Rare gas alkali ionic excimers

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RARE GAS ALKALI IONIC EXCIMERS

BY

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ABSTRACT

RARE GAS ALKALI IONIC EXCIMERS

PAMELA S. MILLAR

The rare gas alkali ionic molecules are established as a new class of ionic excimers which emit in the vacuum ultraviolet (VUV) regime of the electromagnetic spectrum. Temporal and spectral characteristics of these species with (XeRb)+ at 164 nm and (XeCs)+ at 160 nm have been investigated by soft x-ray excitation in a laser-produced plasma and by high energy pulsed electron beam pumping in this work. Soft x-ray pumping of XeF(B→X) and (XeRb)+ yielded the first observation of excimer molecules formed by reactive kinetics in a laser-produced plasma.

The spectrum of (XeRb)+ was observed. The spectral structure could be assigned to 3 dipole allowed transitions originating from the 0+(II), 1(II), 1(I) upper states ending in the 0+(I) ground state. A kinetic study of electron beam pumped mixtures of Ar/Xe/Rb and Ar/Xe/Cs was performed. The observed temporal decays of (XeRb)+ and (XeCs)+ were analyzed. The results suggest that electron deactivation is surprisingly not a dominant quenching process for rare gas alkali ions.

The radiative lifetimes are 150 ± 50 ns for (XeCs)+ and 250 ± 50 ns for (XeRb)+. In addition several quenching rate constants were extracted from the experimental results. These rate constants and lifetimes were incorporated into a kinetic model for these species. This kinetic model reproduced the experimental observations well providing the electron quenching rate coefficient is kept to a maximum of 5 x 10⁻⁹ cm³s⁻¹. Estimates for the upper state densities were computed using this model to be ~4 x 10¹⁵ cm⁻³ for (XeCs)+ and 2 x 10¹⁵ cm⁻³ for (XeRb)+. Including absorption due to the photoionization of the alkali atoms, the net gain coefficients are computed to be on the order of 10⁻² cm⁻¹. Therefore the rare gas alkali ionic excimers appear to be a promising class of candidates as storage media for VUV lasers.
ACKNOWLEDGEMENTS

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A very special thanks to my windsurfing buddies Mack Rhoden and Lisa and Syd Ulvick for introducing me to a sport that is capable of balancing the intensity of experimental research with the indescribable freedom experienced during a broad reach on a 20 knot wind day. Finally I would like to thank my family for their love and support during this work.
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CHAPTER 1
INTRODUCTION

Lasers emitting in the vacuum ultraviolet regime (VUV) (100 - 200 nm), and extreme ultra violet (XUV) (< 100 nm) have many potential scientific and industrial applications. These include high resolution imaging and holography of wet unstained biological specimens [Solem (1986)], high resolution photolithography of integrated circuits, and high energy spectroscopy of atoms, molecules and condensed matter.

Figure 1-1 illustrates the energies and wavelengths of various lasers in the electromagnetic spectrum. It can be seen that there are few emissions in the VUV, mainly some neutral excimer systems. Recently lasing in neutral and ionic atoms has been demonstrated with output energies below 10 μJ per pulse [Matthews et al. (1985), Yin et al (1987)]. Another way to generate coherent radiation in the VUV is to employ laser sources at longer wavelengths which can then be converted into the VUV by nonlinear optical techniques [Hilbig and Wallenstein (1983)]. This means however, although it leads to tuneable VUV sources, is notoriously inefficient.

The search for suitable laser sources in the VUV region with the promise of high output energies has led to the proposals of ionic excimer systems by Sauerbrey and Langhoff (1985), Basov et al. (1985a,b) and Iwata and Sato (1985). These systems, isoelectronic to neutral excimers, should exhibit similar electronic structures while radiating at shorter wavelengths. The shift to shorter wavelengths due to the ionic character of these molecules can be quite large, for example the XeF molecule emits at 351 nm while the isoelectronic alkali halide Cs²⁺F⁻ was observed at 185 nm. This work however is concerned with the rare gas alkali ionic excimers, (RgA)⁺. These species are a new class of ionic excimers which are promising candidates as storage media for VUV lasers.
Fig. 1.1  Lasers in the electromagnetic spectrum with corresponding energy ($h\nu$), wavelength ($\lambda$), and transition mechanism.
The proposed emissions of this type of ionic excimers range from \(-70\) nm for \((\text{HeCs})^+\) to \(-190\) nm for \((\text{XeLi})^+\). This range covers most of the VUV regime. The goal of this work was to establish the feasibility of generating coherent radiation in these species through kinetic and spectroscopic studies of two selected candidates, namely \((\text{XeRb})^+\) at \(164\) nm and \((\text{XeCs})^+\) at \(160\) nm. The results of these studies should be applicable to most rare gas alkali ionic molecules, \((\text{RgA})^+\).

The first experimental verification of the rare gas alkali ionic excimers is demonstrated in this work, using two different excitation methods. Independent, simultaneous experiments were reported by Fiedler et al. (1989) which lead to a spectral classification of these species. In this work the \((\text{XeRb})^+\) ionic molecule was produced through excitation of a \(\text{Xe} / \text{Rb}\) mixture by the soft x-rays from a laser produced plasma. During the course of this work it was established that the laser plasma excitation method can be successfully employed for the generation of new molecules that are formed through a chemical reaction. Pulsed electron beam excitation provides an excellent tool for studying the kinetics of such a system. Kinetic processes for electron beam produced \((\text{XeRb})^+\) and \((\text{XeCs})^+\) are investigated experimentally and a preliminary kinetic model was developed [Millar et al. (1989)], which is comparable to a recent kinetic analysis for the \((\text{KrK})^+\) ionic molecule [Schumann (1989)]. Another method for producing rare gas alkali excimers is using low current ion beam excitation [Fiedler et al. (1989)]. Potential curve calculations partially stimulated by this work by Balasubramanian et al. (1990) and Iwata et al. (1990) have provided a better understanding of the spectroscopy of the rare gas alkali ions.
CHAPTER 2
IONIC EXCIMERS

The excimer systems, such as the rare gas halides, rare gas dimers and the homonuclear halogens are attractive laser species emitting in the visible and ultraviolet (UV) regions of the electromagnetic spectrum [Brau et al. (1984)]. The combination of a bound upper electronic state and a repulsive or weakly bound lower state in these molecules presents ideal conditions for obtaining a population inversion. It has been proposed by Sauerbrey and Langhoff (1985), Basov et al. (1985a) and Iwata et al. (1985) to extend this excimer concept to the far ultraviolet and vacuum ultraviolet (VUV) with ionic excimers. Most of these ionic molecules are isoelectronic to the neutral excimers and therefore similar electronic states are expected. This chapter will discuss the molecular states of some of these ionic molecules followed by a summary of potential curve calculations for these species of increasing complexity.

2.1 MOLECULAR STATES OF IONIC EXCIMERS

To this date, only four classes of ionic excimers have been established in fluorescence experiments: the alkali halides (A2+X-), doubly charged homonuclear rare gas dimers (Rg2)2+, heteronuclear rare gas ions (RgRG')+ and the rare gas alkali ionic excimers (RgA)+. Other proposed ionic excimer systems, such as the rare gas halide ionic molecule (Rg2+X-), which are isoelectronic to halogen and interhalogen laser transitions have not yet been observed.

The most extensive spectroscopic analysis has been performed of the alkali halide excimer molecules (A2+X-) [Steigerwald et al. (1985), Kubodera et al. (1988), Kubodera et al. (1989), Frey et al. (1989), and Kubodera et al. (1990)] which are isoelectronic to the neutral rare gas halide molecules. Emission spectra from Cs2+F- (185 nm, 154 nm) [Steigerwald et al. (1985), Steigerwald et al. (1988), Kubodera et al. (1988), Rb2+F- (130 nm) [Steigerwald et al. (1988), Kubodera et al. (1990)], and Cs2+Cl- (208 nm) [Kubodera et al. (1990)] were observed in excitation by charge transfer from rare gas ions and by direct photoionization using
the soft x-rays from a laser-produced plasma. A doubly ionized alkali ion A\(^{2+}\) has in its
ground state the same electron configuration \((np^5\;^2P)\) as a rare gas ion \((Rg^+)\). It can form
ionically bound compounds with the negatively charged halogen ion \(X^-\) abbreviated by \(A^{2+}X^-\).
In analogy to the rare gas halides, these states may then decay under the emission of photons to
a weakly bound potential curve correlating to the singly charged alkali ion \(A^+\) and the neutral
halogen atom \(X\). The observed alkali halide ionic molecular radiative emissions are due to the
\(A^{2+}X^- (\Sigma, B) \rightarrow A^+X (\Sigma, \Sigma) + h\nu\) transitions between an inner shell ionization state and an
ionic ground state [Sauerbrey and Langhoff (1985)]. It has been determined however, that due
to self absorption it may be very difficult to obtain a positive net gain in these species
[Kubodera et al. (1990)].

The doubly charged homonuclear rare gas dimers have also been observed in
fluorescence experiments [Langhoff (1988)]. These emissions, referred to as the third
continuum emitted after excitation of rare gases by charged particles, are \(Xe_2^{2+}(300\;\text{nm})\), \(Kr_2^{2+}
(200-270\;\text{nm})\), \(Ar_2^{2+} (190-220\;\text{nm})\) and \(Ne_2^{2+} (79\;\text{nm})\). The upper state should correspond to
\((Rg^{2+}Rg)^{2+}\), the \(Rg^{2+}\) has a \(3P\) configuration in the ground state which leads to a \(3\Pi\) or \(3\Sigma\)
state for the \(Rg_2^{2+}\) molecule. In the isoelectronic neutral diatomic halogen molecule \(X_2\), the
analogous \(3\Pi\_g\) state with the same asymptotic configuration \(X^+(3P) + X^-(1S)\), is strongly
bound and decays radiatively to the weakly bound lowest \(3\Pi\_u\) state of \(X_2\) having the
asymptotic configuration \(X(2P) + X(2P)\) which is identical with the corresponding
configuration in \(Rg^+(2P) + Rg^+(2P)\). The states of these molecules are isoelectronic to the
lowest triplet states in the corresponding halogen molecules. These ionic molecules represent
the second class of observed ionic excimers which by pumping with high intensity ion beams
might lead UV lasers which are tunable due to their broad band emission spectrum. The
analogous class of ionic excimers in the alkali metals such as \((Li_2)^{2+} \rightarrow Li^+ + Li^+\) was
proposed by Basov et al. (1985) but has not yet been observed.

The heternuclear diatomic rare gas positive ions \((RgRg)^+\) have been observed in
charged particle beam and discharge excited rare gas mixtures. Tanaka et al. (1975) classified
the spectra of the ten binary mixtures of He, Ne, Ar, Kr and Xe in an electric discharge. The band groups of He/Xe appeared at the shortest wavelengths in the region 100-110 nm; the single band group of Ar/Kr appeared in the region 605-644 nm, at the longest wavelength studied by Tanaka et al. (1975). Due to dominant electron quenching processes that takes place with increasing gas pressures, these ionic species are limited to low gas pressures. The intensities of the emissions observed by Tanaka and co-workers were the strongest at a total pressure of about 10 Torr. Compared with the high pressures required for neutral excimer systems (~3-6 atm), these pressures are considered too small for creating sufficient upper state densities for these ionic excimers.

The rare gas alkali ionic molecules, (RgA)+, represents the fourth class of ionic excimer observed [Millar et al. (1988), Fiedler et al. (1989), Millar et al. (1989) and Schumann and Langhoff (1989)]. They have similar electronic configurations to the homonuclear and heteronuclear rare gas dimers. These ionic species are the main emphasis of this work. The experiments described in chapters 3 and 4 of this work are concerned with two rare gas alkali species, (XeRb)+ emitting at 164 nm and (XeCs)+ emitting at 160 nm. (XeRb)+ emission was observed in both low pressure laser-produced plasma excitation, and in high pressure high energy, pulsed electron beam excitation and the (XeCs)+ emission was observed in electron beam excitation. Fiedler and co-workers have observed fourteen of these species, listed in Table 2.1, by low pressure, low current ion-beam excitation. Schumann and Langhoff (1989) recently observed emissions from (KrK/Cs)+ and (Xe/K/Cs)+ by electron beam excitation with He as a buffer gas.

The spectra observed in this work are in agreement with those of Fiedler et al. (1989). (XeRb)+ and (XeCs)+ were chosen as the best candidates for a kinetic laser feasibility analysis due to their high fluorescence yield. The availability of suitable optics, the relatively high intensities of (XeRb)+ and (XeCs)+ emissions compared with other rare gas/alkali combinations, and the low photoionization cross-sections of Rb and Cs at 164 nm and 160 nm respectively were other selection criteria used for these species.
Table 2.1: Rare gas alkali \((\text{RgA})^+\) ionic excimer emission observed in low current, low pressure, cw ion beam excitation [Fiedler et al. (1989)].

<table>
<thead>
<tr>
<th>((\text{RgA})^+)</th>
<th>(\lambda_{\text{exp}}) (nm)</th>
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<tbody>
<tr>
<td>((\text{ArRb})^+)</td>
<td>114.1</td>
</tr>
<tr>
<td>((\text{ArK})^+)</td>
<td>114.8</td>
</tr>
<tr>
<td>((\text{ArNa})^+)</td>
<td>121.5</td>
</tr>
<tr>
<td>((\text{ArLi})^+)</td>
<td>124.7</td>
</tr>
<tr>
<td>((\text{KrCs})^+)</td>
<td>131.1</td>
</tr>
<tr>
<td>((\text{KrRb})^+)</td>
<td>133.8</td>
</tr>
<tr>
<td>((\text{KrK})^+)</td>
<td>135.5</td>
</tr>
<tr>
<td>((\text{KrNa})^+)</td>
<td>145.3</td>
</tr>
<tr>
<td>((\text{KrLi})^+)</td>
<td>149.5</td>
</tr>
<tr>
<td>((\text{XeCs})^+)</td>
<td>159.9</td>
</tr>
<tr>
<td>((\text{XeRb})^+)</td>
<td>164.1</td>
</tr>
<tr>
<td>((\text{XeK})^+)</td>
<td>167.1</td>
</tr>
<tr>
<td>((\text{XeNa})^+)</td>
<td>182.7</td>
</tr>
<tr>
<td>((\text{XeLi})^+)</td>
<td>189.9</td>
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The upper state of the rare-gas alkali excimers is formed by combining a rare-gas ion \( \text{Rg}^+ \) with an alkali atom \( \text{A} \) in its ground state. The molecule is expected to decay to the lower molecular state correlating to the asymptotic states \( \text{Rg} + \text{A}^+ \). The transition energy is of the order of the difference between the ionization energies of the rare-gas and the alkali-metal. This translates into transition energies in the VUV and XUV, since rare gases have very high ionization energies (12.13 eV for Xe to 24.58 eV for He) while alkali atoms have very small ionization energies (3.89 eV for Cs to 5.39 eV for Li) the transition energies can range approximately from 20 eV to 7 eV. This is equivalent to a wavelength range from 62nm to 178 nm. Therefore these energies are characteristic of the extreme ultraviolet (XUV), VUV regions of the electromagnetic spectrum.

The lower state is weakly bound due to the polarization interaction between the alkali ion \( \text{A}^+ \) and the neutral rare gas atom \( \text{Rg} \). The binding energies are on the order of \(-0.1\) eV and are well known from scattering experiments [Vieland (1984), Radzig and Smirnov (1985), see also Table 2.5]. This state is unambiguously known to be \( ^1\Sigma^+ \) since both the \( \text{Rg} \) and \( \text{A}^+ \) atoms have closed shell \( ^1\text{So} \) configurations. The lowest state of the rare gas dimers also correlates to two closed shell atoms yielding a \( ^1\Sigma^+ \) state. The molecular states arising from the asymptotic atomic states are given in Table 2.2.

