Title

TIME RESOLVED VUV SPECTROSCOPY USING SYNCHROTRON RADIATION: I. FLUORESCENT LIFETIMES OF ATOMIC Kr AND Xe

Author

Matthias, E.

Publication Date

1977-06-01

Submitted to Chemical Physics Letters

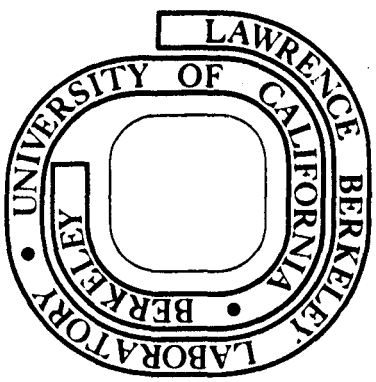
LBL-6605
Preprint

TIME RESOLVED VUV SPECTROSCOPY USING SYNCHROTRON RADIATION: I. FLUORESCENT LIFETIMES OF ATOMIC Kr AND Xe

E. Matthias, R. A. Rosenberg, E. D. Poliakoff, M. G. White, S.-T. Lee, and D. A. Shirley

June 1977

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48



DISCLAIMER

TIME RESOLVED VUV SPECTROSCOPY USING SYNCHROTRON RADIATION: I. FLUORESCENT LIFETIMES OF ATOMIC Kr AND Xe*

E. Matthias,† R. A. Rosenberg, E. D. Poliakoff, M. G. White, S.-T. Lee,‡ and D. A. Shirley

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemistry
University of California
Berkeley, California 94720

June 1977

ABSTRACT

Synchrotron radiation from the Stanford Positron Electron Accelerator Ring (SPEAR) was used to excite the $np^5(n+1)s$ states in Kr (n=4) and Xe (n=5). Utilization of the excellent time structure of this facility made possible the first direct measurements of the lifetimes of these states. The results for Kr are (in $j\ell$ coupling notation): $\tau(5s[3/2]1) = 3.18 \pm 0.12$ ns; $\tau(5s[1/2]1) = 3.11 \pm 0.12$ ns; for Xe, $\tau(6s[3/2]1) = 3.46 \pm 0.09$ ns; $\tau(6s[1/2]1) = 3.44 \pm 0.07$ ns. In addition the lifetime of the Xe $5p^5[3/2]5d[3/2]$ J = 1 state was found to be 1.40 ± 0.07 ns. Effects due to radiation trapping are discussed.

*This work was performed at the Stanford Synchrotron Radiation Project, which is supported by the NSF Grant No. DMR 73-07692 A02, in cooperation with the Stanford Linear Accelerator Center and was done with support from the U. S. Energy Research and Development Administration.

†Permanent address: Freie Universität Berlin, West Germany.

‡Permanent address: Eastman Kodak Research Laboratories, Rochester, NY.

I. INTRODUCTION

Time-resolved spectroscopy in the vacuum ultraviolet (VUV) region has been severely hampered by the lack of suitable pulsed light sources. With the availability of synchrotron radiation from electron storage rings, a pulsed, tunable light source has now become available throughout the VUV energy range. The beam at the Stanford Synchrotron Radiation Project (SSRP) is especially suited to timing experiments because of its short pulse width (.4 ns) and relatively long repetition period (780 ns). It is thus possible to measure lifetimes throughout the subnanosecond to microsecond range. This Laboratory has embarked on a program of time-resolved VUV spectroscopy, with our initial effort directed at determining lifetimes in excited states of the rare gases, Kr and Xe.

Oscillator strengths for the $np^5(n+1)s^1$ levels in Xe and Kr have been the subject of investigations by several methods in the past, and the previously published results are not always mutually consistent (see Tables I and II). Interest in obtaining accurate measurements of the atomic lifetimes has been increasing because the dimers have demonstrated laser potential. The lifetimes of these atomic states enter into the rate equations for formation of the dimers; thus accurate lifetime values are required to quantitatively describe the reaction kinetics.[1,2] In addition, the large spin-orbit splitting of the core hole state of heavier gases requires an alternate coupling scheme. Therefore, reliable experimental results are desirable to facilitate tests of various theoretical approaches.

