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FLUORESCENCE STUDIES OF EXCIPEX MOLECULES
IN THE VACUUM ULTRAVIOLET REGIME

by

PAMELA SEVILLE MILLAR

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

MASTER OF SCIENCE

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May, 1987
ABSTRACT

FLUORESCENCE STUDIES OF EXCIPLEX MOLECULES
IN THE VACUUM ULTRA VIOLET REGIME

by

Pamela S. Millar

This work describes the development of a unique capability for electron beam excitation of hot vapors combined with VUV spectroscopy. The first result obtained with this new facility was the observation of emission from the triatomic rare gas halide Ne$_2$F* at 132 nm. An investigation of the kinetic processes for both Ne$_2$F* and its precursor NeF*, which emits at 108.5 nm, was performed. Several relevant rate coefficients were determined. It was concluded that this system is analogous to the Ar-Cl system, in that it predissociates due to excited halogen dimer formation. Therefore the realization of NeF* or Ne$_2$F* laser action would be difficult due to F$_2$* production. NeF* fluorescence, however, would be more likely to achieve gain due to its higher stimulated emission cross-section.
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Chapter 1: Introduction

A major research area in quantum electronics today is the generation of coherent radiation in the vacuum ultraviolet (VUV), extreme ultraviolet (XUV) and x-ray regions by means of novel schemes that do not require such large costly laser systems [1]. One of the primary objectives of this work, therefore, was to adapt the electron beam facility at Rice University to the VUV regime in order to study possible VUV and XUV laser schemes. Previously the diagnostic instrumentation of this laboratory was operational only in the visible region where several rare gas halide excimer species were discovered and studied. The observation of Ne$_2$F* (132 nm) emission was a significant discovery in the new VUV electron beam laboratory at Rice. The main emphasis of this thesis will be the investigation of the spectroscopy as well as the kinetic processes of Ne$_2$F*.

The spectral region designated by the vacuum ultraviolet extends from 100 to 200 nm. The region between about 100 nm and 10 nm is called XUV. Below about 200 nm there is a region of continuous absorption primarily by the Schumann-Runge bands of oxygen. Therefore spectra in this wavelength region can only be observed in evacuated spectrometers. The need for vacuum instruments is not the only difficulty encountered in the VUV and XUV, as optics in this region are limited by the unavailability of highly reflective or highly transparent materials. Laser systems using optical cavities are not feasible below 100 nm since metal films are limited to values $\leq$ 40% below this wavelength. For this reason the discovery of intense coherent emission [2] from systems without optical cavities is an important development for lasers in the VUV, XUV and x-ray regions. This process is called amplified spontaneous emission (ASE) or sometimes "superfluorescence" and results in just single pass amplification. Systems utilizing this type of amplification are mirrorless. Hence they are important to the realization of short wavelength lasers. An unavoidable difficulty for the generation of short wavelength lasers
is due to the unavailability of appropriate transparent materials. No solid window materials
exist below the cutoff wavelength of LiF at 105 nm. The next lowest cutoff is for MgF$_2$ at
115 nm. Therefore detection below these wavelengths must be windowless. This places
an upper limit on gas medium pressures corresponding to the obtainable spectrometer
pressures. The unavailability of suitable materials for both high transmission windows and
efficient reflectors for resonators is a major impediment for short wavelength lasers,
however ASE enables the alternative of mirrorless lasers systems.

Besides materials problems there are basic physical considerations that require
high pumping powers as well as very rapid pump pulses. To generate radiation in the
desired short wavelength regime a transition energy from about 10-100 eV is needed. This
requires large pumping densities. In general the minimum pumping power density scales
with a high power of the transition frequency [1]:

$$P \sim \nu^\alpha, \quad (\alpha \geq 3).$$  (1.1)

Therefore it appears unavoidable to invest large power densities in order to achieve lasing
in the VUV or XUV regions. Large power densities can be easily achieved by short pulse
pumping sources, i.e. an electron beam accelerator. Short pulses are required in order to
enable the pumping process to compete with quenching processes of the upper transition
level by processes other than radiation to the lower state, such as collisional quenching by
heavy particles or electrons.

Electronic transitions in molecules are considered for coherent radiation in the
VUV spectral region. Exciplex or excimer molecules have the main consideration. An
"exciplex" molecule refers to a molecule consisting of dissimilar atoms which is at an
excited energy level above its ground state. However in literature the term excimer can be a
diatomic molecule (dimer) or a triatomic molecule (trimer) in which the atoms are either
alike or dissimilar. Since these molecules are known as efficient laser media in the visible
and UV regions [3], the extension of the excimer laser principle to shorter wavelengths
appears promising. In this work excimers consisting of a rare gas and a halide are mainly considered. Excited rare gas halides, excimers or exciplexes, have always been considered attractive species for laser action in the visible due to their bound-free transition characteristics. The upper state is an electronically bound state, while the lower potential curve is repulsive. Therefore the basic requirement for laser action, a population inversion, is in principal relatively easy to achieve with excimers as an active medium.

The rare gas halide molecule exhibiting the shortest wavelength emission is NeF* at 108 nm. The triatomic counterpart to this excimer Ne$_2$F$_*$ was predicted to emit at 145 nm [4]. No emission from this trimer had been observed until now. The Ne$_2$F$_*$ emission at 132 nm was observed for the first time in this work. Fig. 1.1 shows the relative locations of these emissions in wavelength and energy compared with other known excimers. The Ne-F excimer system behaves similarly to that of Ar-Cl, as mentioned in chapter 4. This is a direct consequence of the fact that in both systems the lowest excited state of the halogen is lower than that of the rare gas leading to strong predissociation of the rare gas halide. Predissociation of the Ne-F and Ar-Cl systems result in enhanced F$_2$* and Cl$_2$*[5] production respectively.

Another excimer system that appears promising for VUV and XUV emission are the ionic excimers [6]. Ionic excimers composed of alkali halide compounds are isoelectronic to the rare gas halides and are predicted to have similar properties to them, only at shorter wavelengths [6]. Cesium fluoride, isoelectronic to XeF*, has already been observed at 185 nm [7]. These compounds are solids at room temperature and must be heated to about 800°C in order to generate vapor pressures on the order of 1 torr. Therefore techniques were developed that allow for the coupling of an intense electron beam into a hot gas cell. These experimental techniques will be discussed in detail in chapters 2 and 3. Using the unique capability for electron beam excitation of hot
Fig. 1.1

Wavelengths and tuning ranges of the various rare-gas (Rg), rare-gas-halide (RgX), and rare-gas-halide complex (Rg2X) bands, trimeric, and broad.
vapors combined with VUV spectroscopy, core-excited states of alkali atoms were also investigated. Harris et al. [8] proposed that core-excited alkali systems could be used as possible XUV laser schemes. XUV fluorescence has recently been discovered in the transition from the core-excited level Rb(4p$^5$ 5s5p $^4$S$_{3/2}$) to the excited valence level Rb(4p6 5p $^2$P$_{3/2}$) by using a laser produced plasma as a pumping mechanism [9]. At Rice it is intended to investigate whether these states can be populated by collisional energy transfer from metastable rare gas atoms. These metastables may be pumped efficiently by electron beam excitation. A further description of the development of this experimental capability is presented in chapter 3.
Chapter 2: Experimental Apparatus

The experimental apparatus for VUV spectroscopy of room temperature electron beam excited gases is illustrated in Fig. 2.1. The four main components of the apparatus include (1) the electron beam energy source, (2) the reaction cell with (3) backscattering mirror and (4) the vacuum ultraviolet spectrometer with detection equipment. Each component will be individually described in following sections of this chapter starting with the electron beam pumping source.

2.1 Electron Beam Accelerator

The high intensity electron beam was generated by a Physics International Pulserad 110 electron beam accelerator. The Pulserad 110 contains a 10 stage Marx bank high voltage generator, each stage consists of a 0.01875 μF dual capacitor. The stages are charged in parallel to 100kV and switched in series using spark gaps containing SF₆. This yields a 1 MV voltage pulse, which is fed to a Blumlein pulse forming network and then to the vacuum diode. An electron beam is generated with 1 MeV electron energy, a peak current density of 250 A cm⁻², and a pulsewidth of 10 ns (FWHM).

