LOW-POWER PHOTOLYTICALLY PUMPED LASERS

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ABSTRACT

We have carried out an extensive series of measurements of the time-resolved Xe_2^* emission spectra following optical pumping by a short-pulse F_2 laser at 157.6 nm. Most measurements were performed using a gated OMA detector; to increase our confidence in the results, we also made measurements using a scanning monochromator fitted with a photomultiplier and using a boxcar integrator for time resolution. The two sets of results agree well and show that both the singlet and triplet emission bands are broader than expected and have center wavelengths closer together than expected. Curve fits to the data yield the parameters for the fully relaxed states:

$$\text{Triplet: } \lambda_c = 1714 \pm 6 \text{ \AA} \quad \Delta\lambda = 122 \pm 2 \text{ \AA}$$

$$\text{Singlet: } \lambda_c = 1704 \pm 6 \text{ \AA} \quad \Delta\lambda = 131 \pm 3 \text{ \AA}$$

Measurements were performed both at room temperature and at elevated (140°C) and reduced (-27°C) temperatures.

The broad bandwidth of the individual spectral bands was unexpected and, in particular, conflicted with a previous spectral measurement using optical pumping by the Xe^* resonance line from a microwave discharge lamp. Therefore, we also performed a series of spectral measurements using this type of optical pumping. We achieved good agreement with some previous results in the literature, but not with the result in question. We conclude that the present results are reliable.

The results presented in this report therefore provide the first definitive measurement of the individual excimer emissions from each of the $\text{Xe}_2(\text{O}_u^+)$ and $\text{Xe}_2(1_u)$ states. From these measurements and the known ground state potential, we derived a 1_u potential that reproduces the emission band very well. In a similar manner, it will be possible to derive a potential for the O_u^+ state. However, the 1_u potential is in substantial disagreement with the recent 1_u potential derived by the Toronto group [LLS85]. From these potentials, it should be possible to calculate with reasonable accuracy the Xe_2 emission and absorption under various temperature and pressure conditions.

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I INTRODUCTION

Objective

Past work in this laboratory and elsewhere has shown that the pure rare gases can very efficiently convert energy deposited by charged particles (e.g. by a high-energy electron beam) into narrow-band vacuum ultraviolet (VUV) radiation. For example, we have shown that, for many combinations of pumping rate and gas pressure, both krypton and xenon radiate nearly 50% of the energy deposited by a high energy electron beam [ELB82]. This efficient source of VUV radiation can have many applications in photochemistry. The radiation from these rare gases results from bound-free transitions from the lowest lying pair of excimer states consisting of a singlet 0_u^+ state and a triplet 1_u state. In Xe_2^* at room temperature and for pressures above about 1 atm the emission bands from the two states overlap to produce radiation in the so-called second continuum centered at 172 nm and with a FWHM of approximately 13 nm (see Figure 1).

This study was conducted in support of a program in which it is important to know the emission spectrum produced by Xe_2^* when the xenon is at temperatures as high as several thousand degrees kelvin and also to know the emission spectrum as modified by self-absorption in the hot xenon. (At room temperature, absorption occurs on the pressure-broadened atomic transition at 147 nm or from the weakly bound ground state dimer in the first continuum at wavelengths shorter than about 160 nm, as shown in Figure 1. As the temperature increases, transient dimers formed during high speed collisions lead to absorption on the blue edge of the second continuum.) The objective of our work was to establish the temperature dependence of these spectra.

Approach

If the potential curves of the upper and lower states of a transition are known, then both the emission and self-absorption spectra can be calculated for any desired temperature, pressure, and path length. Thus, the most desirable approach to the present problem is to establish those potential

FIGURE 1 SIMPLIFIED SPECTROSCOPY OF XENON ATOMIC AND MOLECULAR EMISSION

From E. H. Fink and F. J. Comes, Chem. Phys. Lett. 30, 267 (1975).

curves through a combination of literature review and evaluation, selected experiments, and analyses. However, because of the uncertainties inherent in that approach, it is also important to verify those results through direct measurement of emission spectra from Xe_2^* produced at high temperatures. We intended to pursue both approaches. The details of the first part, namely, the determination of the potential curves, are described below. We planned to accomplish the second part by measuring emission spectra from xenon excited by a pulsed electron beam where the xenon had been heated by both the incident and reflected shock waves in a shock tube. However, because of the premature termination of the program, we were only able to complete the first part, namely, the determination of the potential curves.

In most cases, it is straightforward to determine the difference between the potential curves for the upper and lower states of a transition by measuring the spectrum of that transition. Then, if the potential curve for either the upper or lower state is known, the other curve can be determined. As we show in Section V, information is available in the literature that allows determination of the potential curve of the repulsive ground state of Xe_2 with sufficient accuracy. However, in xenon, as in all the rare gas excimers, the singlet and triplet bands overlap, so the spectra for the individual 1_u and 0_u^+ states cannot readily be determined from most emission measurements. When we began this study, only two measurements of the Xe_2^* emission spectra were available that purported to represent solely the spectrum of either the pure singlet state [FMC71] or the pure triplet state [ACR74]. There have also been recent high-resolution laser-induced fluorescence spectra of Xe_2^* obtained by pumping at 148.5 and 150 nm [LLS85]; these measurements probed the high vibrational levels (near the dissociation limit) of the 0_u^+ and 1_u states and allowed determination of the spectroscopic constants T_e , x_e , and $\omega_e x_e$ for both states. The only parameter that could not be accurately determined from those measurements was the equilibrium internuclear separation, R_e .

The information from the several studies can be combined to derive potential curves for the singlet and triplet excimer states individually, and that was an early goal of this work. In addition, we planned to perform additional measurements of the emission that would confirm the spectra of the singlet and/or triplet components. Our past measurements of the undispersed

VUV radiation from xenon optically pumped by synchrotron radiation showed that the radiative lifetime of the singlet 0_u^+ state was ~ 5 ns, whereas the triplet 1_u lifetime is ~ 100 ns [BRW80]. Furthermore, those measurements showed that the vibrational relaxation and collisional mixing rates for room temperature Xe_2^* are such that if xenon at pressures of 1 atm or more is excited by a short optical pulse, then the early emission will be dominated by radiation from the vibrationally relaxed singlet, while radiation after about 50 ns will be primarily from the vibrationally relaxed triplet. This separation of the emission into two components, each decaying with its own radiative lifetime, is clearly shown in Figure 2, which is an example of the intensity history from Xe_2^* at 170 nm pumped by synchrotron radiation at 156 nm [BRW80]. Therefore, our first approach to the measurement of individual spectra of the singlet and triplet was through time-resolved emission spectroscopy from xenon pumped by a short-pulse F_2 laser at 157.6 nm.

The experimental details are described in Section II, and the results of those measurements are presented in Section III. Unfortunately, the results we obtained were in conflict with earlier results for the spectrum of the singlet state [FMC71], which was obtained by optically pumping the atomic resonance transition of low pressure xenon at 147 nm with a modulated microwave lamp containing xenon. In an effort to resolve this conflict, we performed a second series of experiments wherein we measured spectra from Xe_2^* optically pumped at 147 nm. The experimental details and the results of this series of experiments are also described in Sections II and III, respectively.

The experimental results are discussed in Section IV. In Section V, we review available information on the potential curves of Xe_2^* and derive new curves that allow us to predict the molecular spectra. A summary and conclusions are presented in Section VI.