In this Letter we report the first values of five excited-state lifetimes in atomic krypton and xenon determined directly by resonance fluorescence. The results are compared with previous experimental values and with theory.

II. EXPERIMENTAL

The experiments were performed on the 8° beam line at SSRP. A detailed description of this facility was given elsewhere.[3] Briefly, 3.2 milliradians of radiation from the storage ring is subtended by a mirror and focused onto the grating of a 1-meter Seya-Namioka monochromator (UHV Design, GCA/McPherson). The dispersed light passes through an exit slit (2 Å band pass) and enters the gas cell through a LiF window. The LiF window serves both to isolate the ultrahigh vacuum (1×10^{-10} torr) of the monochromator from the gas cell and to filter out higher-order light. The excitation energies are restricted, however, to wavelengths longer than 1050 Å because of the LiF cutoff. The light entering the gas cell is 97% plane-polarized and focused to a cross-section of approximately 1mm × 3mm.

The experimental apparatus and associated electronics are shown diagrammatically in Fig. 1. An EMR 541-G photomultiplier (LiF window, CsI cathode), mounted perpendicular to both the propagation vector and the polarization vector, was used to detect the fluorescent radiation. The photomultiplier was placed approximately 2.5cm and 1.0cm from the interaction region for the Kr and Xe studies, respectively. The photomultiplier and associated electronics limited the time resolution of the experiments to ∿1.8 nsec. There was no energy-selective device in

the fluorescence channel because in atomic systems in the low pressure limit only resonance fluorescence occurs. The acceptance range for fluorescence was 1050-1850 Å due to the LiF-cutoff and the CsI response limit of the photomultiplier. Within this range only the spin-orbit doublet of the $4p^5 5s^1$ configuration in Kr could be excited, while in Xe the analogous levels plus several more states could be reached.

The data were recorded by a conventional single photon counting technique. The photomultiplier pulses were amplified and discriminated, then used as the start signals for the time-to-amplitude converter equipped with a single channel analyzer (Ortec model 467). The stop pulse was provided by a signal from an induction coil located in the ring.* The data were accumulated in a multi-channel analyzer.

During these experiments, the electron beam current was between 12 mA and 18 mA, from which we expect a photon flux on the order of 10^{10}/sec. With sample pressure in the 10^{-6} range, the counting rate ranged from 1500 to 2500/sec., of which about one-third was true fluorescence events and two-thirds came from Rayleigh scattering of the incident light. Typical counting times were 60-90 min.

The gases were obtained from Airco Company, and were 99.995% pure. To maintain a fresh sample in the gas cell, the gas was continuously leaked into the sample chamber, which was pumped by a diffusion pump. The base pressure was 1×10^{-6} torr.

III. RESULTS AND DISCUSSION

Typical decay curves are shown in Fig. 2. Data analysis was done by means of a least-square fitting routine in which the background was

*This results in a reversal of the time axis in Fig. 2. It is necessary to avoid reset-time counting losses of the time-to-amplitude converter.

subtracted. The "prompt" peak with a maximum at time t = 0 (ca. channel 860) is due to the large number of Rayleigh scattering events, broadened by instrumental response, which is essentially Gaussian. This form of the response function was confirmed by measurements made off resonance, where Rayleigh scattering was present, but resonance fluorescence was not. The total observed resonance fluorescence decay curve is also broadened by the Gaussian "prompt" curve. Since the "prompt" curve decays very rapidly (FWHM = 1.8 ns), the true lifetime could be found by fitting at times far enough removed from t = 0, that the Gaussian had become negligible. The validity of this procedure was confirmed by analytical techniques.[1]

Lifetime measurements had to be carried out in the 10^{-5} - 10^{-6} torr pressure range to minimize the effects of resonance trapping. Even at these low pressures there is a finite probability for resonance scattering to occur before the fluorescence is detected. Such processes result in an apparent lifetime longer than the true one (see Appendix). To obtain the true lifetime, the pressure dependences were measured and extrapolated to zero pressure. Figures 3 and 4 illustrate this procedure for the $^3P_1$ and $^1P_1$ states of Kr and Xe, as well as for the $5p^5(^2P_{3/2})5d$ J = 1 state in Xe for which the lifetime has not been measured before.