2.2 Electron Backscattering Mirror

An electron beam backscattering reflector [10] was incorporated in the reaction cell to increase the pumping density in the gas. In particular, this is useful at low cell pressures where the energy deposition is small. There are three main reasons to increase pumping density in the reaction medium. The first is due to the fact that the buffer gases used in the neutral and ionic excimer investigations have low atomic numbers. This results in low
Fig. 2.1  Experimental setup for e-beam excitation and diagnosis of species emitting in the VUV and XUV regimes.
stopping powers and small energy deposition. The second motivating factor for using the backscattering mirror is the limited pumping power achievable at low gas pressures. The third reason is to compensate for the considerable amount of electron beam energy lost due to additional physical barriers obstructing the electron beam as in the investigations using the heated cell. In this case the electron beam is required to penetrate two, 50 μm Ti foils and a small layer of insulating air.

A simple backscattering mirror has been designed to conform to transverse pumping to help compensate for the energy deposition losses previously discussed. The principle of this backscattering mirror is to increase the amount of electrons backscattered in the reaction cell. An illustration of such a mirror is shown in Fig 2.2. A 10-cm long piece of lead (Z = 82) was machined into a parabola-like shape. For heated cell experiments, as discussed in chapter 3, tantalum was used instead. The curved inner section is part of a circle that has a continuous transition into a wedge-shaped opening. The approximate focal point, i.e., at about half the radius of curvature of the circle, is located at the optical axis of the reaction cell. The outer surface of the backscattering mirror has a circular shape constructed to fit inside the cell. Free gas circulation is permitted through open space between the cell and the back of the mirror.

During electron beam operation, electrons are accelerated from the carbon cold cathode of 7.5 cm length, towards a highly transparent steel mesh serving as the anode. The electrons penetrate the Hibachi structure, as shown in Fig. 2.2, and pass through a 50-μm-thick titanium pressure foil in order to enter the reaction cell. Since the electron beam is only slightly divergent due to space charge and scattering effects, the backscattering mirror concentrates the electrons in the vicinity of the focal line of the concave mirror. Due to electron beam divergence, the less-than-ideal parabolic shape of the mirror and the relatively broad angular distribution of backscattering, the backscattered electrons do not converge to an ideal line focus, but rather, contribute to an enhanced
Figure 2.2 Cross-sectional view of electron beam diode and reaction cell with back-scattering mirror.
energy density in a finite volume of several millimeters diameter centered around the focus line of the mirror. This concentration of electrons leads to an enhanced pumping density of the medium in the focal region.

In addition to the electron concentration effect, other factors of the backscattering process also contribute to an enhanced pumping density. Below several hundred keV of electron energy, E, the energy loss due to ionization of the gas, which is the dominating loss process in this energy region, varies approximately as $E^{-1}$. Since the backscattered electrons have lower energies than the primary electrons, this effect leads to an increased pumping density of the gas.

Probably more relevant is the production of Bremsstrahlung in the high Z material. The spectral distribution of the bremsstrahlung photons varies over a wide range from almost zero energy up to the incident electron energy, with a peak at about 20%-40% of this energy [11]. The total efficiency of x-ray production for a lead backscattering mirror may be estimated to be about 4% for 1-MeV electrons [11]. This corresponds to about 1J of x-rays for the experimental conditions of this work.

In conclusion, when a surface of sufficiently thick and high Z material is bombarded by electrons in the energy range of 1 MeV, the surface behaves as a lossy mirror with substantial surface scattering. Although the quality of such an electron mirror is far from that of optical mirrors, it is possible to build simple reflector devices for electrons exploiting the effects associated with backscattering.

2.3 Reaction Cell:

The reaction cell for the Ne/F experiments at room temperature is shown in Fig.

2.1. Electron beam energy is injected through a steel mesh anode and the 50 μm Ti support foil into a high pressure stainless steel reaction cell. The stainless steel construction
allows safe handling of corrosive gases such as $F_2$. One end of the cell has a sapphire window. The other side employs a 1" diameter MgF$_2$ window used to separate the high pressures in the cell from the vacuum in the spectrometer. A bellow is placed between the cell and the spectrometer for easy window removal.

The cell is connected to a versatile gas/vacuum system. A baratron gauge is used for precise pressure measurements in the range from one tenth to several hundred torr. Another pressure gauge employed is capable of measuring up to 10 atm. The pressure limit for these experiments is about 6 atm, due to the limited tensile strength of the foil under intense electron beam irradiation. The gas manifold allows convenient selection of several rare gases and halogens. The cell manifold vacuum system consists of a mechanical pump and two diffusion pumps. The gas handling system can be evacuated to about 1 mtorr and the cell to about $10^{-4}$ torr between electron beam shots. The mechanical pump evacuates to 10 mtorr between gas fillings. To avoid severe quenching and absorption by impurities, ultra-high purity neon (99.9995% pure as specified by the vendor) is used. For the donor, a mixture of 10% $F_2$ in He was used. Gas fills were relatively simple as only two constituents, the rare gas, Ne and the halogen $F_2$ needed to be mixed. Initially the donor gas mixture was allowed to flow into the manifold slowly to relatively low pressures up to 50 torr. The buffer gas is then blown into the cell through high flow regulators to allow turbulent mixing. One gas fill lasted up to 5 shots before the detected signal deteriorated.

2.4 Vacuum Ultraviolet Spectrometer:

The optical emission was monitored spectrally by an Acton VM502, Seya Namioka like 0.2 m vacuum ultraviolet spectrometer, equipped with both osmium coated
concave grating and diverter mirror as shown in Fig. 2.1. The model VM502 is designed to use an aberration-corrected concave holographic grating (1200 G/mm), which provides an aperture ratio of f/4.5. The VUV spectrograph is a compact monochromator for the vacuum ultraviolet, in which the spectrum is scanned by rotating the grating about a vertical axis through the grating center. The moveable mirror selects one of the two possible output ports leading to either the photomultiplier (PMT) or the optical multichannel analyzer (OMA I). In the "S" position the mirror is used to reflect the radiation from the grating, forming a "Z" path to the fast photomultiplier (RCA 8575) for temporal information. In the alternate mode, the mirror is turned away from the path of radiation resulting in a "V" path leading to the OMA I (Princeton Applied Research 1205 series D, with a 1205D/01 UV Scintillator). In this version the spectrometer operates like a polychromator yielding time integrated spectra spanning about 40 nm.

The spectrometer is operated under two separate conditions. One configuration is under vacuum, while the other is under pressure, typically 1.2 atm He or N₂. The latter case is for windowless experiments as in NeF*(108 nm) detection, as well as in the He/K experiments. According to the literature [12], LiF transmits down to 105 nm, however LiF could not be used for NeF* detection at 108 nm, since it is not transparent at this wavelength when used in an electron beam pumped system. This is most likely due to radiation damage caused by the intense X-ray pulse associated with the penetration of the electrons in the reaction cell. Since a transmission window is no longer used to separate the corrosive gases in the reaction cell from the spectrometer, another means is sought to protect the optical equipment. The spectrometer grating and VUV mirror are isolated from the gas cell by an automatic shutter which opens the input port of the spectrometer by an electronic solenoid switching mechanism for only 250 ms during electron beam firing. After each shot the spectrometer was evacuated and refilled with inert gas to prevent possible grating damage. The maximum F₂ pressure employed is 0.5% F₂ in neon. Due
to these small partial pressures used diffusion of \( F_2 \) in the spectrometer is negligible.

The spectrometer is also operated under vacuum, in particular for \( \text{Ne}_2 \text{F}^* \) detection at 132 nm. In this case pressures up to six atmospheres were used with the \( \text{MgF}_2 \) window separating the cell pressures from the vacuum in the spectrometer. For such detection the attenuation of the window at 132 nm must be taken into account when analyzing data. The transmission of \( \text{MgF}_2 \) at 132 nm is estimated from manufacturer's data to be about 70%.

2.5 Optical and Electronic Instrumentation:

The OMA I and the PMT used in this work are closed type [13], as they are not directly exposed to the incident radiation. A sodium salicylate scintillator converts the short wavelength VUV radiation into radiation of longer wavelengths. It is prepared by spraying an 80g/l mixture of salicylic acid in methanol on a 0.125" thick plexiglass disc. Numerous tests have established that freshly prepared layers of this scintillator have a constant quantum yield of 0.60 within 10% between 40 and 340 nm [12].

