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TITLE   Time-Resolved Fluorescence Measurements of KrF Emission
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Time-Resolved Fluorescence Measurements of KrF Emission Produced by Vacuum Ultraviolet Photolysis of KrF_2 and Kr/F_2 Mixtures

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ABSTRACT

Vacuum ultraviolet (VUV) light radiation was used to produce electronically excited KrF excimers (in D-, B- and C-states) by the photolysis of KrF_2 and F_2/Kr mixtures at various excitation wavelengths. The excited KrF photoproduct quantum yield was measured over the excitation wavelength range of 120 to 200 nm, and a quantum efficiency of 0.45 was estimated at the peak absorption wavelength of 159 nm for KrF_2. The collision-free fluorescence lifetime of the B-X transition near 248 nm was determined to be 9.9 $\pm$ 0.6 ns when the KrF_2 was excited with the 159 nm light. Near gas kinetic rate constants were measured for the quenching of KrF B-X emission by KrF_2 and CO_2. Using the threshold energy needed for observing excited KrF photofragments, an upper bound for the bond dissociation energy of KrF_2 was determined to be 1.03 $\pm$ 0.1 eV.

INTRODUCTION

In recent years, interest in high power excimer lasers has prompted several studies of light induced reactions between rare gas atoms and halogen containing molecules[1] and photochemistry of excimer producing molecular precursors.[2] Much of the work has aimed at understanding the kinetic processes that are relevant to excimer laser systems, namely, reactive mixtures of Cl_2 and HCl with Ar, Kr, and Xe.[3] The KrF laser system in particular has attracted much attention, since it has been proposed as a fusion driver. Several issues concerning the efficient operation of this laser system are of great importance. The VUV light excitation technique provides a convenient way for quantifying KrF excited state spectroscopic parameters as well as its related kinetic processes. Molecular precursors of KrF such as KrF_2, can be readily synthesized in a stable form and have been proposed as a candidate species for the active medium of an extremely high power amplifier.[4] It is believed that upon modest electronic excitation, favorable dissociation channels open up to provide a high yield of excited KrF excimers. The VUV photochemistry of KrF_2 is particularly interesting since it can furnish the detailed information (e.g. dissociation cross section, quantum yields, and branching channels) pertinent to the operation of a laser amplifier as well as some fundamental spectroscopic information related to KrF. In this paper, we will present a study of the KrF_2 photolysis and the photolytically induced reactions of Kr/F_2 mixtures using tunable VUV light sources in the

110 to 200 nm region. Particular emphasis is directed at investigating the importance of electronic state-specificity in the molecular precursor and its relation to the branching ratio, quantum yield, and the internal energy content of the resultant photoproducts. The VUV excitation method also provides a direct means for examining photochemical processes in a time-resolved manner.

EXPERIMENTAL

Two kinds of experimental apparatus are used for these experiments to excite KrF_2 and Kr/F_2 mixtures of interest in the 110 to 200 nm region. Both a synchrotron light source, the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, and a coherent VUV light source generated via non-linear processes in metallic vapor and/or inert gas media with tunable lasers are used. The two light sources are utilized in a complementary fashion. The synchrotron light provided a broadly tunable and short pulse-width (1 ns) VUV excitation source for the low-resolution excitation and fluorescence study as well as for the fast fluorescence decay measurements. The laser-based coherent light source, on the other hand, allowed a much higher spectral resolution (1 part in $5x10^5$), relatively high peak intensity, and long time window for high resolution excitation and time-resolved kinetic experiments.

Similar experimental apparatuses have been described in detail elsewhere[5,6] and will be outlined briefly here. For this particular experiment, the synchrotron light source (NSLS U9A) was operating in

six-bunch mode (out of the "normal" nine bunches of electrons). The light was dispersed by a 0.5-m monochromator and the sample gas was irradiated in a stainless-steel cell with LiF windows. Under our typical experimental conditions, a spectral resolution of 1 nm was used. Photoproduct emission was detected at right angles using a cooled photomultiplier tube (PMT) with appropriate optical filters or an 0.2-m monochromator and associated photon counting electronics. Fluorescence decays were also monitored as a function of time using a fast time-to-pulse-height converter. Generally, the fluorescence signals were taken synchronously using the last synchrotron pulse of the "multi-bunch" mode allowing a longer time interval with which to measure the decay lifetime. A mini-computer interfaced multichannel analyzer system was used for signal averaging as well as data acquisition and reduction.

For the laser-based coherent light source, a XeCl excimer laser or a Nd:YAG laser pumped tunable dye laser with the option of frequency doubling or mixing was used to generate wavelength in the 300 to 500 nm region. The laser light was then frequency tripled in Hg and/or inert gases (i.e. He, Xe, Kr, and Ar) to produce tunable VUV pulses in the 120 to 180 nm region.[7] A 0.2M VUV monochromator was used to separate the fundamental dye laser beam from the VUV light radiation. The VUV light was then directed to a six-port reaction cell fitted with LiF windows. The photoproduct fluorescence was detected at right angle using a solar blind PMT with appropriate optical filters, and the VUV excitation photon flux was monitored with either a micro-channel plate or a channeltron which was located in a high vacuum housing behind the reaction cell. The electrical

signals from these detectors were then sent to a mini-computer interfaced data acquisition system which included a fast transient digitizer and a box car averager.

The sample pressure was monitored using 1-torr, 10-torr, and 100-torr MKS Baratron heads attached to various cells and manifolds. The gas samples with the exception of F_2 and KrF_2 (i.e. He, Ar, Kr, Xe, and CO_2) were of research grade purity and were used without further purification. The F_2 was from the 5% F_2 in He "excimer laser" mixture of Spectra Gas Inc.. The KrF_2 was synthesized by the INC-4 Group of Los Alamos National Laboratory.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum of the KrF_2 molecules in the 120 to 200 nm region. The absorption reaches a maximum around 159 nm and is determined to have an absorption cross section of approximately 1×10^{-17} cm^2 in rough agreement with a previous measured value.[8] The excitation fluorescence spectra, observing at two different emission wavelengths, the 222-nm D-X transition of KrF and the 248-nm B-X transition, are displayed in Figure 2 and 3, respectively. These spectra seem to mimic the absorption spectrum indicating that the photodissociation channel does not alter markedly in this excitation wavelength range. By examining the excitation spectra at the long wavelength limits for producing KrF emission, threshold wavelengths of 194 $\pm$ 0.5nm and 188 $\pm$ 0.5 nm were determined for producing 248 nm (B-X) and 222 nm (D-X) emission, respectively.