The excited state of the rare gas alkali molecular ion, however correlates into two open shell atoms, a rare gas ion \( \text{Rg}^+ \) and a neutral alkali atom. The electron configuration of the \( \text{Rg}^+ \) ion is \( np^5 2p^2 \) and for the alkali atom \( \text{A} \) is \( n's1 2s \). The orbital angular momentum of the separate atoms can add to give values of 1,0 for the projection of total orbital angular momentum of the molecules along the internuclear axis, giving \( \Lambda = 1,0 \). The spins can add to give values of 0 or 1 for the total spin of the molecule corresponding to singlet and triplet multiplicities. If spin-orbit coupling is weak, then \( \Lambda \) is defined and Hund's case (a) is applied [Herzberg 1950]. The possible molecular orbitals of the upper state are then \( ^1\Sigma, ^3\Sigma, ^1\Pi \) or \( ^3\Pi \). However, for heavy rare gases and alkali metals the spin-orbit interaction is dominant and \( \Lambda \) and \( \Sigma \) (not to be confused with the state \( \Sigma \) corresponding to \( \Lambda = 0, \Sigma = S, S-1, S-2, \ldots S \))
### Dissociation relationship for the electronic states of \((\text{XeRb})^+\)

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<th>Energy (cm⁻¹)</th>
<th>Expt.</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1\Sigma^+_0^+)</td>
<td>Xe⁺ + Rb⁺</td>
<td>5p⁶ + 4p⁶</td>
<td>(1S_0 + 1S_0)</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>(3\Pi_2, 1(2), 0^-, 0^+)</td>
<td>Xe⁺⁺ + Rb⁺</td>
<td>5p⁵ + 4p⁵5s¹</td>
<td>(2P_{3/2} + 2S_{1/2})</td>
<td>64 128</td>
<td>64 745</td>
<td></td>
</tr>
<tr>
<td>(3\Pi_2, 1, 0^-)</td>
<td>Xe⁺⁺ + Rb⁺</td>
<td>5p⁵5s + 4p⁶</td>
<td>(3P_2 + 1S_0)</td>
<td>67 058</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>(1, 0^+)</td>
<td>Xe⁺⁺ + Rb⁺</td>
<td>5p⁵5s + 4p⁶</td>
<td>(3P_1 + 1S_0)</td>
<td>68 045</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>(1, 0^-, 0^+)</td>
<td>Xe⁺⁺ + Rb⁺</td>
<td>5p⁵ + 4p⁵5s¹</td>
<td>(2P_{1/2} + 2S_{1/2})</td>
<td>74 665</td>
<td>75 060</td>
<td></td>
</tr>
<tr>
<td>(0^-)</td>
<td>Xe⁺⁺ + Rb⁺</td>
<td>5p⁵5s + 4p⁶</td>
<td>(3P_0 + 1S_0)</td>
<td>76 197</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>Xe⁺⁺ + Rb⁺</td>
<td>5p⁵5s + 4p⁶</td>
<td>(1P_1 + 1S_0)</td>
<td>77 185</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2 Molecular ionic states of \((\text{XeRb})^+\) arising from low-lying atomic and ionic states of the separated species.
are no longer defined, and Hunds case (c) becomes an appropriate description. For this case
only \( \Omega \) retains meaning \( (\Omega = |\Lambda + \Sigma|) \) in describing the upper state. Since the \( \Sigma \) values can
be 0 or 1, and \( \Lambda \) can also be 0 or 1, then \( \Omega \) can be 2,1 or 0. Also the 0 state can have even or
odd symmetry, with respect to a reflection through any plane passing through both nuclei,
corresponding to a + or - superscript to the right of the \( \Omega \) term value. Table 2.2 shows a list of
possible low-lying molecular ionic states of \((\text{XeRb})^+\) and their energy separations at the
dissociation limits. The experimental energy separations in this table were derived from
Moore's atomic tables [Moore (1971)], while the theoretical energy separations were obtained
from calculations provided by Balasubramanian et al. (1990). The upper electronic states of
the rare-gas alkali ionic molecules are not known, whereas the ground state correlating to \( \text{Xe} + \text{Rb}^+ \) is unambiguously the \( 1\Sigma^+ (0^+) \) state (see table 2.2; also Basov et al. (1985)).

Compared to the well established lower state of the \((\text{RgA})^+\) ionic molecule, the
dissociation energies, \( D_e \), and equilibrium internuclear distances, \( r_e \), are unknown for these
species. One can however estimate a range for these spectroscopic parameters by comparison
to similar molecules. The dissociation energy of \( \text{Rg}^+\text{A} \) should be clearly smaller than the
binding energy of the ionic bond of the isoelectronic alkali halide molecule, \( \text{AX} \) (where \( X \) is the
halogen isoelectronic to \( \text{Rg}^+ \)). Also the binding energy of the \( \text{Rg}^+\text{A} \) potential curve should be
greater than that of the \( \text{Rg}^+\text{Rg'} \) potential, (where \( \text{Rg'} \) is the rare gas atom neighboring the \( \text{A} \) atom) since the polarizability of the alkali is higher than that of the corresponding rare gas, \( \text{Rg'} \).
The equilibrium internuclear distance and the dissociation energy should be similar to that of
the diatomic alkali ion, \((\text{AA'})^+\) (where \( \text{A'} \) is the alkali next to the \( \text{Rg} \) atom in the periodical
system). As an example consider the rare gas alkali ionic molecule \( \text{Xe}^+\text{Rb} \), comparisons of the
dissociation energies and internuclear distances are shown in Table 2.3 below.

The experimental value of the binding energy was determined by Fieldler et al. (1989),
by subtracting the ionization energy of rubidium and the experimental empiricle
<table>
<thead>
<tr>
<th>Molecular Species</th>
<th>$D_e$ (eV)</th>
<th>$R_e$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_g^+A$</td>
<td>0.55$^{(a)}$</td>
<td>4.8$^{(d)}$</td>
</tr>
<tr>
<td></td>
<td>0.30$^{(e)}$</td>
<td>5.48$^{(e)}$</td>
</tr>
<tr>
<td></td>
<td>0.98$^{(f)}$</td>
<td>3.76$^{(f)}$</td>
</tr>
<tr>
<td>$R_g^+R_g$</td>
<td>0.37$^{(b)}$</td>
<td></td>
</tr>
<tr>
<td>$AX$</td>
<td>3.3$^{(b)}$</td>
<td>3.18$^{(b)}$</td>
</tr>
<tr>
<td>$(AA')^+$</td>
<td>0.60$^{(b)}$</td>
<td>4.6$^{(b)}$</td>
</tr>
<tr>
<td>$R_gA^+$</td>
<td>0.13$^{(b, c)}$</td>
<td>3.9$^{(b, c)}$</td>
</tr>
</tbody>
</table>

(a) Fiedler et al. (1989).
(b) Radzig and Smirnov (1985).
(c) Viehland (1984)
(d) Mantel and Langhoff (1990)
(e) Balasubramanian et al. (1990)
(f) Warwar (1989)

Table 2.3 Comparisons of the dissociation energies $D_e$, and equilibrium internuclear distances $R_e$ for $(XeRb)^+$ and similar molecules.
transition energy of 7.575 eV (164.1 nm, see Table 2.1) from the ionization energy of the xenon atom (12.13 eV) and then adding the binding energy of the lower state. This value for the binding energy of Xe+Rb is indeed between the values for the binding energies for Xe+Kr and RbI as and on the order of the binding energy for (CsRb)+. In order to better understand the upperstate molecular orbital configurations for these molecules potential curve calculations are necessary. The following section (2.2) discusses several calculations which vary in accuracy and complexity.

The binding of the upper state is mainly due to the single ns electron of the alkali atom which is expected to be localized between the Rg+ and the A+ ion. The high polarizability of the alkali atom in the presence of a rare gas ion insures a bound upper state. However, in the case of light rare gases and heavy alkalies the asymptotic states of the Rg*(ns) + A+ is energetically below the asymptotic states of Rg+ + A. This may lead to instabilities of these (RgA)+ ionic excimers due to predissociation. Table 2.4 lists the energies of the lowest lying A++, Rg* states along with the ionization energies of the rare gas and the alkalies. It can be seen that in the case of HeCs/Rb/K, NeCs/Rb/K, ArCs/Rb and KrCs rare gas alkali combinations, the Rg + A++ and/or the Rg* + A+ asymptotic values are lower than the ionization energy of the rare gas. These molecules may be unstable. So far however the (KrCs)+, (ArRb)+ and (ArCs)+ ionic excimers have been observed in low pressure ion beam excitation [Fiedler et al. (1989)], also (KrCs)+ has been observed in electron beam excitation by Schumann and Langhoff (1989). According to estimates by, Basov et al. (1985a) and Mantel and Langhoff (1990), the shortest wavelength achievable from these species is ~70 nm in (HeNa)+. This species has not been observed as of yet however, due to the experimental difficulties inherent with performing windowless experiments with high pressure corrosive gases. The longest wavelength is experimentally known to be 189.9 nm from (XeLi)+ emission [Fiedler et al. (1989)], this is considerably shorter then the 250 nm emission originally estimated by Basov et al. (1985a).
<table>
<thead>
<tr>
<th>Rg* + A⁺ (eV)</th>
<th>Cs</th>
<th>Rb</th>
<th>K</th>
<th>Na</th>
<th>Li</th>
<th>¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>A⁺⁺ (eV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Xe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>12.23</td>
<td>12.51</td>
<td>12.68</td>
<td>13.47</td>
<td>13.73</td>
<td>12.13</td>
</tr>
<tr>
<td></td>
<td>a,c,d</td>
<td>a,d,e</td>
<td>a,b,c</td>
<td>a,c</td>
<td>a,c</td>
<td>a,c</td>
</tr>
<tr>
<td></td>
<td>a,b,c</td>
<td>a,b,c</td>
<td>a,b,c</td>
<td>a,b,c</td>
<td>a,b,c</td>
<td>a,b,c</td>
</tr>
<tr>
<td>Ar</td>
<td>15.47</td>
<td>15.75</td>
<td>15.92</td>
<td>16.71</td>
<td>16.97</td>
<td>15.76</td>
</tr>
<tr>
<td></td>
<td>a,c</td>
<td>a,c</td>
<td>a,c</td>
<td>a,c</td>
<td>a,c</td>
<td>a,c</td>
</tr>
<tr>
<td>Ne</td>
<td>20.55</td>
<td>20.83</td>
<td>21.00</td>
<td>21.79</td>
<td>22.05</td>
<td>21.56</td>
</tr>
<tr>
<td></td>
<td>a,c</td>
<td>a,c</td>
<td>a,c</td>
<td>a,c</td>
<td>a,c</td>
<td>a,c</td>
</tr>
<tr>
<td>He</td>
<td>23.76</td>
<td>24.04</td>
<td>24.21</td>
<td>25.00</td>
<td>25.26</td>
<td>24.58</td>
</tr>
<tr>
<td></td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>a</td>
</tr>
</tbody>
</table>

* All values were taken from Moores Atomic Tables [Moore (1974)].

a. The energy of A⁺⁺ and/or Rg⁺⁺ + A⁺ is less then the Energy of Rg⁺⁺ (These combinations of A and Rg should be unstable due to predissociation).

b. These combinations of A and Rg were observed in low current ion beam excitation [Fiedler et al. (1989)].

c. These combinations of A and Rg were observed in e-beam excitation [Schumann and Langhoff (1989)].

d. These combinations of A and Rg were observed in e-beam excitation [Millar et al. (1989)].

e. This combination of A and Rg was observed in soft x-ray excitation [Millar et al. (1988)].

Table 2.4: Stability analysis table for rare gas alkali ionic excimers
2.2 POTENTIAL CURVE CALCULATIONS

Recently several potential curve calculations have been performed for the rare gas alkali ionic molecules [Iwata et al. (1985), Steigerwald (1988), Warwar (1989), Mantel and Langhoff (1990), Balasubramanian et al. (1990) and Iwata et al. (1990)] in an attempt to establish the binding energies and equilibrium internuclear distances of the upper states in these species. Steigerwald utilized the Rittner potential in a semiclassical approach [Rittner (1951)]. Warwar performed a quantum mechanical perturbation calculation similar to the H$_2^+$ calculation for the upper state and incorporated a Rittner calculation for the lower state to predict the transition energies. Mantel and Langhoff utilized a pseudopotential method which gave a 2% accuracy for the transition energies. Balasubramanian performed the most advanced calculation available which both considers and omits spin-orbit coupling for the application of Hunds' coupling cases (c) and (a) respectively [Herzberg (1950)]. Each technique will be discussed and then the results will be compared for the (XeRb)$^+$ ionic molecule.\(^1\)

A semiclassical approach originating from Rittner (1951) is one of the simplest models to describe the binding of an ionic diatomic molecule. This calculation neglects spin-orbit coupling. In this model atoms and ions are treated as polarizable spheres. This treatment has been used successfully to describe the alkali halide ground states [Clementi and Roetti (1974)] and was recently successfully applied to the alkali halide ionic excimers and the rare gas halide ions [Sauerbrey and Langhoff (1985), Steigerwald (1988), Kubodera et al. (1990)].

For a system consisting of a neutral atom and a positively charged ion, the energy is given by:

$$E(r) = A \exp(-br) - \frac{1}{2} e^2/4\pi\varepsilon_0(1/r)^4\alpha_{eff} + I$$ \hspace{1cm} (2.1)
The first term is a repulsive Born-Mayer interaction term which gives the repulsion of two atoms at small internuclear distances. The parameters A and b given by Abrahamson (1969) can be used. The constants A and b can either be calculated from a statistical model of the atom, or fitted to experimental scattering data [Rajan and Gislason (1983)]. The second term gives the energy of the induced dipole moment of the neutral atom, produced from the coulomb field of the ion. \( \alpha_{\text{eff}} \) is the effective polarizability of the neutral atom. The last term "I" is the ionization energy of the ion. For internuclear distances smaller than the radius of the effective radii, \( r_0 \) of the two atoms the polarizability decreases. Different correction factors have been proposed to take this effect into account, Patil (1987) suggests an effective polarizability that can be represented by:

\[
\alpha_{\text{eff}}(r) = \alpha_0 \left( \frac{r}{r_0} \right)^3 \quad r < r_0
\]

\[
= \alpha_0 \quad r > r_0
\]

(2.3)

where \( \alpha_0 \) is the static polarizability of the alkali atom [Radzig and Smirnov (1985)] and \( \Psi(r') \) is its wavefunction. A simpler formula was adopted by Warwar (1989):

\[
\alpha_{\text{eff}}(r) = \alpha_0 \left( \frac{r}{r_0} \right)^3 \quad r < r_0
\]

\[
= \alpha_0 \quad r > r_0
\]

(2.2)

where \( \alpha_0 \) is the static polarizability of the alkali atom [Radzig and Smirnov (1985)] and \( \Psi(r') \) is its wavefunction. A simpler formula was adopted by Warwar (1989):

\[
\alpha_{\text{eff}}(r) = \alpha_0 \left( \frac{r}{r_0} \right)^3 \quad r < r_0
\]

\[
= \alpha_0 \quad r > r_0
\]

(2.3)

Potentials of this type have been calculated for the rare gas alkali ionic molecules [Steigerwald (1988)]. The polarizabilities and expectation values for \( r_0 \) are tabulated in Radzig and Smirnov (1985). Binding energies calculated from this model are in reasonable agreement with experiment. The calculated emission wavelengths for \((\text{XeCs})^+\) and \((\text{XeRb})^+\) deviated by 9% and 5% respectively from the experimentally observed values.

The \( \text{H}_2^+ \) and \( \text{(RgA)}^+ \) diatomic ions are both formed by two open shell atoms sharing an electron. Therefore a calculation, for the \( \text{(RgA)}^+ \) ion, similar to the treatment of \( \text{H}_2^+ \) seemed to be appropriate [Warwar (1989)]. This treatment seeks to take advantage of the fact
that the wave functions for all atoms have been calculated and tabulated [Clementi and Roetti (1974)] using the Hartree-Fock method. These wave functions were used as a starting point for a perturbation calculation.

Since the upper state of the (RgA)⁺ molecular ion correlates to two open shell atoms, the rare gas ion having five electrons in a p-shell, while the alkali atom has one electron in an s-shell, the system can be described as a two center one electron system. The use of Slater orbitals leads to analytic solutions. Due to the polarization of the alkali atom by the rare gas ion, the wave function of the polarized alkali atom is no longer spherically symmetric. This wave function is set to \( \Psi(r) = (1 + \gamma z)\Psi_0(r) \), where \( \gamma \) is the variational parameter. This takes into account that the wave function for the molecule is perturbed along the z-axis which is used as the molecular symmetry axis. This is analogous to the variational treatment of the polarizability of a hydrogen atom [Park (1974)]. The electronic part of the energy of the system is given in terms of \( \gamma \), and the requirement that \( \delta E/\delta \gamma = 0 \) leads to a solution for the electronic energy which is a function of internuclear distance.

A test of this method is presented in Table 2.5 below. The binding energy and equilibrium internuclear distance were calculated for the diatomic alkali molecular ions [Warwar (1989)]. The calculated values are compared to the experimental values [Radzig and Smirnov (1985)], and values calculated by the Rittner method. The quantum mechanical treatment for the energy states of the rare gas alkali ionic excimer molecules seems to support the previously calculated energy states using the Rittner potential method.