The OMA I is an instrument designed to detect a many channel spectrum from single-shot events, such as the fluorescence from the reaction cell. In order to align the focal plane of the grating with the OMA I face plate, the OMA I is tilted at an angle of 30° with respect to the "V" exit port of the spectrometer. The "V" mode output of the spectrometer is detected by an array of photodiodes masked on the vidicon. The output of this array, representing light intensity at 500 different channels is sent to the electronics for processing and digitizing. This information is viewed on a TV screen and then plotted.

The PMT provides temporal information on the reaction cell fluorescence. It detects only one wavelength from the tuned spectrometer output in the "S" position. The PMT is typically biased 1.7 KV DC to give response times of about 5 ns. The output of
the PMT is carried in low noise Heliax Cable through copper conduit to display instrumentation located inside a bronze screened Faraday cage. The cage provides isolation from the strong electromagnetic interference (EMI) generated by the electron beam accelerator. Instruments used to display the PMT output are shielded against EMI as well. These instruments are presently either a fast storage oscilloscope (Tek 7834) or a Tektronix R7912 Transient Digitizer. The digitizer is connected to the PDP 11/23 computer through a fast parallel data bus. Data is displayed and several parameters calculated as part of the storage process. Fluorescent decay rates are calculated from transient digitizer data stored on a diskette. These decay rates are used to calculate the quenching constants and radiative lifetime of the emission detected. Also time integration may be performed by the computer and then compared with OMA I data.

To protect the detectors from electron beam generated x-ray radiation as well as to increase the SNR, a lead shielding was constructed to encase the entire detection system. Also considering the high x-ray sensitivity of the PMT, two lead apertures of 0.2 \( " \) diameter were employed as shown in Fig. 2.1. Despite the lead shielding, in some cases the fluorescence signal could not be distinguished from the x-ray noise. In such instances the x-ray noise signal was subtracted from the total signal by the computer.
Chapter 3: Heated Cell Techniques in the VUV

In an attempt to excite energy levels in the vacuum ultraviolet regime of alkali atoms and ionic excimers, techniques to heat these compounds in a cell and simultaneously excite them transversely by an electron beam were developed. Elevated temperatures are necessary in both schemes to vaporize the alkali or alkali halide particles in an inert gas environment, commonly helium or neon. Experimental procedures and techniques will be discussed in the following sections of this chapter, but first the specific systems in helium-potassium and cesium-fluoride will be described.

3.1 Proposed Excitation schemes for lowest quartet states of alkali atoms and ionic excimer molecules:

The proposed helium-potassium electron beam excited anti-Stokes-Raman laser scheme employs collisional energy transfer processes from excited metastable helium atoms to core-excited potassium atoms [14]. The energy level diagram for this system is shown in Fig. 3.1. The energy level assignments in Fig. 3.1 have been taken from References [15-17]. The lowest lying quartet states of K, i.e. K(3p\(^5\)3d\(4s\)\(^4\)P\(_{3/2, 5/2}\)), are stable against radiative decay as well as autoionization [14]. Therefore these states are metastable and consequently well suited as high lying energy storage levels. It is intended in this study to populate these states by collisions with the He(1\(s_2\)2\(s^3\)S\(_1\)) levels, which will be abbreviated as He(\(2^3S\)). The energy transfer cross section was estimated to be about 10\(^{-16}\)cm\(^2\) [14]. The quartet transition K(3p\(^5\)3d\(4s\)\(^4\)P\(_{5/2}\)) to K(3p\(^6\)3d \(2^D_{3/2, 5/2}\)) at 72.1 nm has a calculated fluorescence yield of about 0.2% due to 5\(\mu\)s radiative time versus 10 ns Penning ionization rate [18]. Of all other depopulating processes, Penning ionization is the
Figure 3.1  Energy level diagram for the proposed K-He laser system.
most important one and should occur on a 10ns time scale for typical potassium pressures of several torr. Hence, the populated quartet states are predicted to store energy on a 10 ns time duration. Within this time scale, the quartet levels can be transferred to higher lying doublet levels via pulsed dye or high power Nd lasers in the visible or IR. Once enough population in the doublet level is achieved a transition to a valence excited state in K may occur and subsequently radiation in the XUV is emitted. Thus the long term goal of this study is to investigate the spectroscopy of these transitions.

Experiments were initiated to excite He/K mixtures with an electron beam. One of the fundamental requirements in such an experiment is the knowledge of the potassium pressure. It is known from vapor pressure curves that a potassium vapor pressure of about 10 torr is accomplished at a temperature of 450°C. A method for its determination will be described in this chapter.

Another proposed VUV laser scheme concerns emission from ionic alkali halide excimer molecules, namely cesium-fluoride. The alkali halides are isoelectronic to the rare gas halide halogen and inter-halogen laser molecules so they are possible candidates for VUV and XUV laser radiation [6].

A doubly-ionized alkali ion like Cs²⁺ has as its ground state the same electron configuration as a rare gas ion Rg⁺. It may form ionically bound compounds with the negatively charged halogen ion F⁻ abbreviated by Cs²⁺F⁻. In analogy to the rare gas halides these states may then decay by the emission of photons to a weakly bound potential curve corresponding to the singly charged alkali ion Cs⁺ and the neutral halogen atom F. Due to the isoelectronic structure of these ionic compounds and the rare gas halides, similar electronic states are expected.

The calculated potential curves for cesium-fluoride [7] as given in Fig. 3.2 qualitatively describe the similarity between rare gas halide electronic states and those of the alkali halide molecule. Cesium-fluoride emits at 185 nm [7]. Its radiative lifetime was
Figure 3.2 Calculated curves for Cesium-Fluoride [7].
estimated to be about 1ns and a stimulated emission cross section of $1.5 \times 10^{-16}$ cm$^2$ was calculated based on a relative linewidth of $\Delta \lambda/\lambda = 0.025$. This value is similar to those of rare gas halides such as ArF$^*$. Experiments were commenced to investigate the fluorescence spectra of CsF$^+$ in a high pressure He/CsF mixture excited by an electron beam. The main difficulty in the experiments is the high temperature required for vaporization of CsF. A temperature of about 800°C is necessary for a CsF vapor pressure of about 10 torr.

3.2 Heated Cell:

In order to perform the He/K and CsF experiments described in the previous section a reaction cell was designed to withstand both high temperatures and high pressures. The main design consideration was to optimize the electron beam energy deposited into the cell. The cold cell used in the NeF$^*/$Ne$_2$F$^*$ experiments is directly coupled to the emission diode by a thin foil. The diode is in vacuum and sealed to the Blumlein housing by a rubber o-ring. However, for the new cell design, contact between the heated cell and the diode is not permissible. There are two factors to consider; first, the o-ring, which seals Blumlein housing and diode, would melt and second, it would be difficult to reach high temperatures in the cell due to losses caused by heat transfer to both the diode and Blumlein housing. The design chosen was to not couple the electron beam directly into the cell, but to guide it through a small layer of air. A thin foil would then seal the cell from air. Since a rubber to metal seal at the foil would melt under the high temperatures considered, a copper gasket was employed. In this configuration the electron beam would then be required to penetrate two thin foils separated by a few mm of air which would reduce pumping density in the reaction cell by at least a factor of two.
The structure designed is illustrated in Fig. 3.3. Stainless steel was chosen because it has a sufficiently high tensile strength, even at 800°C to withstand pressures of several atmospheres. Heating procedures utilize four rod heaters inserted longitudinally on the back plate combined with a "C" shaped rear heater. Temperatures are monitored in two locations via thermocouples as shown in Fig. 3.3. The thermocouple located directly on the foil was used to monitor the cell temperature due to the close correlation between the measured temperatures and the measured vapor pressures using the absorption technique described in section 3.3. Sealing the cell requires the coupling of several components. The backplate which has a slotted knife edge was designed to mate with a Cu gasket. A 50 μm Ti foil is placed on the gasket, the seal is then completed by the top plate which has a knife edge similar to that of the back plate, and has fluted holes resembling a hibachi-like structure. This top plate serves to support the foil when under atmospheric pressures, while still allowing electron beam penetration in the cell.

In order to compensate for the decrease in electron pumping density, due to the additional foil and layer of air, a backscattering mirror, as described in section 2.2, was employed. Due to the high temperatures, lead cannot be used. Another high Z metal available is tantalum, however this metal is difficult to machine, so only a shell of Ta was constructed. The remaining portion of the mirror is composed of stainless steel. The concentrator may increase the pumping density by as much as a factor of three at low gas pressures, typically 1 atm [10]. Since our experiments are estimated to have small yields this mirror is assumed essential.