By subtracting the observed amount of electronic excitation in the KrF photofragment from the amount of energy that was put in the KrF_2 precursor, an upper bound of the energy needed for dissociating KrF_2 to KrF + F can be deduced to be 1.03 eV and 1.3 eV for the 222-nm and 248-nm data, respectively. Since it appears that the threshold energy deduced for the 248nm emission is really limited by the absorption threshold of the KrF_2 molecules rather than the energy needed for bond dissociation, the higher energy channel (222-nm emission) which gives the lower value of 1.03 eV most likely provides a better estimate of the bond dissociation energy. This is in very good agreement with a theoretically calculated value of 1.013 eV.[9] In addition, using the 230-nm CF_2 emission observed in the photolysis of CF_3Br[5] and the quantum yield of CF_3 UV emission deduced by Suto and Lee[10] as a calibration, a quantum yield for producing B-state KrF in the 159-nm photolysis of KrF_2 was estimated to be 0.45. This indicates that KrF_2 can be an extremely good candidate species for generating excimer laser.

KrF emission spectra that were obtained at several excitation wavelengths are shown in Fig. 4 over the range from 180 to 350 nm. The emission bands that are most distinguishable in these spectra are the predominant B-X transition at 248 nm with noticeable vibrational features and the D-X transition at 222 nm. A weak and broad emitting system to the red of the 248 nm band was also observable and can be assigned to the C-A transition. The emission spectra appear to be very similar for the four different excitation wavelengths of 129, 152, 159, and 166 nm. However, it appears that the higher energy channels (e.g. 222 nm emission) become increasingly more important at

the shorter wavelength excitation, indicative of an increase of available excess energy in the photofragments. This is particularly evident in the emission spectrum of KrF using the 129-nm excitation. Also, it was observed that the weak C-A emission tends to be more pronounced at a lower KrF_2 precursor pressure, indicating that KrF molecules in the C-state were nascent photolysis products and were quickly quenched even at modest pressures of a few torr of KrF_2. Figure 5 shows an emission spectrum of a mixture of 16 torr Kr and 44 torr 5% F_2/He with the VUV light source tuned to the 123.6nm resonance of Kr. This spectrum appears to be very similar to that of the KrF_2 photolysis. Unfortunately, in these experiments in order to achieve reasonable signal to noise ratio, the spectra were limited by the wide slits (0.5 to 2 mm) of the emission monochromator (typically operated at low resolution, varied from 15- to 4-nm resolution at 250nm). It was not possible to discern individual vibrational states with a separation on the order of 0.5nm.[11] It should be very interesting to implement a detailed investigation of the vibrational contents of the emission spectra. We are currently improving our apparatus to achieve this objective. Under excitation conditions of relatively highe photon flux, a peculiar emission spectrum was also observed as shown in Figure 6 with an excitation wavelength of 159 nm. The spectrum appears to show a depletion of fluorescence at the peak of 248-nm band, with the bottom of the valley exactly corresponding to the normal fluorescence peak. Interestingly, similar effects were not observed under identical operating conditions when the excitation source was tuned to either 152 or 166

nm. Additional investigations are currently underway to provide a plausible explanation of this phenomenon.

Time-resolved measurements were obtained for the production of KrF emission under various pressure conditions. Figure 7 shows a typical time profile of the KrF 248-nm emission when 0.8 torr of KrF_2 was excited at 159 nm. A fluorescence lifetime can be obtained with a single exponential decay fitted to this curve. Using these fluorescence lifetimes obtained at various KrF_2 pressures, a collisional-free fluorescence lifetime of KrF at 248 nm and a quenching rate constant of KrF emission by KrF_2 were determined, the respective values obtained were 9.9 ± 0.6 ns and 2×10^7 $torr^{-1}sec^{-1}$. However, because the KrF_2 gas is highly reactive, it was difficult to determine the exact concentration of KrF_2, the value of the KrF_2 quenching rate constant has a fairly large uncertainty (20 -30%). The lifetime measurement is in close agreement with a value of $9.0 \pm$ 0.5 ns measured by Burnham and Searles[12] using ArF laser photoysis of KrF_2. However, it is different form a value of 6.8 ns measured by Eden et al.[13] using e-beam excited ArF emission as the photolysis source. This latter value was in agreement with a value of 7 ns calculated by Hay and Dunning.[14] It was predicted by calculations[11] based on the potential energy curves of Hay and Dunning that the upper vibrational manifolds of the B-state of KrF should have longer radiative lifetimes. In view of the large amount of excess energy available in the case of the 159-nm excitation KrF_2 (assuming the a bond dissociation energy of 1 eV, the excess energy is approximately 1.8 eV), it is conceivable that with a spectral resolution of 10 nm at 248 nm, our fluorescence lifetime measurements may see

contributions from vibrationally excited KrF, hence the longer lifetime. However, this argument cannot be applied to the measurement of Burnham and Searles where dissociation occurred very near the threshold energy, only approximately 0.3 eV excess energy was available. Additional experiments with higher resolution in emission wavelength to allow better vibronic state selection will provide a more definite answer. This will also permit the mapping of the lifetime dependence on vibrational levels and will be very useful to validate the results of the theoretical prediction. The quenching of the KrF emission by CO_2 was also measured in real-time. Figure 8 depicts the inverse of KrF fluorescence decay rate as a function of CO_2 pressure. From the slope of the linear least square fit to the points, a CO_2 quenching rate constants can be deduced to be 2.5 x 10^7 $torr^{-1}$ sec^{-1}.

ACKNOWLEDGEMENT

FIGURE CAPTIONS

1. The absorption spectrum of KrF_2 in the 120-200 nm region.

2. The fluorescence excitation spectrum of KrF_2 in the 120-200 nm region by viewing the D-X emission band of KrF at 222 nm.

3. The fluorescence excitation spectrum of KrF_2 in the 120-200 nm region by viewing the B-X emission band of KrF at 248 nm.

4. A series of emission spectra of KrF in the 180 to 350 nm region produced by the photolysis of KrF_2 at four different wavelengths: 129, 152, 159, and 166 nm.

5. The emission spectrum of KrF in the 180 to 300 nm region produced by exciting a mixture of 16 torr of Kr and 44 torr of 5% F_2 in He with 123.6-nm photons.

6. The emission spectrum of KrF in the 180 to 300 nm region obtained with relatively high photon flux excitation of KrF_2 at 159 nm.

7. A typical 248-nm fluorescence decay curve of KrF in the 159-nm photolysis of 0.8 torr of KrF_2

8. A plot of KrF fluorescence quenching rate as a function of CO_2 pressures.

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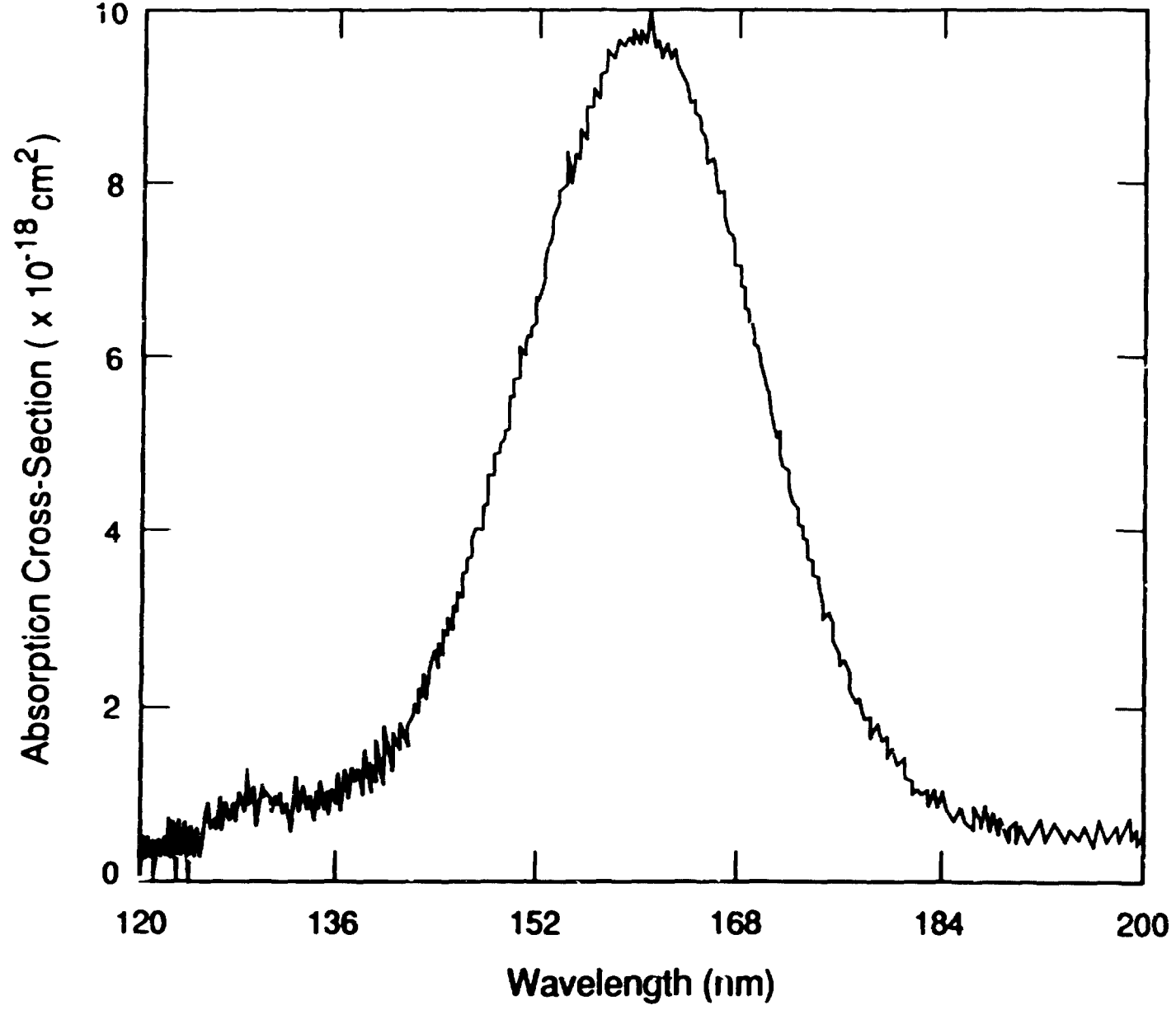
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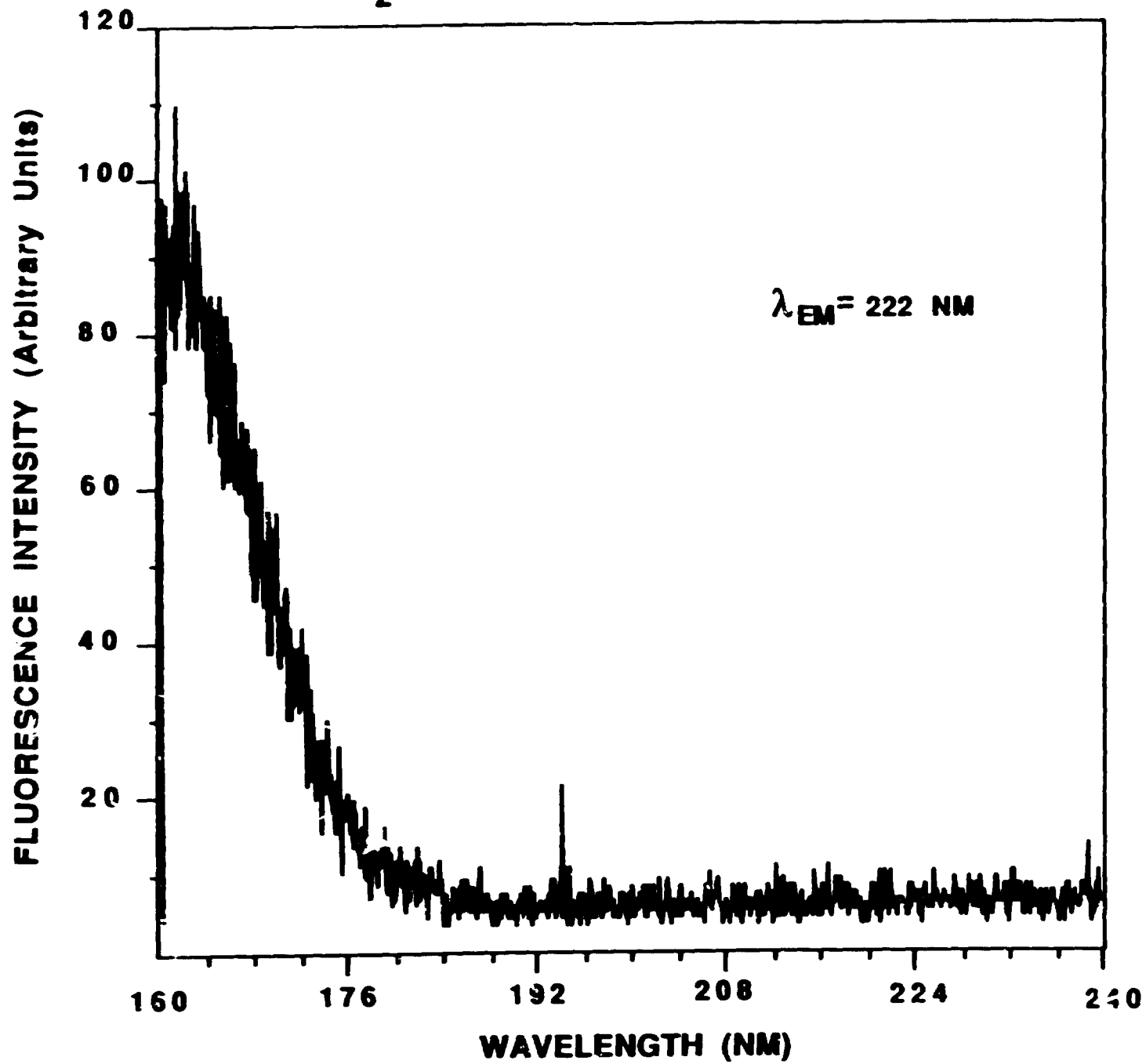

Figure 1.

KrF$_2$ EXCITATION SPECTRUM

λ_{EM}= 222 NM

FLUORESCENCE INTENSITY (Arbitrary Units)

WAVELENGTH (NM)

Figure 2.

KrF$_2$ EXCITATION SPECTRUM

λ_{EM}= 248 NM

FLUORESCENCE INTENSITY (Arbitrary Units)

WAVELENGTH (NM)
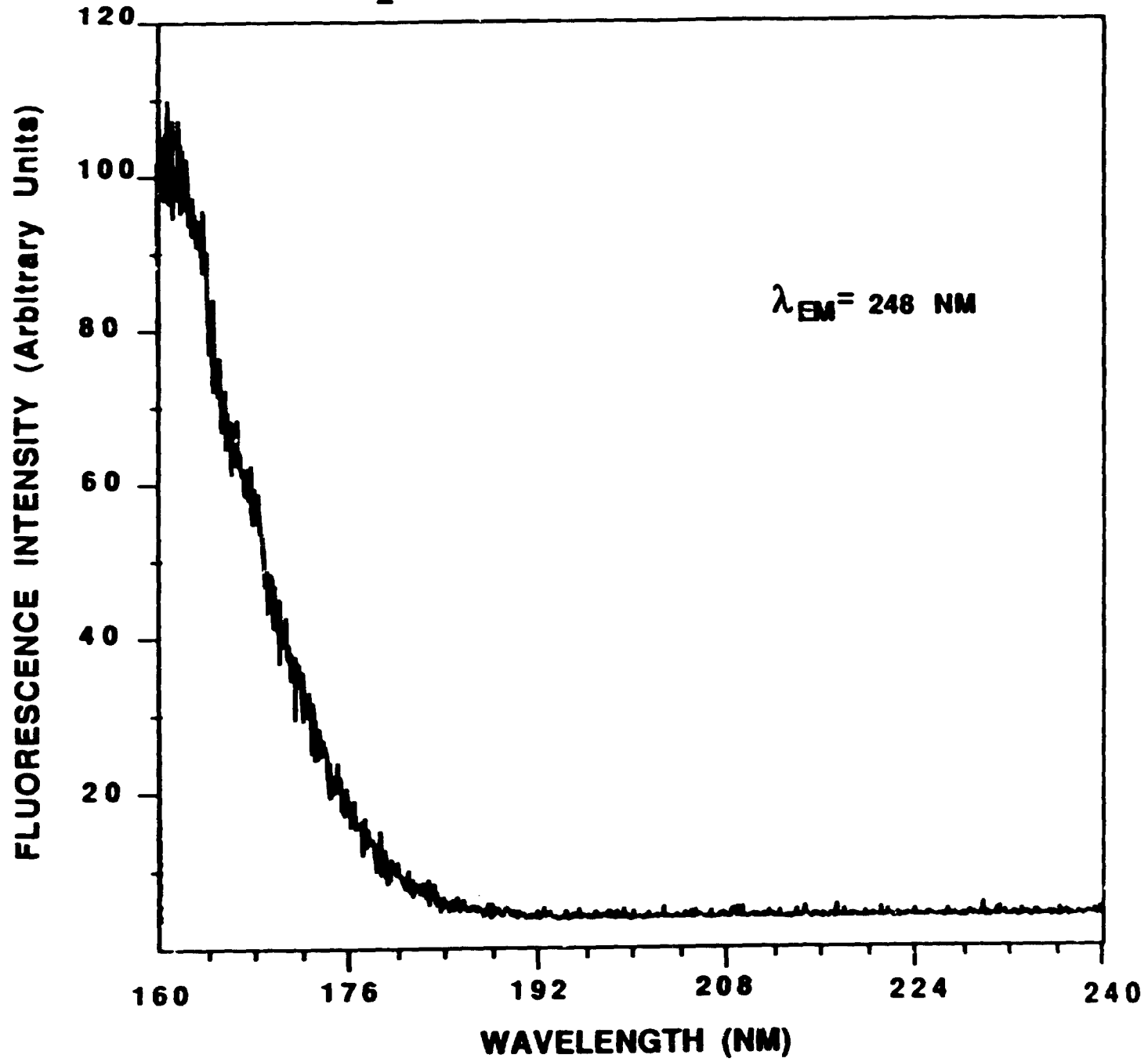
Figure 3.

KrF EMISSION SPECTRUM
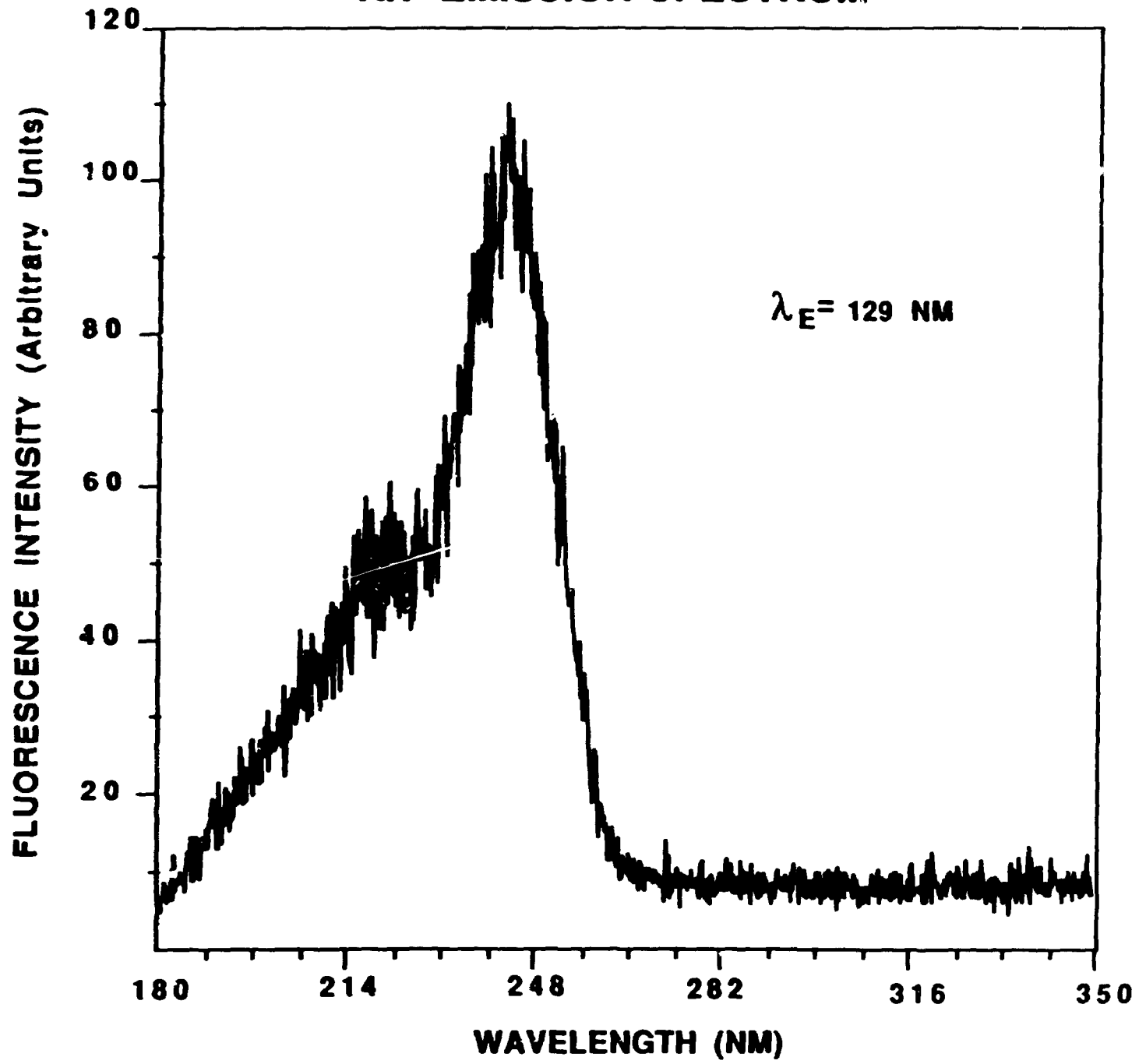
Figure 4a.

KrF EMISSION SPECTRUM

λ_E= 152 NM

FLUORESCENCE INTENSITY (Arbitrary Units)

WAVELENGTH (NM)
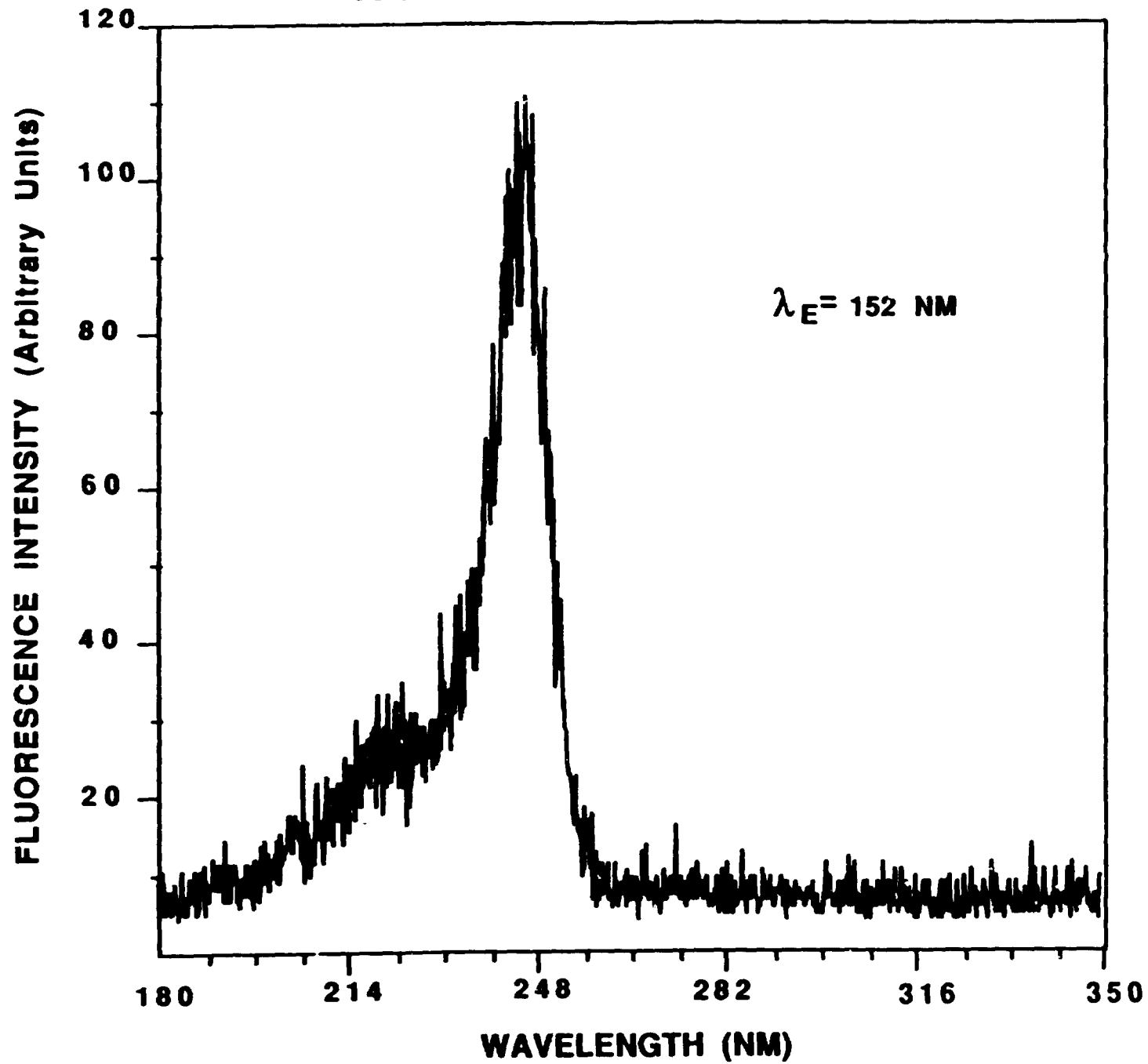
Figure 4b.

KrF EMISSION SPECTRUM

$\lambda_E = 159$ NM
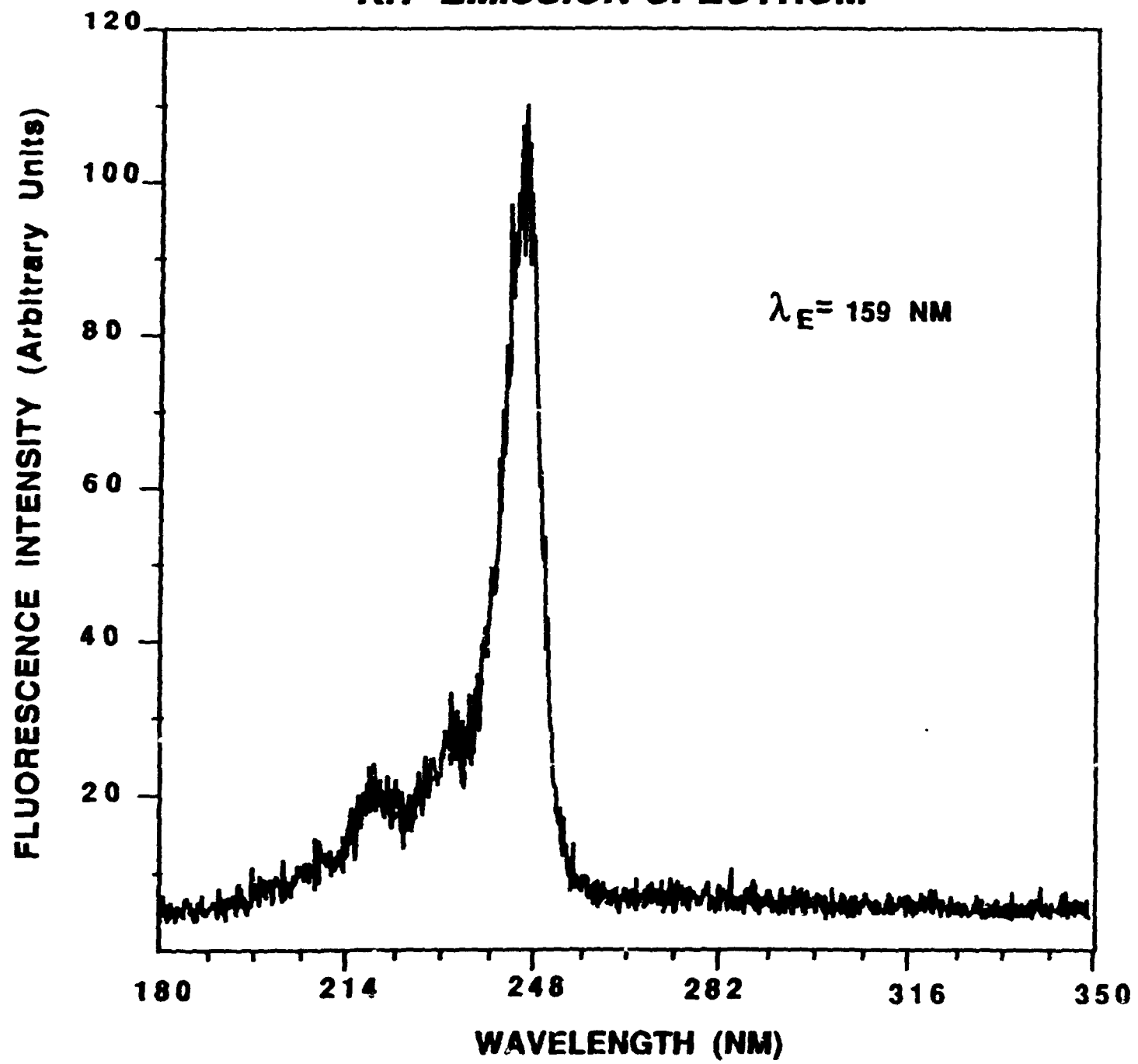
Figure 4c.

KrF EMISSION SPECTRUM
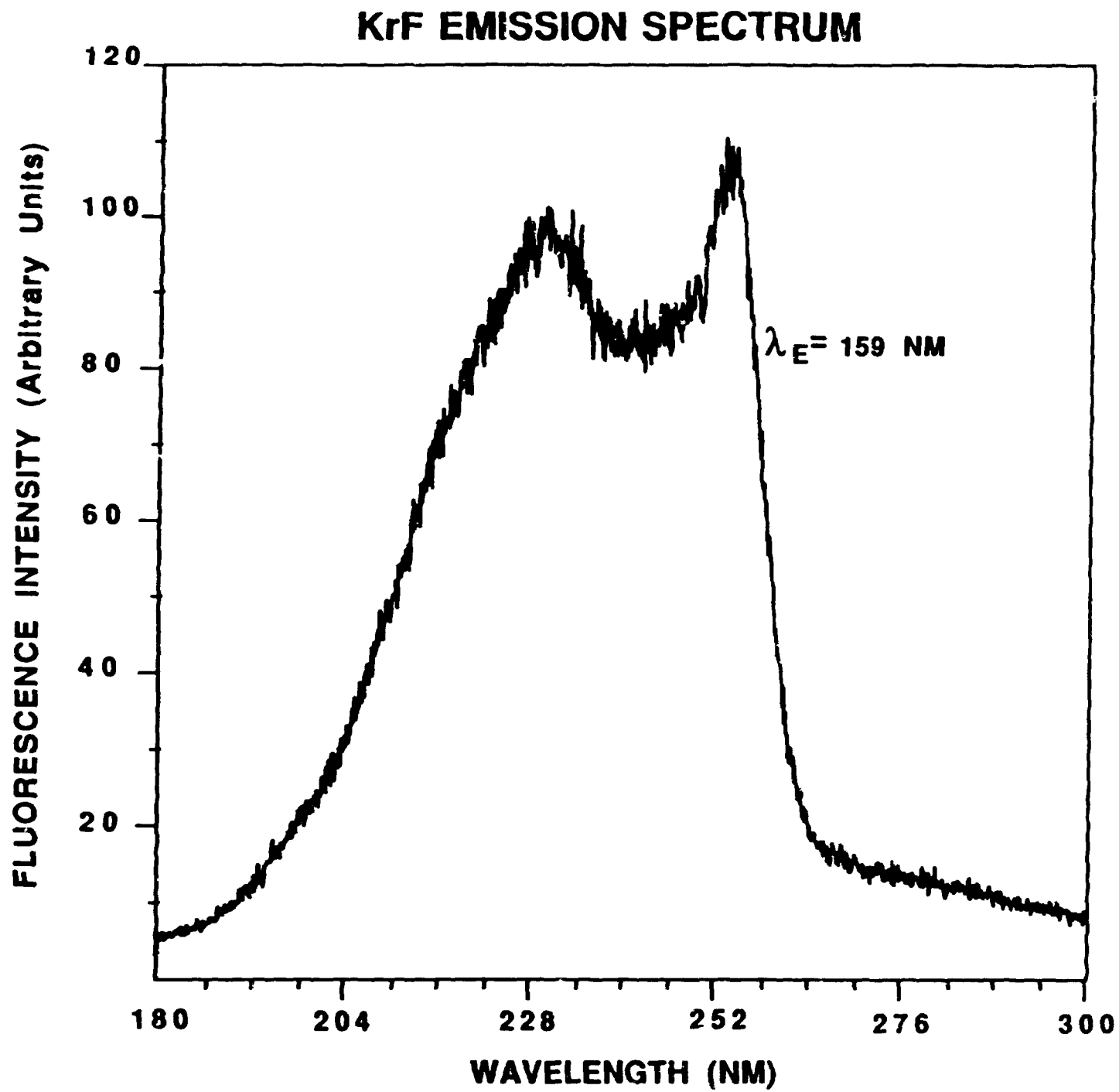
$\lambda_E = 166$ NM
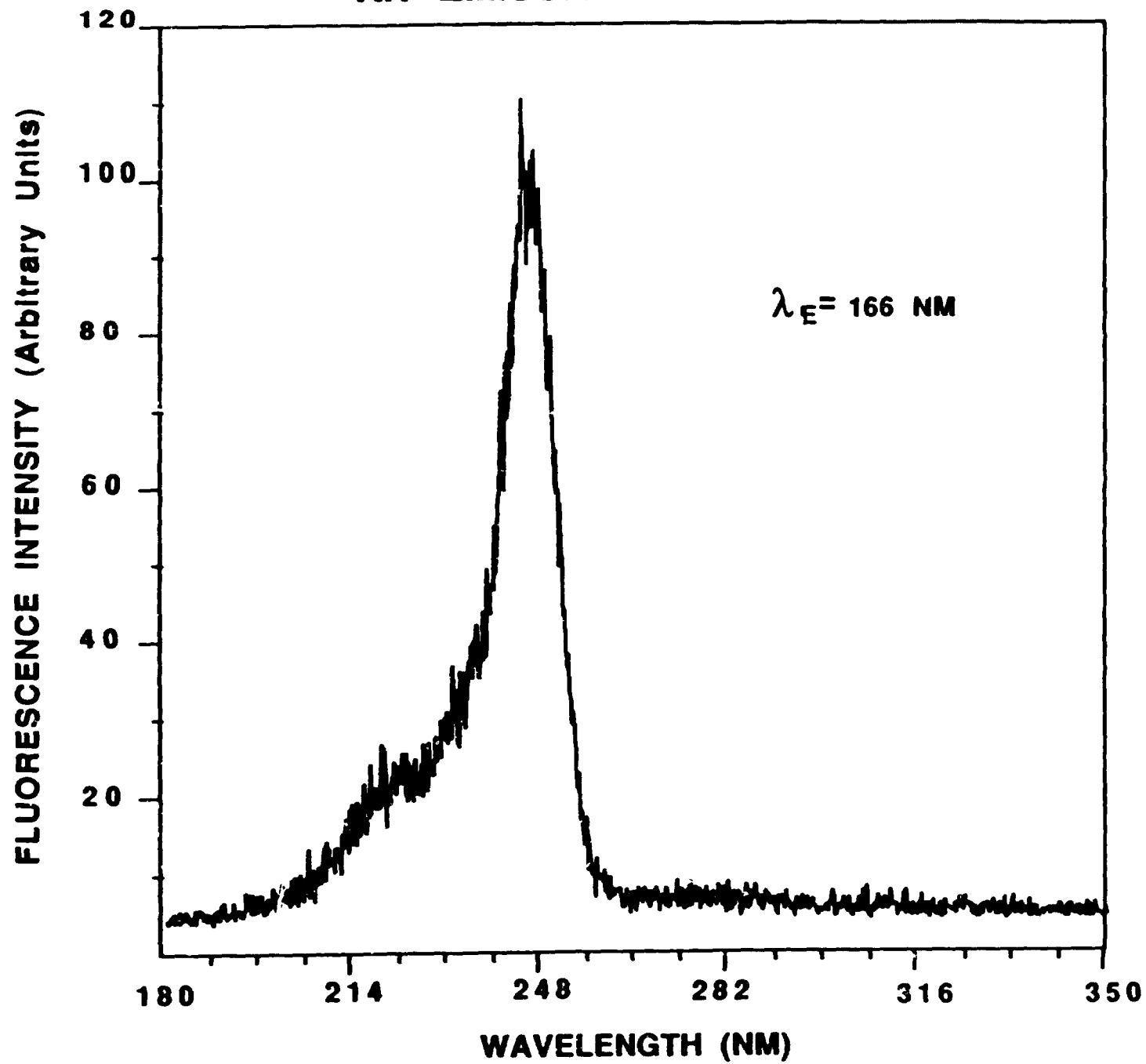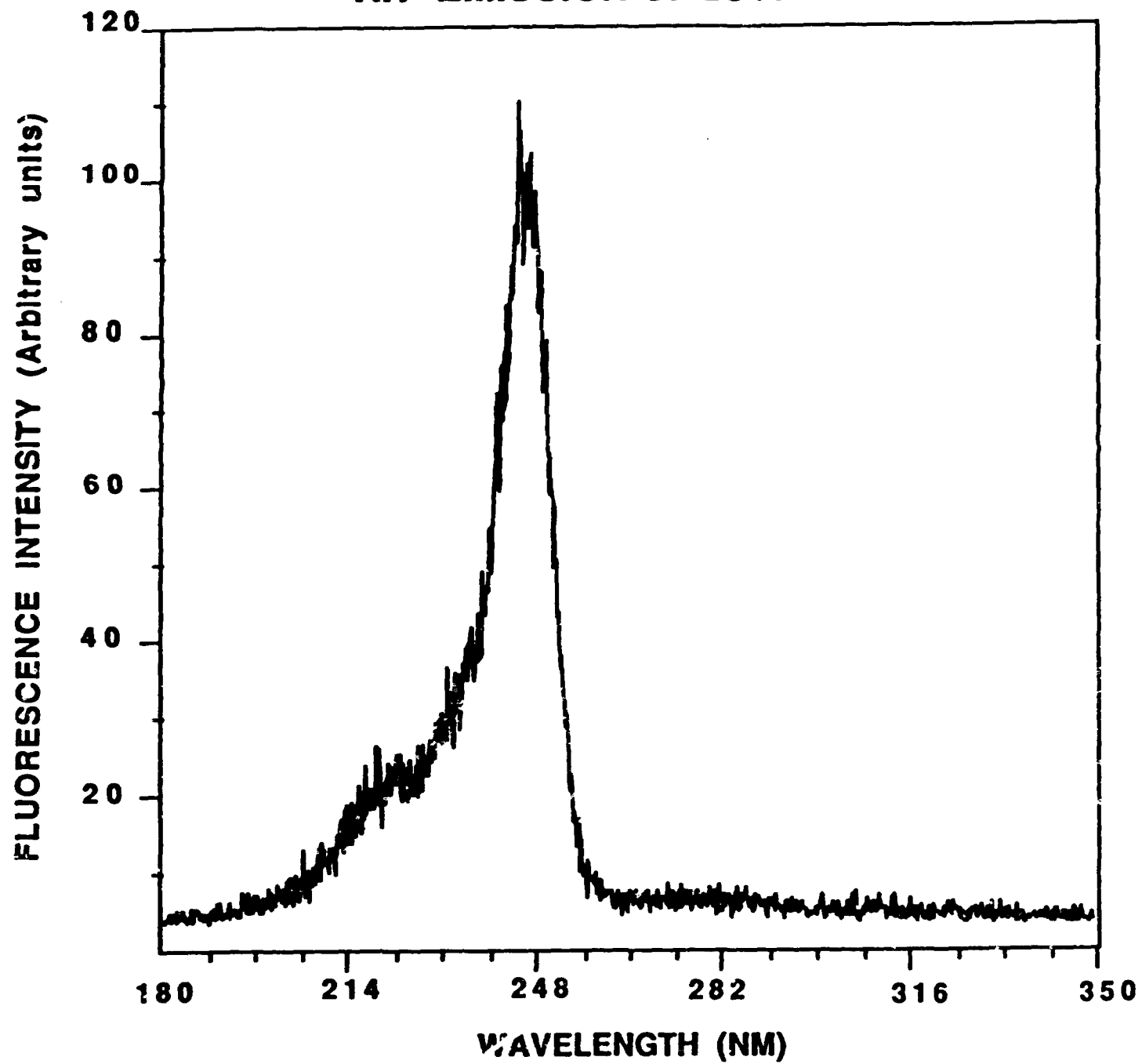
Figure 4d.

Figure 5.

Figure 6.

TEMPORAL PROFILE OF THE KrF EMISSION

Figure 7.

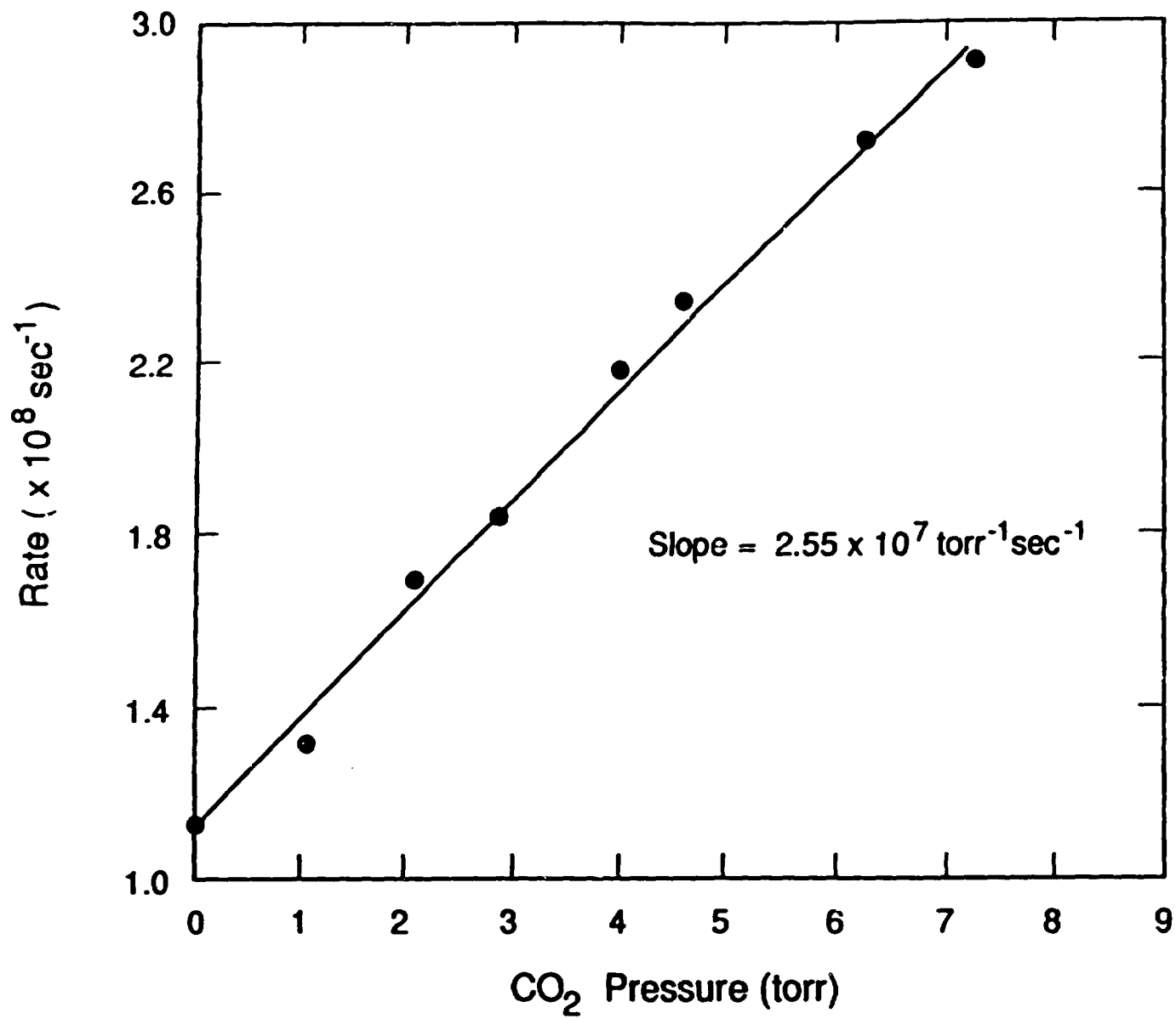Figure 8.

Slope $= 2.55 \times 10^7$ torr^{-1}sec^{-1}

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