For the lower potential curve one can use a Rittner type potential of the form described above, and the variational method for the upper potential. Figures 2-1 and 2-2 show the calculated potential curves for (XeCs)⁺ and (XeRb)⁺ using this method. Table 2.6 gives the calculated binding energies \( D_u \) and \( D_l \) of the upper and lower levels respectively, as well as the equilibrium internuclear distances \( R_u \) and \( R_l \), and compares them with other work and experimental values. Both methods indicate a systematic shift to shorter emission wavelengths.
<table>
<thead>
<tr>
<th>Species</th>
<th>$D_{\text{Quan.}}$ (eV)</th>
<th>$D_{\text{Ritt.}}$ (eV)</th>
<th>$D_{\text{Exp.}}$ (eV)</th>
<th>$R_{\text{Quan.}}$ (Å)</th>
<th>$R_{\text{Exp.}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2^+$</td>
<td>0.94</td>
<td>3.17</td>
<td>0.65</td>
<td>4.07</td>
<td>4.78</td>
</tr>
<tr>
<td>$Cs_2^+$</td>
<td>0.99</td>
<td>3.81</td>
<td>0.74</td>
<td>3.70</td>
<td>4.52</td>
</tr>
<tr>
<td>$Rb_2^+$</td>
<td>1.03</td>
<td>4.98</td>
<td>0.80</td>
<td>3.44</td>
<td>4.14</td>
</tr>
<tr>
<td>$K_2^+$</td>
<td>1.03</td>
<td>6.31</td>
<td>1.00</td>
<td>2.91</td>
<td>3.43</td>
</tr>
</tbody>
</table>

Table 2.5  Quantum calculation for binding energies $D$, and equilibrium internuclear distances $R$ for several diatomic alkali ionic molecules is compared with a simpler Rittner calculation and experiment [Rajan and Gislason (1983)].
Fig. 2.1 Potential energy curves calculated for (XeCs)$^+$. Rittner potential was used to calculate the lower curve while a variational calculation describes the upper state.
Potential energy curves calculated for (XeRb)$^+$. Rittner potential was used to calculate the lower curve while a variational calculation describes the upper state.
Quantum calculation for binding energies $D_{\text{upper}}$ and $D_{\text{lower}}$, and equilibrium internuclear distances $R_{\text{upper}}$ and $R_{\text{lower}}$ of the upper and lower energy states for several rare gas alkali ionic excimers are compared with a simpler Rittner calculation and experiment.

<table>
<thead>
<tr>
<th>Species</th>
<th>$D_{\text{lower}}$</th>
<th>$D_{\text{upper}}$</th>
<th>$R_{\text{lower}}$</th>
<th>$R_{\text{upper}}$</th>
<th>$\lambda_{\text{upper}}$</th>
<th>$\lambda_{\text{lower}}$</th>
<th>$\lambda_{\text{Rittner}}$</th>
<th>$\lambda_{\text{experiment}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NeNa)$^+$</td>
<td>0.01</td>
<td>1.03</td>
<td>3.49</td>
<td>2.91</td>
<td>81</td>
<td></td>
<td></td>
<td>2.4</td>
</tr>
<tr>
<td>(NeK)$^+$</td>
<td>0.01</td>
<td>1.05</td>
<td>3.76</td>
<td>3.39</td>
<td>77</td>
<td></td>
<td></td>
<td>2.8</td>
</tr>
<tr>
<td>(NeRb)$^+$</td>
<td>0.01</td>
<td>1.03</td>
<td>4.02</td>
<td>3.60</td>
<td>76</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NeCs)$^+$</td>
<td>0.01</td>
<td>0.97</td>
<td>4.18</td>
<td>3.91</td>
<td>74</td>
<td></td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>(ArNa)$^+$</td>
<td>0.08</td>
<td>0.99</td>
<td>3.12</td>
<td>2.96</td>
<td>128</td>
<td>0.08</td>
<td>1.62</td>
<td>141</td>
</tr>
<tr>
<td>(ArK)$^+$</td>
<td>0.06</td>
<td>1.03</td>
<td>3.44</td>
<td>3.44</td>
<td>119</td>
<td>0.10</td>
<td>1.78</td>
<td>131</td>
</tr>
<tr>
<td>(ArRb)$^+$</td>
<td>0.04</td>
<td>1.02</td>
<td>3.70</td>
<td>3.65</td>
<td>117</td>
<td>0.05</td>
<td>0.89</td>
<td>116</td>
</tr>
<tr>
<td>(ArCs)$^+$</td>
<td>0.04</td>
<td>0.96</td>
<td>3.86</td>
<td>3.97</td>
<td>113</td>
<td>0.06</td>
<td>1.30</td>
<td>118</td>
</tr>
<tr>
<td>(KrNa)$^+$</td>
<td>0.11</td>
<td>0.93</td>
<td>3.23</td>
<td>3.07</td>
<td>154</td>
<td>0.11</td>
<td>1.50</td>
<td>170</td>
</tr>
<tr>
<td>(KrK)$^+$</td>
<td>0.08</td>
<td>1.01</td>
<td>3.54</td>
<td>3.49</td>
<td>142</td>
<td>0.12</td>
<td>1.62</td>
<td>154</td>
</tr>
<tr>
<td>(KrRb)$^+$</td>
<td>0.06</td>
<td>0.99</td>
<td>3.81</td>
<td>3.70</td>
<td>140</td>
<td>0.06</td>
<td>0.87</td>
<td>138</td>
</tr>
<tr>
<td>(KrCs)$^+$</td>
<td>0.05</td>
<td>0.95</td>
<td>3.97</td>
<td>4.02</td>
<td>135</td>
<td>0.04</td>
<td>1.23</td>
<td>142</td>
</tr>
<tr>
<td>(XeNa)$^+$</td>
<td>0.19</td>
<td>0.90</td>
<td>3.17</td>
<td>3.17</td>
<td>197</td>
<td>0.40</td>
<td>1.39</td>
<td>208</td>
</tr>
<tr>
<td>(XeK)$^+$</td>
<td>0.13</td>
<td>1.00</td>
<td>3.49</td>
<td>3.54</td>
<td>179</td>
<td>0.18</td>
<td>1.50</td>
<td>196</td>
</tr>
<tr>
<td>(XeRb)$^+$</td>
<td>0.10</td>
<td>0.98</td>
<td>3.76</td>
<td>3.76</td>
<td>175</td>
<td>0.11</td>
<td>0.88</td>
<td>173</td>
</tr>
<tr>
<td>(XeCs)$^+$</td>
<td>0.09</td>
<td>0.94</td>
<td>3.91</td>
<td>4.07</td>
<td>168</td>
<td>0.09</td>
<td>1.20</td>
<td>175</td>
</tr>
</tbody>
</table>
for the rare gas alkali excimer \((\text{RgA})^+\) as \(A\) ranges from Na to Cs. Also both methods agree that the binding energy of the molecule is largest with Potassium.

A recent analysis of the \((\text{RgA})^+\) states and potential curves was provided by Balasubramanian et al. (1990). Balasubramanian performed the most advanced calculation available which both considers and omits spin-orbit coupling. The experimental results in this work (see Chapter 4) and in low current ion beam excitation [Fieldler et al. (1989)] reveal three closely spaced peaks. These calculations were motivated by the experimental results described in this work. Their purpose is an accurate determination of the states involved in the observed emissions of the \((\text{RgA})^+\) species. These results were performed for the \((\text{XeRb})^+\) ionic excimer only, as at the start of this work, this was the only spectrum available with a high enough resolution (0.8 nm) to distinguish three peaks.

The theoretical method of calculations performed by Balasubramanian will now be discussed. A complete active space multi-configuration self-consistent field (CASSCF) followed by first-order configuration interaction (FOCI) and relativistic configuration interaction (RCI) calculation procedures were employed. The first two methods take into account electron correlation effects, while the RCI method includes both electron correlations and spin-orbit effects. All calculations were carried out employing relativistic effective core potentials (RECPs) including spin-orbit effects. For Xe the outer 5s\(^2\)5p\(^6\) valence shells were included explicitly in the calculations replacing the rest of the core electrons by RECPs. For Rb the outer 4s\(^2\)4p\(^6\)5s\(^1\) shells were explicitly retained in the calculations. The rest of the core electrons were replaced by RECPs. For Xe and Rb the RECPs generated by La John et al. (1987) were used. These RECPs were generated from relativistic all-electron Dirac-Fock calculations of these atoms. Calculational details are described by Balasubramanian et al. (1990).

Figure 2-3 shows the CASSCF/FOCI potential energy curves for \((\text{XeRb})^+\) obtained in the absence of spin-orbit coupling. These curves are qualitatively useful to comprehend experimental observations as well as to understand the nature of various electronic studies.
Fig. 2.3 CASSCF/FOCI potential energy curves of (XeRb)+ obtained in the absence of spin-orbit coupling. [Balasubramanian et al. (1990)].
including spin-orbit coupling. Furthermore, more electronic states could be obtained using this procedure as opposed to the RCI procedures.

Figure 2-4 shows the CASSCF/FOCI/RCI potential energy curves for the bound states of (XeRb)$^+$ including spin-orbit coupling. There are three electronic manifolds labelled in parenthesis after the term symbol as I, II, III for increasing energy of the electronic levels. As seen from Fig. 2-3, the ground state of (XeRb)$^+$ is of $0^+$ symmetry as expected and is weakly-bound. It corresponds to the $^1\Sigma^+$ curve in the absence of spin-orbit coupling shown in Fig 2-3. There are many bound states correlating into Xe$^+(2P_{3/2})$ + Rb$(2S_{1/2})$ as seen in Fig. 2-4. Higher states such as those correlating to Xe$^+(2P_{1/2})$ + Rb$(2S_{1/2})$ have not yet been calculated in detail, but are expected to lie well above the states shown in Fig. 2-4.

Table 2.7 shows the actual spectroscopic constants of electronic states of (XeRb)$^+$ both in the absence and presence of spin-orbit coupling. Those states are not designated by their $\Omega$ quantum numbers and obtained without spin-orbit coupling. The ground state of (XeRb)$^+$ is of $^1\Sigma^+$ symmetry exhibiting a weak potential minimum. The $D_e$ of the ground state is only 0.08 eV at the CASSCF/FOCI/RCI level, the experimental value is known to be 0.13 eV by scattering experiments [Radzig and Smirnov (1985)].

Table 2.8 compares the spectroscopic parameters determined by each calculation for the upper state of the (XeRb)$^+$ ionic molecule. It appears that the equilibrium internuclear distance for the upper state is much larger than for the lower state. This implies that the radiative transition ends in a vibrationally excited state. Three dipole allowed transitions in (XeRb)$^+$ were found originating from $0^+$(II), 1(II) and 1(I) upper states and ending in the $0^+$(I) ground state. This agrees with the fact that three peaks are observed experimentally under 0.8 nm resolution [Millar et al. (1989), Fieldler et al. (1989)]. The predicted decay energies are higher however than experimentally observed. This is to be expected even though the basis set used for the calculation was sufficiently large and electron correlation effects were treated using CASSCF/FOCI methods. In comparison the Hund's case (a) analysis permits the $^1\Sigma^+$(II) and $^1\Pi$(I,II,III) upper states to radiatively decay to the $^1\Sigma^+$ ground state ($\Delta S = 0, \Delta \Lambda = 0, \pm 1$).
Fig. 2.4  CASSCF/FOCI/RCI potential energy curves of (XeRb)+ including spin-orbit coupling. [Balasubramanian et al. (1990)].
Table 2.7  Spectroscopic properties of low-lying states of (XeRb)$^+$

a) without spin-orbit interaction

<table>
<thead>
<tr>
<th>State</th>
<th>$T_e$ (cm$^{-1}$)</th>
<th>$R_e$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$D_e$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1\Sigma^+$</td>
<td>0</td>
<td>4.02</td>
<td>36.6</td>
<td>0.078</td>
</tr>
<tr>
<td>$^1\Sigma^+$</td>
<td>73480</td>
<td>5.71</td>
<td>35.4</td>
<td>0.63</td>
</tr>
<tr>
<td>$^1\Sigma^+$</td>
<td>74465</td>
<td>5.23</td>
<td>40.6</td>
<td>0.54</td>
</tr>
<tr>
<td>$^3\Pi$</td>
<td>75571</td>
<td>5.30</td>
<td>35.5</td>
<td>0.37</td>
</tr>
<tr>
<td>$^1\Pi$</td>
<td>76172</td>
<td>5.49</td>
<td>37.4</td>
<td>0.26</td>
</tr>
</tbody>
</table>

b) with spin-orbit-interaction

<table>
<thead>
<tr>
<th>State</th>
<th>$T_e$ (cm$^{-1}$)</th>
<th>$R_e$ (Å)</th>
<th>$\omega_e$ (cm$^{-1}$)</th>
<th>$D_e$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0$^+$ (I)</td>
<td>0</td>
<td>4.03</td>
<td>36.7</td>
<td>0.072</td>
</tr>
<tr>
<td>1 (I)</td>
<td>61923</td>
<td>5.48</td>
<td>35.7</td>
<td>0.30</td>
</tr>
<tr>
<td>0$^+$ (II)</td>
<td>62951</td>
<td>5.42</td>
<td>44.0</td>
<td>0.16</td>
</tr>
<tr>
<td>1 (II)</td>
<td>64076</td>
<td>5.50</td>
<td>36.0</td>
<td>0.03</td>
</tr>
<tr>
<td>0$^-$</td>
<td>64935</td>
<td>5.16</td>
<td>48.0</td>
<td>0.05</td>
</tr>
<tr>
<td>0$^+$ (III)</td>
<td>75670</td>
<td>5.32</td>
<td>33.0</td>
<td>0.06</td>
</tr>
</tbody>
</table>

* Balasubramanian et al. (1990)
Table 2.8 Spectroscopic Parameters for (XeRb)⁺

<table>
<thead>
<tr>
<th>Calculation</th>
<th>D (eV)</th>
<th>R (Å)</th>
<th>Calculated (nm)</th>
<th>Experiment (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rittner⁴</td>
<td>0.88</td>
<td>--</td>
<td>173</td>
<td>163.6</td>
</tr>
<tr>
<td>LCAO - QM (variational)⁵</td>
<td>0.98</td>
<td>3.76</td>
<td>175</td>
<td>163.1</td>
</tr>
<tr>
<td>Hellmann⁶</td>
<td>0.55</td>
<td>4.80</td>
<td>166.8</td>
<td>164.1</td>
</tr>
<tr>
<td>0 (II)</td>
<td>0.16</td>
<td>5.42</td>
<td>156</td>
<td>162.6</td>
</tr>
<tr>
<td>With SO Interaction⁷</td>
<td>0.03</td>
<td>5.50</td>
<td>159</td>
<td>163.6</td>
</tr>
<tr>
<td>1(II)</td>
<td>0.30</td>
<td>5.48</td>
<td>161.5</td>
<td>167.6</td>
</tr>
<tr>
<td>1(I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a  Fiedler et al. (1989)
b  Warwar (1989)
c  Mantel and Langhoff (1990)
d  Balasubramanian et al. (1990)
CHAPTER 3
EXCITATION OF NEUTRAL AND IONIC EXCIMERS BY SOFT X-RAYS IN A LASER-PRODUCED PLASMA

3.1 INTRODUCTION

When an intense laser source is focused onto a metal target, a dense plasma is formed [Carroll & Kennedy (1981)]. The spectral characteristics of the plasma depend on the electron temperature, which is in turn dependent on the intensity of the incident laser beam and the target material. For high Z materials the emission spectrum is a continuum with few emission lines Fig. 3-1. It is possible to approximate these spectra as the emission from a blackbody having a temperature of 10-100 eV for laser intensities in the \(10^{10}\) to \(10^{12}\) W/cm\(^2\) range [Carroll et al. (1980)]. For an incident intensity of \(\sim 10^{11}\) W/cm\(^2\) the emission from a tantalum plasma has a characteristic temperature of \(kT = 10-30\) eV [Caro et al. (1984)].

Because of their ability to efficiently convert laser radiation into XUV radiation, laser-produced plasmas are analogous to the flashlamps used to pump other laser sources in the visible and infrared regions. The coherent radiation from the laser can be converted with a reasonably high efficiency (10-20%) [Harris & Young (1987)] into incoherent radiation in the XUV region. A favorable characteristic of XUV radiation is that many photoionization cross-sections for core electrons are high in the 10-50 eV range. Below this range mainly valence states may be ionized. For this reason laser-produced plasmas are particularly attractive for studying core-excited states just below the valence states in atoms as well as in molecules.