In case of the He-K experiment an important consideration is loading potassium into the cell. This highly oxidizing metal is available in standard 5 gram glass ampules, packaged under argon gas at atmospheric pressure. To avoid spontaneous combustion, all handling of potassium took place in a glove bag attached to the cell with a stream of He or N₂ flowing continuously.
Figure 3.3 Exploded view of the heated reaction cell used in electron beam excited alkali halide and alkali systems.
A common occurrence while trying to detect fluorescence in the He-K system is thick condensation of potassium particles during He pressure scans. For example decreasing the He pressure from 1 atm to 0.5 atm or 20 torr induces a thick green mist at the cell ends. This phenomenon occurs, because a decrease in pressure induces a temperature decrease, resulting in potassium condensation. The misting process depletes the K vapor concentration in the central region of the cell; it also coats nearby optics such as the viewing port and spectrometer grating. In an attempt to decrease potassium condensation beyond the electron beam pumped region of the cell a sufficiently long transition zone from the heated portion of the cell to the cold portion is needed to prevent condensation into a fog. It is known from heat pipe technology [19], that the transition zone length should be about three times the tube diameter. In addition a fine mesh stainless steel grid was placed between the cell and the spectrometer to obstruct large streaming potassium particles. Another technique used to prevent potassium vapor from diffusing into the spectrometer region involves the direction control of gas pumping and venting. Pumping on the system is achieved via the port furthest from the spectrometer while He venting is performed through the port inbetween the cell and the spectrometer.

In the case of the cesium-fluoride experiment the main difficulty was foil corrosion. It was presumed that fluorine in the vapor condensed to the foil because it was the coldest spot of the cell. To prevent condensation on the foil a new hibachi plate will be machined to provide space for two rectangular plate heaters. These will replace the function of the large "C" shaped heater formerly placed on the back surface of the cell. The expected result is to make the foil higher in temperature than the other sections of the cell; therefore the CsF vapor is expected to condense in the back region of the cell and foil corrosion will be less probable. Once the foil is able to retain high pressures and temperatures, the next objective will be to determine the vapor pressure in situ as was done in the He/K experiments.
3.3 Potassium Vapor Pressure Determination:

The heated cell used in these experiments does not operate as a conventional heat pipe oven because mixing of the inert gas and alkali vapor is intended for collisional energy transfer. The measurement of alkali vapor pressures in hot cells that do not show the heat pipe effect presents a challenge due to the nonuniformity of both the cell temperature as well as the potassium vapor distribution. A simple method for estimating the vapor pressure would be to measure the cell temperature and inferring the potassium pressure from the vapor pressure curve. However due to the nonuniformity of both the cell temperature as well as the potassium concentration this method is not expected to be very accurate. A more precise method is an absorption measurement. A vapor pressure determination procedure was developed [20], which is used in its simplified form for optically thick samples. Resonance lines usually have high oscillator strengths and become optically thick at relatively low vapor pressures. In case of potassium the 404.5 nm 1s-5p, ground-state-to-valence-level has an oscillator strength of 0.0154 [21]. This resonance line is expected to become optically thick at vapor pressures as low as 1 torr. Such a profile of potassium vapor was obtained by a white light source external to the heated cell. The method developed involves the calculation of equivalent widths of vapor absorption profiles [20]. The concept of equivalent width will be discussed first.

The definition of the equivalent width is illustrated in Fig. 3.4 a. The equivalent width \( W_{eq} \) of the absorption line is defined as the width of a rectangular strip of height \( I_w(0) \) which has the same area as that of the absorption line. \( I_w(0) \) is the intensity of the light source before transmission through the vapor. The area of the strip is equivalent to the area of the absorption dip. From measuring the area of the absorption spectra at the potassium resonance transition, the equivalent width was computed. This leads to the estimation of the K population. A typical experimental result for the potassium 404.5 nm
Figure 3.4 Definition of equivalent width for (a) general case and (b) the optically thick, Potassium 404.5nm line.
(The areas are equivalent, $W_{eq} \approx \sqrt{N_k}$ for the optically thick case.)
absorption dip is illustrated in Fig. 3.4 b. The intensity of the white light source decreases with smaller wavelength. Therefore, the dip area is evaluated as the triangle shown, while $I_w(0)$ is approximated as the average intensity above the dip. Knowing the area in nanometers and the approximate value of $I_w(0)$ the equivalent width may be calculated as:

$$W_{eq} = \frac{\text{Area}}{I_w(0)} \quad (3.1)$$

For the computations $W_{eq}$ is converted into wavenumbers, (cm$^{-1}$) by the following expression:

$$W_{eq} \text{(cm}^{-1}) = W_{eq} \text{(cm)} \times 10^7 / \lambda^2 \quad (3.2)$$

The potassium population in cm$^{-3}$ can be found from the equivalent width using [20]:

$$N_K L = 5.6715 \times 10^{11} W_{eq}^2 / [f_{ik} \Gamma] \quad (3.3)$$

In equation (3.3) $L$ is the length of the vapor zone in cm, $f_{ik}$ is the oscillator strength of the absorption transition, and $\Gamma$ is the transition linewidth in cm$^{-1}$. This equation assumes optically thick samples. This is a good approximation in this case because the optical thickness ($= \sigma NL$) amounts to about 10 for $L = 10$ cm and $N_K$ being only $10^{-14}$ cm$^{-3}$ due to the high absorption cross section of $\sigma = 10^{-14}$ cm$^2$. For experimental conditions of this work $L = 10$ cm, $f_{ik} = .0154$. The line broadening term $\Gamma$, is approximated as:

$$\Gamma = 9.3 \times 10^{-20} (\text{cm}^2)[N_{He}] \quad (3.4)$$
\( N_{\text{He}} \) is the helium concentration in cm\(^{-3}\). This equation neglects natural broadening, doppler broadening as well as line broadening by collisions with potassium. Combining equation (3.4) with values for \( f_{ik} \) and \( L \), equation (3.3) can be simply expressed as:

\[
N_K = 3.96 \times 10^{31} \text{(cm}^{-4}) \left\{ \frac{W_{eq}^2}{[N_{\text{He}}]} \right\} \tag{3.5}
\]

where \( N_K \) is the potassium concentration in cm\(^{-3}\). Table 1 summarizes the results, for an average cell temperature of 430 ± 39°C, the potassium density is about 2.2±1.1x10\(^{17}\) cm\(^{-3}\). According to a vapor pressure curve of potassium, 430°C corresponds to 10 torr or 1.4x10\(^{17}\) cm\(^{-3}\). This is in reasonable agreement with the measured value. The main uncertainty in the measurements is in the determination of \( I_{w}(0) \). The location of the zero transmission baseline was not obvious, due to negative counts detected after background subtraction from the OMA I. This limited the determination of the vapor pressure to within a factor of two. For better accuracy in future experiments an OMA III adapted for VUV spectroscopy will be used.
<table>
<thead>
<tr>
<th>$P_{\text{He}}$</th>
<th>$T^\circ$</th>
<th>$W_{eq}$ (cm$^{-1}$)</th>
<th>$\Gamma$ (cm$^{-1}$)</th>
<th>$N_k$ (cm$^3$)</th>
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<tbody>
<tr>
<td>10.1 Torr</td>
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<td>21.4</td>
<td>0.0126</td>
<td>1.3</td>
</tr>
<tr>
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<td>30.7</td>
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<tr>
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<td>465</td>
<td>65.3</td>
<td>0.049</td>
<td>3.2</td>
</tr>
<tr>
<td>75.0 Torr</td>
<td>460</td>
<td>56.8</td>
<td>0.092</td>
<td>1.3</td>
</tr>
<tr>
<td>0.2 atm.</td>
<td>455</td>
<td>99.35</td>
<td>0.187</td>
<td>1.9</td>
</tr>
<tr>
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<td>396</td>
<td>148.0</td>
<td>0.510</td>
<td>1.6</td>
</tr>
<tr>
<td>0.5 atm.</td>
<td>445</td>
<td>124.0</td>
<td>0.475</td>
<td>1.2</td>
</tr>
<tr>
<td>1.0 atm.</td>
<td>349</td>
<td>185.0</td>
<td>1.10</td>
<td>1.1</td>
</tr>
<tr>
<td>1.0 atm.</td>
<td>400</td>
<td>231.0</td>
<td>1.01</td>
<td>1.9</td>
</tr>
</tbody>
</table>

$$\Gamma(\text{cm}^{-1}) = 9.3 \times 10^{-20} N_{\text{He}}$$
CHAPTER 4: Experimental Observation of NeF* and Ne₂F*