Because these are the first direct lifetime measurements on these systems by this method, we discuss briefly the sources of error. There are two non-negligible error sources: uncertainties in pressure measurements (leading to a typical error of $\sim$2% in the extrapolated value of τ at t = 0), and statistical error (typically $\sim$1%). Cumulative errors

are given in Tables I and II.

A comparison of our results with previous data and theoretical predictions are given in Table I for krypton and in Table II for xenon. The scatter as well as the large limits of error of the previous, less direct methods emphasize the need for direct resonance fluorescence lifetime measurements. An exception is the zero field level crossing measurement by Anderson[5] in Xe which we consider to be the most reliable set of earlier results. Our results for the $^3P_1$ and $^1P_1$ levels in Xe are in good agreement with the values given by Anderson.[5] Comparing our experimental results with theoretical predictions, the nonrelativistic HF calculations of Dow and Knox[18] and of Kim, et al.[11] yield lifetimes that are too long, whereas the intermediate coupling scheme of Gruzdev[19,20] yields values in very good agreement with experiment. A multiple configuration calculation by Gruzdev and Loginov (on Kr only) yields fairly good agreement.

The lifetime of the $5p^5(^2P_{3/2})5d$ $J = 1$ state at 1192 Å in Xe was determined in the same manner. The result $\tau = 1.40 \pm 0.07$ ns reflects the large oscillator strength of this transition. There are no theoretical predictions available for comparison. Calculations of Gruzdev and Loginov[20] however, yield a value of 1.87 ns for the lifetime of the analogous state in krypton, which confirms the trend observed in xenon.

In summary, this work reports the first lifetimes of atomic states excited by synchrotron radiation. No other method used for time-resolved spectroscopy can characterize the system as well as direct optical excitation. Our results demonstrate that the synchrotron radiation available

at SPEAR, has both the necessary timing characteristic and sufficient intensity to study atomic lifetimes at very low pressures. Our measurements yield accurate results for five levels in Kr and Xe, of which the $5p^5(^2P_{3/2})5d$ J = 1 state in Xe has not been previously reported. They also show the intermediate coupling approach to be the most useful for calculating these lifetimes.

APPENDIX: Radiation Trapping

In order to explain the relative slopes of the lines in Figs. 3 and 4, it is necessary to employ one of the theories on imprisonment of resonance radiation.[21-24] If τ_0 represents the true zero pressure lifetime, and τ the coherence time at some pressure, then it is predicted that

$$\tau = \frac{\tau_0}{1-x} \tag{1}$$

where according to D'yakanov and Perel[24]

$$x = 1 - \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-t^2)\exp(-k_0 L e^{-t^2})\,dt \tag{2}$$

and according to Barrat[23]

$$x = 1 - \exp[-(\pi/6)^{1/2} k_0 L] \tag{3}$$

and in both cases[21]

$$k_0 = \frac{2}{\Delta\nu_D}\left(\frac{\ell n 2}{\pi}\right)^{1/2} \frac{\lambda_0^2}{8\pi} \frac{N}{\tau_0} \tag{4}$$

The quantity x represents the fractional absorption of resonance radiation by a layer of vapor of density N and thickness L; $1/k_0$ may be thought of as the minimum mean free path for absorption of resonance radiation of wavelength λ_0 and Doppler width $\Delta\nu_D$. For comparative purposes, the expression developed by Barrat will be used.*

Substituting Eq. (3) into Eq. (1) and expanding the exponential, one obtains†

*According to Nussbaum and Pipkin (see Ref. 25), both theories give equivalent results at sufficiently low values of the optical thickness, $k_0\ell$. For these measurements, $k_0\ell \sim 0.3$.

