DyI₃ is increased up to an order of magnitude by the described method. Also, the warm-up time of the lamp would be reduced as its operating temperature could be lower.

3.3 Analysis of the ScI₃ 900 nm Fluorescence Feature

The broad asymmetric peak present at 914 nm in the fluorescence spectrum of ScI₃ visible on Figure 3.4, with several ripples appearing on its blue tail, is characteristic of a bound→free transition that is tentatively assigned to emission from the diatomic molecule ScI. The peak wavelength, indeed, matches closely the energy gap between the ground state \( ^2D_{3/2} \) (electronic configuration 3d⁴s²) and the first excited state \( ^4F_{3/2} \) (electronic configuration...
3d\(^2\)(\(^3\)F\)4s) of neutral scandium lying at 11519.99 cm\(^{-1}\) (corresponding to a transition at a wavelength of 868 nm).

![Emission spectrum of the bound→free transition of ScI. The positions of the peaks of several undulations in the spectrum are indicated. Offsets have been added to the curves for legibility.](image)

Figure 3.4: Emission spectrum of the bound→free transition of ScI. The positions of the peaks of several undulations in the spectrum are indicated. Offsets have been added to the curves for legibility.

### 3.3.1 Vibrational Motion

The vibrational motion of a diatomic molecule in a bound energy state can be approximated by the harmonic oscillator model associated with a parabolic potential energy. However, this model is valid only around the minimum of the well but a more accurate model is given by the Morse potential that is in reasonable agreement with the real potential over a larger range in the internuclear separation \(l\) (see Figure 3.5). For both of these potentials, an exact solution to the Schrodinger equation exists. It can be expressed as

\[
V_M = D_e \left( 1 - e^{-a_e(l-l_0)} \right)^2
\]
where \( l \) is the internuclear separation. An energy level is described by three independent parameters associated with the Morse potential: \( \omega_e \) the harmonic vibrational frequency, \( \chi_e \omega_e \) the anharmonicity constant, and \( l_0 \) the equilibrium internuclear distance. The dissociation energy \( D_e \) can be deduced from the other variables using the relationship \( D_e = \hbar \omega_e / 4 \chi_e \). The factor \( a_e \) controls the width of the potential and is obtained using the equation \( a_e = \sqrt{k_e / 2D_e} \), where \( k_e \) is the bond force constant equal to the second derivative of the potential at the minimum of the well. Notice that performing a Taylor expansion of the exponential to the first order, the Morse potential reduces to the harmonic oscillator for \( l \approx l_0 \):

\[
V_M \approx D_e a_e (l - l_0)^2 = \frac{k_e}{2} (l - l_0)^2
\]

The Morse parameters are not available in the literature for ScI diatomic molecule, but it is possible to infer those assuming that the observed emission is related to a transition from a bound excited state of ScI to its dissociative ground state.

First, the harmonic vibrational frequency is the wavelength spacing between the secondary peaks from Figure 3.4 and can roughly be determined.
as 17 nm in average, which represents a frequency bandwidth of 200 cm\(^{-1}\) or 6 THz. Knowing the reduced mass of the scandium iodide system

\[
\mu = \left(1/m_{Sc} + 1/m_I\right)^{-1} = 33.2 \text{ u} = 5.51 \times 10^{-26} \text{ kg}
\]

the force constant is derived as \(k_e = \mu \omega^2_e = 78 \text{ kg/s}^2\). The dissociation energy is the depth of the potential minimum and is estimated by the difference of the energy of the first excited state of ScI with the photon energy of the 914 nm emission recorded (see Figure 3.6):

\[
D_e = E_{ScI^*} - E_\gamma = 11520 - 10941 = 579 \text{ cm}^{-1} = 17.4 \text{ THz}
\]

Now the anharmonicity constant can be computed

\[
\chi_e \omega_e = \frac{a_e^2 h}{2\mu} = \frac{\hbar \omega^2_e}{4D_e} = 17.3 \text{ cm}^{-1} = 5.18 \times 10^{11} \text{ Hz} = 8.6 \% \omega_e
\]

![Figure 3.6: Energy diagram of the ScI bound→free transition.](image)

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3.3.2 Rotational Motion

The simplest approach to analyze the rotational motion of a diatomic molecule is to use the rigid rotator model. It assumes that the distance between the two masses is fixed and the molecule simply rotates about its center of mass. This is a reasonable approximation as vibrational amplitudes are small compared with the bond length. The discrete energy levels are given according to the formula $E_J = \frac{\hbar^2}{8I} J(J+1)$, where the positive integer $J$ is the rotational quantum number. Postulating an $r = 200 \text{ pm}$ internuclear separation, which is the order of magnitude for ionic diatomic molecules, the momentum of inertia is inferred

$$I = m_\text{Sc}r_\text{Sc}^2 + m_I r_I^2 = \mu r^2 = 2.2 \times 10^{-45} \text{ kg.m}^2$$

Therefore, the spacing between energy levels is

$$\Delta E_J = E_{J+1} - E_J = \frac{\hbar^2}{I} (J + 1) = \frac{\hbar^2}{4\pi^2 I} (J + 1) = 2B\hbar (J + 1)$$

This leads to a spectrum consisting in a series of lines with an constant separation of $2B = 0.25 \text{ cm}^{-1} = 7.6 \text{ GHz}$. This value is almost one thousand times smaller than the spacing between vibrational levels. It is too tiny to be singled out by the laboratory spectrometer and only contributes to the width of the vibrational lines. Thus, the bond length of the molecule could be determined from an accurate measurement of the width of the spectral lines, taking into consideration the number of rotational energy levels involved.
CHAPTER 4

CONCLUSION AND FUTURE WORK

Emission from molecules in various form photoexcited in the ultraviolet has been achieved. Some spectral features have been attributed to atomic lines, but at least one is considered to be a bound→free transition of the ScI diatomic molecule.

There are still a number of promising experiments to be performed. The use of a monochromator having a finer resolution than the spectrometer utilized to record the spectra displayed in this thesis could confirm some hypothesis. The measurement of the fluorescence lifetime of the 914 nm line would be useful to determine the lasing potential of ScI at that wavelength. Furthermore, it would be of interest to perform photopumping using ArF on the vapor phase sample to see if other energy levels are reached leading to the detection of new wavelengths in the fluorescence measurements. Simulations and alternative experimental methods to obtain parameters of the Morse potential could also be carried out in order to confirm the suggested bound to free transition.
REFERENCES