4.1 Rare Gas Halide Exciplexes:

Diatomic and triatomic excimers have been studied extensively since the mid seventies. Their bound free transition characteristics caused by a repulsive ground state, enables them to have population inversion when excited by a high power pumping source such as an electron beam accelerator or gas discharge. Triatomic rare gas halides, which will be referred to simply as trimers, are observed on the long wavelength side of most B-X and C-A RgX (Rg = rare gas, X = halogen) transitions [3]. They were initially viewed as a loss mechanism for the diatomic rare gas halogen lasers. The trimers have a steeply repulsive potential energy surface in the ground state resulting in an inherently broadband fluorescence. Typical bandwidths are 50-80 nm, as compared to the narrow 1-2 nm spectral linewidth of the diatomic B-X transitions. Therefore some of these triatomic molecules were developed into tunable laser sources [3,22,23]. Another characteristic common to all trimers is their long radiative lifetimes, of typically more than 200 ns. This property combined with the broad bandwidth results in relatively low stimulated emission cross section and therefore low effective gain. For the KrF(B-X) transition one obtains $\sigma_{SE} = 2 \times 10^{-16} \text{cm}^2$ [3], while for the Kr₂F trimer emission $\sigma_{SE} = 3 \times 10^{-18} \text{cm}^2$ [3]. This is a cross section approximately two orders of magnitude smaller than for the dimer. Due to their long radiative lifetimes the Rg₂X* species are vulnerable to quenching by other constituents of the gas mixture, in particular the halogen donor. On the other hand, trimers have favorable laser media properties since a long
radiative lifetime would permit laser operation after the decay of possible absorption due to a short intense excitation pulse. Another advantage is low gain cross section leads to high saturation energies which leads to good amplifiers.

Of the ten rare gas halide combinations whose emissions are well characterized, nine of the corresponding trimers have been previously detected [3]. For Ne$_2$F*, only two potential curve calculations were available [24,25] at the start of this work. In this chapter the first observation of Ne$_2$F* fluorescence is reported. It is identified through the characteristic behavior of its fluorescence radiation and that of its precursor, NeF*.

4.2 NeF*:

Emission from NeF* was detected from electron beam pumped mixtures of high purity Ne (99.9995%) and 10% F$_2$ in helium. The fluorescence spectrum as measured by the OMA I is shown in Fig. 4.1. The peak emission occurs at 108.0 nm with a bandwidth of 1.9 ± 0.2 nm. Both the peak wavelength and full width at half maximum (FWHM) are in agreement with previous reports by Rice and Hays [26] and Walter [27]. Rice and Hays observed NeF* at 108.0 nm with a FWHM of 1.9 ± 0.2 nm in gas mixtures of neon and F$_2$ [27]. Walter on the other hand observed NeF* spectra at 108.4 nm with a bandwidth of 1.7 ± 0.3 nm using He in addition to Ne and F$_2$ [27]. Theoretical, \textit{ab initio} calculations confirm these findings [4,28] as well. Winter and Bender predict that NeF*(B-X) should emit in a 1.5 nm wide band centered at 108.0 nm [4], while Dunning and Hay predict an emission at 114 nm [28]. The assignment of the emission at 108 nm to NeF*(B-X) is thus strongly supported by other observations as well as theoretical calculations.
Figure 4.1 Fluorescence spectrum of NeF emitting at 108nm.
4.2.a Potential curves:

Relevant NeF* potential curves as given by Walter [27] are summarized in Fig 4.2. Common to almost all RgX species, the ground states are repulsive. The two lowest bound levels $^2\Sigma_{1/2}$ and $^2\Pi_{3/2,1/2}$ are ionic and cross with covalent curves which correlate to the excited states of both Ne and F. As a result of electron beam excitation, NeF* is primarily formed by three body ion recombination:

$$\text{Ne}^+ + \text{F}^- + \text{Ne} \rightarrow \text{NeF}^* + \text{Ne} \quad (4.1)$$

This is true for all RgX with the Rg light and X heavy including ArCl. The term "light" alludes to high lying excited energy levels, while "heavy" refers to less energetic excited states. An alternative formation reaction is through excited neutrals:

$$\text{Ne}^* + \text{F}_2 \rightarrow \text{NeF}^* + \text{F} \quad (4.2)$$

or:

$$\text{Ne} + \text{F}^* + \text{M} \rightarrow \text{NeF}^* + \text{M} \quad (4.3)$$

where M is a third body.

In case of NeF*, the crossing of potential curves correlating to ionic states and those correlating to neutrals occurs at relatively small internuclear distances, as shown in Fig. 4.2. Also the energy separations between ionic and covalent states are bigger compared with other rare gas monohalides. This is essentially due to the greater ionization and excitation energies of Ne compared with those of Ar, Kr and Xe. Due to the energy separations there is a certain probability at each crossing for the ionic Ne$^+$ and F$^-$ atoms to neutralize in the covalent channels, and there are two such crossings, therefore only a small fraction of the population is expected to be bound. Fig. 4.3 shows the
Figure 4.2 Calculated NeF* potential curves [28].
Figure 4.3 Rate coefficients for mutual neutralization and three body recombination of NeF²⁺ [30].
pressure dependence of the rates for both predissociation, also called mutual neutralization, as well as three body recombination compiled by Whitten et al. [29]. At 1 atm the rate coefficient for mutual neutralization is more than 10x that of three body recombination, while at higher pressures the difference is not as great. Therefore higher rare gas pressure favors both NeF* and thus Ne2F* formation due to increased populations of third bodies.

A notable competition between the formation of NeF* and F2* exists as a consequence of the potential curve characteristics mentioned. The NeF* formation process begins with the highly excited Ne2F** produced by ionic recombination. Then this molecule can either relax to a lower excited state of NeF*, or it may predissociate into excited F* levels. Once the excited atomic F* levels are formed, they may collide with energetic Ne or F* atomics. The latter predissocation case subsequently leads to the formation of F2*. However the former covalent channel results in recombination by third bodies, namely Ne, which produces low energy NeF* molecules. This is similar to the ArCl/Cl2* competition reported by Liegel et al. [5].

4.2.b Fluorescence Studies of NeF*:

The NeF*(B-X) emission was monitored as a function of both F2 and Ne pressures. NF3 was ruled out as a possible donor due to its high absorption cross section, \( \sigma = 3.4 \times 10^{-18} \text{cm}^2 \), at 108 nm as measured by Walter [27]. F2 however is an attractive donor. It has no characteristic absorptions above 102 nm [30], and an 85% higher yield than NF3 as reported by Walter [27]. As mentioned in chapter 2, NeF* fluorescence
experiments were performed windowless, thus limiting total gas pressures in the reaction cell to 1 atm. The spectrometer however was filled with helium or neon at slightly higher pressures of 1.2 atm. Therefore only pressures up to 1 atm could be used for neon while pressure ranges from 0.01 - 5.0 torr for F₂ were employed. Figure 4.4 depicts NeF* time integrated intensity measured at 108.0 nm with varied F₂ pressure. The NeF* fluorescence peaks at very small F₂ pressures of 0.4 to 0.6 torr and rapidly falls off with increasing pressure. Similar findings are reported in Walters' investigation of NeF* [27]. Most rare gas halides undergo rapid donor quenching, only at higher F₂ concentrations typically 1-10 torr. A strong loss channel of NeF* is by F₂* formation. F₂* production is a direct consequence of mutual neutralization, since the F₂* population is presumably produced in F*/F₂ collisions. NeF* production is a function of three body ion recombination. Therefore the ratio of NeF* intensity to that of F₂* should correlate with the ratio of recombination to mutual neutralization at the appropriate pressures from Fig. 4.3.

