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VACUUM ULTRAVIOLET STUDIES OF RARE GASES AND RARE GAS MIXTURES
EXCITED WITH PULSED HIGH ENERGY ELECTRON BEAMS

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VACUUM ULTRAVIOLET STUDIES OF RARE GASES AND RARE GAS MIXTURES EXCITED WITH PULSED HIGH ENERGY ELECTRON BEAMS*

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Preliminary studies are reported on the properties of the rare gas systems argon, krypton, and xenon excited with high current density, energetic, pulsed electron beams. The excited media are examined through observation of the vacuum ultraviolet spontaneous emission originating from the molecular species formed in the excited medium. Experimental data are presented concerning energy transfer processes in Ar/Xe mixtures as well as time resolved spectra of pure Ar, Kr, and Xe in the wavelength region from 1100Å to 2500Å. For the case of 1500Å band arising from transitions in the krypton dimer, we present evidence of gain narrowing of the spontaneous emission line at a pressure of five atmospheres.

INTRODUCTION

The ultraviolet continua of the excited rare gas systems have been known since the 1930's.¹ These continuum emissions have also been examined more recently² and have found application as convenient light sources covering essentially the entire vacuum ultraviolet for wavelengths longer than approximately 1000Å. These continuous radiations originate from bound-free transitions of the molecular dimers (e.g. Ar₂, Kr₂, or Xe₂). In typical cases of interest the excited state is characterized by a potential function $V^*(R)$ which has a substantial potential minimum at an internuclear separation R_0 and which supports several vibrational levels. In contrast, the ground state interatomic potential $V(R)$ is generally strongly repulsive for $R \sim R_0$ although it does exhibit a relatively shallow van der Waals minimum at internuclear distances substantially greater than R_0 . Figure (1) schematically illustrates these potential curves. It is characteristic that the triplet state lies somewhat below the singlet level due to exchange. In the literature the data on He₂ and Xe₂ are the most complete although large uncertainties nevertheless do exist in the precise location of many of the potential curves even in these

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cases.³ The complex nature of these molecular systems is immediately recognized by the fact that over 60 electronic states are currently known for even the simplest system He_2^+ .

To a very good approximation, these excited molecular dimers can be regarded as Rydberg states. In this view the molecular configurations are then comprised of two parts; the molecular ion core (e.g. He_2^+) and a single excited electron orbiting largely outside of the region occupied by the core. One then has a relatively simple Rydberg series⁴ characteristic of that core state. This model predicts that the equilibrium internuclear separation R_0 , the molecular vibrational frequency, and the molecular moment of inertia are determined largely by the corresponding properties of the molecular ionic core. The potential curves given by Ginter and Battino³ for He_2^+ quite strikingly indicate the validity of this approximate model. It would appear that this feature introduces a very desirable simplification into an otherwise rather complicated situation, since it should be possible to formulate meaningful estimates of matrix elements on the basis of an essentially one electron picture.

Figure 1

Plot of potential energy vs. internuclear separation (R) for ground state ($V(R)$) and typical lowest excited molecular states ($V^*(R)$).

An interesting property of these systems derives from the fact that certain of these continuous bands are observed with very similar characteristics in all three phases, gas, liquid, and solid. For example, the argon continuum centered near $1300\text{\AA}$ resulting from excitation by Americium α -particles exhibits essentially identical lineshapes (within $\sim 10\%$) for all three phases.⁵ On the basis of this observation, one is strongly motivated to conclude that the excited species in all cases very closely resemble the gaseous dimer which is only negligibly influenced by the weak van der Waals forces of the surrounding neighbors in the liquid and solid. This immediately suggests the possibility that these systems may be successfully operated at liquid or solid density. In this connection it is useful to note that at an active density of $2 \times 10^{19} \text{ cm}^{-3}$ (~ 1 atmosphere) and assuming roughly one Rydberg per system the stored energy density corresponds to nearly 50 kilojoules/liter.

Recent Soviet experiments with xenon excited by high energy electrons reported by N.G. Basov et al⁶ have demonstrated the feasibility of coherent generation with these systems at liquid density. The Russian workers have also indicated in private communication⁷ that they have obtained similar results in high pressure xenon gas. It is anticipated that oscillation may be obtained from the other rare gases in a similar manner.