†Including terms only to first order introduces an error of $\sim(k_0\ell)^2$ or less than 10%. The data is insufficient to warrant inclusion of higher order terms.

$$\tau = \tau_0(1 + (\pi/6)^{1/2} k_0 L + \ldots . \quad (5)$$

or

$$\tau = \tau_0 + KLN \quad (6)$$

where

$$K = (\pi/6)^{1/2} \frac{2}{\Delta\nu_D} \left(\frac{\ell n 2}{\pi}\right)^{1/2} \left(\frac{\lambda_0^2}{8\pi}\right) \frac{g_2}{g_1} \quad .$$

Thus, a plot of τ - vs. - N should yield to first order a straight line of slope KL.

Since in these experiments L was not well defined, and to account for the different isotopes,[25] the only meaningful comparison is a ratio of the slopes of the lines for a given gas.

Equation (6) predicts the slopes of the 5s[3/2]1 line and the 5s[1/2]1 line of Kr to be in a ratio of 1.2 : 1; the experimental result is 1.2 ± 0.2 : 1 for Xe; the predicted value of the slopes of the 5s[3/2]1 to 6s[1/2]1 to 5d[3/2]1 are 1.9 : 1.3 : 1.0, while experimentally the values are 1.9 ± 0.5 : 1.0 ± 0.3 : 1.0.

The experimental results are more than adequately explained by the theory, thus justifying the linear extrapolation used to obtain the zero pressure lifetime.

REFERENCES

1. E. D. Poliakoff, M. G. White, R. A. Rosenberg, S.-T. Lee, E. Matthias, and D. A. Shirley, submitted for publication.
2. R. Brodman and G. Zimmerer, to be published.
3. H. Winick, VUV Radiation Physics, edited by E. E. Koch, et al. (Pergamon Viewpeg, 1974), p. 776; V. Rehn, et al., ibid. p. 780.
4. R. Turner, Phys. Rev. 140, A426 (1965).
5. D. Kent Andersson, Phys. Rev. 137, A21 (1965).
6. P. G. Wilkinson, J. Quant. Spectr. Rad. Transfer 5, 503 (1965).
7. P. G. Wilkinson, J. Quant. Spectr. Rad. Transfer 6, 823 (1966).
8. G. I. Chashchina and E. Ya. Shreider, Opt. Spectr. 20, 283 (1966).
9. G. I. Chashchina and E. Ya. Shreider, Opt. Spectr. 22, 284 (1967).
10. J. M. Vaughan, Phys. Rev. 166, 13 (1968).
11. Y. K. Kim, M. Inokuti, G. E. Chamberlain, and S. R. Mielezarek, Phys. Rev. Letters 21, 1146 (1968).
12. P. M. Griffin and J. W. Hutcherson, J. Opt. Soc. Am. 59, 1607 (1969).
13. J. Geiger, Phys. Letters 33A, 351 (1970).
14. K. T. Lu, Phys. Rev. A4, 579 (1971).
15. J. P. de Jough and J. van Eck, Physica 51, 104 (1971).
16. W. Wieme and P. Mortier, Physica 65, 198 (1973).
17. A. Delage and J. D. Carette, Phys. Rev. A14, 1345 (1976).
18. J. D. Dow and R. S. Knox, Phys. Rev. 152, 50 (1966).
19. P. F. Gruzdev, Opt. Spectr. 22, 170 (1967).
20. P. F. Gruzdev and A. V. Loginov, Opt. Spectr. 38, 611 (1975).

21. A. C. E. Mitchell and M. W. Zemonsky, Resonance Radiation and Excited Atoms, (Cambridge University Press, Cambridge, England, 1964).

22. T. Holstein, Phys. Rev. 72, 1212 (1947).

23. J. P. Barrat, J. Phys. Radium 20, 541, 633, 657 (1959).

24. M. I. D'yakanov and V. I. Perel, Zh. Eksperim. i Teor. Fiz. 47, 1483 (1964) (Translation: Soviet Phys.-JETP 20, 997 (1965)).

25. Gilbert H. Nussbaum and Frances M. Pipkin, Phys. Rev. Letters 19, 1089 (1967).

Table I. Compilation of lifetimes and oscillator strengths for the two transitions $^3P_1 \rightarrow {}^1S_0$ and $^1P_1 \rightarrow {}^1S_0$ in Krypton.

$^3\tau$(ns)	^3f(1263Å)	$^1\tau$(ns)	^1f(1165Å)	method	authors	
4.14	0.166			resonance imprisonment	Turner[4]	(1965)
4.32 ± 0.33	0.159 ± 0.01	4.52 ± 0.35	0.135 ± 0.01	total absorption	Wilkinson[6]	(1965)
3.3 ± 0.8	0.21 ± 0.05	2.9 ± 0.7	0.21 ± 0.05	linear absorption	Chashchina and Shreider[9]	(1966)
3.37 ± 0.33	0.204 ± 0.020	3.32 ± 0.36	0.184 ± 0.020	optical line broadening	Vaughan[10]	(1968)
3.67 ± 0.12	0.187 ± 0.006	3.16 ± 0.15	0.193 ± 0.009	total absorption	Griffin and Hutcherson[12]	(1969)
4.0 ± 0.8	0.173 ± 0.035	3.5 ± 0.7	0.173 ± 0.035	electron energy loss	Geiger[13]	(1970)
		4.2 ± 0.4	0.142 ± 0.015	self-absorption	de Jongh and van Eck[15]	(1971)
3.18 ± 0.12	0.208 ± 0.006	3.11 ± 0.12	0.197 ± 0.006	resonance fluorescence	present work	
4.98	0.138	4.49	0.136	nonrel. Hartree-Fock	Dow and Knox[18]	(1966)
3.43	0.20	3.05	0.20	intermediate coupling calc.	Gruzdev[19]	(1967)
3.61	0.190	3.45	0.177	multiple conf. appr.	Gruzdev and Loginov[20]	(1975)

Table II. Compilation of lifetimes and oscillator strengths for the two transitions $^3P_1 \rightarrow {}^1S_0$ and $^1P_1 \rightarrow {}^1S_0$ in Xenon.

$^3\tau$(ns)	^3f(1470Å)	$^1\tau$(ns)	^1f(1296Å)	method	authors
3.79 ± 0.12	0.256 ± 0.008	3.17 ± 0.19	0.238 ± 0.015	zero field level crossing	Anderson[5] (1965)
3.5 ± 0.6	0.28 ± 0.05	3.3 ± 0.7	0.23 ± 0.05	linear absorption	Chashchina and Shreider[8] (1965)
3.74 ± 0.25	0.260 ± 0.20	2.80 ± 0.20	0.270 ± 0.020	total absorption	Wilkinson[7] (1966)
		3.89 ± 0.10	0.194 ± 0.005	total absorption	Griffin and Hutcherson[12] (1969)
3.73 ± 0.75	0.260 ± 0.052	4.0 ± 0.8	0.190 ± 0.038	electron energy loss	Geiger[10] (1970)
3.57	0.272	3.99	0.189	low-energy electron impact	Lu[14] (1971)
4.6 ± 0.5	0.213 ± 0.020	4.2 ± 0.9	0.180 ± 0.040	resonance imprisonment	Wieme and Mortier[16] (1973)
5.31	0.183	4.47	0.169	low-energy electron impact	Delage and Carette[17] (1976)
3.46 ± 0.09	0.263 ± 0.007	3.44 ± 0.07	0.229 ± 0.007	resonance fluorescence	present work
5.00	0.194	5.13	0.147	nonrel. Hartree-Fock	Dow and Knox[18] (1966)
3.47	0.28	3.02	0.25	intermediate coupling calc.	Gruzdev[19] (1967)
4.58	0.212	3.99	0.189	nonrel. Hartree-Fock	Kim, et al.[11] (1968)

FIGURE CAPTIONS

Fig. 1. Schematic representation of experimental apparatus.

Fig. 2. Fluorescence decay curve of Kr.

Fig. 3. Lifetime vs. pressure for Kr.