The NeF* fluorescence was measured for varying neon pressures up to 1 atm. The maximum fluorescence intensity as a function of Ne pressure is plotted in Fig. 4.5. The experimental results suggest that the maximum NeF* intensity scales stronger than linearly with the Ne pressure. If NeF* production via the F* channel dominates, this dependence can be tentatively described by the following simple kinetic model:

\[
\frac{d[F^*]}{dt} = k_2[\text{Ne}_2^+][F^-] - \frac{[F^*]}{\tau_2}
\]  

(4.4)

\[
\frac{d[\text{NeF}^*]}{dt} = k_1[F^*][\text{Ne}]^{(1-2)} - \frac{[\text{NeF}]}{\tau_1}
\]

(4.5)
Figure 4.4 Dependence of NeF$^+$ time-integrated fluorescence intensity upon F$_2$ pressure at 1 atm. Ne.
Figure 4.5 NeF* intensity as a function of Ne pressure.
Three body quenching is neglected in this model due to the smallness of the \([\text{Ne}]^2\) term at low the neon pressures used. The neon dependence in equation 4.5 may be quadratic due to additional neon collisions. In an attempt to explain this behavior the differential equations will be solved for \(F^*\) and \(\text{NeF}^*\) fluorescence yields. First the integration of equation 4.4 yields:

\[
I_{F^*} = k_2/\tau_2 \int [\text{Ne}_2^+] [F^-] dt \cdot \tau_2
\]

(4.6)

where \(I_{F^*}\) is the fluorescence yield of \(F^*\). Integration of equation 4.5 results in :

\[
I_{\text{NeF}^*} = \tau_1 k_1 I_{F^*} [\text{Ne}]^{(1-2)}
\]

(4.7)

The power of Ne may be 1 or 2 depending on how high the probability is for forming \(\text{NeF}\) from 2nd collisions with Ne after the first predissociation. Assuming the \(F_2\) concentration is high enough so that most of the plasma electrons are attached to \(F_2\) to form \(F^-\) ions and \(\text{Ne}_2^+\) is the dominant positive ion, the \(\text{Ne}_2^+\) concentration is approximately the same as the \(F^-\) concentration because the plasma is neutral. With these assumptions equation 4.6 is simplified to :

\[
I_{F^*} \sim \tau_2 [\text{Ne}]^2
\]

(4.8)

Providing the recombination with neon is the dominant process that determines the \(F^*\) lifetime, a further simplification can be achieved. \(\tau_2\) can be taken as the inverse of the neon concentration, simplifying equation 4.8 to :

\[
I_{F^*} \sim [\text{Ne}]
\]

(4.9)

Substituting equation 4.8 into 4.9 yields an expression for the \(\text{NeF}\) intensity as measured
by the PMT:

$$I_{\text{NeF}} \sim [\text{Ne}]^{2-3}$$  \hspace{1cm} (4.10)

This expression shows that the NeF intensity has a stronger than linear dependence on the neon pressure. This agrees qualitatively with the fluorescence data shown in Fig. 4.5.

A typical plot showing the temporal behavior of the NeF* fluorescence, after the subtraction of x-ray noise is depicted in Fig. 4.6. The risetime is about 25 ns with a pulsewidth FWHM of 65 ns for an F_2 pressure of 0.5 torr at 1 atm Ne. The decay time is about 130 ns, which is much longer than the pumping pulse. Since the radiative lifetime as predicted by Winter and Bender [4] is only 2.4 ns it must be assumed that the extracted lifetime is that of a precursor of NeF*. The tail of the pulse does not show the common exponential decay. A simplified analysis however reveals a possible second order kinetic reaction. It is proposed that the temporal development of NeF* will be inclined to follow that of F*, by ionic recombination. This is because only small concentrations of F_2, about 1-2 torr for maximum NeF* emission, are mixed with Ne. Earlier it was proposed that F* is the precursor of NeF*, however the following discussion considers that F* might in fact be limited by the F* production. This would result in the decay of the temporal pulse of NeF* following that of the F* ion. The decay will not be exponential but will be determined by the following second order differential equation:

$$\frac{d[F^*]}{dt} = -k_3[F^*]^2$$  \hspace{1cm} (4.11)

k_3 is the ion recombination constant and neutrality of the plasma is assumed. For an initial F* concentration, at the beginning of the exponential decay (t=0), of F_0^*, the solution to this equation yields the following expression:

$$[F^*] = [F_0^*]/\{1 + [F_0^*]k_3t\}$$  \hspace{1cm} (4.12)
Fig. 4.6 Time-resolved fluorescence from NeF* (108 nm).
This matches the decay of Fig. 4.6.

In conclusion the temporal data of NeF* revealed a non-exponential decay tail at low Ne pressures up to 1 atm, which led to the proposition that the NeF* emission follows the temporal decay of the F* population. Also the NeF* intensity varies non-linearly, probably quadratically with neon pressure. This was previously explained by the first order F* process.

4.3 Ne$_2$F*:

For the first time since trimers were discovered in 1977, Ne$_2$F* emission has been observed in electron beam pumped mixtures of Ne/F$_2$ at 132 nm. This emission is the shortest wavelength trimer ever reported. Fig. 4.7 illustrates the spectral characteristics of Ne$_2$F* accompanied by its precursor NeF* ranging in wavelength from 105 - 145 nm. The broad continuum centered at 132 nm with a bandwidth of 10 nm is verified as Ne$_2$F* and the narrow emission at 108 nm is NeF*. The emissions were not viewed simultaneously however, due to the scarcely visible Ne$_2$F* emission at 1 atm. The highest Ne pressure used for Ne$_2$F* observation was 6 atm, the optimum pressure may be higher.

4.3.a Ne$_2$F* Spectroscopy:

Ne$_2$F* had not been observed until now, but theoretical calculations have been available for about ten years [3]. Ne$_2$F* is expected to be bound since Ne$_2^+$ has a
Fig. 4.7 Fluorescence spectra of NeF* (108 nm) and Ne$_2$F* (132 nm) from e-beam-excited mixtures of Ne and F$_2$. 
binding energy of about 1.65 eV. This energy is high compared to the binding energies of \( \text{Ar}_2^+, \text{Kr}_2^+, \) and \( \text{Xe}_2^+ \), from which common trimers are found such as \( \text{Ar}_2\text{F}^+ \). Bender and Schaefer III have done the first theoretical study of the \( \text{Ne}_2\text{F}^* \) system [24]. Via \textit{ab initio} calculations they find a \( C_{2v} \) geometry for \( \text{Ne}_2\text{F}^* \) and predict the \( 2^2B_2 \) state of \( \text{Ne}_2\text{F}^* \) to be bound relative to the \( \text{Ne}^+\text{F}^+ \text{Ne} \) by 0.76 eV [24]. Electronic transition moments were also computed for the permitted transitions of \( 2^2B_2 \) to the ground states \( 2^2A_1 \) and \( 2^2B_2 \). For electronic transitions to the repulsive ground state an emission between about 120 nm and 160 nm is expected [24]. Other theoretical calculations were published by Huestis and Schlotter [25]. They performed the less elaborate DIM calculations including spin orbit coupling. They predicted an emission wavelength of 145 nm for \( \text{Ne}_2\text{F}^* \).

There has been an observation of the \( \text{NeF}^* \) spectrum by Rice and Hays. They have also reported weak emissions at 119.5 nm and 122.0 nm [26]. It was concluded by Bender and Schaeffer III [24] that these weak emissions might be due to \( \text{Ne}_2\text{F}^* \) which happens to coincide well with their calculations. However, no kinetic behavior of these transitions has been investigated in order to consolidate this assignment.

Electron beam excited \( \text{Ne}/\text{F}_2 \) mixtures between 105 nm and 145 nm is presented in Fig. 4.7. The broad continuum centered at 132 nm with a bandwidth of 10 nm is assigned to \( \text{Ne}_2\text{F}^* \) and the narrow emission at 108 nm is \( \text{NeF}^* \). The narrow lines superimposed on the broad continuum can be assigned to NII and CI emission lines, originating from impurities in the gases and backscattering mirror. These atomic lines were used to calibrate the system. The broadband spectrum centered at 132 nm is
attributed to Ne\textsubscript{2}F* emission for several reasons. First, it appears only with gas mixtures of neon and F\textsubscript{2}. Gas mixtures of just Ne or He with F\textsubscript{2} were used and no fluorescence was observed at 132 nm. Second, the broadband spectrum is observed to the red of the NeF* emission by an energy shift of 1.51 eV, this is in agreement with other known dimer/trimer systems. Third, the measured energy width is 0.174 eV, which is comparable to other trimers, namely Ar\textsubscript{2}F* (0.765 eV) as shown in table II. The assignment of Ne\textsubscript{2}F* is further supported by kinetic studies. Therefore the weak emission observed by Rice and Hays [26] cannot be assigned to Ne\textsubscript{2}F* as this work solidly reports Ne\textsubscript{2}F* fluorescence at 132 nm.