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FIGURE 2 VACUUM ULTRAVIOLET EMISSION FROM XENON OPTICALLY PUMPED
BY SYNCHROTRON RADIATION AT 156 nm

II EXPERIMENTAL DETAILS

Mechanical Setup

The experimental setup for fluorescence measurements using optical pumping by the F_2 laser is shown schematically in Figures 3 and 4. The cell used was a standard mini-Conflat six-way cross made of stainless steel. The laser inlet and outlet windows were of UV-grade sapphire mounted on a mini-Conflat flange. Because the 157-nm laser wavelength is absorbed by oxygen, the laser output window was connected to the cell by a tube purged with N_2 . We tried at first to apply the laser beam (whose cross section is $\sim 5 \times 1 \text{ cm}^2$) directly to the cell ($\sim 0.75 \text{ cm}$ dia.), but the resulting small fluorescence signal forced us to install a 50-cm focal length focusing lens about 20 cm from the center of the cell. The emitted (and scattered) light was input to the entrance slit of a McPherson Model 218 1/3-m vacuum monochromator through a LiF window. The monochromator was fitted with a 1200 g/mm grating blazed at 150 nm, so that the dispersion was 2.65 nm/mm. A sapphire window directly opposite the monochromator allowed application of wavelength calibration lamps. Above the cell was a second six-way cross which served as a "utility" input for pumpout, gas supply, pressure measurement (using a Baratron 0-10,000 torr capacitance manometer) and a Cu/Co thermocouple for measuring gas temperature inside the cell. Below the cell, a vacuum photodiode or, later on, a fast photomultiplier tube was attached to the cell through a flange containing a LiF window. Their intended use was to monitor the total (spectrally unresolved) time-dependent emission and/or to provide a triggering source for detection electronics.

For the experiments using optical pumping by xenon atomic resonance emission ($\sim 147 \text{ nm}$) from a microwave lamp, the setup was modified slightly as shown in Figure 5. The sapphire window that had admitted the F_2 laser light was removed and was replaced by a re-entrant window design consisting of a small stainless steel tube to whose end a LiF window was attached using a low-vapor-pressure, high temperature epoxy. A standard mini-Conflat flange was welded to the other end and was used to seal the window mount to the cell body. The space between the resonance lamp window and the LiF input window

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FIGURE 3 SCHEMATIC OF EXPERIMENTAL SETUP FOR LASER EXPERIMENTS

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FIGURE 4 DETAILS OF CELL DESIGN

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FIGURE 5 SCHEMATIC OF EXPERIMENTAL SETUP FOR MICROWAVE LAMP EXPERIMENTS

was purged with N_2 . The inside surface of the window was located ~ 1 -2 mm off the cell centerline and was within the field of view of the monochromator, which subtended a square of ~ 10 mm linear dimension about the center of the cell. The absorption coefficient of 5 torr Xe (lowest pressure used) at a wavelength $\sim 10\text{ cm}^{-1}$ below the resonance line (the probable wavelength emitted by the microwave-discharge resonance lamp) is estimated to be $\sim 2/\text{cm}$ [Ca81], so in experiments at this or higher pressure most of the exciting radiation was absorbed within the monochromator field of view.

Emission spectra were recorded over a modest range of gas temperatures by heating or cooling the six-way crosses that constituted the test cell. For elevated temperature measurements (140°C), a standard laboratory heating tape was wrapped over the cell and was operated by a Variac transformer to obtain the desired temperature. The temperature inside the cell was measured by the Cu/Co thermocouple situated just above the viewed gas volume. Wall temperatures were monitored by two Cr/Al thermocouples attached to the cell's outside surface.

For low temperature measurements (-40°C), a cooling coil of Tygon tubing was wrapped over the cell and an insulating Fiberglas blanket covered the coil. Cool methanol was forced through the coil by a laboratory Neslab cooler. The temperature was determined by the Neslab controller and measured by the same thermocouple arrangement mentioned above. The laser input and output windows were carefully flushed with nitrogen to prevent condensation, yet some condensation could not be avoided.

We modified the high-vacuum pumping system supplied with the McPherson monochromator to also pump independently both the cell and the vacuum photodiode chamber to a vacuum better than $\sim 10^{-5}$ torr. The path between the cell and the monochromator was pumped through the entrance slit. Matheson research grade Xe was used to fill the cell; each fill was used only once and no attempt was made to re-use the gas to ensure gas purity.

For optical multichannel analyzer (OMA) experiments, the monochromator exit slit unit was removed and the Princeton Applied Research optical multichannel analyzer Model 1205D detector head was installed (after modifying the entrance slit lateral position to precisely align the image on the

detector active area). For the boxcar experiments, the exit slit was re-installed and re-aligned, and a photomultiplier tube was used for signal detection.

Excitation Sources

For the laser excitation experiments, we used a Lambda Physik Model EMG 102 excimer laser modified for F_2 use to produce $\lambda = 157.6$ -nm radiation. The laser gas mixture consisted of 100 mbar of 5% F_2 in He and 2900 mbar pure He. The laser power was ~5 mJ for a fresh mix, but it decreased to about 1 mJ after several minutes of lasing at 30 Hz. Measurements were usually taken at 20-30 Hz repetition rate. The pulse duration was nominally about 5 ns, but that parameter not measured in the present work.

For the microwave lamp excitation experiments, the light source used was the 147-nm resonance emission line of Xe obtained by a microwave discharge inside a sealed off quartz tube containing ~1 torr of pure Xe. The microwave source was a 2.450-GHz commercial unit manufactured by Riva, Inc. Power was coupled to the gas tube by a McCarroll-type cavity made by Opthos Instruments, Inc. The power coupled into the discharge was 50 to 70 watts. The power unit could operate either in a continuous mode or in a modulated mode, which resulted in a chopped light output of approximately rectangular waveform. Both duty cycle and modulation frequency were adjustable and a synchronization pulse outlet at the power supply provided a reference waveform to be input into a Princeton Applied Research Model 126 lock-in amplifier. The modulated source detection scheme was expected to improve the signal/noise ratio.

Detectors

Optical Multichannel Analyzer--In the first set of experiments, we detected the fluorescence signals dispersed by the vacuum monochromator using a PAR Model 1205A OMA console in conjunction with a Model 1205D detector head. This detector consists of a vidicon together with a silicon intensified target (SIT) detector tube. For VUV use, the detector faceplate is coated with a plastic scintillator. Because this original scintillator appeared to be damaged, we removed it and applied a new scintillator coating consisting of TPB (1,1,4,4-tetraphenyl-1,3-butadiene, scintillation grade) by airbrush spraying a solution of TPB in dichloromethane over the face plate. The

detector consists of 500 elements of 25- μm width each. This size, combined with the dispersion of the monochromator, gives a nominal resolution of the detector of 0.65 $\text{\AA}$, but the actual resolution is about three times lower. This resolution was verified by measuring the Hg and N_2 atomic emission line widths from calibration lamps (after carefully aligning the detector to be parallel to the entrance slit).

The OMA can work either CW or in a gated mode. In the gated mode, the SIT is biased off and is actuated by a negative voltage pulse so that detection occurs only during the duration of this gating pulse. The OMA triggering scheme is shown in Figure 6. A synchronizing pulse from the OMA console is used to trigger a Datapulse pulse/delay generator and to trigger the F_2 laser through the laser control module. The high-voltage gate generator, being triggered by the Datapulse after an adjustable delay, applies a negative voltage (1000-1500 V, adjustable) to the OMA detector. The gate width can be adjusted to vary from ~ 10 ns to several milliseconds. The gate width and the delay times were set to detect Xe_2^* emission either in the early part of the fluorescence decay (thus measuring primarily singlet emission) or late in the decay (to measure primarily the longer lived triplet emission). Two pulse generators were used: first, a Cober high voltage pulse generator and, later on, a PAR Model 1211 pulse generator that has better rise- and fall-time characteristics. Because the voltage applied affects the focusing of the image and therefore the resolution of the detector, the value of this voltage was adjusted to obtain a symmetrical profile of the narrowest possible width for the 157.5-nm scattered laser light. However, as a consequence of nonuniform focusing during pulsed operation, the best resolution observed in the gated mode was 5 $\text{\AA}$, compared with ~ 2 $\text{\AA}$ in the CW mode.

Synchronizing the gating pulse to the the OMA e-beam scanning waveform results in accumulation of signal only during the 600 μs "dead time" when the beam is not scanning, thus avoiding interference with the preamp and video processor and ensuring equal charge accumulation time for all detector elements. This procedure restricts the laser repetition rate to the OMA scanning rate of 30 Hz, which does not entail any special problem.

FIGURE 6 DETECTION SCHEME USING OPTICAL MULTICHANNEL ANALYZER

An important feature of the (ideal) OMA is the uniformity of its sensitivity over the entire array. We checked the uniformity of response in both operating modes by slowly scanning the monochromator to sweep a narrow spectral line from a calibration lamp through the array while monitoring the peak intensity on the console scope. We found a significant deviation from uniformity, exceeding 25%, on the short-wavelength side of the detector. This restricted the useful range of the detector to about 200 nm and necessitated determining the spectra by overlapping several measurements taken with different monochromator settings.

Spectra were obtained using the accumulation and background subtraction features of the OMA processor. First, the signals resulting from a given number of shots without the laser firing (100-1000, depending on the amount of signal relative to various noise sources) were accumulated in the first of two memories to establish a background. Then the laser was fired for the same number of pulses, and signals (including the Xe_2^* fluorescence) were accumulated in the second memory. Subtraction of the first memory from the second gave a background-corrected spectrum. The displayed spectrum was then recorded using an x-y recorder to obtain a plot of accumulated number of counts versus element number. The wavelength was calibrated in the CW mode using atomic emission lines from a standard mercury pen lamp and from a nitrogen microwave excited lamp. In the gated mode, only the 253.7-nm Hg line and the scattered laser line could be used because of the much lower signals of the other lines in this mode.

Boxcar Integrator--Some uncertainties in the OMA results (discussed in Section III), combined with deviation of the experimental results from the calculated separate contributions of 1_u and 0_u^+ states to vibrationally relaxed emission spectra (see Section V) motivated us to use a different detection scheme for obtaining the spectrum. In this second series of experiments, the OMA detector was removed and the exit slit assembly re-installed on the monochromator. The exit slit port was sealed with a window that was coated with sodium salicylate scintillator. An EMI Model 9514 photomultiplier tube (PMT) was mounted behind the window to record the fluorescence signals. The wavelength dependence of the fluorescence was determined by scanning the monochromator, while time resolution was easily achieved using the gating feature of the boxcar integrator.

The detection scheme is shown schematically in Figure 7. The laser was triggered from a Datapulse pulse generator at a variable repetition rate of ~30 Hz. A second photomultiplier (Hamamatsu Model R1645SU-01) viewing the fluorescence cell from below was used to record the undispersed fluorescence and the scattered laser light and to trigger the boxcar. The signal from the EMI photomultiplier was input to the boxcar through a much longer coaxial cable to provide a delay relative to the triggering pulse. The boxcar signal at each wavelength was averaged over 10 to 100 laser pulses using a gate width that varied from ~10 to 200 ns and was output to a chart recorder. The monochromator was slowly scanned over the relevant wavelength range (1550-1850 Å). The scanning rate was set so that the wavelength increment scanned during the averaging time (i.e., the number of pulses averaged divided by the laser repetition rate) was less than the monochromator resolution set by the slit width. In the present measurements, the resolution was about 10 Å and the scanning speed was usually 20 Å/min.

Because a boxcar measurement required about 15 minutes to complete one scan, it was necessary to correct for the change of laser power. Accordingly, a Scientec power meter was mounted at the cell output window, again connected to the window flange by a nitrogen purged tube, as shown in Figure 3. The power meter output signal was detected by a microvoltmeter and was recorded on a second channel of the chart recorder simultaneously with the boxcar output. We found that as much as 40% of the power measured by the laser power meter came from the F-atom laser transitions at ~700 nm that occur simultaneously with the F₂ laser transition at 157 nm. This was taken into account when normalizing the fluorescence signal to the VUV laser power.

CW/Modulated Detection--In the third set of experiments, the pulsed F₂ laser excitation was replaced by resonance pumping of atomic xenon using a microwave discharge lamp. In these measurements, the fluorescence was again detected by a photomultiplier mounted behind the scintillator-coated window on the exit slit of the scanning monochromator. Initially, an EMI 9558 photomultiplier was used, but it was replaced later by an EMI 9514S photomultiplier which produced a larger output signal. In each case, the photomultiplier was inserted into a thermoelectrically cooled housing (Products for Research, Inc.), which was attached to the monochromator exit slit. The measured dark current for the cooled photomultipliers was in the

FIGURE 7 DETECTION SCHEME USING BOXCAR INTEGRATOR

range of $(1 \text{ to } 5) \times 10^{-10}$ A. The slit widths used corresponded to a spectral resolution of 10 to 15 Å. In the DC detection mode, the photomultiplier signal was directly input into a microammeter (Hewlett-Packard 425A or Keithley 414S), and the output was fed to a chart recorder after proper attenuation. In the AC detection mode, the output signal was input into the signal channel of the PAR Model 126 lock-in amplifier while a synchronized rectangular waveform from the microwave power supply served as a reference signal. The modulation frequency and filter bandwidth were varied about 500 Hz to obtain the best output signal, which was fed into a chart recorder. Initially, spectra were taken using both modes and were found to be almost identical. Because the AC detection mode did not show significant signal/noise improvement over the DC mode (probably because of noise generated in the modulation process itself, which could not be easily filtered out), we decided to use the simpler DC mode for all subsequent measurements. The chart recorder data were digitized and stored for further computer analysis.

Data Reduction

The OMA system accumulates data in the form of counts per detector channel. We plotted these results using an x-y recorder, taking care to document absolute magnitudes of signals for each graph so that results taken under identical experimental conditions could be compared. We then digitized each plot using a Houston Instruments digitizer and a digitizing program operating on our laboratory VAX computer. The digitized data were stored on hard disc memory for subsequent manipulation, which included normalizing the results to a common scale, superposition of results on a common graph, and plotting.

In the experiments in which F_2 -laser-induced fluorescence intensities were measured using the boxcar recorder, both the fluorescence intensities and the laser intensities were recorded on a strip-chart recorder. These data were also digitized and stored. Normalized fluorescence spectra were then determined by computing the ratio of the two signals.

In the experiments in which the excitation source was a xenon microwave lamp, the lamp power was assumed to be constant, and the digitized fluorescence spectra were used without further modification.

III RESULTS

Laser Excitation/OMA Detection

In principle, any recorded OMA spectrum centered on 1700 Å should be sufficient to determine the entire relevant emission spectrum. Indeed, when we superimposed emission spectra taken at several center wavelengths displaced by 50 Å each, we found good agreement in the spectra if the wavelengths corresponded to pixels near the center of the OMA detector. However, portions of spectra recorded using pixels near the edges of the OMA array differed from those recorded using the center of the array. This problem was much more severe in the gated mode of operation than in the CW mode, so it cannot be attributed solely to the nonuniformity of response problem mentioned above (which should affect both modes equally). We do not completely understand the cause of increased nonuniformity in the gated mode, but it may be a temporal effect caused by the relatively slow charging time of the silicon target, which reduces the apparent sensitivity at the edges of the array. To circumvent this shortcoming, we recorded the spectra at least three times, each time with a different center wavelength shifted by 50 or 100 Å, and the different spectra were superimposed such that only the central part of each was taken into account.