The basic purpose of this work is to provide a more detailed experimental analysis of the rare gas systems excited by pulsed, high current, relativistic electron beams. In order to achieve this goal we have begun experiments which enable us to measure the time resolved spontaneous emission spectrum of the material excited by the electron beam. In this way we have obtained data concerning the kinetic steps and time scales associated with these systems. Herein we present some preliminary data and analysis relating to our experiments examining Ar, Kr, and Xe at pressures from zero to five atmospheres.

DISCUSSION OF SOME MECHANISMS OPERATIVE IN THE RARE GAS MOLECULAR SYSTEMS

Although the rare gases are normally considered to comprise one of the simplest classes of materials, we nevertheless find that several processes contribute to the kinetic scheme which leads to neutral molecular formation. Some of these processes, illustrated by the example of Xe, are the following:

Reactions (1) and (2) represent the excitation and ionization generated by both the high energy primary electrons as well as the sufficiently energetic secondaries. Electrons can also lose energy radiatively. However, for the electron energies of interest, this loss is low being less than $\sim 8\%$ in the highest Z case, xenon.⁸ Of course, for the lighter materials this figure is even smaller. Thus, we neglect radiative loss processes. These excited and ionized atoms will then subsequently combine in 3-body processes to form the corresponding molecule and molecular ion as represented by (3) and (4). The dissociative recombination process (5) then provides a channel to convert the ionized material into excited atomic species. For the rare gases this process is quite fast except for the case of helium.⁹ The abnormally slow rate for helium is believed to be related to the lack of an appropriate curve crossing of a dissociative neutral molecular state with the ionic bound potential curve.¹⁰ Process (6) illustrates a spontaneous radiative bound-free transition of the molecular system corresponding, for example, to the $3\Sigma_u^+ \rightarrow 1\Sigma_g^+$ transition shown in Fig. (1). This transition is an allowed electric dipole process through spin-orbit coupling. Indeed, in the higher Z materials (e.g. Kr_2^* and Xe_2^*) it is anticipated that the spin selection rule is quite ineffective as it is in the atomic case.¹¹ Atomic and molecular relaxation processes are indicated in (7), (8), and (9). In the atomic case it is desired to collapse the manifold of excited states to the $3P_2$ level which correlates with lowest molecular excited state^(3b) ($1S_0 + 3P_2 \leftrightarrow 3\Sigma_u^+$). Both electrons and atoms can participate in these processes. Slow electrons can be very important particularly involving magnetic transitions and transitions requiring a change in the electronic spin state. For instance in neon, Phelps¹² has determined the relaxation rates of $3P_1 \rightarrow 3P_2$ through collisions with neon atoms and electrons. For the atomic collision partners the cross section is of the order of $\sim 10^{-19} \text{ cm}^2$ while for the electrons the cross section is $\sim 10^{13} \text{ cm}^2$ which is essentially the theoretical maximum imposed by unitarity¹³ for S-wave scattering of thermal electrons. Molecular vibrational relaxation is illustrated as reaction (8). It is anticipated that this may be a very efficient process requiring only a few gas kinetic collisions on account of the possibility of resonant atom

exchange. Helium, however, apparently constitutes an exception to this expectation. Callear and Hedges¹⁴ report that the vibrational relaxation of the $\text{He}_2(a^3\Sigma_u^+, v=1)$ state is "abnormally slow." A long range repulsive potential which keeps the atom and molecule at relatively large distances, and thus preventing the exchange process, could account for this observation in helium. Finally, processes (10) and (11) illustrate photoionization and Penning ionization of the excited dimer states. Taken together these reactions represent losses of both photons and radiating molecular systems. Since the lowest excited molecular state is more than half way up from the molecular ground state to the convergence of the Rydberg series at the ground molecular ionic state,¹⁵ the frequency of the $^3\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ transition is sufficient to photoionize the $^3\Sigma_u^+$ state. This will then be a stimulated loss process diminishing the optical gain on the $^3\Sigma_u^+ \rightarrow ^1\Sigma_g^+$ transition. The Penning process is also undesirable. Given a time scale for pumping, the rate of the Penning process will establish an upper bound on the attainable energy density storage. Although these cross sections are not presently known for the rare gas systems, the rate has been measured for the process¹⁶