Only gas mixtures containing Ne and F\textsubscript{2} were used for optimization. NF\textsubscript{3} as a donor was tried, but emissions were considerably weaker by at least a factor of two. This is attributed to the depletion of the NeF population due to NF\textsubscript{3} absorption at 108 nm. Helium was also used as a buffer gas resulting in weaker Ne\textsubscript{2}F* emissions as well. The maximum pressure gas mixture attainable was 6 atm neon and 0.9 torr F\textsubscript{2}, with 6 atm Ne as an upper limit.

The 10 nm bandwidth of Ne\textsubscript{2}F* is relatively narrow compared with other known trimers such as Ar\textsubscript{2}F*. It might be considered that the MgF\textsubscript{2} window used attenuated the emission on the short wavelength side causing narrowing. However the emission appears to be symmetric. Also the Ar\textsubscript{2}* emission at 126 nm was observed without noticeable distortion, as shown in Fig. 4.8. Walter stated in his investigation that via extrapolation of spectral widths of other trimers [27], a width for Ne\textsubscript{2}F* emission should be in the
Table II  Triatomic $Rg_2F^*$ emissions and computed energy widths
$\lambda = $ Center wavelength, $\Delta \lambda = $ Spectral width, $E = $ Emission energy,
$\Delta E = $ Energy width.

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<td>9.42 a)</td>
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<td></td>
<td>145 b)</td>
<td>40 c)</td>
<td>8.57 b)</td>
<td>2.85 c)</td>
</tr>
<tr>
<td>Ar$_2$F</td>
<td>285</td>
<td>50</td>
<td>4.36</td>
<td>0.765</td>
</tr>
<tr>
<td>Kr$_2$F</td>
<td>420</td>
<td>70</td>
<td>2.96</td>
<td>0.493</td>
</tr>
<tr>
<td>Xe$_2$F</td>
<td>610</td>
<td>130</td>
<td>2.04</td>
<td>0.435</td>
</tr>
</tbody>
</table>

(a) Observed in this work  
(b) Calculated [25]  
(c) Proposed [27]
Fig 4.8 \( \text{Ar}_2^* \) (126 nm) spectrum at 3 atm. Ar.
neighborhood of 40 nm. This "extrapolation" certainly follows the trend that the bandwidth of the trimer exciplexes decrease with decreasing center wavelength. However, another important characteristic to consider is the energy bandwidths. Table II shows computed energy bandwidths of most trimers. Column five exhibits an increasing energy width for decreasing center wavelength. For a Ne$_2$F* emission at 145 nm with FWHM of 40 nm predicted by Walter [27], the energy width is computed to be 2.85 eV. On the other hand for the 10 nm wide 132 nm emission observed in this work an energy bandwidth of 0.714 is computed. Compared with energy widths of other trimers it seems that 2.85 eV may be too high for Ne$_2$F* while a bandwidth of 0.714 eV is comparable to that of Ar$_2$F*.

The 132 nm center wavelength of the Ne$_2$F* fluorescence observed in this work is shorter than the predicted value. According to the DIM calculations by Huestis and Schlotter [25] the Ne$_2$F* emission should be near 145 nm. This corresponds to an energy difference of 0.85 eV between the observed and predicted levels of Ne$_2$F*. This indicates either a smaller binding energy of Ne$_2$F*, relative to NeF* + Ne, or larger bond lengths of the excited state than expected from calculations.

4.3.b Kinetic Reactions of Ne$_2$F*:

Temporally resolved as well as time integrated fluorescence emissions of Ne$_2$F* were monitored as a function of both rare gas Ne and donor F$_2$ pressures. From the results, quenching constants by F$_2$ and Ne, the three body production rate from NeF*, and
the radiative lifetime of Ne$_2$F* were determined.

The temporal behavior of the Ne$_2$F* fluorescence is illustrated in Fig. 4.9 for typical conditions. Even at a neon pressure of 6 atm the Ne$_2$F* fluorescence shows a risetime of about 60 ns, which is considerably larger than the NeF* risetime at only 1 atm total pressure. The fluorescence pulse decays exponentially on a timescale of several hundred nanoseconds.

The Ne$_2$F* effective decay rates, i.e. the inverse effective lifetimes are plotted as a function of quenching gas pressures. These decay rate plots, or Stern-Volmer plots, of Ne$_2$F* intensity versus F$_2$ and Ne are shown in Fig. 4.10 a, b respectively. The effective decay rate $[\tau_{\text{eff}}]^{-1}$ is given in the following equation:

$$[\tau_{\text{eff}}]^{-1} = [\tau_{\text{rad}}]^{-1} + k_{F_2}[F_2] + k_{Ne}[Ne] \quad (4.13)$$

when three body quenching processes are neglected. Here $\tau_{\text{rad}}$ denotes the radiative lifetime and $[F_2]$ and $[Ne]$ the fluorine and neon concentrations respectively. The quenching coefficients, $k_{F_2}$ and $k_{Ne}$ are computed from the slopes of the Stern-Volmer plots. Since the decay rate of Ne$_2$F* is essentially constant for different Ne pressure, only an upper limit for $k_{Ne}$ of $k_{Ne} \leq 10^{-14}$ cm$^3$s$^{-1}$ can be determined. This value is consistent with two body rare gas quenching coefficients, and for other trimers [31]. The slope from Fig. 4.10a yields $k_{F_2} = 1.8 \pm 0.2 \times 10^{-10}$ cm$^3$s$^{-1}$. This decay rate coefficient is also on the same order of magnitude as halogen donor two body quenching coefficients for other comparable systems [31]. From the decay rate intercept of Fig. 4.10a the radiative lifetime
Fig. 4.9 Time-resolved fluorescence from Ne₂F*(132 nm).
Figure 4.10  Stern-Volmer plots of Ne₂F⁺ against (a) F₂ pressure and (b) Ne pressure.
may be computed. This analysis yields a lifetime of 280±55 ns. The maximum lifetime is
determined by neglecting $k_{Ne}$ and the minimum corresponds to $k_{Ne}=10^{-14} \text{cm}^{3}\text{s}^{-1}$. This
value is much greater than 2.4 ns [4], the predicted radiative lifetime of the precursor
NeF*, which is typical for triatomic rare gas halides.

To confirm the validity of the calculated rate coefficients, a comparison can be
made between the observed effective lifetime in Fig.4.9 and the calculated effective lifetime
from equation 4.13. From the tail of the temporal plot in Fig. 4.9, an exponential decay fit
is made yielding a $\tau_{eff}$ of 137 ns. For 6 atm Ne and 0.6 torr $F_2$ with an averaged
radiative lifetime, $\tau_{rad} = 266.7$ ns, the computed effective lifetime from equation (4.13) is
129 ns. This is only 8 ns lower than measured, a difference well within the experimental
error.

The $F_2$ donor pressure dependence of $\text{Ne}_2F^*$ is illustrated in Fig.4.11. The
maximum emission occurs at about 0.4 torr $F_2$. This pressure coincides with the
maximum NeF* signal. Also the Ne pressure dependence of $\text{Ne}_2F^*$ is shown in Fig.
4.12. The Ne dependence of $\text{Ne}_2F^*$ is stronger than linear just like its precursor NeF*.
This indicates that two body as well as three body quenching of $\text{Ne}_2F^*$ by Ne is small.

To determine the three body production constant of $\text{Ne}_2F^*$ by NeF*, the intensity
ratio of $\text{Ne}_2F^*$ to NeF* is taken as a function of neon pressure for the given reaction :

$$\text{NeF}^* + 2\text{Ne} \rightarrow \text{Ne}_2F^* + \text{Ne} \quad (4.14)$$

which leads to the following rate equation:
Fig. 4.11 Ne\textsubscript{2}F* intensity as a function of F\textsubscript{2} pressure.
Figure 4.12 $\text{Ne}_2\text{F}^*$ intensity as a function of Ne pressure.
\[
d\left(\text{Ne}_2\text{F}^*\right)/dt = k_4 [\text{NeF}][\text{Ne}]^2 - [\text{Ne}_2\text{F}] / \tau_3, \quad (4.15)
\]

The fluorescence yield ratio of Ne$_2$F* to that of NeF* is:

\[
I\{\text{Ne}_2\text{F}^*\}/I\{\text{NeF}^*\} = k_4 [\text{Ne}]^2 \tau_3 
\quad (4.16)
\]

In this case $I\{\text{Ne}_2\text{F}^*\}$ and $I\{\text{NeF}^*\}$ represent the fluorescence yield of Ne$_2$F* and NeF* respectively, while $k_4$ is the three body rate constant and $\tau_3$ is the radiative lifetime of Ne$_2$F*. Equation (4.16) describes a possible quadratic dependence on neon pressure. Due to experimental limitations, the NeF* intensity ratio could be computed only for 1 atm Ne, a pressure in which Ne$_2$F* fluorescence is weak. Nevertheless, the calculated $k_4 = 2.2 \pm 1.1 \times 10^{-33} \text{ cm}^3 s^{-1}$ is in reasonable agreement with a theoretical value [27], $k_4 \sim 6 \times 10^{-33} \text{ cm}^3 s^{-1}$. The rate constants and lifetime of Ne$_2$F* are compiled in table III. Inaccuracies in the experimentally measured $k_4$ may be caused by the low signal to noise ratio of Ne$_2$F* fluorescence compared with x-ray noise at 1 atm of Ne.