As discussed in the Introduction section, the objective of these measurements was to determine separately the singlet and triplet emission spectra, and the approach was to use time gating in which the early time emission ($t \leq 10$ ns) is identified with singlet emission and late time emission with triplet emission. Accordingly, we recorded OMA data in three regimes as described below. In these experiments, xenon pressures ranged from 1500 to 3000 torr. The OMA gate width was varied from 500 to 2000 ns and the number of accumulated pulses from 100 to 1000 depending on signal levels. Generally, the signal levels for the triplet regime were about an order of magnitude lower than for the singlet regime (depending on the time delay), so accumulation times were always longer in the triplet measurements. In each case, the spectra presented are composites of spectra taken at different

center wavelength settings of the monochromator and superimposed as described above. Results presented here are representative of all those obtained.

Time-Integrated Spectra--We first measured the time-integrated spectrum using a gate width of 1 μ s. The timing was set so the scattered laser light occurred about in the center of the gate. Spectra obtained with this gate position are shown in Figure 8 for three cell temperatures. The center wavelengths and bandwidths of these spectra are as follows:

<u>T ($^{\circ}$C)</u>	<u>λ_c ($\text{\AA}$)</u>	<u>$\Delta\lambda$ ($\text{\AA}$)</u>
-40	1715	115
20	1710	120
140	1690	150

Singlet Spectra--To obtain the singlet spectrum, we set the gate to close 10 ns after the laser pulse. A room temperature spectrum is shown in Figure 9. The band center is at 1700 $\text{\AA}$ and the bandwidth is 135 $\text{\AA}$. Because the time gate encompasses the laser pulse, scattered laser light again appears in the spectrum.

Triplet Spectra--To obtain the triplet spectrum, we delayed the start of the gate 50 to 200 ns from the laser pulse. A room temperature spectrum is shown in Figure 10, and superimposed spectra for three different temperatures are shown in Figure 11. The absence of scattered laser light in these spectra confirms that early-time emission is excluded. The center wavelengths and bandwidths of these spectra are as follows:

<u>T ($^{\circ}$C)</u>	<u>λ_c ($\text{\AA}$)</u>	<u>$\Delta\lambda$ ($\text{\AA}$)</u>
-35	1715	115
20	1710	120
140	1685	110

Laser Excitation/Boxcar Detection

In this series of experiments, spectra were measured for the same three time regimes as for the OMA measurements. In these experiments, the gate widths and especially the delay times were determined to better accuracy than in the OMA experiments.

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FIGURE 8 Xe_2^+ SPECTRA MEASURED WITH OMA: TIME INTEGRATED

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FIGURE 9 Xe_2^+ SPECTRA MEASURED WITH OMA: GATED TO OBSERVE SINGLET EMISSION ($P = 1640$ torr, $T = 20^\circ\text{C}$)

RA-2206-8

FIGURE 10 Xe_2^+ SPECTRA MEASURED WITH OMA: GATED TO OBSERVE
TRIPLET EMISSION (P = 1690 torr, T = 15°C)

RA-2206-9

FIGURE 11 Xe_2^+ SPECTRA MEASURED WITH OMA: GATED TO OBSERVE
TRIPLET EMISSION

Time-Integrated Spectra--Figure 12 is an example of a time-integrated spectrum, taken at zero delay with a relatively long (200-ns) gate width. The center wavelength is 1710 Å and the bandwidth is 133 Å.

Singlet Spectra--Figure 13 shows three spectra taken within the singlet time regime, with the gate set to 0 delay and 15 or 20 ns duration so that the scattered laser pulse is observed. One of these spectra was obtained with a reduced laser power achieved by removing the focusing lens. Again, the center wavelength is approximately 1710 Å and the bandwidth is approximately 130 Å.

Triplet Spectra--Figure 14 presents three different spectra taken with varying delay times following the laser pulse. Each of these spectra is considered to be in the triplet time regime, although traces of scattered laser light are observed, particularly for 20 ns time delay. The center wavelength is 1710 Å and the bandwidth is 120 Å.

Generally, the reproducibility of the boxcar results was somewhat less than that for the OMA data, which we attribute to the following effects: (1) jitter in the apparent peak wavelengths, which stems from the error in manually starting both monochromator and strip chart recorder scans simultaneously, (2) inaccuracy in normalizing for laser power decrease during measurement, and (3) drift of background level in the boxcar.

Xenon Resonance Line Excitation/PMT Detection

As we will discuss in more detail in the next section, the singlet and triplet spectra deduced from the laser-excited emission studies reported above were different from our expectations. In particular, the singlet and triplet spectra are similar to each other in center wavelength and bandwidth, whereas we expected the two components to be offset by as much as 50 Å in center wavelength and to have a bandwidth of about 90 Å compared with a value of 120 Å for the combined spectrum. Our expectation was based on the success of preliminary spectral modeling in fitting various experimental spectra (see Section V), and this preliminary model was strongly reinforced by a measurement reported in the literature in which atomic xenon resonance fluorescence from a microwave discharge lamp was used to produce what was asserted to be a molecular singlet emission spectrum from xenon at 500 torr [FMC71]; that spectrum was indeed shifted and narrowed compared with other measurements.

RA-2208-10

FIGURE 12 Xe_2^+ SPECTRA MEASURED WITH PMT/BOXCAR: TIME INTEGRATED
($P = 2005 \text{ torr}$, $T = 20^\circ\text{C}$)

RA-2206-11

FIGURE 13 Xe_2^+ SPECTRA MEASURED WITH PMT/BOXCAR: GATED TO OBSERVE SINGLET EMISSION

RA-2206-12

FIGURE 14 Xe_2^+ SPECTRA MEASURED WITH PMT/BOXCAR: GATED TO OBSERVE TRIPLET EMISSION

In view of potential uncertainties in our laser-excitation results, we decided to repeat the microwave lamp excitation experiment. Because atomic xenon resonance radiation is strongly absorbed by xenon, these measurements are of necessity restricted to rather low pressures; furthermore, a reentrant window design in which the window is in the field of view of the monochromator, as described above, is required. During this work, we obtained measurements over an extended range of xenon pressures, which allow us to compare our results with other literature results. We also studied xenon/helium mixtures.

Pure Xe--Emission spectra of pure Xe were measured over the spectral range from 1450 to 1900 Å at several gas pressure up to 1200 torr and at temperatures of 20°C and -13°C. Representative results are presented in Figures 15 and 16. At the lowest Xe pressures, only a narrow band starting at the excitation wavelength of 1470 Å was observed. The peak of this band shifted to the red with increasing pressure and gradually evolved into the well known first continuum of Xe_2^* (see Figure 1 above). At 50 torr the second continuum at ~1700 Å was observed, and its intensity increased with increasing pressure, as shown in Figure 16. At the same time, the intensity of the first continuum decreased and disappeared completely at ~600 torr.

It is interesting to compare our results to previous measurements of the emission following optical excitation of Xe. In Figure 17 we compare our spectrum measured at 50 torr with one measured by Fink and Comes [FC75] for 60 torr, and in Figure 18 we compare our result at 500 torr with the result by Freeman, et al [FMC71] for that same pressure. The agreement is very good in the first case and very poor in the second, even though our experimental conditions essentially duplicated the earlier ones. In particular, our spectrum taken at 500 torr shows a center wavelength of 1720 Å and a bandwidth of 130 Å, in good agreement with our previous measurements reported above, but in sharp contrast to values of 1680 Å and 85 Å reported by Freeman et al. We are forced to conclude that the latter work must have contained an experimental artifact that led to an erroneous result.

To elucidate the pressure and temperature dependence of the second continuum features, specifically its relative intensity, bandwidth, and peak position, we fit the relevant portion of the spectra (1630-1900 Å) to a Gaussian band shape, using a nonlinear least-squares curve fitting routine

RA-2206-22

FIGURE 15 Xe_2^+ SPECTRA RESULTING FROM OPTICAL PUMPING
BY MICROWAVE LAMP: 5 torr TO 106 torr

RA-2206-23

FIGURE 18 Xe_2^+ SPECTRA RESULTING FROM OPTICAL PUMPING
BY MICROWAVE LAMP: 22 torr TO 620 torr

RA-2206-16

FIGURE 17 COMPARISON OF Xe_2^+ SPECTRUM AT 50 torr WITH RESULTS OF FINK AND COMES AT 60 torr

From E. H. Fink and F. J. Comes, Chem. Phys. Lett. **30**, 267 (1975).

RA-2206-17

FIGURE 18 COMPARISON OF Xe_2^+ SPECTRUM AT 500 torr WITH RESULTS OF FREEMAN et al. AT 500 torr

Ref.: C. G. Freeman, M. J. McEwan, R. F. C. Claridge, and L. F. Phillips, Chem. Phys. Lett. 10, 530 (1971)

developed in our laboratory. A good fit was obtained in all cases. When both the first and second continuum could be discerned, the Gaussian best fit for the second continuum was subtracted from the overall spectrum to single out the part corresponding to the first continuum (and, possibly, to broadened atomic emission). Figure 19 shows an example of such analysis, including the quality of the Gaussian fit to the second continuum spectrum. For each spectrum, the integrated intensities of the overall spectrum and of the Gaussian fit part were measured, and their ratio was calculated. Table 1 summarizes the results of this analysis for several Xe pressures at both temperatures studied. In this table, the best fit parameters for peak wavelength and full width at half maximum (FWHM) for the second continuum are listed together with the ratio of integrated intensities.

From Table 1, the spectra at the lowest Xe pressures clearly show a marked pressure dependence of the fit parameters and the intensity ratio. The peak wavelength increases and the band width decreases with increasing pressure while the intensity ratio goes up rapidly. Above ~500 torr, the peak wavelength and the bandwidth are effectively pressure independent at 1715 ± 2 Å and 130 ± 2 Å, respectively. The peak wavelength determined by the fitting program is not very sensitive to the choice of the fitting range (usually chosen as 1640-1890 Å), whereas the Gaussian bandwidth is more sensitive and can vary by ~5 Å for a reasonable change of that range.

The temperature dependence of the best fit parameters is less marked, mainly because the two temperature values are close together; thus, no clear temperature dependence can be established. At lower Xe pressures, the width is somewhat smaller and peak wavelength longer at the lower temperature. At higher Xe pressures there is not any pronounced temperature effect.

A similar Gaussian fitting analysis was performed also on the data from Fink and Comes [FC75]. The resulting parameters, given for comparison in Table 1, are in good agreement with the present data.

Xe/He Mixtures--We measured the emission spectra of xenon mixed with helium gas over the Xe pressure range from 6 to 800 torr and for He pressures up to 3900 torr. Most data were taken at room temperature, but a series of measurements at -27°C is also reported. Figure 20 shows one such series of spectra taken at ~50 torr Xe with various He pressures. Although the relaxation of the first continuum into the second continuum is clearly

RA-2206-24

FIGURE 19 FIT OF GAUSSIAN BAND SHAPE TO SECOND CONTINUUM SPECTRUM FOR 106 torr Xe

Table 1

BEST FIT GAUSSIAN PARAMETERS FOR PURE Xe

P_{Xe} (torr)	Temp. (°C)	<u>Fit Parameters</u>		Intensity Ratio (Gaussian/Overall)
		<u>Width</u> (Å)	<u>Peak</u> (Å)	
55	20	154	1703	0.55
106	20	151	1708	0.79
250	20	143	1712	0.96
504	20	134	1714	
620	20	132	1716	
800	20	126	1715	
1000	20	134	1716	
1190	20	128	1715	
50	-12	166	1701	0.51
104	-14	142	1713	0.81
256	-13	132	1719	0.86
565	-12	128	1717	0.98
620	-14	129	1717	
60*	20	154	1704	0.59
100*	20	152	1710	0.85

*From [FC75]

RA-2206-25

FIGURE 20 Xe_2^+ SPECTRA RESULTING FROM OPTICAL PUMPING BY
MICROWAVE LAMP FOR Xe/He MIXTURES: 55 torr Xe

observed, its rate is much slower than for the pure Xe spectra (Figure 16). At the highest He pressure of 2250 torr, there is still a first continuum contribution to the spectrum, whereas no such contribution was observed above 500 torr of pure Xe. The same trend is observed for other Xe pressures and at lower temperature. For example, in Figure 21 the spectra taken at -100 torr Xe are displayed.

The effect of Xe pressure on the spectra is shown more clearly in the data obtained at similar He pressures of 1300 to 1700 torr and various Xe pressures as presented in Figures 22 and 23 for room temperature and -27°C, respectively.

To again elucidate the important second continuum parameters and their pressure dependences, we performed a nonlinear least-squares fit of the 1640-1900 Å part of the spectra to a Gaussian line shape. The overall fit is good in all cases, as is evident from Figures 24 and 25, which show the result of applying such a procedure to spectra for Xe/He mixtures of 6/2570 torr and 56/1510 torr, respectively.

The best fit Gaussian parameters, as well as the ratio of the Gaussian integrated intensity to the overall spectral intensity, for several Xe/He mixtures are summarized in Table 2. The general trend is of increasing peak wavelength and decreasing bandwidth for increasing He pressure at constant Xe pressure. These parameters tend to converge to the totally relaxed (high pressure) pure Xe parameters at high He pressures. However, it is important to note that the relaxation by He is much slower than for pure Xe, Xe in Ar mixtures [ACR74] or Xe in Kr mixtures [FC75].

As for the effect of temperature, the peak wavelength shifts to a higher value and the bandwidth to a slightly lower value at the lower temperature (-27°C). Because the temperature change is small, the effects are not pronounced.

Again, the value of the peak wavelength is fit somewhat more accurately than the bandwidth for these data.

RA-2206-26

FIGURE 21 Xe_2^+ SPECTRA RESULTING FROM OPTICAL PUMPING BY MICROWAVE LAMP FOR Xe/He MIXTURES: 105 torr Xe

RA-2206-27

FIGURE 22 Xe_2^+ SPECTRA RESULTING FROM OPTICAL PUMPING BY MICROWAVE LAMP FOR Xe/He MIXTURES: 1300 torr to 1600 torr He, $T = 17^\circ\text{C}$ (He pressure in parentheses)

RA-2206-28

FIGURE 23 Xe_2^+ SPECTRA RESULTING FROM OPTICAL PUMPING BY MICROWAVE LAMP FOR Xe/He MIXTURES: 1200 torr to 1800 torr He, $T = 27^\circ\text{C}$ (He pressure in parentheses)

RA-2206-29

FIGURE 24 FIT OF GAUSSIAN BAND SHAPE TO SECOND CONTINUUM SPECTRUM
FOR 6 torr Xe AND 2570 torr He

RA-2206-30

FIGURE 25 FIT OF GAUSSIAN BAND SHAPE TO SECOND CONTINUUM SPECTRUM
FOR 56 torr Xe AND 1510 torr He

Table 2

BEST FIT GAUSSIAN PARAMETERS FOR PURE Xe/He MIXTURES

<u>P_{Xe}</u> <u>(torr)</u>	<u>P_{He}</u> <u>(torr)</u>	<u>Temp.</u> <u>(°C)</u>	<u>Fit Parameters</u>		<u>Intensity Ratio</u> <u>(Gaussian/Overall)</u>
			<u>Width</u> <u>(Å)</u>	<u>Peak</u> <u>(Å)</u>	
6	2570	20	137	1710	0.65
23	740	20	144	1703	0.31
22	1515	20	141	1712	0.63
57	253	20	150	1707	0.69
55	783	20	149	1710	0.74
56	1510	20	142	1712	0.87
55	2253	20	137	1713	0.91
102	265	20	146	1711	0.84
104	750	20	145	1713	0.88
107	1320	20	139	1712	0.91
106	2210	20	138	1714	0.94
55	1275	-27	141	1716	0.81
100	1260	-27	134	1716	0.91
100	2480	-27	127	1721	0.94
270	1250	-28	127	1723	0.99
565	1515	-26	126	1720	0.99
265	725	20	132	1714	
265	1505	20	135	1715	0.97
265	2245	20	128	1712	
505	755	20	128	1717	
505	1605	20	127	1714	
537	2235	20	127	1715	
800	700	20	126	1716	
795	1485	20	124	1717	
795	2210	20	128	1717	

IV DISCUSSION OF EXPERIMENTAL RESULTS

Comparison of OMA and Boxcar Results

The boxcar measurements were motivated by the uncertainty encountered during OMA experiments because of the lack of overlap of spectra taken at different center wavelength values. Therefore, comparison of data obtained by these two independent measuring techniques can serve as a good criterion for the reliability of the results. Comparing the data for each of the three timing categories mentioned above (Figures 8 and 12 for "integrated" spectra, Figures 9 and 13 for the "singlet" case, and Figures 10 and 14 for the "triplet"), we can see that the agreement is good in each case. Thus, we conclude that both the OMA and the boxcar data are reliable; however, because the scatter is less in the OMA data, we have the greatest confidence in those results.

Comparison of "Singlet" and "Triplet" Spectra

In the previous section, we presented both OMA and scanning monochromator/boxcar results obtained using gated detection in which we identified early-time results (≤ 10 ns) as representing singlet spectra and late-time results (≥ 20 ns) as representing triplet spectra. In each case, we listed the center wavelength and the full-width-half-maximum for the spectra.

In comparing those results (Figures 9 and 10 for OMA detection and Figures 13 and 14 for boxcar detection), we observe some shift of the singlet to the short-wavelength direction, but the shift appears to be unsymmetrical; the "blue" wing is displaced more than the "red" wing. The resulting shift of peak wave length is about 10 Å, and the singlet emission band is somewhat broader than the triplet band. A more elaborate measurement of peak position and bandwidth (FWHM) based on Gaussian curve fits to the spectra gives the following results:

$$\begin{array}{lll} \text{Triplet:} & \lambda_c = 1714 \pm 6 \text{ \AA} & \Delta\lambda = 122 \pm 2 \text{ \AA} \\ \text{Singlet:} & \lambda_c = 1704 \pm 6 \text{ \AA} & \Delta\lambda = 131 \pm 3 \text{ \AA} \end{array}$$

These data were taken from room temperature (20°C) spectra, and the error limits cited here reflect the scatter of these parameters over the rather small number of spectra analyzed. Thus, these data should not be considered as reliable statistical error limits.

Figure 14 shows triplet spectra taken using the boxcar at three delay times from 20 to 150 ns. No dependence of the spectral features on the delay time is observed within the boxcar data error limits. The only change is in the weak peak of scattered laser light at 157.6 nm, which is clearly observed only in the 20-ns delay experiment. This apparent insensitivity to delay time is consistent with our assumption that because the singlet lifetime is much shorter than the shortest gate delay used in these measurements, the singlet state does not contribute to any of these three spectra.

From these results we conclude that the singlet is indeed shifted by ~ 10 Å to the "blue" side and is wider by ~ 9 Å compared with the triplet spectrum. However, this shift is much less than expected from the calculations (see Section V) or from the previous experimental results of [FMC71] using resonance excitation (Figure 18).

Temperature Effects

Most of our data were obtained at room temperature, with only a few measurements made at lower (-40°C) and higher (140°C) temperatures (and only with OMA detection), so the thermal effects observed are far from being conclusive. Nevertheless, a marked temperature effect is observed, both in the "integrated" spectra (Figure 8) and the "triplet" spectra (Figure 11). In both cases, the blue side of the band shifts to shorter wavelength with increasing temperature while the red side changes much less. This results in broadening of the emission band with increasing temperature. The high temperature spectrum of the triplet seems to be an exception, but this spectrum is of rather low quality and the red wing of it is not reliable. Because only room temperature data were obtained in the singlet case, no temperature effects on this spectrum can be presented.

Laser Power Effects

Ideally, the excitation source should have produced only the two excited molecular states of concern here without any "by-products." The most probable

exception to this desired situation is if the laser power is high enough to photoionize those atoms and/or molecules already optically pumped into an excited state. In that case, recombination could produce singlets and triplets long after the laser pulse ended. This should not affect our assumption that the early-time emission is primarily singlet because that assumption is based on radiative decay rates, but it could negate our assumption that singlet emission is confined to 10 ns following the pulse and that all late-time emission is from the triplet.

We estimate the photoionization yield starting with an estimated laser fluence in the cell of $\phi = 5 \times 10^{15}$ photons/cm². If we assume a square pulse, the ratio of ions to excited states is given as

$$N^+/N^* = \phi \sigma / 2$$

where σ is the cross section for photoionization of the excited states. A probable upper limit for that value is $\sigma < 10^{-17}$ cm², so $N^+/N^* \leq 0.025$. Thus, the emission that could be produced from late-time recombination must have been a small fraction of the total and should not interfere with measurement of the triplet spectrum.

The second way photoionization could interfere with the spectral measurements is if the electron density was high enough that electron collisions could alter the excited state kinetics, for example, by collisionally exciting excimers from the triplet to singlet state. We estimate the absolute electron density by assuming that 10% of the incident laser photons are absorbed to produce excited states. Then the peak excited-state densities are 5×10^{14} /cm³, which leads to peak electron densities of $\leq 1.2 \times 10^{13}$ /cm³. In previous laser studies at SRI [ELB82], we deduced a rate for this process of 1.8×10^{-6} cm³/s. The product of this rate times the above electron density is 2×10^5 /s, which is a time constant of 4 μ s. Because our measurements were confined to less than 500 ns, it is unlikely that this process could have interfered with the spectral measurements either.

In the experiments, we tried at first to use the unfocused laser beam for the excitation, but a poor S/N ratio, especially in the "triplet" gate position where the signal is down by an order of magnitude or more, forced us to use a lens to partially focus the laser beam (the beam was focused about 25

cm beyond the cell). All spectra but one were taken with this setup. The only result using an unfocused beam is a measurement of the singlet spectrum using the boxcar; this result is presented in Figure 13. Comparing the other results in that figure, no discernable "power effect" is observed; however, this observation should be applied cautiously because there is just a single result with a reduced power level. As just noted, no reliable data for the triplet could be measured at such low power.

Pressure Effects on Spectra Produced by Microwave Lamp Excitation

As demonstrated in Figures 19, 24, and 25, the shape of the second continuum at ~ 1700 Å resulting from optical pumping of xenon by the xenon resonance emission from a microwave lamp is well fit by a Gaussian for both pure Xe and Xe/He mixtures, both for unrelaxed spectra (i.e., where the first continuum to the red side of 1470 Å is present) and for completely relaxed spectra. The latter result, pertaining at higher pressures, is expected because it corresponds to the usual second continuum spectrum resulting from transitions from the lower vibrational levels of the excited singlet and triplet states to the repulsive ground state. However, it is significant that the spectrum stays symmetrical at lower pressures because contributions from higher vibrational levels should be increasingly important as the pressure decreases, and the asymmetry of the excited-state and ground-state potential curves could lead to asymmetric spectra as well. Emission from the higher vibrational levels does lead to broadened spectra, as evidenced by the increasing bandwidths with decreasing pressure listed in Tables 1 and 2.

We also see from Tables 1 and 2 that the peak wavelengths of the unrelaxed (low pressure) spectra are shifted by ~ 10 Å to shorter wavelength compared to the fully relaxed spectra. This shift could be accounted for by emission from higher vibrational levels, but because the shift is not accompanied by any observable band asymmetry, it might also be explained as the result of varying relative contribution of the triplet and singlet excited states to the emission.

The width of the best-fit Gaussian for the high Xe pressure (fully relaxed) spectrum is 126 - 130 Å (see Table 1). Compared with the results of our previous study of the time-resolved spectra, this range of values is

between the widths ascribed to the singlet and triplet states. On the other hand, the bestfit peak wavelength of 1716 Å is close to what was termed the triplet peak in that study.

V XENON EXCIMER POTENTIALS AND CALCULATED EMISSION SPECTRA

As with any true excimer molecule, the Xe_2^* emission and absorption spectra, because of their continuum nature, make the job of determining accurate potentials very difficult, and so far no spectroscopically accurate excimer potentials are available for this molecule. However, recent spectroscopic measurements on the Xe_2 0_u^+ and 1_u potentials, together with the emission measurements reported here, now provide a basis for a reevaluation of the Xe_2 excimer potentials using all the available data.

Ground State of Xe_2

The ground state of Xe_2 has been the subject of many studies involving spectroscopic, atom-atom scattering, and transport measurements. These have been reviewed in detail by Barker [BWL74, BKB76], who used all the available data to generate the best ground state potential for large internuclear separations ($R \geq 3.3$ Å). We consider the Barker X_4 potential fitted to a Morse potential using the parameters given by Castex [Ca81] to be sufficiently accurate for our purposes. Unfortunately, this potential does not extend to small enough internuclear separation, R , to be useful for the excimer spectral calculations because the excited state potentials have equilibrium separations in the 3.0 to 3.1 Å range. It does, however, provide a magnitude and slope that must be matched in a continuous manner by any potential that extends to smaller R . In the range where the potential is strongly repulsive, several studies all seem to give similar slopes but different magnitudes. We used the experimental results of Foreman, Lee, and Rol [FLR75], which, although unpublished, are the most reliable experimental Xe - Xe scattering data providing information in the steep repulsive region ($2.15 \leq R \leq 3.14$ Å) of the ground state. These data are plotted in Figure 26, which shows that the two sets of data approach each other smoothly although their regions of validity do not overlap and the slopes differ slightly. We have fit the slopes of the two potentials with a spline fit and integrated to obtain a smooth continuous transition between the two sets of data; the result

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FIGURE 26 POTENTIAL ENERGY CURVE FOR THE Xe₂(X¹Σ_g) GROUND STATE

is shown as the solid curve in Figure 26. The potential is thus in tabular form, and no analytic fit has been attempted.

Excited State Potentials

Excited state potentials have been the subject of detailed theoretical calculations [ELP78] that provide valuable insight and a reasonable estimate of the potentials. However, the resulting potentials are not of spectroscopic accuracy. Absorption measurements were also used to explore the excited state potentials, but they are limited because of the repulsive ground state to probing only the long-range part of the potential. These measurements also suffer from the inability to distinguish the two upper states to which the absorption occurs and thus provide only a single upper potential that is averaged in an undetermined manner over the two states. However, they do help to determine the long-range part of the 0_u^+ potential that dissociates to the $\text{Xe}(^3P_1) + \text{Xe}$ limit. Castex [Ca81] has provided the most recent and definitive measurements of this type. Emission measurements, of course, also contain useful information about the excited state potentials, but the spectral overlap and broad lineshape caused by the repulsive lower state makes the inversion problem very difficult.

The recently reported measurements of high-resolution VUV laser spectroscopy of Lipson, LaRocque, and Stoicheff [LLS85] provide the first really spectroscopically valuable data on the upper states. Although their spectroscopic measurements cover only a narrow range of wavelengths and corresponding internuclear separation, the resolution was high enough to resolve the high vibrational levels and the isotopic shifts. The resolution of individual isotopic vibronic bands permitted an absolute identification of the v' levels from which they originated. These levels are in the range $v' = 38$ to 45 , but from a fitting of all the vibronic and isotopic lines, a set of spectroscopic constants (T_e , ω_e , and $\omega_e x_e$) was derived for the 1_u and 0_u^+ states. If we accept these potentials as the best available, the only remaining uncertainty is the equilibrium internuclear spacing, R_e , which could not be determined because the rotational spectra were not resolved.

We used the constants derived from [LLS85] to calculate Morse potentials, which we then used to calculate Morse wavefunctions and Franck-Condon factors for the v' levels. The resulting potentials shown in Figure 27 are based on

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FIGURE 27 POTENTIAL ENERGY CURVES FOR THE Xe_2^+ ($1_u, 0_u^+$) STATES
BASED ON SPECTROSCOPIC MEASUREMENTS OF LIPSON et al.

R_e values chosen to provide reasonable fits to the emission data, as discussed below. This information was used to calculate the emission spectra from each of the upper levels to the ground state. In this calculation, the R_e of each state is critical in determining both the position and width of the 170-nm continuum emission. Thus, the R_e was regarded as a parameter that could be varied to obtain agreement with the emission experiments. However an additional variable that is difficult to determine for any given experimental situation is the relative contribution of each of the states. Unfortunately, the published data on the emission spectra are seldom taken under conditions conducive to isolating either of the states or knowing their relative intensities.

Calculated Spectra Based on Previous Data

At the beginning of this program, we believed that the emission data of Freeman et al. [FMC71] obtained at 500 torr of xenon pressure by exciting with a Xe resonance lamp at 147 nm produced an emission spectrum that could be interpreted as only from the O_u^+ state. As discussed in Section IV and shown in Figure 18, this spectrum is much narrower and peaked at shorter wavelength than the spectrum from e-beam excited gas. Because excitation at the 3P_1 resonance line should yield predominantly the singlet O_u^+ molecular state, that spectrum was used to determine the R_e of that state. As shown in Figure 28, the calculated spectrum of the LLS O_u^+ state with an R_e of 3.13 Å fits that data very nicely. However, as discussed in Section III, we were unable to reproduce the results of Freeman et al., and so we no longer regard those results as reliable. Thus, this means of determining the R_e of the O_u state is not valid. Nevertheless, using the assumed R_e 's of 3.13 Å together with an inferred value of $R_e \sim 3.07$ Å for the l_u state and assuming equal contributions from the l_u and O_u^+ states, we calculated an "integrated" spectrum at 300 K. This spectrum is shown Figure 29 and compared with data taken by Koehler et al. [KFR74] with both X-ray and e-beam excitation. The agreement is reasonable, particularly on the blue side where the O_u state is the predominant contributor, and seems to confirm the R_e assignment for that state.

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FIGURE 28 THEORETICAL AND EXPERIMENTAL SPECTRUM OF THE $\text{Xe}_2^+ (0_u^+)$ STATE BASED ON DATA OF FREEMAN et al.

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FIGURE 29 THEORETICAL SPECTRUM OF THE Xe_2^+ ($1_u + 0_u^+$) STATES COMPARED WITH EXPERIMENTAL RESULT OF KOEHLER et al.

In addition to the lack of confidence in the spectrum of Freeman et al. [FMC71], another uncertainty arises in these derived potential parameters because of the lack of knowledge of the ratio of populations of 1_u to 0_u^+ . Our earlier studies using synchrotron radiation to excite Xe_2 in the red wing of the atomic resonance transition [BRW80] clearly show from the lifetime measurements that the two states are populated approximately equally at excitation wavelengths in the 150- to 160-nm range. This was shown in Figure 2, which indicates the substantial (~50%) contribution from the long-lived 1_u state when excited by 156-nm photons. That result was the basis for our assumption of equal contributions from the 1_u and 0_u^+ states in calculating the integrated spectrum above. Table 3 lists the ratio of 1_u to 0_u^+ emission intensities as a function of excitation wavelength and shows that the 1_u state is being strongly excited throughout this wavelength range, which is contrary to expectations based solely on the relative radiative lifetimes of the singlet and triplet excimer states. This result has important implications for the experiments described in this report, where excitation occurred at the F_2 laser wavelength of 158 nm.

Calculated Spectra Based on Present Experiments

The spectra presented in this report provide a substantial new data base of Xe_2 emission spectra that have been state-identified by their time dependence. In particular, the late-time data that are identified as the 1_u emission spectra provide a clear means of evaluating the 1_u potential given that the ground state is well established. The surprising feature of these results is the width of the continuum band from a single state. Figure 30 presents a calculated spectrum for the 1_u state based on the 1_u potential from [LLS85]; clearly, this potential cannot produce such broad spectra from a single state. The data could only be fit if both states are contributing. In Section IV, we discussed the possibility that both states could be contributing at very late times after the excitation pulse because of photoionization of the excited dimers during the laser pulse. We concluded that singlets could contribute less than 2% to the late-time emission because of this process. Also, because of the high pressure at which these data were obtained, we conclude that the emission spectra are representative of a thermally relaxed 1_u state at 300 K.

Table 3

RATIO OF 1_u TO 0_u^+ INTENSITIES AS A FUNCTION OF EXCITATION WAVELENGTH
FROM SYNCHROTRON STUDY

<u>Transition, Energy (cm⁻¹)</u>	<u>0_u^+ Intensity</u>	<u>1_u Intensity</u>	<u>Ratio of $1_u/0_u^+$</u>
63404	580	1000	1.72
63801	607	993	1.64
64204	606	929	1.53
65525	623	1049	1.68
65276	663	1028	1.55
65570	644	1180	1.84

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FIGURE 30 THEORETICAL SPECTRUM OF THE $\text{Xe}_2^* (1_u)$ STATE USING POTENTIALS BASED ON LLS DATA COMPARED WITH PRESENT EXPERIMENTAL LATE-TIME SPECTRUM

Accepting the conclusion that our late-time decay spectra are truly representative of the thermally relaxed 1_u state, we proceed to find a potential that will produce the spectrum. We assume that the ground state potential discussed above (Figure 26) is valid and use it as a basis for determining the necessary parameters. To calculate the very wide bandwidth, it is necessary to move the R_e inward where the ground state is steeper, but to maintain the mean transition wavelength of 171.5 nm, we must reduce the well depth. We found that a Morse potential with the following characteristics gives an excellent reproduction of the experimental spectrum: $D_e = 2300 \text{ cm}^{-1}$, $\omega_e = 110 \text{ cm}^{-1}$, and $R_e = 3.04 \text{ \AA}$. The spectrum calculated from this potential is shown in Figure 31 together with two experimental late-time spectra taken under differing conditions. This 1_u potential is shown in Figure 32 along with the [LLS85] potentials.

Status of Other Parameters Required to Calculate Spectra

In the same way as we derived a potential curve for the 1_u state that allows us to calculate spectra that fit the late-time data, we will be able to derive a potential curve for the 0_u^+ state that will allow us to calculate spectra that fit the early-time results. As noted above, these spectra are assumed to be from fully relaxed Xe_2^* , so only the lowest vibrational levels are populated, and R is close to R_e for all levels. The calculation of spectra at high temperature then requires two additional pieces of information. The first is the transition probability versus internuclear spacing (corresponding to high degrees of vibrational excitation) for each of the two excimer states, and the second is the vibrational populations in each of the two states.

The lifetimes of the relaxed excimer states of Xe_2 have been accurately measured [BRW80], but the transition rate as a function of R is uncertain in the intermediate region between R_e and the atomic limits. Castex [Ca81] estimated the R -dependent transition moments and compared them with the theoretical values calculated by Ermler et al. [ELP78]. Recently, the Toronto group [MHS86] measured the transition lifetime of the $\text{Xe}_2 1_u$ state at large R (4.3 $\text{\AA}$) to be about half of the lifetime at R_e .

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FIGURE 31 THEORETICAL SPECTRUM OF $\text{XeO}_2^+ (1_u)$ STATE BASED ON NEW POTENTIAL CURVES COMPARED WITH EXPERIMENTAL LATE-TIME SPECTRUM

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FIGURE 32 COMPARISON OF NEW POTENTIAL CURVE WITH CURVES
BASED ON RESULTS OF LIPSON *et al.*

Determining the vibrational populations in both states is a complex kinetic calculation requiring rates for mixing both the pair of molecular states and the pair of atomic states, as well as the vibrational relaxation rates. Some of these rates were measured by Bonifield et al. [BRW80] in our previous synchrotron radiation study. They include the rate for $1_u - 0_u^+$ mixing, which is very slow ($k_d = 1.3 \times 10^{-13}$ and $k_u = 4.6 \times 10^{-15} \text{ cm}^3/\text{s}$). Similarly, the collisional transition of $\text{Xe}(^3P_1)$ to the 3P_2 state is also slow ($\approx 3 \times 10^{-13} \text{ cm}^3/\text{s}$).

VI SUMMARY AND CONCLUSIONS

We conducted an extensive series of measurements of the time-resolved Xe_2^* emission spectra following optical pumping by a short-pulse F_2 laser at 157.6 nm. Most measurements were performed using a gated OMA detector; to increase our confidence in the results, we also made measurements using a scanning monochromator fitted with a photomultiplier and using a boxcar integrator for time resolution. The two sets of results agree well and show that both the singlet and triplet emission bands are broader than expected, and have center wavelengths closer together than expected. Curve fits to the data yield the parameters for the fully relaxed states:

$$\begin{array}{lll} \text{Triplet:} & \lambda_c = 1714 \pm 6 \text{ \AA} & \Delta\lambda = 122 \pm 2 \text{ \AA} \\ \text{Singlet:} & \lambda_c = 1704 \pm 6 \text{ \AA} & \Delta\lambda = 131 \pm 3 \text{ \AA} \end{array}$$

Measurements were performed both at room temperature and at elevated (140°C) and reduced (-27°C) temperatures.

The broad bandwidth of the individual spectral bands was unexpected and, in particular, conflicted with a previous spectral measurement using optical pumping by the Xe^* resonance line from a microwave discharge lamp. Therefore, we also performed a series of spectral measurements using this type of optical pumping. We achieved good agreement with some previous results in the literature, but not with the result in question. We conclude that the present results are reliable.

The results presented in this report therefore provide the first definitive measurement of the individual excimer emissions from each of the $\text{Xe}_2(0_u^+)$ and $\text{Xe}_2(1_u)$ states. From these measurements and the known ground state potential, we derived a 1_u potential that reproduces the emission band very well. In a similar manner, it will be possible to derive a potential for the 0_u^+ state. However, the 1_u potential is in substantial disagreement with the recent 1_u potential derived by the Toronto group [LLS85]. From these potentials, it should be possible to calculate with reasonable accuracy the Xe_2 emission and absorption under various temperature and pressure conditions.

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