involving the helium metastable $\text{He}(2^3S_1)$. The cross section σ was determined to be $\sigma \approx 10^{14} \text{ cm}^2$, a quite substantial value. For the moment assume that the molecular process (11) possesses a similar value and that the available pumping time τ is $\sim 50 \times 10^{-9}$ seconds. We may then roughly estimate the bound on the excited particle density n by equating $n\nu\sigma \approx 1/\tau$ where ν is the mean relative intermolecular speed. This gives $n \approx 10^{17} \text{ cm}^{-3}$ which, assuming a Rydberg per system, corresponds to only ~ 250 joules/liter. This is a fundamental limitation which emphasizes the need for a rapid means of excitation.

The loss processes (10) and (11) may be considered from a unified point of view. Diagrammatically, the photoionization process (10) can be represented as

10a

where I denotes the appropriate intermediate autoionizing state. In a similar manner the amplitude for the Penning reaction (11) may be symbolized as

in which the photon now appears as a propagator rather than an external line. In a certain sense, the latter (11a) may be regarded as a photo-ionization process quite similar to the former (10a), but with the photon not necessarily on the mass shell (i.e. $\omega \neq c|k|$).

EXPERIMENTAL APPARATUS

A schematic of the experimental apparatus is shown in Fig. (2). The basic parameters of the electron beam which provides the primary excitation are a mean particle energy of approximately 1.5 MeV, a current density of $\sim 2 \times 10^3$ amps/cm², and a pulse duration of $\sim 40 \times 10^{-9}$ seconds. This device, known as a Febetron, is an 80 stage capacitor bank arranged in a Marx configuration. Each stage was charged to ~ 30 KV producing 2.5 megavolts across a field emitting diode consisting of a thin (1.5 mil) titanium anode and a fork-like array of needles serving as the cathode; the effective impedance of the tube being $\sim 400 \Omega$. The machine contains an internal D.C. solenoid which serves to guide the electron beam formed by the tube repeatedly through the titanium output windows. This arrangement, although putting severe limitations on the repetition rate due to overheating, provided the uniformity of characteristics assuring the repeatable performance necessary to conduct these experiments.

Triggering of the machine is accomplished by a low jitter trigger amplifier consisting of a precharged length of coaxial cable switched by a hydrogen filled thyatron thereby providing a 20 KV pulse to the trigger electrodes of the first Marx stage. The total energy output is 400 joules (measured at the tube output face), the peak total beam

output current is 9000 amps (measured with a Faraday cup) with a current rise time of 10^{-8} nanoseconds.

The output of the electron beam machine enters the gas chamber through another thin (~ 3 mil) titanium window where it is guided magnetically through the use of a focusing coil energized by a 20 kilovolt capacitor bank. Since the response time of the magnetic guide field circuit is very long (> 50 μ sec) on the time scale of interest (≤ 400 nsec), the value of the magnetic field during the experiment can be regarded as constant. At the far end of the magnetic coil it is observed that the electron beam rapidly expands and terminates on the tube walls. The time integrated electron current density spatial profile for the beam propagating in one atmosphere of air is illustrated in Fig. (3). The profiles correspond to various distances along the axis of the gas chamber tube in the region where the axial external

Figure 2
Schematic representation of important system interconnections

Figure 3

Isodensitometer recordings of time-integrated electron deposition (1.0 Atm. Air) as a function of distance from the electron beam source plane. Numbers to the side of each disc indicate distance in inches. The beam profile is roughly gaussian with 90% of its energy inside a 2 cm diameter. This figure scale is very nearly 1:1.

guide field is effective. These densitometer readings show that the beam propagates with essentially cylindrical symmetry very nearly down the center of the tube. Further indications concerning the propagation characteristics of the electron beam appear in figures (4) and (5). Figure (4) illustrates the ionization trace in 10 atmospheres of helium while Figure (5) shows the results obtained in 5 atmospheres of xenon.

Optical observations of the active medium are made through the LiF window terminating the gas chamber and located at a sufficient distance from the magnetic coil so that very little, if any, flux is incident upon it. Inspection of this window after more than 200 shots showed it to be perfectly clear and completely free of any signs of radiation damage. The emission from the excited gas is then viewed along the axis of the electron beam through an evacuated light pipe equipped with a turning mirror (front surfaced with Al and MgF_2 overcoated).

Figure 4

Time integrated, visible emission generated by electron beam propagated through 10 atmospheres of He gas for a magnetic guide field of 15 Kgauss.

The radiation so observed then fell on the entrance slit of an evacuated spectrometer.¹⁷ A photomultiplier encased in 1 1/2 inches of lead¹⁸ with a sodium salicylate disc was used to register the output signal. The signals were photographed on two oscilloscopes; one (a Tektronix 454 or a 7904) recorded the photomultiplier output while the other, a dual beam Tektronix 556, registered both a timing pulse from the electron beam machine as well as the photomultiplier output. Figure (6) illustrates a typical trace from the former corresponding to a measure of 850 torr of xenon at 1700A with a horizontal setting of 100 nsec/cm. In order to eliminate the presence of electromagnetic transients, all the sensitive electronic components were enclosed in a screen room. The remaining noise signal, primarily due to x-rays, was always less than 10 millivolts and entirely negligible in these experiments. The vacuum system was connected to a turbo-molecular pump and the pressure in the gas chamber was measured with a capacitance manometer.

Figure 5
Time integrated visible emission generated by electron beam propagated through 5 atmospheres of xenon gas for a magnetic guide field of 15 Kgauss.

Figure 6

Polaroid recording of typical timing trace. Lower trace shows voltage history of the field emitting diode. Upper trace shows typical spontaneous emission with a horizontal scale of 100 ns/cm.

EXPERIMENTAL RESULTS

Data were taken on pure Ar, Kr, and Xe as well as Ar-Xe mixtures at gas pressures between zero and 5 atmospheres. In addition, some preliminary measurements were performed on H_2 and H_2 -Ar mixtures.

In order to reduce the raw photographic data, the experimental traces of intensity versus time, along with the other relevant parameter (e.g. spectrometer wavelength, gas composition, gas density) were converted to digital form and stored in a multi-dimensional array. This facilitated various elementary operations on the data which otherwise would have been rather tedious. For example, this enabled us to examine the spectral intensity distribution $I(\lambda)$ as a function of wavelength λ for particular values of time t after the beginning of high energy current pulse.

Ar-Xe Mixtures

Rapid energy transfer between $\text{Ar}_2^* (^1\Sigma_u^+)$ and xenon atoms in the process

has been reported by the group working at Tel-Aviv.¹⁹ They describe a strong quenching of the 1300Å Ar_2 continuum²⁰ through the addition of a xenon impurity. The Israeli work involved conditions of relatively weak excitation densities in comparison to these attainable ($\sim 10^{10}$ watts) with the pulsed electron beam. It was desired to observe this energy transfer process under the conditions of substantially augmented excitation possible with this apparatus.

Figure (7) shows the observed emission at 1300Å from pure argon at 850 torr pressure at a horizontal setting of 100 nsec/cm. Considerable

Figure 7

Polaroid recording of 1300Å ($\pm 5\text{\AA}$) argon emission, 850 torr (12 Kgauss diatnetic field). Horizontal scale: 100 nsec/cm. Vertical scale: 400 mv/cm. $S/N \geq 80/1$, where the noise (N) is defined as the residual signal with the detector blinded.

radiation attributable²¹ to the lower vibrational levels of the $1\Sigma_u^+ \rightarrow 1\Sigma_g^+$ transition of Ar_2^* is present.²¹ Tanka and Yoshino²¹ conclude that the contribution of the $3\Sigma_u^+ \rightarrow 1\Sigma_g^+$ transition should be small in argon. However, in the higher Z systems krypton and xenon the triplet and singlet transitions are anticipated to have comparable strength. The influence of the addition of 30 torr of xenon to 820 torr of argon on the intensity of the 1300Å argon continuum is illustrated in Figure (8). All other parameters including the vertical sensitivity are identical to those of Figure (7). The argon molecular continuum is essentially eliminated by the presence of the xenon additive. The xenon atoms, once excited to the $1P_1$ level, are strongly trapped²² and should eventually relax by both collisional quenching to the triplet states and by molecular formation of Xe_2^* in the process²³

Figure 8
 Polaroid trace of 1300Å ($\pm 5\text{\AA}$) argon emission from a mixture of 820 torr argon + 30 torr xenon (12 Kgauss magnetic field). Compare with Figure 7. Horizontal scale: 100 nsec/cm. Vertical scale: 200 mvolt/cm. $S/N \geq 40/1$, where the noise (N) is defined as the residual signal with the detector blinded.

We observe that this reaction is quite similar to process (3) except that the third body is argon instead of xenon. In the approximation that the third body participates largely through the relatively long range van der Waals interaction, it should be possible to estimate the ratio of the rates for (3) and (14), since the van der Waals force involves the atomic polarizabilities in a known manner.²⁴ This aspect is presently under examination. The signature of Xe_2^* formation²³ is the appearance of the molecular xenon emission at $\sim 1700 \text{ \AA}$. Since the xenon partial pressure is considerably less than that of the argon, it is anticipated that the formation rate of the Xe_2^* species will be less than for the Ar_2^* observed without the xenon present. Figure (9) shows the time dependence (100 nsec/cm) of the emission observed at

Figure 9
Polaroid trace of $1700\text{\AA} (+5\text{\AA})$ emission of Xe_2^* produced from a mixture of 820 torr argon + 30 torr xenon (12 Kgauss magnetic field). Horizontal scale: 100 nsec/cm. Vertical scale: 200 mvolt/cm.

1700Å in the mixture consisting of 30 torr Xe and 820 torr Ar. These conditions are identical to those existing in Figure (8). Figure (10) illustrates the data of Figure (9) with a horizontal sweep of 500 nsec/cm enabling observation of the complete time development of the emission at 1700Å. These data are completely consistent with the conclusions of Gedanken et al¹⁹ concerning the efficient energy transfer process (13). A quantitative appraisal of the rates is currently in progress. We do find however, that significantly greater concentrations of xenon impurity are required to fully quench the 1300Å Ar₂ emission than was necessary in the experiments of Gedanken et al¹⁹ where an impurity level of less than 100 ppm was completely effective. Although no quantitative analysis has yet been performed, we believe that this observation is fully consistent with the enormously greater excitation rates of our experiments and which would lead to a saturation of the excited state density of a sufficiently low level xenon impurity. It

Figure 10

Identical to Figure 9 with the exception that the horizontal scale is increased to 500 nsec/cm.

is significant in this connection to observe that the curve in Figure (9) very closely approximates the integral of the trace shown in Figure (7). This is consistent with an efficient transfer from the Ar_2^* to the Xe atoms generating a population of $^3\text{P}_2$ Xe atoms through collisional cascade from the $^1\text{P}_1$ level. Under such circumstances an essentially complete inversion of the xenon $^3\text{P}_2 - ^1\text{S}_0$ system is expected.¹⁹ It is sufficient that in order to achieve this condition the rate of process (13) must substantially exceed the single radiative rate (untrapped) for the allowed $1295\text{\AA}$ $^1\text{P}_1 \rightarrow ^1\text{S}_0$ xenon transition. This certainly represents the worst case, since we have ignored the role played by cascade relaxation from the $^1\text{P}_1$ level which will clearly tend to reduce radiative losses. An active density of Ar_2^* corresponding to only a few torr is required to satisfy this condition with the rates given in Ref. (19), a situation that would appear to be fairly readily achieved with this experimental apparatus.

Pure Argon, Krypton, and Xenon Studies

Pure argon, krypton, and xenon samples were studied over a wide range of densities. These investigations examined the spectral features of these materials in order to appraise the detailed properties including the time dependence of the atomic and molecular populations. The major fraction of the data was taken in the wavelength region from $1100\text{\AA}$ to $2500\text{\AA}$ with a resolution of $50\text{\AA}$ at gas pressures varying from 250 torr to 850 torr. In the later stages of these experiments a strengthened gas chamber was used enabling the examination of material up to pressures of ten atmospheres.

Argon. The spectra of pure argon at 850 torr are illustrated in Figure (11) and Figure (12). The data of Figure (11) show the spectrum for relatively early times (50, 75, 100, 125, 150 nsec) after the initiation of the electron beam. Figure (12) follows the development of the spectrum out to substantially greater times (150, 200, 250, 300, and 400 nsec). The feature centered at $1300\text{\AA}$ corresponds to the principal continuum²⁵ attributable to low vibrational states of the $1\Sigma_u^+ \rightarrow 1\Sigma_g^+$ transition²¹ as discussed earlier. However, a main feature of these results is the observation of considerable emission at longer wavelengths between approximately $1800\text{\AA}$ and $2400\text{\AA}$. Moreover, the structure of this radiation has a rather marked time dependence. Similar longer wavelength components have also been observed under other experimental conditions^{21, 26} Hurst et al suggest that these observations can be explained as recombination spectra "involving the formation of argon excimers with binding energies of about 4 eV." In view of the curves available on helium^(3a) and xenon^(3b) and the anticipated systematics of the rare gas systems, a binding energy of this magnitude would appear to be somewhat excessive. We will return to a discussion of these inadequately understood continua at a later point.

Figure 11

Computer generated, time resolved spectra for argon at 850 torr, time is given in nanoseconds, for $t < 150$ ns. ($t=0$ taken as the 50% point on the rise of the voltage across the field emitting diode) Magnetic field 12 Kgauss. Vertical scale: Intensity in arbitrary units. Horizontal scale: wavelength in thousands of angstroms. 1 $\equiv$ 50 ns. 2 $\equiv$ 75 nsec. 3 $\equiv$ 100 nsec. 4 $\equiv$ 125 nsec. 5 $\equiv$ 150 nsec.

Figure 12

Same as Figure 11 but for later times as noted below.

1 $\equiv$ 150 nsec. 2 $\equiv$ 200 nsec. 3 $\equiv$ 250 nsec. 4 $\equiv$ 300 nsec. 5 $\equiv$ 400 ns.

Krypton. Spectral data for pure krypton at 850 torr are plotted in Figure (13) for early times (50, 100, and 150 nsec) and in Figure (14) at correspondingly later intervals (150, 200, 250, 300, and 400 nsec). The spectral feature located at 1500Å is at the position of the expected molecular continuum originating from transitions between the lowest lying bound excited states and the repulsive ground state. Very probably this radiation arises primarily from a set of completely vibrationally thermalized levels of the $^3\Sigma_u^+$ state although we cannot rule out the presence of a contribution from the $^1\Sigma_u^+$ state on the basis of these and other data taken at higher resolution. As in the case of argon, a substantial amount of radiation centered at approximately 2200Å is observed at longer wavelengths. The component at 2200Å which is strong and broad at early times relaxes initially to a narrower feature and then decays in amplitude at longer times. The time dependence of the 1500Å continuum, however, is observed to have a roughly reciprocal behavior in relation to the 2200Å component;

Figure 13

Same plot as Figure 11 but for Krypton gas at 850 torr for times noted below. 1 $\equiv$ 50 nsec. 2 $\equiv$ 75 nsec. 3 $\equiv$ 100 nsec. 4 $\equiv$ 125 nsec. 5 $\equiv$ 150 nsec.

at early times it is relatively weak and grows to its maximum as the 2200Å emission diminishes in strength. This type of response is very suggestive of a radiative cascade process in which the higher states radiating at $\sim$ 2200Å produce population in the levels responsible for the 1500Å continuum. Nevertheless, it has not been possible to unambiguously identify the origin of the longer wavelength 2200Å component. In certain respects this situation is analogous to the observations in argon and to other experimental results reported for xenon.(3b) We will return to this point later.

Since the molecular formation process(3) is a three body event, the rate should scale like the square of the gas density. The excited state populations of Kr_2^* should then be greatly enhanced at higher densities. With this in mind, it was decided to examine the 1500Å continuum of krypton under higher resolution as a function of density in order to detect the presence of gain narrowing of the spontaneous emission line.²⁷ Krypton was selected largely on the basis of certain

Figure 14

Same plot as 11 but for Krypton gas at 850 torr for times noted below.
 1 $\equiv$ 150 nsec. 2 $\equiv$ 200 nsec. 3 $\equiv$ 250 nsec. 4 $\equiv$ 300 nsec. 5 $\equiv$ 400 ns.

experimental considerations. In order to optimize the observation of gain narrowing, it is desired to maximize the product $g_0 l$ of the gain coefficient g_0 and the effective length l . For a variety of reasons including the propagation properties of the electron beam at pressures above one atmosphere and the need for a relatively high Z to break the spin selection rule for $3^2P_{1/2} + 1^2P_{1/2}$ transitions, the optimum material for our experimental conditions appeared to be krypton. The normalized line profiles of the Kr 1500Å continuum at one atmosphere and five atmospheres are illustrated in Figure (15). The instrumental resolution in both cases is $<5.0\text{\AA}$. The wings of the line are very nearly the same while a clearly discernible narrowing occurs in the vicinity of the maximum of the five atmosphere curve. This is precisely the type of behavior expected for a gain narrowed resonance; the greatest effect should occur at the peak of the line. There is, however, another effect which could cause a density dependent line narrowing simulating the narrowing effect due to optical gain. This

Figure 15

Normalized line profiles for krypton gas at 1 atm. (outer curve) and at 5 atm. (inner curve). Magnetic field strength at all points was 12 Kgauss. is vibrational relaxation of the excited Kr_2^* dimer according to process (8). It is easily seen from the potential curves shown in Figure (1) that the radiation pattern characteristic of an ensemble of vibrationally excited systems will be broader than that for a vibrationally relaxed ensemble. This is simply due to the Franck-Condon principle; the vibrationally excited systems correspond to a greater energy breadth on the repulsive ground state potential curve. In order to check this possibility, we have made estimates based on Mulliken's^(3b) curves for xenon of the linewidth expected for the krypton 1500Å continuum radiated by a completely thermalized distribution of vibrational levels in the excited $^3\Sigma_u^+$ state. This is necessarily an approximate statement based on the expected similarity of the krypton and xenon potential curves, but we believe that it is sufficient for our purposes. Within the framework of this assumption we find that the linewidth observed at one atmosphere is consistent with that anticipated from a vibrationally thermalized distribution

of electronically excited krypton dimers. Moreover, it is suspected that the rate of vibrational relaxation of the excited molecules is very fast on account of atom exchange. On this basis, we conclude that the data illustrated in Figure (15) constitute reasonably definitive evidence of genuine optical gain and that it is very improbable that the line narrowing effect is due to vibrational relaxation. In order to conclusively verify this preliminary interpretation, we are currently fabricating a high pressure cell in a transverse geometry (optical axis perpendicular to electron beam axis) which will enable an optical cavity to be coupled to the excited medium. If optical gain is present, coherent oscillation should be observed under these conditions.

Xenon. Experiments were conducted on pure xenon under conditions identical to the argon and krypton studies. Figure (16) illustrates

Figure 16

Same plot as 11 but for xenon gas at 850 torr for times noted below.

1 = 50 nsec. 2 = 75 nsec. 3 = 100 nsec. 4 = 125 nsec. 5 = 150 nsec.

a typical result for the spectrum observed in xenon at 850 torr for times of 50, 75, 100, 125, and 150 nanoseconds after the initiation of the electron beam. Under these circumstances the peak emission is located somewhat longward of $1800\text{\AA}$. In the spectral region from $1100\text{\AA}$ to $2500\text{\AA}$ essentially all of the observed radiation is confined to the interval between $1600\text{\AA}$ and $2000\text{\AA}$. On the basis of Mulliken's approximate curves,^(3b) and to within the $50\text{\AA}$ resolution of these measurements, it is possible to associate the peak $\sim 1850\text{\AA}$, from the lowest vibrational levels of the $^3\Sigma_u^+$ state undergoing a transition to the repulsive $1\Sigma_g^+$ state. Of course, since the $1\Sigma_u^+$ state is believed to be relatively close to the $^3\Sigma_u^+$ level, a component due to this state may also be present. However, the shape of the observed spectrum in xenon has somewhat different properties at lower density (e.g. 400 torr). Under these conditions a second peak is seen at $\sim 1700\text{\AA}$. In this connection it is interesting to note that the laser oscillation recently observed²⁸ in high pressure xenon gas occurred at the wavelength of $1716\text{\AA}$ with an approximate width of $\sim 17\text{\AA}$. This indicates that the transitions involved in the stimulated emission process $\sim 1716\text{\AA}$ differ from those generating the peak of the spontaneous emission spectrum in our experiments at the pressure of 850 torr. The wavelength difference suggests a differential of $\sim 4000\text{ cm}^{-1}$ in the degree of excitation of these two sets of states. Again, on the basis of Mulliken's potential curves^(3b), the $1700\text{\AA}$ component may be due to the high vibrational levels of the $1\Sigma_u^+$ and $^3\Sigma_u^+$ states.²⁹ This is consistent with the more marked appearance of the $1700\text{\AA}$ peak in spontaneous emission at lower pressure, since rapid vibrational relaxation at the higher pressures will have a tendency to broaden the band causing the $1700\text{\AA}$ peak to merge with the adjacent continuum at $\sim 1850\text{\AA}$. The shoulder visible at $1700\text{\AA}$ in Figure (16) is indicative of this type of behavior.

DISCUSSION OF RESULTS

The continua of argon, krypton, and xenon at approximately $1300\text{\AA}$, $1500\text{\AA}$, and $1700\text{\AA}$ respectively have been observed in these materials excited with relativistic electron beams. These bands are attributed to transitions from the lower excited states of the excited homonuclear dimers to the $1\Sigma_g^+$ ground repulsive state. In addition, we have seen the appearance of considerable radiation displaced to longer wavelengths in argon^{21,26} and krypton. A similar result has also been reported^{3b} in xenon at $\sim 3000\text{\AA}$.³⁰ Such longer wavelength continua then appear to systematic phenomena.³¹ In these experiments it seems quite unlikely that they are generated by impurities or fluorescence of the LiF window. Although the evidence for this conclusion is presently far short of a proof and further diagnostics will be required to explicitly verify this issue, this view appears quite reasonable in light of the fact that these continua are characteristic of the specific materials and that the LiF window showed no indication of radiation damage.

At this point the precise origin of these longer wavelength continua is not clear. Initially, it is tempting to associate them with transitions between higher excited states of the first Rydberg

series of the excited dimers. Difficulty with this interpretation, however, is encountered immediately. For example in krypton, the available energy range between the Kr_2 ($^3\Sigma_u^+$) state and the lowest corresponding ionic state $\text{Kr}_2^+ + e^-$ is not sufficient to accommodate a transition at 2200Å. The same conclusion follows in argon and also for xenon in the case of the $\sim 3000\text{\AA}$ continuum as pointed out by Mulliken.^{3b} If one wishes to assign the origin of these spectral features to the rare gas dimer states, it appears that an alternative description is required. One possibility, although quite speculative, is the presence of additional states based upon an excited core configuration³² as suggested by Mulliken in the example of xenon.^{3b} Although the correctness of this particular hypothesis cannot be established at the present time, the systematic features of the experimental observations provides a strong impetus for the supposition that the origins of these emissions are related in a correspondingly regular fashion in the three materials under study.

From the point of view of energy storage for pulsed laser applications, the heavier rare gas molecular systems (i.e. Kr_2^* and Xe_2^*) do not have conveniently long radiative lifetimes. To a very considerable extent this difficulty is circumvented by energy transfer to a metastable state which may occur with impressive efficiency as the measurements on the Ar-Xe mixtures appear to indicate. From the curve illustrated in Figure (10) it is observed that the energy content in the lowest excited atomic xenon levels, presumably mainly the 3P_2 state, has a lifetime of nearly two microseconds. This is considerably longer than the lifetimes of the corresponding molecular states which radiate strongly to the ground state.

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