The Ne$_2$F* system is more simplified compared to most trimers since neon acts both as the buffer gas for electron beam energy deposition and as rare gas for build up of NeF* and Ne$_2$F*. The observed decay of Ne$_2$F* under high pressure is exponential, therefore it does not follow the decay of its precursor NeF* at low pressure. A possible reason for this discrepancy is that at high pressures NeF* may be exponential due to the production of many more F* ions.

In addition to the investigations of the dimer and trimer emissions in gas mixtures
Table III  Rate Constants of $\text{Ne}_2\text{F}^*$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NeF}^* + 2\text{Ne} \rightarrow \text{Ne}_2\text{F}^* + \text{Ne}$</td>
<td>$k_1 = 4.0 \pm 2 \times 10^{-33} \text{cm}^6\text{s}^{-1}$</td>
</tr>
<tr>
<td>$\text{Ne}_2\text{F}^* \rightarrow 2\text{Ne} + \text{F} + \text{hv (132 nm)}$</td>
<td>$k_1 = 6.0 \times 10^{-33} \text{cm}^6\text{s}^{-1}$ (a)</td>
</tr>
<tr>
<td>$\text{Ne}_2\text{F}^* + \text{F}_2 \rightarrow \text{Quenching}$</td>
<td>$\tau_{132} = 280 \pm 55 \text{ns}$</td>
</tr>
<tr>
<td>$\text{Ne}_2\text{F}^* + \text{Ne} \rightarrow \text{Quenching}$</td>
<td>$k_F = 1.8 \pm 0.3 \times 10^{-11} \text{cm}^3\text{s}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$k_{\text{Ne}} \leq 1.0 \times 10^{-14} \text{cm}^3\text{s}^{-1}$</td>
</tr>
</tbody>
</table>
of neon and F$_2$, a search was conducted for the Ne$_3$F$^*$ exciplex. Ar$_3$F$^*$ was recently observed [32]. The binding energy for Ne$_3^+$ was calculated to be only 0.15±0.02 eV [33]. Therefore Ne$_3$F$^*$ might be thermally less stable than Ar$_3$F$^*$. If Ne$_3$F$^*$ exists and radiates, its emission is expected to lie on the long wavelength side of Ne$_2$F$^*$ (132 nm) between about 150 and 170 nm. One experimental difficulty encountered, however, is the strong F$_2^*$ emission at 157.5 nm. Only regions below 148 nm and above 165 nm could be observed as a consequence of this strong emission. Fluorescence was not observed in these regions. It cannot be excluded that the Ne$_3$F$^*$ fluorescence, if it exists, is hidden by the strong F$_2^*$ emission. However the pressure dependence of the Ne$_2$F$^*$ emission does not indicate a strong three body quenching of Ne$_2$F$^*$ by neon, which would be expected if Ne$_3$F$^*$ exists as a stable exciplex [32].
**Chapter 5: Conclusions and Proposed Future Work**

The main result of this work was the first observation and characterization of \( \text{Ne}_2\text{F}^* \) at 132 nm. A VUV detection and e-beam pumping system was developed. Also heated cell techniques were developed for investigations of ionic excimers as well as core-excited alkali metals, both of which require high temperatures to reach the vapor state. With the addition of heated cell techniques this system will provide unique capabilities for future work in this field. The conclusion of this work is divided into three molecular and atomic schemes. The results obtained will be summarized along with propositions for future investigations.

In gas mixtures of Ne and \( \text{F}_2 \) the shortest wavelength trimer, \( \text{Ne}_2\text{F}^* \) was observed for the first time. A 132 nm emission with a FWHM of 10 nm is reported. \( \text{NeF}^* \), the precursor of \( \text{Ne}_2\text{F}^* \), was also observed at 108 nm with a FWHM of 1.9 nm. The fact that \( \text{Ne}_2\text{F}^* \) has a longer wavelength and broader emission than that of \( \text{NeF}^* \) is consistent with other related trimer and dimer pairs.

From spectral and temporal data, a kinetic model for \( \text{NeF}^* \) was proposed. Production of \( \text{NeF}^* \) by ion recombination as well as harpooning reactions was considered. The competition between \( \text{NeF}^* \) and \( \text{F}_2^* \) is analogous to that of \( \text{ArCl}^* \) and \( \text{Cl}_2^* \) [5]. The similarity is due to the fact that both have lower lying excited donor energy levels than rare gas levels. This tends to induce a high excited donor concentration which, depending on the donor, is favorable for producing excited fluorine, \( \text{F}_2^* \) or chlorine, \( \text{Cl}_2^* \).

Typical of all trimers, \( \text{Ne}_2\text{F}^* \) emission is optimal at high pressures due to three body recombination with its precursor \( \text{NeF}^* \). Spectral and temporal measurements were taken of \( \text{Ne}_2\text{F}^* \) to compute quenching and formation coefficients as summarized in Table
III. Temporal data of Ne$_2$F$^*$ fluorescence at high pressures reveal an exponential decay. Just as with NeF$^*$ the Ne dependence of Ne$_2$F$^*$ is stronger than linear and a possible quadratic dependence is proposed. It can be concluded that Ne$_2$F$^*$ is not capable of laser action, just like many other trimers. This is a direct consequence of their characteristic long spontaneous lifetimes as well as broad spectral widths leading to a small stimulated emission cross section. The computed stimulated emission cross section for Ne$_2$F$^*$ is about 10$^{-19}$ cm$^2$. It may on the other hand be possible to induce laser action in NeF$^*$ as the cross section for stimulated emission is about 2x10$^{-17}$ cm$^2$, requiring a NeF$^*$ population of about 10$^{15}$ cm$^{-3}$ for amplification. In order to attempt this, a spectrometer which can withstand high pressure up to at least 6 atm is needed. Also the existence of Ne$_3$F$^*$ was investigated. A strong F$_2^*$ signal which emits in the expected spectral region prevents detection of this four atomic excimer, if it exists.

In addition to studying neutral excimers, ionic excimers composed of doubly ionized alkali metals with singly ionized halogen atoms will be investigated. To avoid corrosion problems in the future experiments, the foil will be made the hottest spot of the cell. This will be achieved by attaching high power heaters directly to the foil retaining hibachi plate. With this improvement fluorescence of CsF$^+$ should be observed at 185 nm at higher vapor pressures.

Since the apparatus was developed for the VUV under high temperatures, another promising laser scheme in alkali vapors could be investigated. The expected emission of core-excited alkali atoms is in an attractive spectral region, below 100 nm. The excitation transfer system of potassium in a helium environment was used in an initial study to perfect measurement techniques. The main difficulty in these systems is producing large populations of the quartet levels, which are attractive for storage due to their relatively long lifetimes compared to the higher lying doublets.
A technique for measuring vapor pressure via the equivalent width method was developed. Recently promising new results from Stanford [9] were obtained for core-excited Rb. An XUV emission from Rb(4p⁵ 5s⁵p ⁴S₃/₂) to Rb(4p⁶ 5p ⁴P₃/₂) levels was observed from laser produced plasmas. The Ne(³P₂) energy level is coincident with the Rb (⁴S) level. Therefore a Ne/Rb system seems promising for XUV emission under electron beam pumping. This scheme appears more promising than He/K because the properties of the upper quartet manifold is well known. Also Ne should be able to transfer energy more effectively to the quartet Rb states. Since Ne is heavier than He, it is more effective in producing slow electrons which leads to an overall higher energy deposition.
BIBLIOGRAPHY:


