Title

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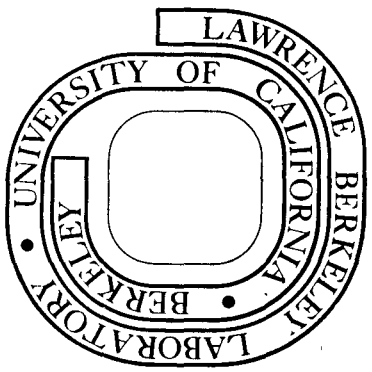

DISCLAIMER

TIME-RESOLVED VUV SPECTROSCOPY USING SYNCHROTRON RADIATION III. RADIATIVE DECAY MEASUREMENTS OF ELECTRONICALLY EXCITED STATES OF Xe_2^* †

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ABSTRACT

Synchrotron radiation from the Stanford Positron-Electron Accelerating Ring (SPEAR) was used to measure the radiative decay constants of the lowest lying excited electronic levels of Xe_2. Lifetimes of the 0_u^+ and 1_u manifolds were found to be 1.58(5) nsec and 317(13) nsec, respectively. Reversible intersystem crossing between these two electronic manifolds explains the pressure dependence of the lifetimes correctly. Values for intersystem crossing rate constants are derived and discussed.

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I. INTRODUCTION

There has been a great deal of recent interest in electronically excited excimer systems as ultraviolet lasing media.[1] For the continued development of these lasers, a detailed knowledge of the dynamics of the lasing transitions is essential. In particular, the lasing efficiency is dictated by the population inversion, which depends strongly on the lifetime of the upper level.[1,2]

In this paper we report measurements that were undertaken to evaluate the feasibility of utilizing the time structure of synchrotron radiation at the Stanford Positron-Electron Accelerator Ring (SPEAR) to determine the lifetimes of molecular levels. Because excimer lasers have been constructed using Xe_2 as the lasing medium,[1c] we chose to study the radiative decay of the Xe_2^* molecule. The 1720 Å emission of the Xe_2^* laser results from the radiative relaxation of low vibrational levels of the 0_u^+ and 1_u states to the repulsive wall of the ground state. Figure 1 shows the transitions of interest, after the work of Fink and Comes.[3] The expected asymmetric tail is well borne out in the typical absorption/excitation spectrum shown in Fig. 2.

Section II describes the experimental apparatus and technique. Section III gives qualitative results from the measurements. Section IV presents a quantitative discussion and comparison with other investigators.

II. EXPERIMENTAL

To study the decay of electronically excited molecular states quantitatively, a pulsed, tunable UV source is necessary. Synchrotron

radiation is an ideal source for probing molecular decay dynamics because the method of excitation is well-defined, and the fluorescence decay observations are direct. Electron-bombardment excitation, while convenient and efficient, is not highly selective. Populating highly excited species via electron bombardment leads to cascading decays through lower lying states and convolutes the time evolution of these lower states.

The experimental set-up has been described in detail elsewhere,[4] but a brief description follows. The synchrotron radiation was dispersed by a Seya-Namioka monochromator (GCA/McPherson, UHV design) and entered the sample chamber through a LiF window. Detection of the fluorescent radiation was done perpendicular to the beam axis without energy discrimination. Only photons with $1050\,\text{Å} \leqslant \lambda \leqslant 1800\,\text{Å}$ were detected, with the upper and lower wavelength limits determined by the photocathode response[4] and photomultiplier tube window material (LiF), respectively.

The radiation from SPEAR was pulsed, with a pulse width of 0.4 nsec and a pulse repetition period of 780 nsec. A photon coincidence technique, which measured the time between the initial excitation pulse and a single fluorescent photon pulse, generated the decay curve. This time was measured by a time-to-amplitude converter, which was then analyzed and stored in a multichannel analyzer operating in the pulse-height mode.

The Xe sample gas and Kr buffer gas used in this experiment were supplied by Airco with purities exceeding 99.995% and were used without further purification. All experiments were carried out at ambient

laboratory temperatures, approximately 293°K.

Fluorescent decay curves were generated under two conditions: pure Xe with pressure varying between 5 and 75 Torr, and Xe with pressure fixed at 25 Torr, and Kr buffer gas varying between 0 and 400 Torr. The excitation energy varied between 1471Å and 1479Å for the pure Xe measurements, and was kept fixed for the Kr buffer gas measurements at 1478 Å.

All excitation was done off-resonance from the $^3P_1$ atomic transition but higher in energy than the $^3P_2$ atomic transition. Exciting off-resonance from the $^3P_1$ atomic level insured that excited molecules were formed only by direct transitions from ground state (0_g^+) molecules. Resonant atomic excitation would allow excited molecules to form by three-body atomic collisions, where one of the collision partners is an atom in the $^3P_1$ state.[5] To insure that all excited molecules were created in the 0_u^+ state, excitation was done above the $^3P_2$ resonance.

For the ambient conditions used in these experiments, Xe_2 molecules represent approximately 0.001% of the total pressure. This was deduced from classical statistical thermodynamics,[6] using the data of Lee.[7] The equilibrium partial pressure of Xe_2 increases quadratically with pressure, which implies that the highest operating pressure possible is desirable. A judicious choice of pressure was made to prevent collision events from dominating the radiative decay. Pressures of Xe of the order of 25 Torr proved to be adequate.

III. RESULTS

The Kr buffer gas decay curves were recorded on a 1 μsec time scale and illustrate all of the salient features of the decay dependence on pressure. Figure 3 shows the results of the Kr buffer gas measurements. These decay curves clearly indicate the presence of two major components. Initial attempts at least-squares fitting of the decay curves to two exponentials, however, gave fits that were not completely satisfactory. By introducing a third component, excellent agreement was obtained. The results of these fits are summarized in Table 1.

Both lifetimes, τ_1 and τ_2, decrease with increasing buffer gas pressure, although the shorter component, τ_1, appears to have reached a limiting value ($\sim$1 nsec) for total pressures above 125 Torr. Since the ultimate timing capabilities of our system is $\sim$1 nsec, these values for the short component are in fact upper limits of the true lifetime. Asymmetry in the time-response curve limited the ultimate time resolution of the apparatus. To assess this effect, the instrumental response function was measured experimentally using "prompt", Rayleigh-scattered non-resonant radiation. The curve obtained in this way is illustrated in Fig. 4. In order to obtain the pressure dependence of the short-lifetime component it was necessary to utilize previously recorded decay curves for pure Xe at pressures below 100 Torr.[8] A typical pure Xe lifetime measurement is given in Fig. 4. These curves were generated using a shorter time scale (100 nsec) than the Kr buffer gas studies (1 μsec), thus precluding accurate measurement of the long lifetime, τ_2. The values of the short lifetimes are listed in Table 2. A steady

decrease in the short lifetime with increasing pressure is clearly evident.

For both the pure Xe and Kr buffer gas measurements, the third component, τ_3, had a lifetime intermediate between the other two components and an integrated intensity an order of magnitude smaller than either of the other two. No systematic variation with pressure was observed. The origin of this third may well be instrumental and needs to be re-checked with a faster time-response detector. It does not alter the conclusions of this paper, and will not be discussed further.

IV. DISCUSSION

Because there are two electronic manifolds with dipole-allowed transitions in the wavelength region probed, 0_u^+ and 1_u, a two-component decay is expected. Furthermore, the 1_u lifetime is expected to be longer than the 0_u^+ lifetime, because the 1_u state has a separated atom limit which is dipole-forbidden to fluoresce[9] ($^3P_2 \rightarrow {}^1S_0$). Thus, the long- and short-lived decays are assigned to the 1_u and 0_u^+ manifolds, respectively. The model proposed below must be consistent with these assignments, and must explain the observed variations of the two lifetimes with pressure.

Direct population of the 1_u manifold in this experiment is precluded because the excitation radiation was at a sufficient energy to populate only the 0_u^+ manifold. Because a long-lived decay component was observed (see Table 1), there must exist an indirect route that populates the 1_u state. Fink and Comes[3] and Brodmann and Zimmerer[5,10] have shown that vibrational relaxation occurs at Xe pressures as low

as 20 Torr. In the notation of Brodmann and Zimmerer,[5] vibrational relaxation of the upper levels of the 0_u^+ manifold populates the $^{1,3}\Sigma^+$ manifold (see Fig. 1). Their work suggests that intersystem crossing is possible for the 0_u^+ state due to high efficiency of inelastic collisions.

Observation of the 1_u component implies that there is a non-radiative route depleting the 0_u^+ population, thus decreasing the 0_u^+ lifetime as the pressure is increased. Since the 1_u decay component has a lifetime that also decreases with increasing pressure, we surmise that the 1_u molecules can collisionally decay as well, to the 0_u^+ state. Thus, reversible intersystem crossing qualitatively explains the pressure dependence of the two decay components.

To quantify the model, the following equations are introduced:

$$Xe_2(0_g^+) + h\nu \longrightarrow Xe_2^*(0_u^+) \quad \text{(instantaneous)} \tag{1}$$

$$Xe_2^*(0_u^+) \xrightarrow{k_1} Xe_2(0_g^+) + h\nu \tag{2}$$

$$A + Xe_2^*(0_u^+) \xrightarrow{k_2} Xe_2^*(1_u) \tag{3}$$

$$A + Xe_2^*(1_u) \xrightarrow{k_3} Xe_2^*(0_u^+) \tag{4}$$

$$Xe_2^*(1_u) \xrightarrow{k_4} Xe_2(0_g^+) + h\nu \tag{5}$$

where A is a collision partner (either Kr or Xe atoms) and k_1^{-1} and k_4^{-1} are the radiative lifetimes of the 0_u^+ and 1_u states, respectively.

The intensity of emitted radiation, I(t), is

$$I(t) = \frac{\partial N_{0^+_u}}{\partial t} = k_1 N_{0^+_u} + k_4 N_{1_u} \tag{6}$$

The time dependence of $N_{0^+_u}$ and N_{1_u} is given by

$$\frac{\partial N_{0^+_u}}{\partial t} = -(k_1 + k_2 N_A) N_{0^+_u} + k_3 N_A N_{1_u} \tag{7}$$

$$\frac{\partial N_{1_u}}{\partial t} = -(k_4 + k_3 N_A) N_{1_u} + k_2 N_A N_{0^+_u} \tag{8}$$

These coupled differential equations both have the approximate solution:

$$N_i(t) = C_1^i \exp[-(k_1 + k_2 N_A)t] + C_2^i \exp[-(k_4 + k_3 N_A)t] \tag{9}$$

provided

$$4k_2 k_3 N_A^2 \ll (k_1 + k_2 N_A - k_3 N_A - k_4)^2 \quad .$$

This condition is insured by the large value of k_1. Substituting Eq. (9) into Eq. (6), one obtains

$$I(t) = a_1 \exp[-(k_1 + k_2 N_A)t] + a_2 \exp[-(k_4 + k_3 N_A)t] \quad . \tag{10}$$

The exponential decay parameters, $(k_1 + k_2 N_A)$ and $(k_4 + k_3 N_A)$, can be identified with τ_1^{-1} and τ_2^{-1} of Table 1, respectively. Similarly, $(k_1 + k_2 N_A)$ is identified with τ_1^{-1} of Table 2. THus, the slope of the plot of τ_1^{-1} versus N_A will yield k_2 and the intercept k_1 (A = Xe). Similarly, the slope and intercept of the τ_2^{-1} versus N_A will give k_3 and k_4 (A = Kr + Xe), respectively. A least-squares fit of the data

is presented in Fig. 5 (τ_1^{-1}) and Fig. 6 (τ_2^{-1}). The results of the analysis lead to a value of $\tau_{rad}^{0_u^+}$ = 1.58(5) nsec (= k_1^{-1}) and k_2 = 1.2(1) × 10^{-10} cm^3 S^{-1} (for Xe buffer gas), and $\tau_{rad}^{1_u}$ = 317(13) nsec (= k_4^{-1}) and k_3 = 2.5(1) × 10^{-13} cm^3 S^{-1} (for a mixture of Xe and Kr buffer gas).

Table 3 shows a compilation of lifetime measurements on the lowest lying states of Xe_2^*. The large amount of scatter in lifetime values demonstrate the need for a reliable experimental technique. Pulsed photon excitation is the most reliable, since the states being populated are well defined, and the resulting decays from these states are observed directly.

Brodmann and Zimmerer[5] and Fink and Comes[3] determined values of $\tau_{0_u^+} \cdot k$, where k is the vibrational relaxation rate constant. Employing the lifetimes derived from this work, the vibrational relaxation rate of Brodmann and Zimmerer is redetermined as $k = 3.25 \times 10^{-10}$ cm^3 S^{-1}. The vibrational relaxation rate of Fink and Comes is similarly redetermined as $k \cdot 2.5 \times 10^{-10}$ cm^3 S^{-1}. We note that these relaxation rates are similar to our k_2 value. This is not unexpected, because both vibrational relaxation and intersystem crossing are collisionally-induced processes de-populating the upper levels of the 0_2^+ state.

Actually, our slope in Fig. 5 represents a total depletion rate of the upper vibrational levels of the 0_u^+ state. Because we have not shown that this depletion only feeds the 1_u state, k_2 really represents an upper limit to the intersystem crossing rate.

In this discussion we have not considered radiation trapping explicitly. Based on the equilibrium concentration of dimers,[6,7] the distance between the fluorescent volume and our detector, and the absorption

cross-section of Xe_2, apparent lifetimes greater than one μsec would be expected from resonantly trapped fluorescent radiation.[4] Decay processes on such a slow time scale should appear as a constant background in our decay curves. Thus, we assert that we have observed decays from vibrationally relaxed dimers, for which the probability of photon re-absorption on its path to the detector is negligible, and not from radiation trapping processes. This contention is supported by the high constant background for the 25 Torr Xe measurement (see Table 1). Because the buffer gas pressure is zero in this instance, less vibrational relaxation occurs, causing the fluorescence to be more nearly resonant than in the cases with higher buffer gas pressure. We attribute this higher background at least in part to radiation trapping.

The ratio k_2/k_3 ($\sim$500) determined in this work implies that the $1_u \rightarrow 0_u^+$ intersystem crossing rate is much less efficient than the reverse process. The reasons for this are not obvious and indicate the need for further examination.

Implicitly, we have neglected variations of lifetimes with emission wavelength, which changes as vibrational relaxation occurs. A more refined model, which incorporates this vibrational dependence is needed to thoroughly explain the dynamics of the molecular states.

The decay dynamics of Xe_2 are accounted for on the basis of reversible intersystem crossing between the 0_u^+ and 1_u manifolds. Based on this model, accurate lifetimes have been demonstrated for the 0_u^+ and 1_u states, allowing a refinement of non-radiative decay constants associated with these important lasing states.

TABLE 1. Parameters from least-squares fits of Kr buffer gas decay curves.

P_{Kr} (Torr)	C_o	τ_1 (nsec)	C_1	τ_2 (nsec)	C_2	τ_3 (nsec)	C_3
0	2.06	1.4	1000	300	0.691	4.62	25.4
100	0.30	$\leq 0.9^*$	1000	253	0.268	3.25	10.9
200	0.53	$\leq 0.9^*$	1000	188	0.413	3.33	9.9
300	0.42	$\leq 0.9^*$	1000	176	9.32	3.72	1.10
400	0.50	$\leq 1.0^*$	1000	154	2.01	7.91	3.96

The data from Fig. 3 were fitted to an equation of the form $I(t) = C_o + \sum_{i=1}^{3} C_i\, e^{-t/\tau_i}$. C_i's are normalized to $C_1 = 1000$. Statistical uncertainties of τ values are less than 2%.

*These τ_1 values are not reliable, as discussed in text.

TABLE 2. Lifetimes from least-squares fits of pure Xe decay curves.

P_{Xe} (Torr)	λ_{ex} (Å)	τ_1 (nsec)
5	1477	1.64
10	1479	1.41
25	1478	1.38
44	1471	1.24
75	1471	1.10

The sum of three exponentials and a constant were used to fit these data. The short lifetimes are given.

TABLE 3. Compilation of lifetime measurements of lasing manifolds of Xe_2.

$\tau_{0_u^+}$ (nsec)	τ_{1_u} (nsec)	τ (nsec)†	Ref.
5.5(1.0)	96.5(50)		9
		50 ± 20	11
		130 ± 20	2
		2000 ± 500	12
4(1)	16(2.5)		13*
		16 ± 2	14
2	60		1b
1.58(5)	317(13)		present work

All measurements except present work and reference 1b employed pulsed electron bombardment excitation.

*Observed 280 nsec decay and assigned it to lifetime of highly excited state.

†Unspecified.

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FIGURE CAPTIONS

Fig. 1. Potential curves of Xe_2, showing van der Waals ground state and two lowest excimer levels.

Fig. 2. Absorption and excitation spectrum of Xe at 10 Torr.

Fig. 3. Kr buffer gas decay curves. The excitation wavelength for all these decay curves was 1478Å. P_{Xe} is 25 Torr for all decay curves. Least-squares fits are drawn over experimental points. Parameters of fits are discussed in text and listed in Table 1.

Fig. 4. Typical pure Xe decay curve. Fit is drawn over experimental data points. Slashes indicate where the fit starts and stops. The lower curve is the instrumental response function, as discussed in text.

Fig. 5. Short lifetime pressure dependence (pure Xe).

Fig. 6. Long lifetime pressure dependence (Kr buffer gas).

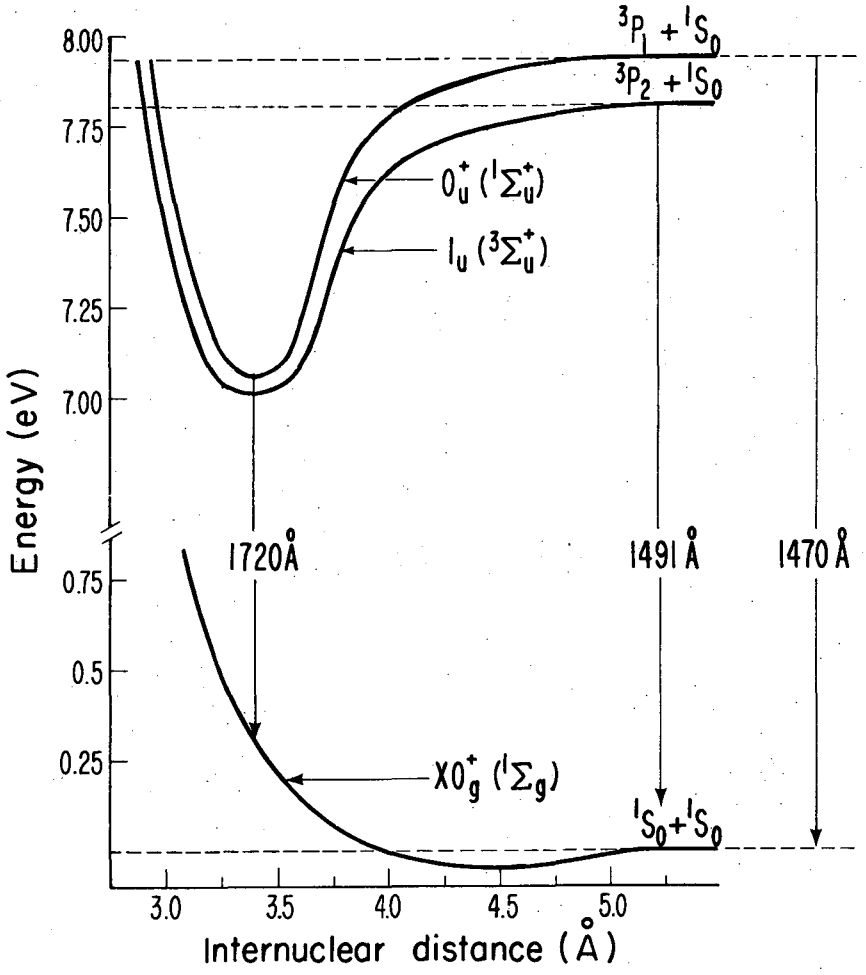

8.00
7.75
7.50
7.25
7.00
0.75
0.5
0.25
Energy (eV)
$^3P_1 + {}^1S_0$
$^3P_2 + {}^1S_0$
$0_u^+ ({}^1\Sigma_u^+)$
$1_u ({}^3\Sigma_u^+)$
$X0_g^+ ({}^1\Sigma_g)$
$^1S_0 + {}^1S_0$
1720Å
1491 Å
1470 Å
3.0
3.5
4.0
4.5
5.0
Internuclear distance (Å)

Fig. 1

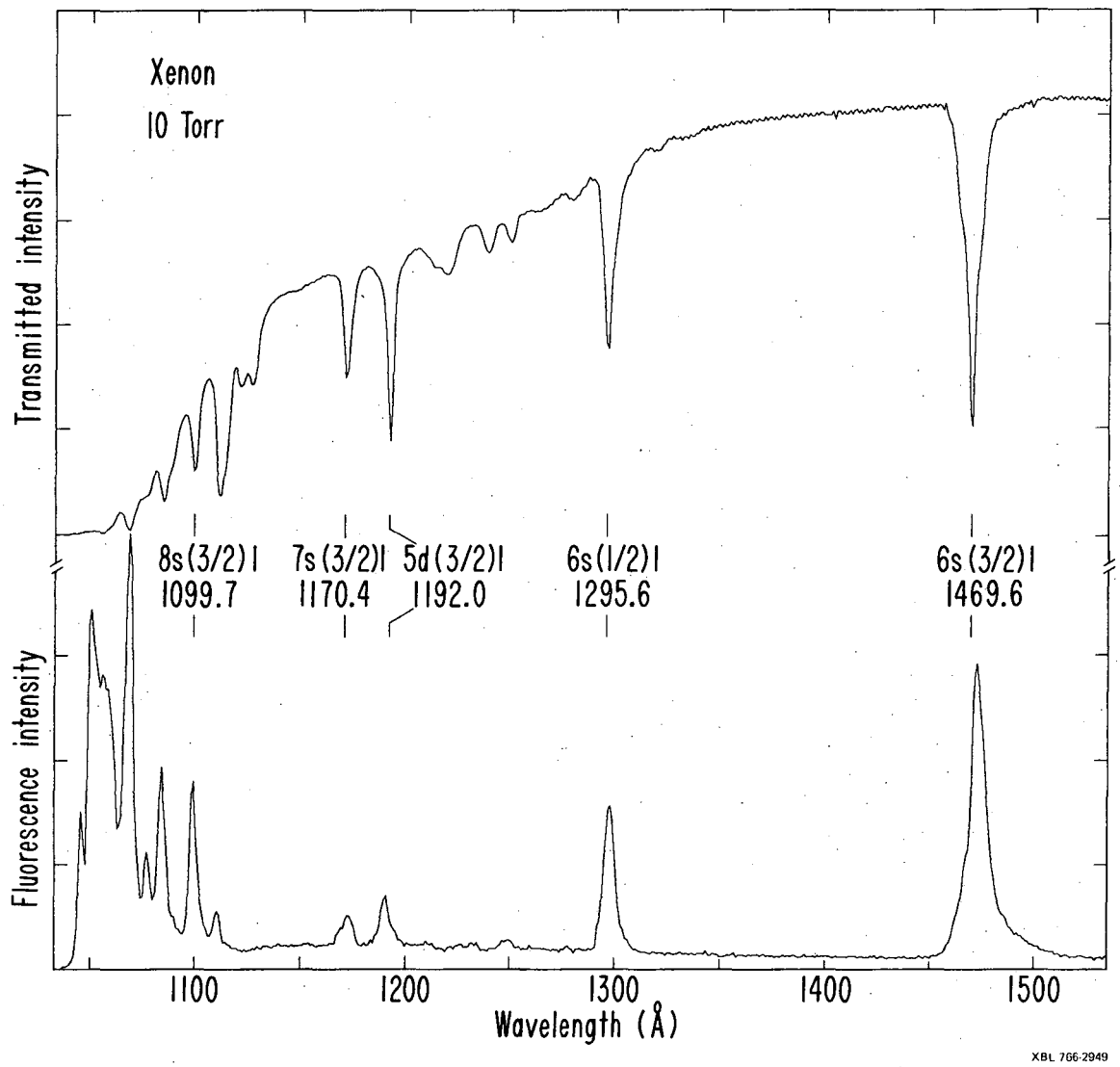


Fig. 2

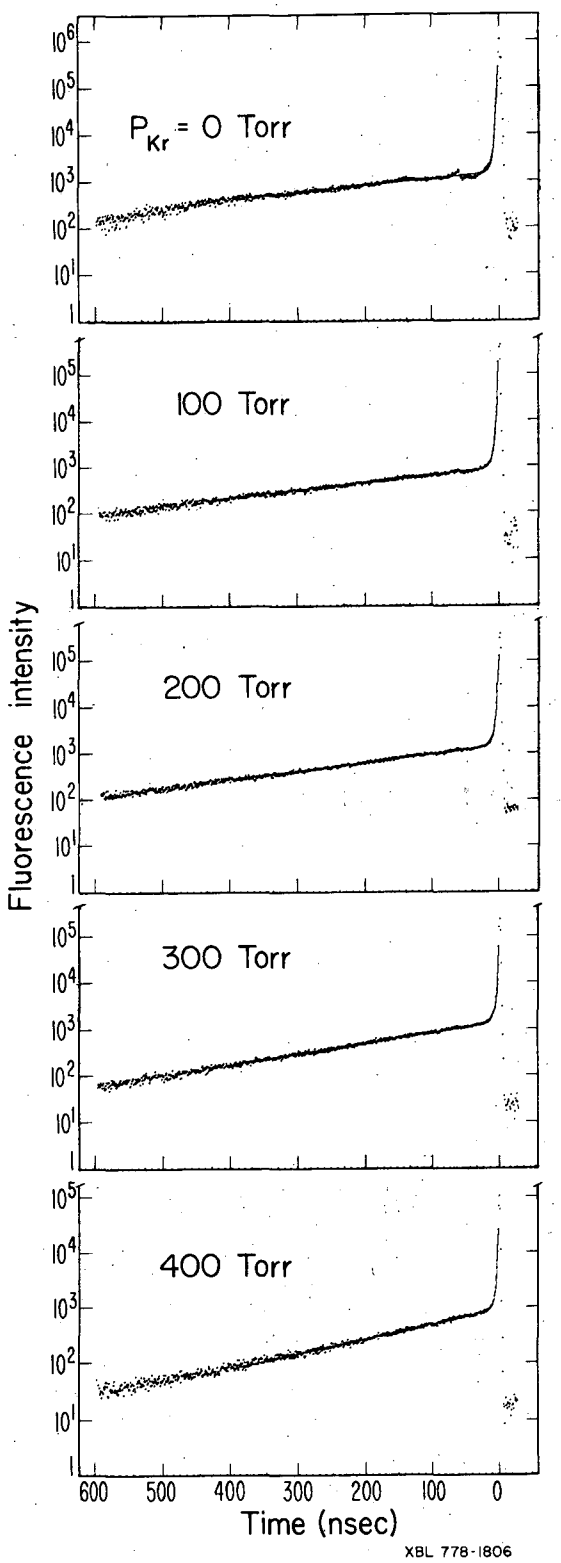

P_{Kr} = 0 Torr
100 Torr
200 Torr
300 Torr
400 Torr
Fluorescence intensity
Time (nsec)
600
500
400
300
200
100
0
XBL 778-1806

Fig. 3

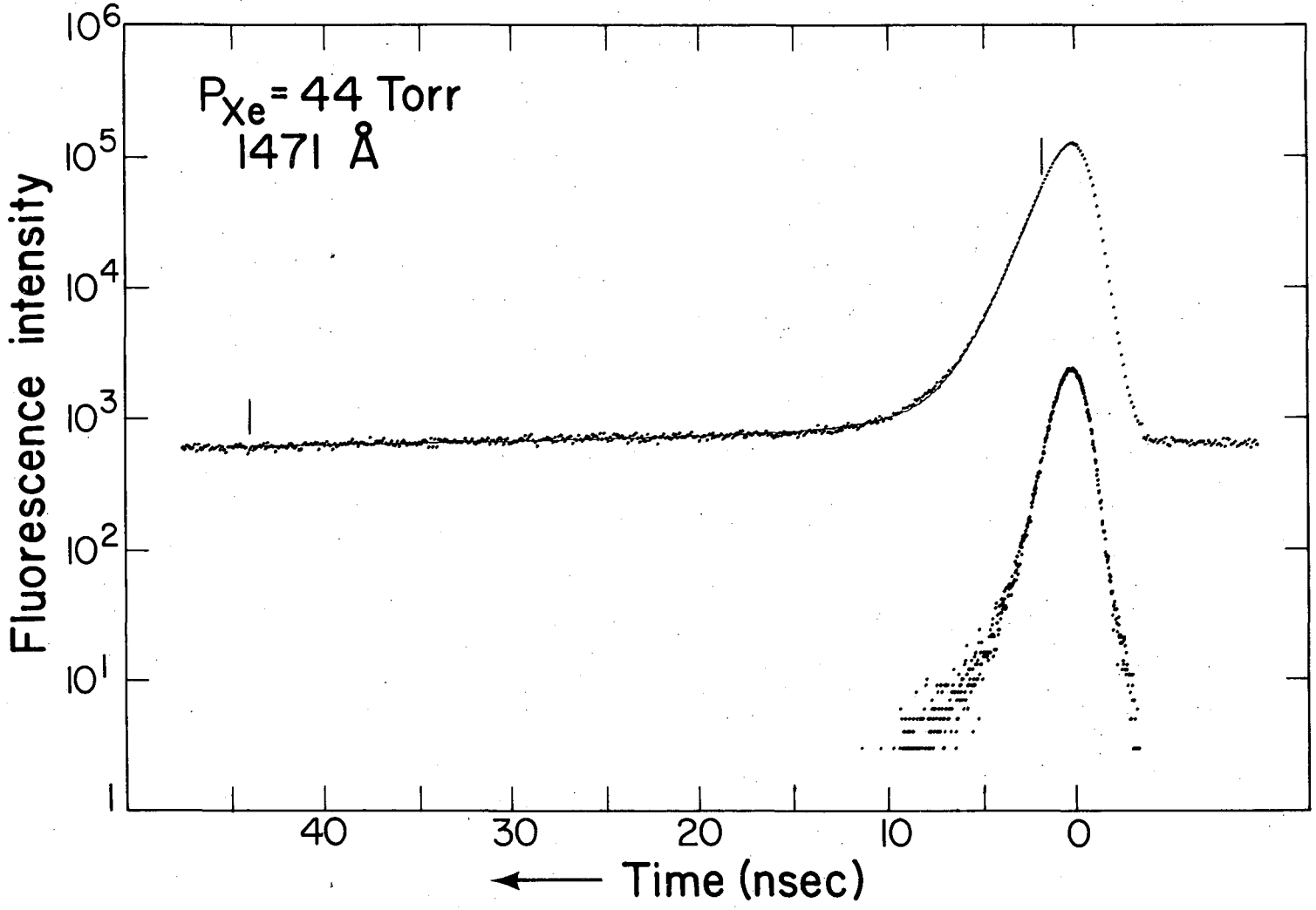
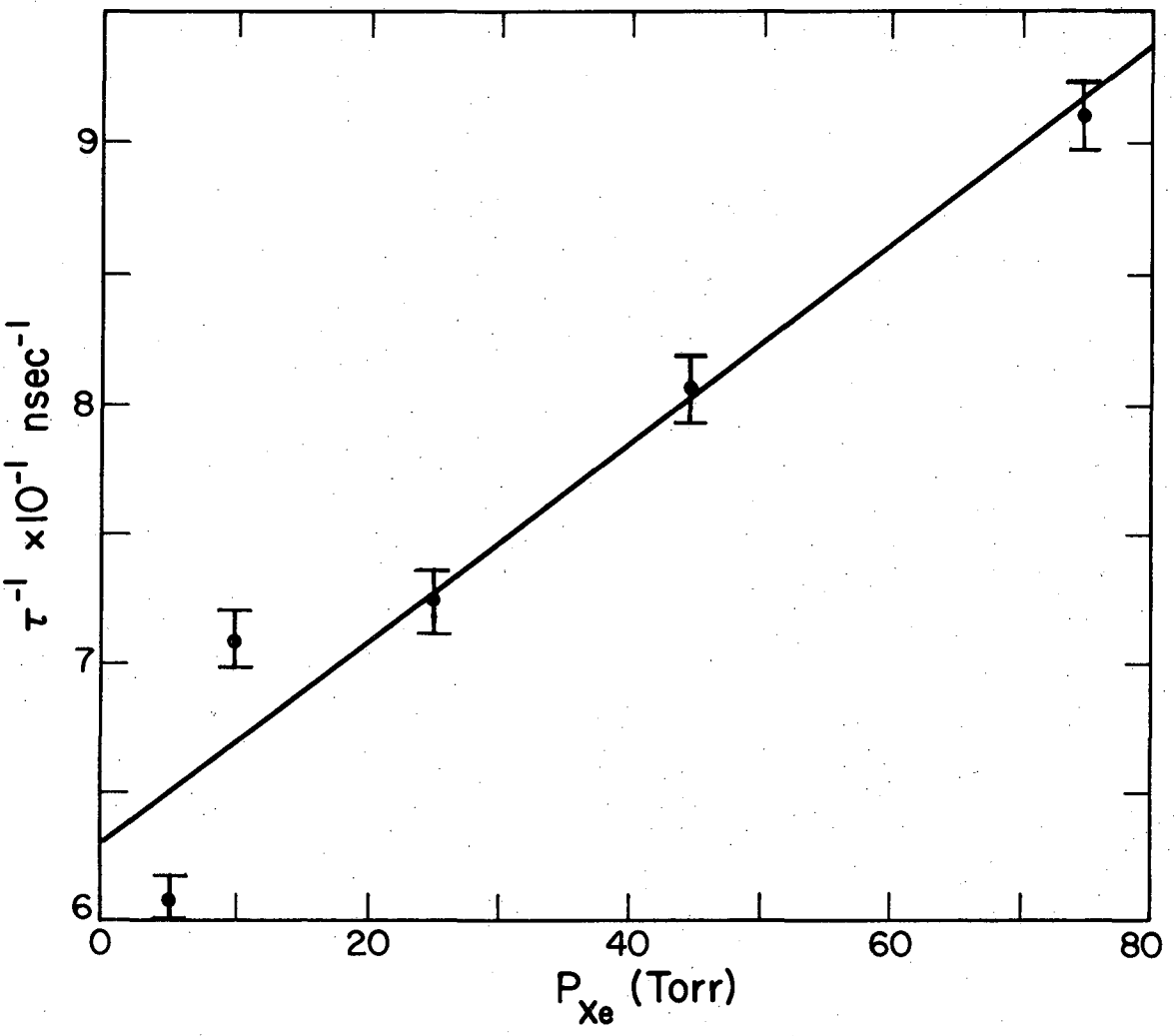


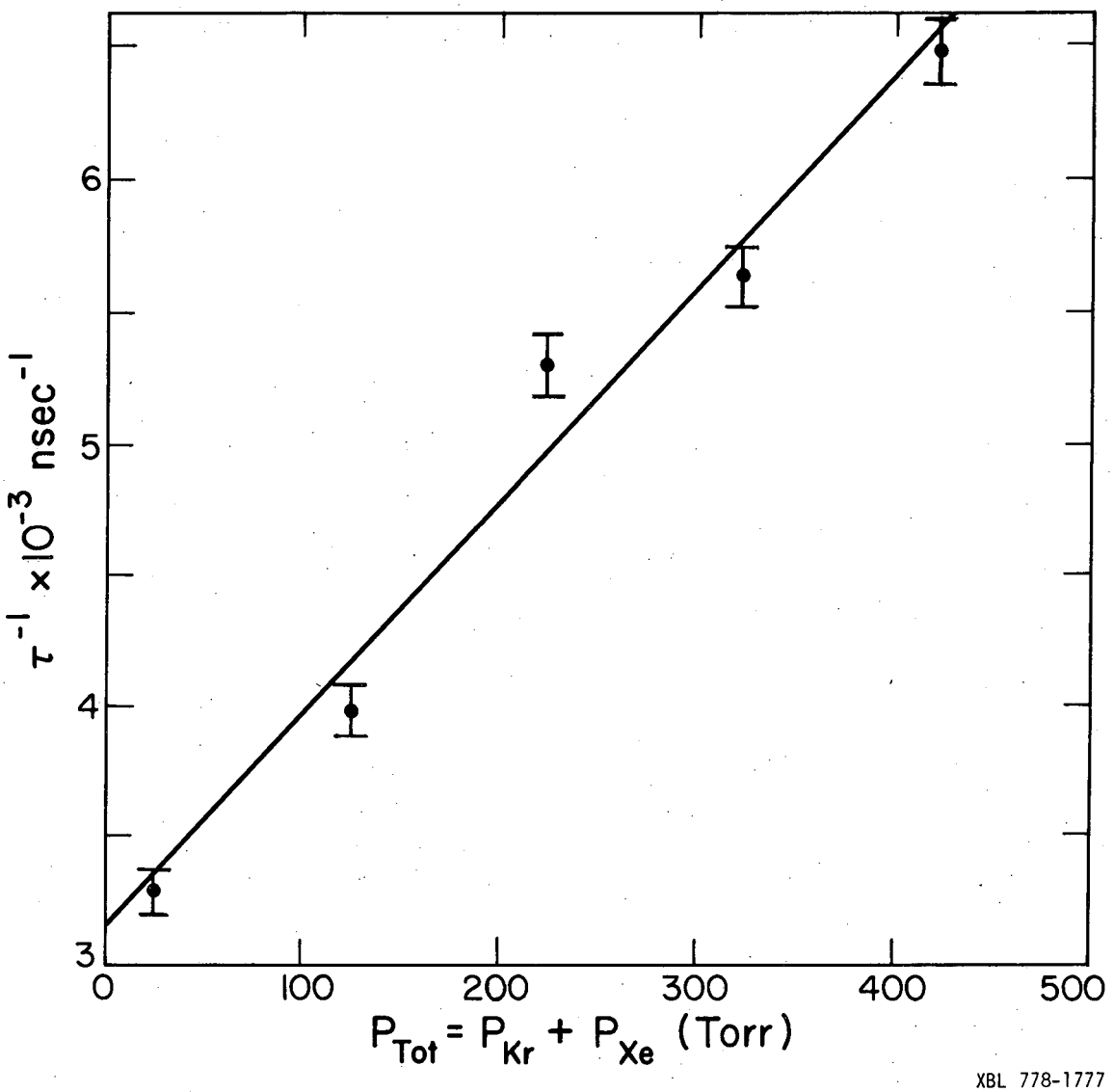
Fig. 4

XBL 778-1779 A



XBL 778-1776

Fig. 5



XBL 778-1777

Fig. 6

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