Recently laser produced plasmas have been used to excite molecular systems through direct photionization, i.e. Cs\(^{2+}\)F\(^-\) emission at 185 nm [Kubodera et al. (1988), Frey et al. (1989)]. In this work the formation of a new ionic excimer molecule (XeRb)\(^+\) and the well known XeF molecule by reactive kinetics initiated by photoionization from a laser-produced plasma is reported. To the best of our knowledge this is the first reported
Fig. 3.1 Spectral and temporal characteristics of a 10 ns, 1 J Nd:Yag laser-produced plasma on a tantalum target. Spectral scan shows a broad continuum in the XUV. The spectral scan is not corrected for the variation in grating reflectivity which accounts for the decline in signal below 50 nm.
observation of molecular formation from constituent atomic species a result of laser-plasma pumping. In addition an attempt to observe the Xe\(^{2+}\mathrm{F^-}\) ionic excimer using this method is reported.

3.2 EXPERIMENTAL APPARATUS

The apparatus used in this work consists of a reaction cell, the laser source and data acquisition electronics as shown below in Fig. 3-2. The reaction cell design could be used for electron beam as well as for laser produced-plasma excitation.

The cell was constructed from stainless steel and, for rare gas alkali investigations, could be heated to temperatures in excess of 450°C. The ends of the cell were water cooled to prevent condensation of Rb vapor on the windows. Although the cell was constructed to allow for heat pipe operation, it was used as an oven because gas mixtures of Xe and Rb were excited, whereas in a heat pipe the inert buffer gas is used to confine the vapor to the heated volume of the cell. A tantalum target was mounted on a rotating shaft inside the cell and could be adjusted with respect to the optical axis of the perpendicular cell arm. During the (XeRb)+ experiments the target was heated to prevent condensation of Rb on it, and also rotated to provide a new surface for successive laser shots. The output of an oscillator-amplifier injection-controlled KrF excimer laser provided a 750 mJ pulse with a duration of 30 nsec in a 1.5 cm x 3 cm rectangular mode at a repetition rate of 2 Hz. The laser output beam was focused by a UV fused silica lens with a focal length of 225 mm at 248 nm (this was determined by measuring the distance required for the beam to break down in air). The focal spot size was measured to be approximately square with sides 100 \(\mu\)m in length, by Petersen (1989). These dimensions were determined by mounting a razor blade on a translation stage and scanning through the focus. Due to mirror and transmission window losses, the energy deposited into the cell was about 250 mJ, corresponding to an intensity of approximately \(5 \times 10^{10}\) W/cm\(^2\) at the focus.
Fig. 3.2 Experimental setup. A focused KrF excimer laser generates a plasma on a tantalum target inside a heatpipe cell. The soft x-rays emitted from the plasma ionize the surrounding vapor, leading to the formation of excimer or ionic excimer species.
A 10 cm focal-length CaF$_2$ of MgF$_2$ lens was used to collect the fluorescence from the interaction zone and to focus it onto the entrance slit of a 0.2-m VUV spectrometer. The Ta target was located approximately 0.5 cm from the optical axis of the spectrometer. The observable volume within the cell was determined, with an empty cell by varying the position of a small constant light source (an LED) with respect to the optical axis. The cross-sectional rectangular area for maximum observation is 1.5 cm in the x-direction by 1.0 cm in the y direction centered about the optical axis of the cell. The detection set-up is more sensitive in the vertical direction since it has a slit height of 250 mm compared to a width of 0.5 mm. A photomultiplier tube equipped with a sodium salicylate scintillator in conjunction with a high-speed storage scope, provided time-resolved fluorescence data. The measured rise time of this detection system was approximately 10 nsec. Time-averaged spectra were obtained by using a boxcar integrator with a 50-nsec gate to discriminate against recombination radiation from the Ta plasma, which appeared approximately 200ns after the laser pulse [Kubodera et al. (1988)].

Using this apparatus, the ionic excimers Cs$^2+$F$^-$ at 185 nm, Cs$^2+$Cl$^-$ at 208 nm, and Rb$^2+$F$^-$ at 130 nm by direct photoionization of CsF, CsCl and RbF vapors were previously produced [Kubodera et al. (1988), Sauerbrey et al. (1988), Frey et al. (1989), Kubodera et al. (1990)]; however, excimer formation requiring reactive kinetics in a laser plasma had not been demonstrated until the XeF and (XeRb)$^+$ experiments reported in this work [Millaret al. (1989a)].

3.3 EXPERIMENTAL RESULTS

3.3.1 XeF (B-X) Emission Excited by a Laser-Produced Plasma

The XeF(B-X) transition is a well known excimer emission in terms of emitted wavelength, lifetime and formation and quenching rate constants [Rhodes et al. (1984)].
Therefore this species was chosen as an initial candidate for forming molecules from constituent atomic species as a result of laser plasma pumping. This experiment is simple in the sense that the cell is not heated.

A three-component gas mixture of F₂, Xe, and He was used in the cold cell to produce XeF fluorescence at 351 nm in the laser-produced plasma. The emission spectrum of the XeF(B-X) transition in a gas mixture optimized for maximum fluorescence intensity (2 Torr of F₂, 10 Torr of Xe, and 38 Torr of He) is shown in Fig. 3-3. The spectrum has a 14 nm width (FWHM) and is asymmetric with respect to the peak, falling off sharply with increasing wavelength. This asymmetry is due to vibrational excitation of the upper state, which has been observed at low pressures [Brashears and Setser (1982)]. At higher pressures (>2 atm) the vibrational manifold is relaxed and the asymmetry decreases [Rhodes et al. (1984)]. Another contributing factor to the asymmetry in the XeF spectrum could be the decrease in average signal many rod rotations for a single gas fill; the spectrum in Fig. 3-3 was obtained from a single gas fill with 17 rod rotations while the spectrometer scanned from 334-nm to 360-nm.

The XeF pressure dependence of the observed 351 nm fluorescence on F₂ (5% in He) and Xe are shown in Figures 3-4 and 3-5 respectively. While maintaining a constant pressure of 10 Torr Xe, the emission peaks at about 40 Torr total of the F₂/He. Using this peak pressure of 40 Torr F₂/He, Xe was varied as shown in Fig. 3-5. The peak emission in this case takes place in Xe pressure between 10 and 20 Torr. After the peak, both plots display rapid decay with increasing pressure. This is due to collisional de-excitation of the XeF excimer, however the decrease in x-ray penetration depth with increasing pressure probably also plays an important role.

This x-ray range can be estimated from the total photoionization cross-sections and concentrations of Xe and He. The total cross-section for photoionization σₚᵢ of Xe for photon energies of ~20 eV is 10⁻¹⁷ cm² [Yeh and Landau (1985)], therefore the range of soft x-rays in 10 Torr Xe is 3 mm decreasing to 1.5 mm in 20 Torr. In a 38 Torr F₂/He (95% He) mixture
Fig 3.3  XeF(B-X) spectrum obtained from laser-produced plasma excitation in 38 Torr He, 10 Torr Xe and 2 Torr F₂. The target rod was 5.5 mm from the optical axis.
Fig 3.4  Averaged intensity of XeF(B-X) emission at 351 nm as a function of 5%F₂/He gas-mixture pressure.
Fig. 3.5  Averaged intensity of XeF(B-X) emission at 351 nm as a function of Xenon pressure for 40 Torr gas-mixture 5%F₂/He.
without Xe the range of the soft x-rays is ~8 mm (σ_pl for He is ~7 \times 10^{-18} \text{ cm}^2). Further increasing pressure reduces the x-ray penetration depth to ~≤1 mm from the target. It has been shown in previous work [Frey et al. (1989)] that the electron density ~ 1 mm from the target approaches 10^{16} \text{ cm}^3. For an electron quenching rate constant of 10^{-7} \text{ cm}^3s^{-1} the corresponding deactivation time of XeF is 1 ns compared to the radiative lifetime of 15 ns, so increasing the Xe or He pressure will result in x-ray ranges that confine the emission region to regions of high electron density which results in quenching the XeF.

For the optimal mixture of 2 Torr of F_2, 10 Torr of Xe, and 38 Torr of He, Fig. 3-6 illustrates the temporal behavior of the fluorescence of XeF. There are several formation channels which may lead to population of the XeF upper state. These reactions are represented by the following rate equations:

<table>
<thead>
<tr>
<th>REACTION</th>
<th>RATE CONSTANT</th>
</tr>
</thead>
<tbody>
<tr>
<td>F_2 + e^- \rightarrow F^- + F,</td>
<td>K_1 = 4.0 \times 10^{-9} \text{ cm}^3\text{sec}^{-1} (3.1)</td>
</tr>
<tr>
<td>Xe^+ + Xe + Xe \rightarrow Xe_2^+ + Xe</td>
<td>K_2 = 2.0 \times 10^{-31} \text{ cm}^6\text{sec}^{-1} (3.2)</td>
</tr>
<tr>
<td>Xe^+ + Xe + He \rightarrow Xe_2^+ + He</td>
<td>K_3 = 1.1 \times 10^{-31} \text{ cm}^6\text{sec}^{-1} (3.3)</td>
</tr>
<tr>
<td>Xe_2^+ + F^- \rightarrow XeF + Xe</td>
<td>K_4 = 1.0 \times 10^{-6} \text{ cm}^3\text{sec}^{-1} (3.4)</td>
</tr>
<tr>
<td>Xe^+ + F^- + M \rightarrow XeF + M,</td>
<td>K_5 = 1.5 \times 10^{-25} \text{ cm}^6\text{sec}^{-1} (3.5)</td>
</tr>
</tbody>
</table>

where M is either Xe or He. For high pressure gas mixtures in electron beam and gas discharge pumping the indirect channel through reactions (3.1) - (3.4) are dominant [Rhodes (1984)] in XeF formation. For the present low pressure conditions however, the formation of Xe_2^+ by route of equations (3.2) and (3.3) is built up on a time scale of about 10 μs, which is much slower than the observed temporal behavior. The rise time of the signal shown in Fig. 3-6 is 65 ns. Therefore the direct recombination of the atomic ions in reaction (3.5) should be
Fig. 3.6  Time-resolved fluorescence from XeF at 351 nm. The dots correspond to an experimentally observed fluorescence trace, and the solid curve is calculated from the model discussed in the text.
the dominant formation channel for the XeF excimer in low pressure laser-produced plasma excitation.

For the present conditions, assuming that $K_t = 4 \times 10^{-9}$ cm$^3$/sec for an electron temperature, $T_e = 1$ eV [Chantry (1982)], dissociative attachment represented in reaction (3.1) proceeds on a time scale of a few nanoseconds. Thus electrons are rapidly converted into F$^-$ ions, which are subsequently recombined with Xe$^+$ ions to form XeF (equation (3.5)). The detected XeF(B-X) emission decays with a lifetime $\tau$ that depends on the collisional mixing between the XeF(B) and XeF(C) states; therefore, the decay times should lie between 15 and 100 nsec, the radiative lifetimes of the B and C states, respectively. A simple kinetic model was made using reactions (3.1) and (3.5) assuming the positive xenon ion density Xe$^+$ is equivalent to the negative fluorine ion density F$^-$ and the electron density e$^-$. The solution obtained is in the following form:

$$\text{XeF} (t) = \text{Xe}_0^+ \alpha e^{-t/\tau} \int_0^1 \frac{e^{t'/\tau}}{\left(1 + \alpha t'/\tau\right)^2} \, dt'$$  \hspace{1cm} (3.6)$$

where Xe$^+_0$ is the Xe$^+$ density at the onset of the laser pumping pulse, prior to the formation of F$^-$ ions, it is assumed that at this point in time the Xe$^+_0$ density is equivalent to the electron density. The solid curve in Fig. 3-6 was calculated from this simple model, assuming that $K_5 = 1.5 \times 10^{-25}$ cm$^6$/sec$^{-1}$ [Flannery & Yang (1978)], where $\tau = 31$ nsec and $\alpha = 0.44$. The fast rise time of the solid curve in Fig. 3-6 is due to the assumption of a delta-function-like excitation pulse that produces an initial Xe$^+$ and e$^-$ population of $10^{14}$ cm$^{-3}$. The kinetic model reproduces the non-exponential decay, characteristic of the three body recombination reaction in equation (3.5). Since at the low constituent gas pressures used in this experiment, formation of XeF from diatomic molecular xenon ions is too slow to be compatible with the observed behavior, the rapid formation of excimers through direct ionic channels, as in reaction
(3.5), is promising for the production of a wide variety of excimer molecules in laser-produced plasmas, since relatively low-pressure gases must be used to absorb the soft x-rays in the observable volume.

In addition to optimizing the individual gas components, the dependence of the XeF emission on the target location was investigated in 10 Torr Xe and 40 Torr F2/He. A Helium-Neon (HeNe) laser beam was sent through the V-exit port of the spectrometer set to zero order. The point in which the target intersects the HeNe beam gives the location of the optical axis of the reaction cell. From this location the target was pulled back and the distance was measured. The target position with respect to the optical axis was found to be best at 5±2 mm as shown in Fig. 3-7.

3.3.2 Investigation of Xe2+F- Ionic Excimer Excited by a Laser-Produced Plasma

The ionic rare gas halogen molecules Rg2+X-, have been proposed by Sauerbrey and Langhoff (1985). Since the XeF(B-X) emission was observable in LPP excitation an investigation over the proposed wavelength regions for Xe2+F- was performed. The same gas mixture that was optimized for maximum XeF fluorescence was employed (2 Torr F2, 10 Torr Xe and 38 Torr He). The spectral regions scanned were 120-225 nm and 330-400 nm. The only spectra observed was from tantalum ion lines at 160-186 nm and from XeF, at 340-360 nm. A possible explanation for this result could be the fact that XeF is the precursor to Xe2+F-.

Assuming that every Xe+ ion is converted to XeF the average XeF density can be estimated from the kinetic model to ~1013 cm⁻³, i.e. less than about 10⁻⁴ of the Xe atoms are ionized over the observed volume. If Xe+F has the same photoionization cross-section as Xe this would yield about 10⁻⁹ cm⁻³ Xe2+F- excimers which is below our detection threshold.
Averaged Intensity of XeF(B-X) emission at 351 nm as a function of the target distance from the optical axis of the cell.
3.3.3 (XeRb)+ Emission Excited in a Laser-Produced Plasma

Using this soft x-ray excitation technique, a new ionic excimer molecule (XeRb)+ has been produced and studied. A mixture of Xe and Rb was excited by using the excimer-laser-produced plasma. The Rb vapor pressure was monitored by using the equivalent width of the absorption from a spectrally broad light source on the 4202- and 4216-Å resonance lines [Corney (1977)]. Because the oven cell was not operated in a heat pipe mode, this measurement was only approximate since the uniformity and length of the vapor zone were not independently measured. The cell could be operated with vapor pressures from 1 to 10 Torr of Rb, and the Rb vapor pressure could be measured with an accuracy of ±10% by the absorption technique [Millar (1987)]. As shown in Fig. 3-8 the Rb vapor pressures measured in this manner corresponded well with the measured outside cell temperature and the established vapor pressure curve of Rb up until 10 Torr. Figure 3-8 shows that even with increasing temperatures above 650 K vapor pressures, above 10 Torr could not be achieved. This effect is due to alkali diffusion into the cold zone resulting in a depletion in the heated pumping region of the cell.

In analogy to the XeF formation, the formation and radiative decay of the (XeRb)+ molecule were expected to proceed by the reactions

\[
\begin{align*}
\text{Xe}^+ + \text{Rb} + \text{M} & \rightarrow \text{Xe}^+\text{Rb} + \text{M} \quad (3.7) \\
\text{Xe}^+\text{Rb} & \rightarrow \text{Xe} + \text{Rb}^+ + \text{hv} \quad (3.8)
\end{align*}
\]

where in these experiments M was Xe. As in the case of XeF, formation through diatomic molecular channels is not expected to play a significant role at the pressures used in this investigation. This is supported by the weak emission of Xe₂⁺ at 172 nm that was observed in these experiments.

The emission from a mixture of 76 Torr of Xe and 10 Torr of Rb excited by a laser breakdown or by a laser plasma on a Ta target is shown in Fig. 3-9. When the excimer laser is
Measurement of Rb vapor pressure inside the heated cell as a function of temperature for ~100 Torr of He buffer gas pressure. Resonance line absorption was used to measure the ground state density of Rb, and thermocouples were used to measure the temperature. The Rb vapor pressure curve is taken from [Nesmeyanov (1963)].
Fig. 3.9  
(a). Time-integrated fluorescence from (XeRb)$^+$ produced by a laser breakdown in 10 Torr of Rb and 76 Torr of Xe.  
(b). Time-integrated fluorescence from (XeRb)$^+$ produced by a laser plasma on a Ta target in 10 Torr of Rb and 76 Torr of Xe.
focused to produce a laser breakdown, i.e., with the Ta target removed, a broadband VUV emission is seen along with a weak feature at 166 nm, as illustrated in Fig. 3-9(a). This feature becomes much stronger and centered at 165 nm when a Ta target is placed in the cell and the Xe-Rb mixture is excited by the soft x-rays from the laser plasma on the target. This emission at 165 nm was not present when the cell contained only Xe or only a mixture of Rb and Ar. It was, however, observed in Xe-Rb-Ar mixtures. This implies that the emission is due to a Xe-Rb molecule. Furthermore, the emission wavelength is in good agreement with the approximate value of 170 nm calculated from the data in Basov et al. (1985a) and Radzig & Smirnov (1985) for the ionic molecule (XeRb)+. A neutral molecule such as XeRb* is expected to predissociate.

A broad, intense continuum was observed in the whole VUV region from laser-produced-plasma-excited Xe and Xe-Rb mixtures. It was not present in Ar-Rb mixtures. Similar continua in pure Xe were observed previously at longer wavelengths with laser-produced plasmas and laser breakdown by Silfast & Wood II (1974), and Damany et al. (1985). This continuum is clearly visible as a broad unstructured background in Fig. 3-9. This intense background emission followed the temporal development of the excitation pulse. Therefore the gate on the boxcar integrator had to be delayed 100 nsec after the laser pulse. The plasma recombination light began ~200 nsec after the excimer laser pulse, and therefore, for the (XeRb)+ emission to be seen clearly, the boxcar gate had to be limited to a 50-nsec width. Although in these experiments, owing to the VUV continuum and the plasma recombination light, the (XeRb)+ emission could be viewed only 100 nsec after the laser plasma formation, the emission is quite distinct.

Figure 3-10 shows a strong Rb vapor pressure dependence of the emission at 165 nm. In addition, the wavelength of peak emission appears to narrow in width and to shift from 166 to 165 nm with increasing Rb vapor pressure, while an unknown feature at about 176 nm appears to decrease. For these figures, the resolution of the spectrometer was 2 nm (500-μm
Fig. 3-10  Time-integrated fluorescence from (XeRb)+ for different pressures of Rb at 76 Torr of Xe.
slit width); however, higher-resolution scans (1.2 nm) indicate a FWHM of 3.3 nm for the (XeRb)+ emission. The Rb vapor is expected to have a photoionization cross section of only 0.11 Mb in this region of the spectrum [Marr & Creek (1968)] and therefore should not significantly affect the shape of the observed emission.

3.4 SUMMARY

In summary, the emission of excimer and ionic excimer species produced through reactive kinetics by excitation from a laser plasma has been observed. The emission from the new ionic molecule (XeRb)+ has been identified at 165 nm. This excitation technique should be generally applicable to the study of a wide variety of proposed ionic excimer molecules [Sauerbrey & Langhoff (1985), Basov et al. (1985a), Iwata et al. (1985)].

Since in laser-produced plasma excitation relatively low-pressure gases must be used to absorb the soft x-rays in the observable volume (up to 100 Torr) it was not possible to create enough upper state population to generate coherent radiation from the XeF and (XeRb)+ emissions. Mainly the laser-produced plasma served as a spectroscopic tool for studying the new rare-gas alkali emission as well as a new means for studying low pressure excimer kinetics. A more appropriate source for operating in the high pressure regime (>2 atm), however, is the high energy, high current density, pulsed electron-beam accelerator.
CHAPTER 4
EXCITATION OF RARE-GAS ALKALI IONIC EXCIMERS
BY AN ELECTRON BEAM

Like neutral excimer species rare gas alkali ionic excimers are created by three body collisions. Estimates for the cross-sections for these collisions [Basov et al. (1985b)] indicate that gas pressures in excess of 1 atm are desirable to generate upper state densities sufficient for lasing. A high energy, high current electron-beam generator was proposed as an appropriate source for such high pressure gas excitation [Basov et al. (1987)]. It was one of the objectives of this work to demonstrated intense electron beam excitation of the rare gas alkali excimers [Millar et al. (1989b)]. One of the technical problems to be solved was the coupling of a high current electron beam into a high temperature reaction cell. The experimental apparatus used for e-beam excitation of (RgA)+ species is shown in Fig 4-1. The system consists of three major parts: 1. the electron-beam accelerator with guiding magnet, 2. the heated reaction cell, and 3. the detection apparatus. The electron-beam characteristics and diagnostics are discussed as well as two different electron beam diode-cell coupling geometries. Experimental results were obtained for (XeCs)+ at 160 nm and (XeRb)+ at 164 nm, a kinetic analysis of these results will be given in the following chapter.

4.1 ELECTRON-BEAM ACCELERATOR

A 1 MeV, 20 kA electron beam with a pulse width of 10 ns full width at half maximum (FWHM) (Physics International Pulserad 110 electron-beam generator) was used to transversely excite high pressure and temperature rare-gas/Alkali gas mixtures. Basically, the system consists of five components: a DC power supply and controls, a triggering source and its delivery system, a Marx bank, a coaxial Blumlein pulse generator, and a field emission diode. In order to insulate the high voltage, the capacitors and sparkgaps forming the Marx
Experimental Apparatus for $e$-Beam Pumping Ionic Excimers

Fig. 4-1  Top view of heated cell, VUV detection apparatus and electron beam machine with guide magnet for electron beam excitation of (RgA)$^+$ ionic excimers.
bank as well as the Blumlein pulse forming network are immersed in insulating oil. The field emission diode is contained in a high vacuum chamber ($\sim 10^{-5}$ Torr).

The Marx bank consists of 10 dual capacitor stages, with a capacitance of 0.01876 mF at 100 kV ($\pm$ 50 kV on each half). These capacitors are charged in parallel yielding a total stored energy of $\sim 940$ J. Breakdown of the SF$_6$ filled spark gaps initiated by a fast rising trigger pulse ($\sim 40$ kV) connects the capacitors in series and results in voltage multiplication; i.e. 1MV at the final stage of the Marx bank. The SF$_6$ pressure should be as small as is consistent with the requirement that the sparkgaps do not self breakdown; i.e. 32.5-33 psi.

The Blumlein pulse generator acts as a resonantly charged tuned transmission line. With this design, load voltages nearly same as the Marx bank voltage can be reached. The oil gap between the inner and intermediate cylinders acts as an output switch discharging the Blumlein circuit. The setting of this gap is critical since it determines how efficiently energy is coupled into the diode. For 1 MV charging voltage, an oil gap of $\sim 2$ cm is recommended corresponding to 4-6 counter-clockwise turns of its adjustment knob from zero gap. The typical current pulse duration across the load is $\sim 10$ ns (FWHM).

The field emission diode consists of a cold carbon felt cathode, which is connected to the Blumlein inner cylinder. Electrons are emitted from the cathode by field emission and travel through a false anode, drift region, and thin titanium foil into the cell. A cross-sectional view of the single foil reaction cell and electron beam machine diode is shown in Fig. 4-2. The cathode was constructed of carbon felt bonded to an aluminum chuck by a conductive nickel filled epoxy. In previous experiments [Hamada (1988)] the cathode was constructed from a rectangular shaped, solid block of carbon mechanically attached to the aluminum chuck. Use of carbon felt for the cathode material rather than solid carbon provides a more uniform energy deposition along the optical axis of the reaction cell. This increase in deposition uniformity is attributed to the larger number of 'micro-points' or 'whiskers' at which field emission can occur in carbon felt [Ericson & Mace (1983)] as opposed to solid carbon.
Fig. 4-2  Cross-sectional view of heated cell and electron beam cathode. The single 50\(\mu\)m Ti foil seals both the cell and cathode region. The cell is thermally isolated from the diode by a drift region tube with thin walls, the diode plate kept at room temperature by cooling rings shown.
The impedance of the vacuum diode could be adjusted by varying the spacing between
the cathode and false anode, however it was necessary to open the diode to air to do these
adjustments. During previous work with this electron beam generator [Cheville et al. (1989)] it
was found that use of a false anode prolongs the foil lifetime. The false anode is a conductive
plane located before the titanium foil, that is highly transparent to electrons. The previous
experimental arrangement used a false anode constructed of a thin stainless steel mesh. This
material was supported by the hibatchi plate < .5 cm from the titanium foil. Careful
examination of the stainless steel mesh show that small rips in the false anode material occurred
after several hundred shots. These rips resulted in localized variations of the anode-cathode
spacing. We believe this resulted in areas of increased electron current density at the foil and
premature foil failure.

For the single foil diode-cell configuration the false anode illustrated in Fig. 4-3 is a
rectangular grid of 3 mm spacing constructed of 0.2 mm diameter stainless steel wire. The
wire is pulled tight over an aluminum frame and tension is maintained by bolts spaced evenly
about the perimeter of the frame. The false anode greatly resembles an ordinary tennis racket in
method of construction. This false anode has several significant advantages. It is mechanically
strong- over 2000 shots have been taken so far and there is no indication of damage. The area
occluded by the structure of this false anode is significantly less than that of the previous mesh
material, hence fewer electrons are blocked or scattered resulting in increased energy deposition
at the reaction cell. Furthermore the stainless steel mesh material used previously is rather
expensive, this anode is much more cost efficient.

After passing through the false anode the electrons enter a field free 'drift region'
approximately 3 cm in length before passing through the foil. The walls of the drift region
were 3 mm thick stainless steel to provide sufficient mechanical support with minimal heat
transfer; a calculation for determining the appropriate thickness is discussed in section 4.3.

In order to prevent space charge effects from causing significant divergence of the
Fig. 4-3  Top view of the false anode, which provides a uniform conductive plane for electron field emission.
electron beam in the drift region a DC magnetic guide field was employed. A semi-steady state field was used rather than a pulsed field to avoid misalignment of the cell due to mechanical shocks. The magnetic field was provided by an electromagnet (Stanganeze Industries #S1 5585) in a race-track shape with bent ends. The magnet was powered by a 60 V, 0-1500 A DC welding power supply (Lincoln Electric Co. #DC-1500). The field strength of the guide field was measured by a Hall-probe and could be varied from 0 to 2200 gauss between shots. This provided a means of varying the energy deposition without changing the pressure or temperature within the reaction cell.

4.2 ELECTRON-BEAM DIAGNOSTICS

The Marx bank signal, Rogowski coil signal, Faraday cup signal and chlorostyrene film measurements are diagnostic techniques which are useful in evaluating electron beam machine performance.

The charge up and breakdown waveform can be monitored by the "Marx bank monitor" signal shown in Fig. 4-4. By observing the breakdown level and its timing, the charge condition of the capacitors and the oil gap setting of the Blumlein can be diagnosed. A breakdown voltage of ~1.0 volt should be monitored using the oil encased 1200:1 resistor voltage divider along with 50 dB attenuation.

The Blumlein and impedance matching condition inside the diode can be evaluated by measuring the total diode current by means of the Rogowski coil placed around the cathode supporting rod. The typical peak current should be ~25 kA with the sensitivity of the Rogowski coil of 2 kA/volt as shown in Fig. 4-5 (a).

The actual current density in the reaction cell can be measured with the Faraday cup probe. The probe consists of simple inner and grounded outer conductors separated by an insulator. The conversion factor from the voltage output to current density value is given by \((A R)^{-1}\) where \(A\) is the area of the inner conductor (0.12 cm\(^2\)) and \(R\) is the terminator impedance.
Fig. 4.4  Temporal development of the Marx bank voltage signal.
Fig. 4.5 Rogowski coil and Faraday cup signals. The Rogowski coil signal is used to trigger data acquisition electronics, and the Faraday cup signal measures the current density of the electron beam after penetrating into the reaction cell.
A typical current density value at 0.6 cm behind the optical axis position is 250 A/cm² as shown in fig. 4.5 (b) for a 50 μm foil with 7.6 cm cathode at 6.0 atm argon buffer gas pressure. Although it requires some assumptions to convert the current density to energy deposition into the gas mixtures, it is the easiest and most sensitive relative measure of electron beam pumping performance.

In order to evaluate the upper state density of any excimer species, the energy density of the pumping source must be known. Several three dimensional computer models for electron-beam energy deposition [Hart & Searles (1976), Eckstrom & Walker (1980)], and several direct measurement methods such as gas pressure rise method [Eckstrom & Walker (1980)], calorimetry, and film exposure dosimetry [Bishop et al. (1972)] have been used. Chlorostyrene film dosimetry has been adopted as an easy and reproducible energy deposition measurement technique after confirming less than 20% measurement error with the calorimetry. The film is evaluated by measuring the transmitted power of a HeNe laser beam (λ = 632.8 nm) before and after the electron-beam exposure. The logarithm of the transmitted power ratio ND is linearly related to the logarithm of electron-beam dose D(J/gram) according to a calibration by the manufacturer given by Equation (4.1):

\[ D = 10 \cdot ND^{1.082} \text{ (J/g)} \quad (4.1) \]

where,

\[ ND = \log_{10}(T_B/T_A) \quad (4.2) \]

and \( T_B \), \( T_A \) are HeNe transmission before and after electron beam exposure. The dynamic range of the log-log scale linearity extends over two orders of magnitude. Conversion from the dose D to the energy deposition unit E (J/liter) can be realized using buffer gas pressure P (atm) and its density \( \rho \) (gram/liter-atm) as given by Equation (4.3):

\[ E = (d_0/d)D \cdot P \cdot \rho = (d_0/d)10 \cdot P \cdot \rho \cdot ND^{1.082} \text{ (J/l)} \quad (4.3) \]
where \( d \) is the actual film thickness and \( d_0 = 50\mu\text{m} \).

For a typical experimental condition the buffer gas is \( \sim 3.0 \) atm argon; therefore, \( P = 3.0 \) atm and \( \rho = 1.677 \text{ g/cm}^3 \) yielding

\[
E = (d_0/d)(50.3)\cdot ND^{1.082} \ (\text{J/l}) \tag{4.4}
\]

A typical average energy deposition value for a single 50 \( \mu \text{m} \) titanium foil with a 7.6 cm long cathode and a magnetic confining field of 1.3 kG is \( \sim 150 \) J/liter. If the double foil configuration is employed (25-\( \mu \text{m} \) plus 50-\( \mu \text{m} \) titanium), then the energy density reduces to \( \sim 50 \) J/liter under the same conditions.

### 4.3 HEATED CELLS FOR ELECTRON BEAM EXCITATION

The fluorescence experiments of electron beam excited rare-gas alkali ionic excimers were performed in a double-foil heated cell configuration. A cross-section of this experimental arrangement, shown in Fig. 4-6, employs an air gap with an additional foil to thermally isolate the cell from the diode. This second foil limited the pump energy to 50 J/l at 3 atm buffer gas pressure. For higher energy deposition, a single-foil diode cell configuration was designed and constructed as shown in Fig. 4-2.

Also to enhance the energy deposition in both diode-cell configurations, a backscattering mirror, or concentrator [Sauerbrey et al. (1987)] was used. The concentrator shown in Figs. 4-2 and 4-6 consisted of a 10-cm-long piece of stainless steel machined into a parabolic shape. This device was then fitted to a similarly shaped tantalum shield. Because tantalum is a high Z material, the shield served to effectively backscatter the incident electrons into the focus of the parabola. The approximated focal point was located along the optic axis of the reaction cell. Due to the electron beam divergence, the imperfect parabolic shape of the
Fig. 4-6 Cross-sectional view of heated cell and electron beam cathode in a double foil configuration. The heated cell is sealed with 50 \( \mu \text{m} \) Ti foil, and the cathode region is sealed with 25 \( \mu \text{m} \) Ti foil. The small air gap acts as a thermal isolator.
mirror, and the relatively broad angular distribution of backscattering, the backscattered electrons did not converge to an ideal line focus, but rather contributed to an enhanced energy density in a finite volume of several millimeters diameter centered around the focal line of the parabolic mirror.

The single foil diode-cell configuration, shown in Fig. 4-2, was constructed of type 316 stainless steel, which has sufficient tensile strength to withstand pressures of several atmospheres at high temperatures, and is not attacked by the highly corrosive molten alkali metals contained within the cell. The cell was constructed of a half cylindrical section welded to a rectangular plate. The rectangular plate was bolted to a matching plate attached to the vacuum diode with the titanium foil sandwiched between and sealed by a copper gasket. This cell is routinely operated at buffer gas pressure of 3 atm argon with foil lifetimes of > 200 shots. A similar cell which operates at room temperature has demonstrated operation at pressure of > 10 bar; the foil lifetime is significantly reduced at these pressures however.

Several methods of sealing the cell were attempted. An oval copper gasket constructed of 1.5 mm diameter, round wire provided a good seal over many heating and cooling cycles. Since it is necessary to provide a vacuum seal on both sides of the foil over a wide range of temperatures, standard knife edge seals cannot be used reliably.

The cell was heated by a combination of four rod heaters installed near the foil, and a half-cylindrical heater attached to the back of the cell. It was necessary to keep the titanium foil at least as hot as the remainder of the cell to prevent condensation of alkali metal upon it. Alkali metal condensing on the foil significantly decreases foil lifetime and possibly degrades energy deposition.

To protect the optics and spectrometer from the alkali vapor the heated section of the cell was separated from the optic mounts by a unheated 8 cm long section of 20 mm diameter tubing with water cooling rings on the end. A wick constructed of stainless steel mesh served to transport condensed alkali metal back to the heated portion of the cell. Water cooling rings
are attached to the vacuum diode assembly to further provide cooling the diode and prevent
damage to the viton o-rings. Also, to protect the diode cavity from hot corrosive alkali vapors,
a diode safety circuit was designed to automatically close the diode gate valve, flush the diode
cavity with nitrogen, and set off a loud alarm upon foil breakage. The thermal characteristics
and the energy deposition capabilities were tested. The results of these experiments will be
described in the following sections.

4.4 THERMAL CHARACTERISTICS

Since temperatures as high as 500°C are required to vaporize alkali metals up to 10
Torr, thermal losses to the diode flange, which was connected to the cell by the drift region
tube, were a major concern in designing the single-foil diode cell configuration. Therefore a
simple isothermal calculation [Sears et al. (1977)] was made to determine the thickness of the
walls of the drift region. The equation for the heat current in a rectangular tube is:

\[ H = k \cdot t \cdot \frac{\Delta T}{\Delta X} \]  \hspace{1cm} (4.5)

where,

\( H \) [heat current \( \leq \) total power of cell heaters] = 1800 W
\( k \) [thermal conductivity of the material, Stainless Steel] = 0.5024 W cm\(^{-1}\) K\(^{-1}\)
\( t \) [thickness of the tube]
\( l \) [circumference of the cross-section of the tube] = 35.5 cm
\( \Delta T \) [maximum temperature - room temperature] = 470°C - 743 K
\( \Delta X \) [tube length] = 2.54 cm

If the heat current is equated to the maximum power that can be achieved by the shell and rod
heaters, then the maximum tube thickness required can be estimated to be 3.4 mm. Since the
environment of the heated cell is not completely insulated from room temperature, a smaller
thickness of 3 mm was chosen for the drift region tube. The heat distribution measured from the heated cell and drift region tube to the diode flange is shown in Fig. 4-7. The temperature profile decreases from the cell to the diode. With the aid of water cooling tubes on the diode flange and on the drift region tube, the heated cell is able to achieve a temperature in excess of 800°C while the diode remains at room temperature. Since only 546°C is needed for 10 Torr of Na, the maximum cell temperature is higher than is required for the rare-gas alkali experiments, thus leaving a large thermal margin.

The heat distribution along the optical axis of the cell was also a concern since it is important to have uniform heating in the electron beam pumped region of the cell while maintaining close to room temperature at the flanges. This is to confine the alkali metal to the central volume of the cell, to prevent optics damage at the flanges, and to maintain a constant uniform alkali vapor in the e-beam pumped region of the cell. While under vacuum the thermal distribution along the optical axis in the heated cell was measured in Fig. 4-8. The temperature in the central zone of the cell is almost constant (TC #'s 4 & 5) while the end tube connected to the flanges remained relatively cool ~36°C. Thus it was considered safe to mount optical elements, such as dielectric mirrors, inside the cell.

The densities of the alkali vapors were estimated from vapor pressure curves [Nesmeyanov (1963)] and the cell temperature, which was monitored by five thermocouples. Also absorption profiles of alkali resonance lines were measured by illumination of the heated zone with a broadband light source [Petersen et al. (1988)].

4.5 ENERGY DEPOSITION

Energy deposition measurements were performed for various Ar buffer gas pressures and magnetic field strengths as shown in Figs. 4-9 through 4-16. To assure reliable data, the electron beam current and charging voltage were continuously monitored by a Rogowski coil and Marx bank resistive voltage divider. The maximum achieved energy deposition was about
Fig. 4-7. Thermal distribution of heated cell and electron beam diode flange along the electron beam axis. The lower picture shows the locations of the numbered thermocouples.
Fig. 4-8  Thermal distribution of heated cell along the optical axis, transverse to the electron beam axis. The left half of the heated cell has identical temperature distribution as the right half, which is shown. The bottom picture is a frontal view of the heated cell and diode flange, which shows the locations of the numbered thermocouples.
Fig. 4-9  Energy Deposition along the optical axis as a function of applied magnetic field for 1 atm of argon.
Fig. 4-10  Energy Deposition along the optical axis as a function of applied magnetic field for 3 atm of argon.
Fig. 4-11 Energy Deposition along the optical axis as a function of applied magnetic field for 5 atm of argon.
Fig. 4-12 Energy Deposition along the optical axis as a function of applied magnetic field for 6 atm of argon.
Fig. 4-13  Energy deposition along the optical axis as a function of argon pressure with a 0.9 kG applied magnetic field.
Fig. 4-14  Energy deposition along the optical axis as a function of argon pressure with a 1.3- kG applied magnetic field.
Fig. 4-15 Energy deposition along the optical axis as a function of argon pressure with a 1.7-kG applied magnetic field.
Energy Deposition vs. Ar Pressure
B=2.2 kG

Energy Deposited, J/l

Distance, cm

P=1 atm
P=3 atm
P=5 atm
P=6 atm

Fig. 4-16  Energy deposition along the optical axis as a function of argon pressure with a 2.2- kG applied magnetic field.
260 J/l for 5 - 6 atm of Ar with a 2.2 kG magnetic guide field as shown in Fig. 4-16. Without the magnetic confining field the energy profile is peaked and the maximum energy achieved was 85 J/l with 5 atm argon (see Fig. 4-17). The energy deposition decreased with lower Ar pressures and smaller magnetic fields, i.e., Figs. 4-9 and 4-10. Furthermore, magnetic field strengths of 0.9 kG were insufficient for obtaining uniform energy deposition as shown in Fig. 4-13. Overall the magnetic field increases the energy deposition and adds uniformity to the energy profile along the optical axis (see Figs. 4-13 to 4-16). Note that by varying the magnetic guide field the energy deposition in the cell can be varied by a factor of two from one shot to the next.

4.6 DETECTION APPARATUS

The detection apparatus is shown as a component in Fig. 4-1. A MgF₂ window separated the high pressure rare-gas/alkali vapor mixture from the vacuum in the detection apparatus. The VUV emissions of Xe₂⁺(172nm), Ar₂⁺(126nm), (XeCs)⁺(160 nm) or (XeRb)⁺ (164 nm) were spectrally resolved with a 0.2 meter VUV spectrometer (Acton YM-502). A sodium salicylate scintillator coupled to an output port of the spectrometer then converted the VUV photons to visible photons which were then temporally resolved by a fast photomultiplier (PMT) (RCA 8575) connected to a high speed transient digitizer (Tektronix 7912AD). Data collected from the detection system was stored on a microcomputer for subsequent analysis. To protect the PMT from electron-beam-generated x-ray radiation, the entire detection system was encased in lead shielding. Further suppression of the x-ray noise on the data was accomplished using background subtraction techniques. Also to prevent signal distortion due to the magnetic guide field, the PMT was placed inside three concentric tubes, with a large magnetic susceptibility.

Recently, a vacuum photo diode (VPD)(Hammamatsu R1193U-04) with spectral sensitivity of 115-nm to 320-nm, was attached to the opposite side of the reaction cell. A filter
Fig. 4-17 Energy deposition along the optical axis as a function of argon pressure without a guiding magnetic field.
for either Xe₂* or (XeCs/Rb)⁺ can be used for spectral discrimination. The temporal response of this detector is ~0.3 ns, which should enable a more accurate analysis of the decays of the (RgA)⁺ species compared to the PMT detector. Fig. 4-18 compares the response of the VPD to the PMT for Xe₂* fluorescence. The decay constants and temporal widths are in excellent agreement. Also the VPD is less sensitive to x-ray radiation and magnetic field distortions than the PMT.

4.7 EXPERIMENTAL RESULTS

In this section, the observation and analysis of emission from electron beam excited (XeCs)⁺ at 160-nm and (XeRb)⁺ at 164-nm is presented. Fluorescence from these ionic excimers has been studied in xenon-alkali and argon-xenon-alkali mixtures as a function of constituent gas pressures. This investigation yields information on the origin of the observed emissions, radiative lifetimes, and the relevant production and quenching mechanisms of (XeCs)⁺ and (XeRb)⁺ emissions.

The fluorescence from (XeCs)⁺ and (XeRb)⁺ was investigated mainly in argon-xenon-alkali mixtures as a function of argon, xenon and cesium or rubidium. These emissions were not observed in pure rare gases or rare gas combinations. Throughout the experiments the relative intensity of Xe₂* excimer was monitored. Fluorescence from (XeCs)⁺ and (XeRb)⁺ was also observed in the absence of the argon buffer gas, however a Xe and Cs or Rb dependence of these species was not performed under these conditions.

The temporal development of both the (XeCs)⁺ and (XeRb)⁺ fluorescence for typical gas mixtures and temperatures are shown in Figs. 4-19 and 4-20 on linear and semilogarithmic scales. These time resolved signals were obtained by subtracting the short-lived (~20 ns) and small (<0.1 volt) signal caused by the x-rays due to the electron beam. The straight line fitted to the semilogarithmic plots suggests single exponential decays for the
Fig. 4.18 Comparison of decay constant, $\tau$ and temporal width (FWHM) for $\text{Xe}_2^*$ fluorescence yield at 172 nm determined by a photomultiplier (PMT) and a vacuum photodiode (VPD).
Fig. 4-19 Temporal behavoir of the VUV fluorescence of (XeCs)+ at 160 nm. The upper plot displays the logarithm of the observed temporal profile. The line fitted through this plot results from a single exponential decay with an effective decay time $\tau$. 

$Xe^+Cs, 160\ \text{nm}$

$\tau = 127\ \text{ns}$

FLUORESCENCE INTENSITY, arb. units

TIME, ns

100 Torr Xe
1 Torr Cs
3 atm Ar
Fig. 4-20 Temporal behavior of the VUV fluorescence of (XeRb)$^+$ at 164 nm. The upper plot displays the logarithm of the observed temporal profile. The line fitted through this plot results from a single exponential decay with an effective decay time $\tau$. 

$Xe^+Rb, 164 \text{ nm}$

$\tau = 101 \text{ ns}$

FLUORESCENCE INTENSITY, arb. units

TIME, ns

25 Torr Xe
7 Torr Rb
3 atm Ar
fluorescence of both species. The rapid rise time (~20 - 50 ns) supports the argument that these excimers are indeed ionic.

4.7.1 Spectrum of \((XeRb)^+\) and \((XeCs)^+\)

The measured spectrum of \((XeRb)^+\) is shown in Fig. 4-21. A distinct structure of three peaks could be resolved in the case of \((XeRb)^+\) whereas, due to the lower spectral resolution in early experiments [Millar et al. (1989a)], the \((XeCs)^+\) spectrum shown in Fig. 4-22, exhibits one 4-nm-wide peak centered at 160 nm. Each experimental point in the spectra of Fig. 4-22 corresponds to a temporally resolved fluorescence measurement. The spectral position of the three peaks of \((XeRb)^+\) agrees approximately with the position of the spectral features observed with low-current ion beam excitation [Fiedler et al. (1989)]; however, the short-wavelength peak of 162.6 nm is the most intense feature with low-pressure (~100 Torr) ion beam excitation, whereas the middle peak at 163.6 nm has the highest intensity under the present excitation conditions. Within the resolution of the detection apparatus, no change in the temporal behavior of the emission could be detected when the spectrometer was tuned between 161 and 168 nm; i.e., all three peaks of \((XeRb)^+\) show the same temporal characteristics. Measurements were also made in the vicinity of 170 nm where \(Xe2^*\) emission was expected. In this region, as shown in Fig. 4-22 at 172 nm, the fluorescence decay time becomes much longer and for small alkali pressures the signal resembles the \(Xe2^*\) emission observed at room temperature. For Xe pressures below 100 Torr and for alkali pressures above 8 Torr, the \(Xe2^*\) signal is completely quenched by the presence of alkali vapor.

4.7.2 Pressure dependences of \((XeCs)^+\), \((XeRb)^+\) and \(Xe2^*\)

The pressure dependence of \((XeCs)^+\) and \(Xe2^*\) intensities on Ar, Xe and Cs are shown in Figs. 4-23 (a), (b) and (c). From Fig. 4-23 (a) it is observed that both \((XeCs)^+\) and \(Xe2^*\) time integrated fluorescence signals increase approximately linearly with argon pressure, while
Fig. 4-21  Fluorescence spectrum of electron beam excited mixture of Ar/Xe/Rb. The resolution is 0.8 nm. Each data point corresponds to an individual electron beam shot. The solid line is for presentation purposes.
Fig. 4-22  Fluorescence spectrum of electron beam excited mixture of Ar/Xe/Cs. The resolution is 2 nm. Each data point corresponds to an individual electron beam shot. The solid line is for presentation purposes.
Fig 4.23 (a,b) Integrated intensity of (Xe Cs)\(^+\) (160 nm) and Xe\(^*\)\(_2\) (172 nm) as a function of gas pressure: a) Argon  b) Xenon.
Fig 4.23 (c) Integrated intensity of (Xe Cs)$^+$ (160 nm) and Xe$^+_2$ (172 nm) as a function of Cesium density.
maintaining constant xenon pressure and temperature (cesium pressure). Argon pressures above 3 atm were not employed due to an unpractical decrease in foil lifetime. These species are also found to increase with xenon pressure as shown in Fig. 4-23 (b). However, the Xe$_2^*$ emission dominates at xenon pressures above 150 Torr, in fact the Xe$_2^*$ signal spectrally overlaps at 160 nm, preventing an accurate measurement of (XeCs)$^+$. If cesium pressures above 8 Torr are employed, then the Xe$_2^*$ signal is quenched even at xenon pressures above 150 Torr, however the (XeCs)$^+$ signal also decreases with increasing cesium density, as shown in Fig.4-23 (c).

Similar experiments were performed using rubidium as the alkali donor. Increasing the xenon pressure from 25 to 150 Torr resulted in a 30% signal increase of (XeRb)$^+$. Also increasing the argon pressure from 1 to 3 atm increased the (XeRb$^+$) output signal by 80%. A rubidium vapor pressure dependence of (XeRb)$^+$ is shown in Fig. 4-24. The output increases until ~3 Torr Rb is reached, at higher pressure the signal levels off and slowly decreases. Experiments by Schumann et al. (1989) show similar results in He/Kr/K mixtures. In the present experiments this effect may possibly be due to alkali coating of the transmission window, and a depletion of the alkali from the pumping region of the cell. Therefore the pressure ranges were limited due to foil problems (argon pressure ≤ 3 atm), Xe$_2^*$ signal overlap (xenon pressure ≤ 150 Torr) and coated optics (cesium, rubidium pressure ≤ 10 Torr).

4.7.3 Absolute measurement of (XeRb)$^+$ and Xe$_2^*$ fluorescence yield

An absolute measurement was made of (XeRb)$^+$ and Xe$_2^*$ fluorescence observed with a vacuum photodiode (VPD) coupled to a narrow band interference filter for spectral discrimination. The photodiode sensitivity is 5mA/W, the measured signal is in milli-volts (mV) so the power(W) = [signal(mV)(W)] / [50(Ω) 5(mA)] = signal(mV)(W) / 250(mV). The power is then corrected for the transmission of the filter, the solid angle from the pumping zone to the detector, and estimated pumping volume. The transmission curves for these filters are
Fig. 4-24  Peak Intensity of (XeRb)+ fluorescence signal at 164 nm as a function of rubidium density.
shown in Figs. 4-25 and 4-26. For an Ar/Xe mixture of 3 atm, and 100 Torr respectively the measured power density for Xe$_2^*$ was 14.4 KW/cm$^3$. In the same gas mixture with the addition of 5 Torr Rb, (XeRb)$^+$ yielded 10 KW/cm$^3$. The pumping power for the present conditions is 6 MW/cm$^3$ yielding a 0.5 - 1% fluorescence efficiency for Xe$_2^*$ and (XeRb)$^+$. These power density values will be compared to kinetic calculations performed in the next chapter.
Fig. 4.25  Calibration curve for 163 nm very-narrow band transmission filter for (XeRb)$^+$ or (XeCs)$^+$ detection. The bandwidth is 60 Å. The maximum transmission is 6.8% at 162.9 nm.
Fig. 4.26 Calibration curve for 172 nm narrow band transmission filter for Xe₂* detection. The bandwidth is 200 Å. The maximum transmission is 15 % at 173 nm.
CHAPTER 5
KINETIC MODEL OF ELECTRON BEAM PUMPED RARE GAS ALKALI IONIC EXCIMERS

5.1 INTRODUCTION:

As was discussed in the previous chapter, experiments using electron beam excitation of (RgA)+ excimers were performed with the objective to obtain information on the production and quenching processes and the radiative lifetimes of (XeRb)+ and (XeCs)+ molecules. In this chapter a kinetic model similar to that proposed by Warwar (1989) is developed for the (XeRb)+ species. One of the main objectives in formulating a kinetic model is to determine the excited state densities. With the knowledge of radiative lifetimes wavelengths, linewidths and excited state densities one can investigate the feasibility of generating coherent radiation. This possibility will be discussed at the end of the chapter.

In 1985, before any experimental evidence of the rare gas alkali ionic excimers was available, Basov et al. (1985b, 1987) proposed two kinetic models for electron beam pumping (NeNa)+ and (XeCs)+ species. The main production channels suggested were:

\[ \text{Rg}^+ + A + \text{Rg}^' \rightarrow (\text{RgA})^+ + \text{Rg}^' \] 
\[ (\text{RgA})^+ + \text{Rg}^' \rightarrow (\text{RgA})^+ + \text{Rg} \] 
\[ (\text{RgA})^+ + \text{Rg} \rightarrow (\text{RgA})^+ + \text{Rg} \] 

(5-1)

(5-2)

with the estimated rate constants shown. Equation (5-2) should proceed only in the reverse direction however, since the binding energies of the (RgA)+ ions have been found from experiments (see chapter 2) to be smaller than for Rg2+. For (RgA)+ the binding energy is on the order of 0.5 eV, whereas for Rg2+ it ranges from 1.34 eV for Ar2+ to 0.98 eV for Xe2+. The second reaction will therefore be a loss channel and not a production reaction for the rare gas alkali ions.
The main non-radiative quenching reaction was expected to be electron-ion dissociative recombination:

\[(\text{RgA})^+ + e^- \rightarrow \text{Rg} + \text{A} \quad (3.0 \times 10^{-7} \text{ cm}^3/\text{s}) \quad (5-3)\]

The rate constant for this reaction was estimated in analogy to similar processes, such as dissociative recombination of $\text{Rg}_2^+$, (for Rg = Xe, the rate constant is known to be $3.0 \times 10^{-7}$ cm$^3$/s [Bardsley and Biondi (1970)]). A reaction rate of $10^{-7}$ to $10^{-8}$ cm$^3$/s however would quench the long decay of the ionic molecule which has been observed experimentally in e-beam pumped (XeRb)$^+$ and (XeCs)$^+$ ionic excimers [Millar et al. (1989b,c)].

In addition Basov proposes that the radiative lifetimes should be on the order of 1 - 5 ns in analogy to the lifetimes of the rare gas dimer $^1\Sigma(\sigma_u^+) \rightarrow ^1\Sigma(\sigma_g^+)$ [Keto et al. (1974)] optical transition.

### 5.2 Radiative Lifetime and Quenching Rate Analysis

The decay of the fluorescence signal is an effective decay which includes the radiative decay of the species as well as collisional de-excitation of the upper excited state by constituent gases and charged particles contained within the reaction cell. The fact that the fluorescence signals of (XeCs)$^+$ and (XeRb)$^+$ show single exponential decays with decay constants of about 100 ns is surprising (see Figs. 4-19 and 4-20). For an electron beam excited ionic species, one would expect recombination with electrons to play an important role in the decay, which would lead to a non-exponential decay. The differential equation expressing the decay of the upper state density is thus approximated as first order,

\[i.e.,\]
dy/dt = -b·y \hspace{1cm} (5.4)

where,

\[ y = [(RgA)^+] \], the upper state density \hspace{1cm} \]

\[ b = 1/\tau_{\text{eff}}, \text{the inverse of the effective decay constant, also known as the decay rate.} \hspace{1cm} \]

solving for \( y \) yields:

\[ y(t) = y(0)\cdot e^{-bt} \hspace{1cm} (5.5) \]

The decay rate can also be expressed by the following equation:

\[ 1/\tau_{\text{eff}} (s^{-1}) = 1/\tau_{\text{rad}} (s^{-1}) + K_{\text{Ar}} [\text{Ar}] + K_{\text{Xe}} [\text{Xe}] + K_{\text{A}} [\text{A}] \hspace{1cm} (5.6) \]

where,

\[ \tau_{\text{rad}} = \text{radiative lifetime of the } (\text{XeA})^+ \text{ excimer,} \hspace{1cm} \]

\[ [\text{Ar}] = \text{argon density, } (\text{cm}^3), \hspace{1cm} \]

\[ [\text{Xe}] = \text{xenon density, } (\text{cm}^3), \hspace{1cm} \]

\[ [\text{A}] = \text{cesium, rubidium, density } (\text{cm}^3), \hspace{1cm} \]

and,

\[ K_{\text{Ar}} = \text{quenching rate constant by Ar, } (\text{cm}^3s^{-1}), \hspace{1cm} \]

\[ K_{\text{Xe}} = \text{quenching rate constant by Xe, } (\text{cm}^3s^{-1}), \hspace{1cm} \]

\[ K_{\text{A}} = \text{quenching rate constant by A, } (\text{cm}^3s^{-1}). \hspace{1cm} \]

The quenching rate constants can be determined by plotting the decay rates as a function of the constituent gas pressures or densities. These Stern-Volmer plots are illustrated in Figs. 5-1 (a), (b), and (c), for (XeCs)+ experiments and Figs. 5-2 (a) and (b) for (XeRb)+ experiments. The quenching rate constants are determined by the slopes and the radiative lifetimes can be computed from the decay rate intercepts. Table 5.1 contains the rate equations
Fig. 5-1 (a)  
(XeCs)$^+$ fluorescence decay rate as a function of argon density.
Fig. 5-1 (b)  \((\text{XeCs})^+\) fluorescence decay rate at 164 nm as a function of xenon density.
Fig. 5-1 (c)  

(XeCs)$^+$ fluorescence decay rate as a function of cesium density.
Fig. 5-2 (a) (XeRb)$^+$ fluorescence decay rate as a function of xenon density for 3.6 and 5 Torr rubidium with 3 atm argon. The two lines have almost identical slopes indicating a constant decay rate constant for xenon quenching of (XeRb)$^+$. 
Fig. 5-2 (b)  
(XeRb)$^+$ fluorescence decay rate at 164 nm as a function of rubidium density.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Temperature/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Xe^+Cs + Cs \to \text{Products}$</td>
<td>$2.4 \pm 1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$</td>
<td>581-650</td>
</tr>
<tr>
<td>$Xe^+Cs + Xe \to \text{Products}$</td>
<td>$3 \pm 2.5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$</td>
<td>623</td>
</tr>
<tr>
<td>$Xe^+Cs + Ar \to \text{Products}$</td>
<td>$4 \pm 3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$</td>
<td>633</td>
</tr>
<tr>
<td>$Xe^+Cs \to XeCs^+ + \text{hv}$</td>
<td>$150 \pm 40 \text{ ns}$</td>
<td></td>
</tr>
<tr>
<td>$Xe^+Rb + Rb \to \text{Products}$</td>
<td>$2.3 \pm 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$</td>
<td>550-663</td>
</tr>
<tr>
<td>$Xe^+Rb + Xe \to \text{Products}$</td>
<td>$2.9 \pm 2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$</td>
<td>618</td>
</tr>
<tr>
<td>$Xe^+Rb + Ar \to \text{Products}$</td>
<td>$9 \pm 4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$</td>
<td>618</td>
</tr>
<tr>
<td>$Xe^+Rb \to XeRb^+ + \text{hv}$</td>
<td>$280 \pm 35 \text{ ns}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.1  Decay mechanisms for (XeRb)$^+$ and (XeCs)$^+$
and their respective constants, and lifetimes of (XeCs)+ and (XeRb)+ which were experimentally measured and calculated using equation (5.6).

The simplest kinetic model of the (RgA)+ species does not consider electron quenching, this type of analysis yields a single exponential decay of the temporal behavior of these species. Such behavior was observed, and noted in Chapter 4 in the temporal decays of electron beam pumped (XeCs)+ and (XeRb)+ (see Figures 4-19 and 4-20). If electron quenching did play a significant role then a kinetic of second order would be more appropriate for modeling the upper state time dependence of (RgA)+. One can assume that the electron density is at the least, equal to the Rg+ A density. In this case a second term can be added to equation (5-4) in the following second order differential equation:

\[
\frac{dy(t)}{dt} = -a \cdot y^2 - b \cdot y
\]

(5-7)

The solution of this equation is then:

\[
y(t) = \frac{b \cdot y_0 \cdot \exp(-b \cdot t)}{a \cdot y_0 \cdot (1 - \exp(-b \cdot t)) + b}
\]

(5-8)

The "a" coefficient is proportional to the formation rate constant of the upper state, and \( y_0 \) is the value of the temporal pulse taken during the decay of the pulse at a selected time. This solution was fitted by selecting starting and stopping points on the decay portion of the temporal pulses shown in chapter 4, values for the "a" and "b" coefficients were then determined. The analysis was performed for increasing constituent gas pressures for both (XeRb)+ and (XeCs)+ species. The "a" coefficients changed in sign and the "b" coefficients increased and decreased in a non-systematic way with increasing gas pressures. One would expect the "b" coefficients to increase with increasing gas pressures, however. Also the "a" coefficients should maintain a
positive value. Therefore, it can be said that this second order solution does not present a physical explanation of the data. The temporal profiles did however fit well with a single exponential decay as shown in Fig. 5-3.

In the previous analysis it was assumed that the observed effective decays of the temporal plots of the \((\text{RgA})^+\) species were due to both radiative and collisional quenching of the upper state. This analysis leads to the belief that these ionic excimers have long radiative lifetimes. On the other hand it is also possible that the effective decays represent the build up time of these molecules instead of the decay. The likely production reaction for the rare gas alkali ionic excimers is:

\[
\text{Rg}^+ + \text{A} + \text{Rg}' \rightarrow (\text{RgA})^+ + \text{Rg}'
\]

with \(\text{Rg} = \text{Xe}\) and \(\text{Rg}' = \text{Ar}\). Therefore if the decay is characteristic of the production process then equation (5.6) would be replaced by the following equation:

\[
\frac{1}{\tau_{\text{eff}} (\text{s}^{-1})} = K [\text{Ar}] [\text{Xe}^+]
\]

where \(K\) is the rate constant for three body production of the rare gas alkali. A plot of the decay rate as a function of argon pressure would result in a line intercepting the origin. This was not observed from the Stern-Volmer plots representing the data in this work (Figs. 5-1 and 5-2).

Hence it is proposed that the rare gas alkali ionic excimers have long radiative lifetimes, and electron quenching is negligible for these species. It is quite surprising that electron quenching does not appear to influence the lifetime of the excited ionic rare gas alkali molecules, as it does play a significant role in the quenching of the ionic rare gas dimers \([\text{Brau et al. (1984)}]\).
Fig. 5.3  First and second order fits to an electron beam excited (Xe+Rb) emission in 3 atm Ar, 150 Torr Xe and 4 Torr Rb at 164 nm. The second order fit yields an "a" coefficient equivalent to \(-1.9 \times 10^{-6}\) (v/s) and a "b" coefficient of \(5.5 \times 10^{6}\) (s\(^{-1}\)). The first yields a "b" coefficient of \(4.9 \times 10^{6}\) (s\(^{-1}\)).
5.3 KINETIC MODEL OF ELECTRON BEAM PUMPED (XeRb)+

The processes for a kinetic model of a (XeRb)+ electron beam pumped system based on previous models [Basov et al. (1985 b, 1987), Warwar (1989)] and the experimental results presented in this work are given below in Table 5.2.

Table 5.2 Kinetics processes of electron beam pumped Ar/Xe/Rb mixtures

I. Initial Conditions

<table>
<thead>
<tr>
<th></th>
<th>Ar</th>
<th>Xe</th>
<th>Rb</th>
<th>Pump</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.0</td>
<td>50</td>
<td>5.0</td>
<td>100 A/cm², 1 MeV, 10 ns</td>
</tr>
</tbody>
</table>

II. Pumping Processes

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ar + ep → Ar⁺ + e + ep</td>
<td>0.78 Pump</td>
</tr>
<tr>
<td></td>
<td>Ar + ep → Ar⁺* + ep</td>
<td>0.22 Pump</td>
</tr>
<tr>
<td></td>
<td>Xe + ep → Xe⁺ + ep + e</td>
<td>0.80 Pump</td>
</tr>
<tr>
<td></td>
<td>Xe + ep → Xe⁺* + ep</td>
<td>0.20 Pump</td>
</tr>
</tbody>
</table>

III. Production and Quenching of (XeRb)+

1. Xe⁺ + Rb + Xe → (XeRb)+ + Xe 1.0 x 10⁻²⁸ cm⁶/s [a]
2. Xe⁺ + Rb + Ar → (XeRb)+ + Ar 1.0 x 10⁻²⁸ cm⁶/s [a]
3. (XeRb)+* + Ar → Xe + Rb + Ar 9.0 x 10⁻¹⁴ cm³/s [b]
4. (XeRb)+* + Xe → Xe + Rb + Xe 2.0 x 10⁻¹² cm³/s [b]
5. (XeRb)+* + Rb → Xe + Rb⁺ + Rb 2.3 x 10⁻¹¹ cm³/s [b]
6. (XeRb)+* + Xe → Xe₂⁺ + Rb 5.0 x 10⁻¹² cm³/s [b]
7. (XeRb)+* + e → Xe + Rb 5.0 x 10⁻⁹ cm³/s [b]
8. (XeRb)+* → Xe + Rb⁺ + hv 1.0 / 250 ns [b]

IV. Rare Gas Kinetics

9. Xe⁺ + Xe + Xe → Xe₂⁺ + Xe 1.8 x 10⁻³¹ cm⁶/s [c]
10. Ar⁺ + Ar + Ar → Ar₂⁺ + Ar 2.0 x 10⁻³¹ cm⁶/s [c]
11. Xe₂⁺ + e → Xe⁺ + Xe 3.7 x 10⁻⁷ cm³/s [c]
12. Ar₂⁺ + e → Ar⁺ + Ar 1.0 x 10⁻⁷ cm³/s [c]
13. Xe⁺ + Rb → Rb⁺ + Xe 3.0 x 10⁻¹⁰ cm³/s [b]
(14) $\text{Ar}^+ + \text{Rb} \rightarrow \text{Rb}^+ + \text{Ar}$ \hspace{1cm} $3.0 \times 10^{-10}$ cm$^3$/s \hspace{1cm} [b]
(15) $\text{Xe}_2^+ + \text{Rb} \rightarrow \text{Rb}^+ + 2\text{Xe}$ \hspace{1cm} $3.0 \times 10^{-10}$ cm$^3$/s \hspace{1cm} [b]
(16) $\text{Ar}_2^+ + \text{Rb} \rightarrow \text{Rb}^+ + 2\text{Ar}$ \hspace{1cm} $3.0 \times 10^{-10}$ cm$^3$/s \hspace{1cm} [b]
(17) $\text{Ar}^* + \text{Xe} \rightarrow \text{Ar} + \text{Xe}^*$ \hspace{1cm} $3.0 \times 10^{-10}$ cm$^3$/s \hspace{1cm} [c]
(18) $\text{Ar}_2^* + \text{Xe} \rightarrow \text{Ar} + \text{Ar} + \text{Xe}^*$ \hspace{1cm} $4.4 \times 10^{-10}$ cm$^3$/s \hspace{1cm} [c]
(19) $\text{Ar}^* + \text{Ar} + \text{Ar} \rightarrow \text{Ar}_2^* + \text{Ar}$ \hspace{1cm} $1.0 \times 10^{-32}$ cm$^3$/s \hspace{1cm} [c]
(20) $\text{Xe}^* + \text{Ar} + \text{Ar} \rightarrow \text{Xe}_2^* + \text{Ar}$ \hspace{1cm} $7.2 \times 10^{-11}$ cm$^6$/s \hspace{1cm} [c]
(21) $\text{Xe}^* + \text{Ar} + \text{Ar} \rightarrow \text{Xe}_2^* + \text{Ar}$ \hspace{1cm} $2.3 \times 10^{-32}$ cm$^6$/s \hspace{1cm} [c]
(22) $\text{Ar}_2^* + \text{e} + \text{e} \rightarrow \text{Ar}_2^* + \text{e}$ \hspace{1cm} $1.0 \times 10^{-29}$ cm$^6$/s \hspace{1cm} [c]
(23) $\text{Xe}^* + \text{Ar} + \text{Ar} \rightarrow \text{Xe}_2^* + \text{Xe}$ \hspace{1cm} $2.5 \times 10^{-32}$ cm$^6$/s \hspace{1cm} [c]
(24) $\text{Xe}_2^* \rightarrow \text{Xe} + \text{Xe} + \text{hv}$ \hspace{1cm} $1.0 / 50$ ns \hspace{1cm} [b,c]
(25) $\text{Ar}_2^* \rightarrow \text{Ar} + \text{Ar} + \text{hv}$ \hspace{1cm} $1.0 / 4.0$ ns \hspace{1cm} [c]

V. Alkali Quenching

(26) $\text{Xe}^* + \text{Rb} \rightarrow \text{Rb}^+ + \text{Xe} + \text{e}$ \hspace{1cm} $5.0 \times 10^{-10}$ cm$^3$/s \hspace{1cm} [d]
(27) $\text{Ar}^* + \text{Rb} \rightarrow \text{Rb}^+ + \text{Ar} + \text{e}$ \hspace{1cm} $5.0 \times 10^{-10}$ cm$^3$/s \hspace{1cm} [d]
(28) $\text{Ar}_2^* + \text{Rb} \rightarrow \text{Ar} + \text{Ar} + \text{Rb}^+ + \text{e}$ \hspace{1cm} $5.0 \times 10^{-10}$ cm$^3$/s \hspace{1cm} [d]
(29) $\text{Xe}_2^* + \text{Rb} \rightarrow \text{Ar} + \text{Ar} + \text{Rb}^+ + \text{e}$ \hspace{1cm} $5.0 \times 10^{-10}$ cm$^3$/s \hspace{1cm} [d]

VI. Alkali Recombination

(30) $\text{Rb}^+ + \text{Rb} + \text{Ar} \rightarrow \text{Rb}_2^+ + \text{Ar}$ \hspace{1cm} $1.0 \times 10^{-29}$ cm$^6$/s \hspace{1cm} [a]
(31) $\text{Rb}^+ + \text{Rb} + \text{Xe} \rightarrow \text{Rb}_2^+ + \text{Xe}$ \hspace{1cm} $1.0 \times 10^{-29}$ cm$^6$/s \hspace{1cm} [a]
(32) $\text{Rb}_2^+ + \text{e} \rightarrow \text{Rb} + \text{Rb}$ \hspace{1cm} $3.0 \times 10^{-8}$ cm$^3$/s \hspace{1cm} [a]

[a] Basov et al. (1985b).
[b] This experimental work.

The model utilized the kinetic program developed by Warwar (1989), which was derived mostly from rate constants suggested by Basov et al. (1987). The main differences in the two previous models were in the electron-ion dissociative recombination constants (see equation (7) in Table 5.2), and the radiative lifetimes of the species. Rate constants of
equations (3) and (4) in Table 5.2 differ slightly from those used by Warwar (1989) due to more recent experimental results [Millar et al. (1989b,c)].

The initial conditions represent gas pressures optimized for (XeRb)+ emission, and the electron beam pumping parameters. The pumping processes describe the reactions of the primary electrons (ep) with the rare gases. The production of the (XeRb)+ upper state is due to equations (1) and (2), with a rate constant similar to that proposed by Basov et al. (1985b, 1987).

The kinetic model yields the photon densities of (XeRb)+ and Xe2* emissions in units of (s⁻¹cm⁻³), which must be multiplied by the transition energies to obtain the power density (W/cm³). In addition to the power density, the decay constant of the emission and the temporal width (FWHM) can be determined. Table 5.3 shows the results of this analysis compared with the absolute measurement discussed in section 4.6.3:

Table 5.3 (XeRb)+ and Xe2* emission parameters experimentally determined by a vacuum photodiode (VPD) measurement and calculated from the kinetic model presented by Table 5.2. Xe2* experiments were with 3 atm Ar and 100 Torr Xe, (XeRb)+ experiments had the same fill with the addition of 5 Torr Rb.

<table>
<thead>
<tr>
<th></th>
<th>Power Density (KW cm⁻³)</th>
<th>τ (ns)</th>
<th>FWHM (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe₂⁺* (172 nm)</td>
<td>Experiment</td>
<td>14.4</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td>MODEL</td>
<td>10.4</td>
<td>280</td>
</tr>
<tr>
<td>Xe⁺Rb (164 nm)</td>
<td>Experiment</td>
<td>10.0</td>
<td>~10-20</td>
</tr>
<tr>
<td></td>
<td>MODEL</td>
<td>6.0</td>
<td>20</td>
</tr>
</tbody>
</table>
The (XeRb)$^+$ emission measured by the VPD was not sufficiently above the noise level for an accurate determination of the decay constant, the temporal width could only be estimated as well. In the case of Xe$_2^*$ emission, Fig. 5-4 shows output of the kinetic model. The observed fluorescence pulse of Xe$_2^*$ was well above the noise level so the decay constants and temporal widths could be measured. The power densities measured for both species agree quite well with the results of the kinetic model, $\sim 25\%$, where the error in the measured intensity is caused by the shot to shot variation ($\sim 20\%$).

The time dependence determined from the model for 3 atm Ar, 100 Torr Xe and 5 Torr Rb, can be seen in Fig. 5-5. The results are scaled so that the temporal pulses all fit on the same graph. Below, the peak density of each species is given:

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>MAXIMUM DENSITY [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe$^+$</td>
<td>$1.29 \times 10^{14}$</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>$2.53 \times 10^{14}$</td>
</tr>
<tr>
<td>Xe$_2^*$</td>
<td>$3.87 \times 10^{13}$</td>
</tr>
<tr>
<td>(XeRb)$^+$</td>
<td>$1.31 \times 10^{15}$</td>
</tr>
<tr>
<td>$h\nu_{\text{Xe}_2^*}$</td>
<td>$7.74 \times 10^{20}$ (s$^{-1}$)$^a$</td>
</tr>
<tr>
<td>$h\nu_{(\text{XeRb})^+}$</td>
<td>$5.22 \times 10^{21}$ (s$^{-1}$)$^a$</td>
</tr>
</tbody>
</table>

$^a$ The Photon densities were differentiated with respect to time and are in units of s$^{-1}$cm$^{-3}$ therefore a multiplication by the emission energy yields power density in W/cm$^3$.

The results of the kinetic model with varied pressures are shown in Figs. 5-6, 5-7 and 5-8. The calculated and experimentally measured rubidium pressure dependence of the (XeRb)$^+$ species is depicted in Fig. 5-6. The solid line shows the (XeRb)$^+$ calculated yield peaking at about 1-2 Torr Rb pressure, while the dotted line, representing experimental results.
Fig. 5.4. $\text{Xe}_2^*$ calculated time dependence for 3 atm Ar and 100 Torr Xe.
Fig. 5.5 Kinetic model outputs of $\text{Ar}^+$, $\text{Xe}^+$, $(\text{XeRb})^+$ and $\text{Xe}_2^*$ for 3 atm Ar, 100 Torr Xe and 5 Torr Rb.
Fig. 5.6 Calculated and experimentally determined Rb pressure dependence of (XeRb)$^+$. 
Fig. 5.7 Calculated Xe$_2^*$ fluorescence yield as a function of Rb pressure for 3 atm Ar and 100 Torr Xe.

Fig. 5.8 Calculated (XeRb)$^+$ and Xe$_2^*$ yield as a function of argon pressure for 100 Torr Xe and 5 Torr Rb.
from this work, peaks at about 4 Torr. Both results then slowly fall off with increasing pressure. These results are also in agreement with the work of Schumann et al. (1990). Figure 5-7 shows the calculated \( Xe_2^* \) yield decreasing sharply with increasing rubidium pressure. This effect was observed experimentally in this work and also by Schumann et al. (1990) with the \((KrK)^+\) ionic excimer (where K is replaced by Rb). The most probable explanation of the quenching of \( Xe_2^* \) is due to the penning ionization process in Table 5.1, equation (29).

The calculated results for an argon, buffer gas pressure dependence is shown in Fig. 5-8. The \( Xe_2^* \) yield increases quadratically with increasing buffer gas pressure while the \((XeRb)^+\) yield increases slowly and linearly, this result also with \((XeCs)^+\) experiments [Millar et al. (1989b,c), Schumann et al. (1990)], and with a recent kinetic model developed by Schumann et al. (1990) of He/Kr/K admixtures.

Preliminary results from kinetic model described in Table 5.2, suggest a maximum \((XeRb)^+\) population of \(2 \times 10^{15} \text{ cm}^{-3}\) for a mixture consisting of 3 atm Ar, 50 Torr Xe and 4 Torr Rb. The population of \((XeCs)^+\) was also calculated by varying a few rate constants which were determined experimentally in section 5.2. The maximum population for \((XeCs)^+\) was determined to be \(4 \times 10^{15} \text{ cm}^{-3}\). Now that the upper state populations have been calculated, an analysis for the feasibility of laser radiation in these species can be discussed.

5.4 LASER PROSPECTS OF RARE GAS ALKALI IONIC EXCIMERS

When considering the feasibility of developing a laser, one of the most important parameters is the net small signal gain coefficient,

\[
G = [\sigma_{SE} N_{(Rg^+A)}] - [\sigma_{abs} N_A],
\]

(5-9)

where \( \sigma_{SE} \) is the cross-section for stimulated emission:
\[ \sigma_{SE} = \frac{\lambda^2 A_{12}}{8 \Pi} g(v) \]  

(5-10)

\( A_{12} \) is the Einstein coefficient, which is the inverse of the spontaneous lifetime of the molecule, \( \lambda \) is the transition wavelength. \( N(Rg^+A) \) and \( N_A \) in equation (5-9) represent the concentrations of the excited state rare gas alkali ionic molecules and the alkali atoms respectively. Assuming a normalized gaussian lineshape \( g(v) \), the value at the linecenter \( g(v_0) \) is given by:

\[ g(v_0) = \{2[\ln(2/\Pi)]^{1/2}\} / \Delta v \]  

(5-11)

where,

\[ \Delta v = c \Delta \lambda / \lambda^2 \]  

(5-12)

and \( c \) is the speed of light. Substituting equations 5-11 and 5-12 into equation 5-10 results in a cross-section for stimulated emission represented by:

\[ \sigma_{SE} = 0.037 A_{12} \lambda^4 / (c \Delta \lambda). \]  

(5-12)

The value for \( N(Rg^+A) \) was calculated from the kinetic model. The second term in parenthesis in equation (5-9) takes absorption into account. Photoionization of the alkali atoms should be the dominant process for absorption since the radiative emissions are not energetic enough to ionize the rare gas atoms. Figure 5-9 shows the atomic absorption cross-section \( \sigma_{abs}(cm^2) \) for the alkali metals [Marr and Creek (1968)]. \( N_A \) was estimated from vapor pressure curves [Nesmeyanov (1963)] and the cell temperature.

Using equation (5-9), a calculation for the small signal gain coefficient of \((XeRb)^+\) and \((XeCs)^+\) emissions was performed, for a gas fill optimized for greatest fluorescence yield, the
Fig. 5.9  Measured atomic absorption cross-sections for alkali metals [Marr and Creek (1968)].
results are summarized in Table 5.4. Although the Xe⁺Cs ionic excimer has a higher calculated density, the absorption cross-section of Cs at 160 nm is greater than Rb at 164 nm resulting in a higher positive net gas for the (XeRb)⁺ species. A gain coefficient of 0.02 cm⁻¹ should be sufficient to generate coherent radiation.
Table 5.4  (RgA)$^+$ Gain Parameters

<table>
<thead>
<tr>
<th></th>
<th>$\lambda$ (nm)</th>
<th>$\Delta \lambda$ (nm)</th>
<th>$\tau_{rad}$ (ns)</th>
<th>$\sigma_{se}$ ($10^{-18}$ cm$^2$)</th>
<th>$\sigma_{abs}$ ($10^{-19}$ cm$^2$)</th>
<th>GAIN ($10^{-2}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(XeCs)$^+$</td>
<td>160</td>
<td>1.5 ± 0.5</td>
<td>150 ± 50</td>
<td>4.0 ± 3</td>
<td>2.7</td>
<td>0.5</td>
</tr>
<tr>
<td>(XeRb)$^+$</td>
<td>164</td>
<td>1.5 ± 0.5</td>
<td>280 ± 50</td>
<td>2.5 ± 1</td>
<td>1.1</td>
<td>2.1</td>
</tr>
</tbody>
</table>
CHAPTER 6
SUMMARY

The main objective of investigating ionic excimers is to extend the well known excimer technology of bound free transitions in order to make lasers at shorter wavelengths (below 200 nm). Figure 6.1 represents an overview of the different classes of ionic excimers and their isoelectronic neutral counterparts along with the different excitation sources employed. Due to the higher pumping requirements of lasers at shorter wavelengths [Waynant and Elton (1976)], high energy pulsed electron beam pumping seems to be the most promising method of excitation. Low current ion beams and laser-produced plasmas have been proven to be excellent for spectroscopic analysis [Millar et al. (1989a), Fiedler et al. (1989)], however they are unable to create high upper state densities in this species due to the low pressures that are employed.

To this date lasing has not been observed in any class of ionic excimer. The alkali halide molecules have the problem of self absorption [Kubodera et al. (1990)] and the diatomic rare gas ions exhibit low fluorescence yields [Langhoff (1988)]. Other ionic excimer species have not yet been observed [Sauerbrey and Langhoff (1985), Basov et al. (1985a,b)]. The rare gas alkali ionic excimers, investigated in this work however appear to be promising species for generating coherent radiation in the VUV. The kinetic analysis provided by electron beam excitation yielded an estimated upper state population up to $10^{15}$ cm$^{-3}$ and cross-section for stimulated emission of $\sim 2 \times 10^{-18}$ cm$^2$. With photionization cross-sections for the alkalies $\sim 10^{-19}$ cm$^2$ at the fluorescence wavelengths of the (RgA)$^+$ species, the resulting net gain coefficients are $\sim 10^{-2}$ cm$^{-1}$. Since mirrors are available at these wavelengths, laser radiation from these species should be possible.

Our group is in the process of setting up a laser experiment for (XeRb)$^+$ at 164 nm using the newly designed single foil reaction cell which has demonstrated energy depositions
<table>
<thead>
<tr>
<th>Ionic Excimer</th>
<th>Isoelectronic Neutral Excimer</th>
<th>Experimental Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali Halide</td>
<td>Rare Gas Halide</td>
<td>Ion Beam</td>
</tr>
<tr>
<td>Cs$^{2+}$F$^-$</td>
<td>XeF</td>
<td>Laser Produced Plasma</td>
</tr>
<tr>
<td>185 nm</td>
<td>351 nm</td>
<td></td>
</tr>
<tr>
<td>Rare Gas Alkali</td>
<td>Diatomic Rare Gas</td>
<td>Laser Produced Plasma</td>
</tr>
<tr>
<td>Xe$^+$Cs</td>
<td>Xe$_2^*$</td>
<td>Ion Beam</td>
</tr>
<tr>
<td>160 nm</td>
<td>172 nm</td>
<td>e-Beam</td>
</tr>
<tr>
<td>Diatomic Rare Gas</td>
<td>Diatomic Halogen</td>
<td>e-Beam</td>
</tr>
<tr>
<td>Ar$_2^{2+}$</td>
<td>Cl$_2^*$</td>
<td>Ion Beam</td>
</tr>
<tr>
<td>213 nm</td>
<td>258 nm</td>
<td>Laser Produced Plasma</td>
</tr>
<tr>
<td>Rare Gas Halide</td>
<td>Diatomic Halogen</td>
<td></td>
</tr>
<tr>
<td>Xe$^{2+}$I$^-$</td>
<td>I$_2^*$</td>
<td></td>
</tr>
<tr>
<td>132 nm</td>
<td>342 nm</td>
<td></td>
</tr>
</tbody>
</table>
of up to 250 J/l at 5 atmospheres of buffer gas pressure, compared to \( \sim 80 \) J/l with the double foil cell. Providing that electron quenching really is not a dominant process in these species, this increased pumping energy should facilitate the observation of laser radiation by increased upper state densities.
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