● 5s[3/2]1

■ 5s[1/2]1

Fig. 4. Lifetime vs. pressure for Xe.

● 6s[3/2]1

■ 6s[1/2]1

▲ 5d[3/2]1

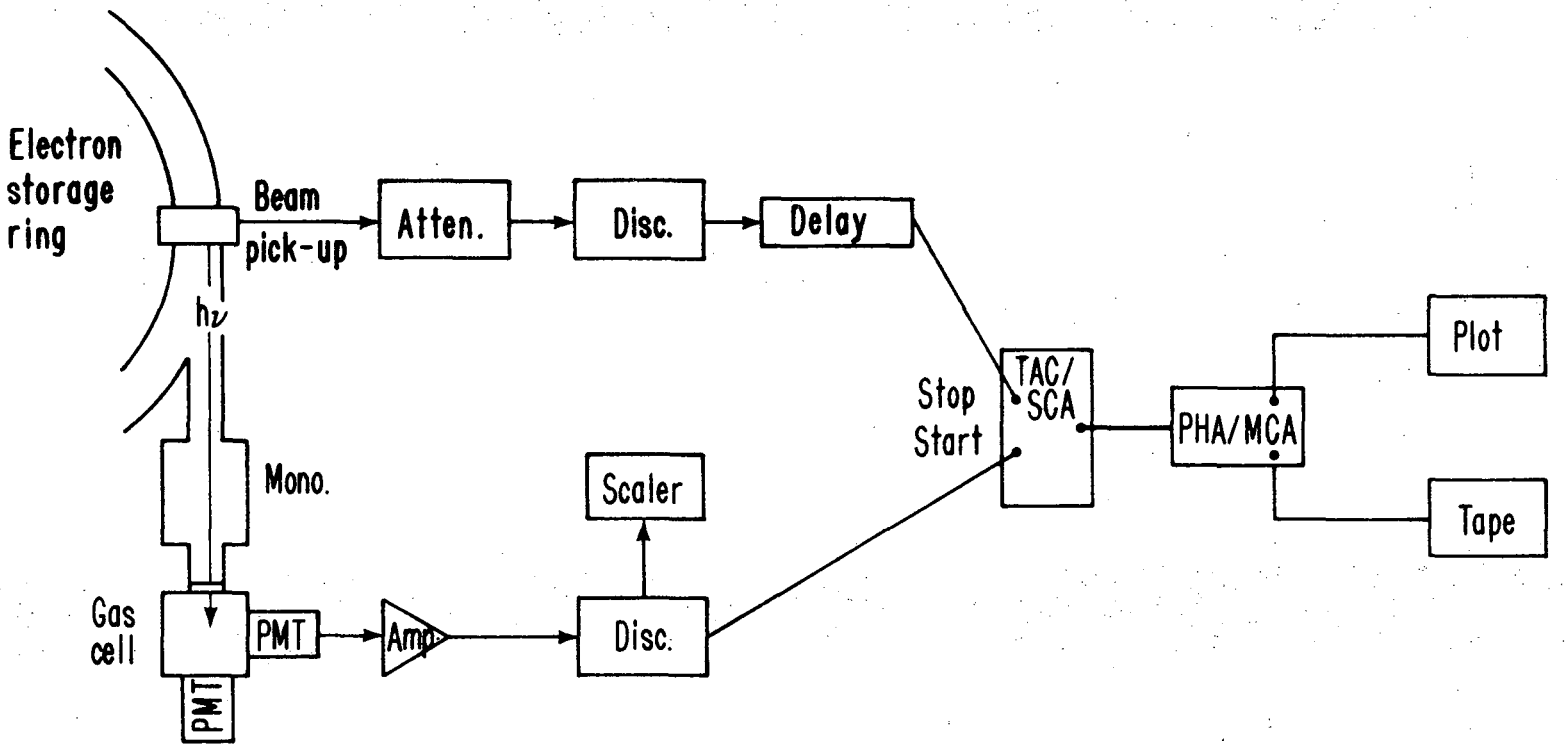


Fig. 1

XBL-7612-4530

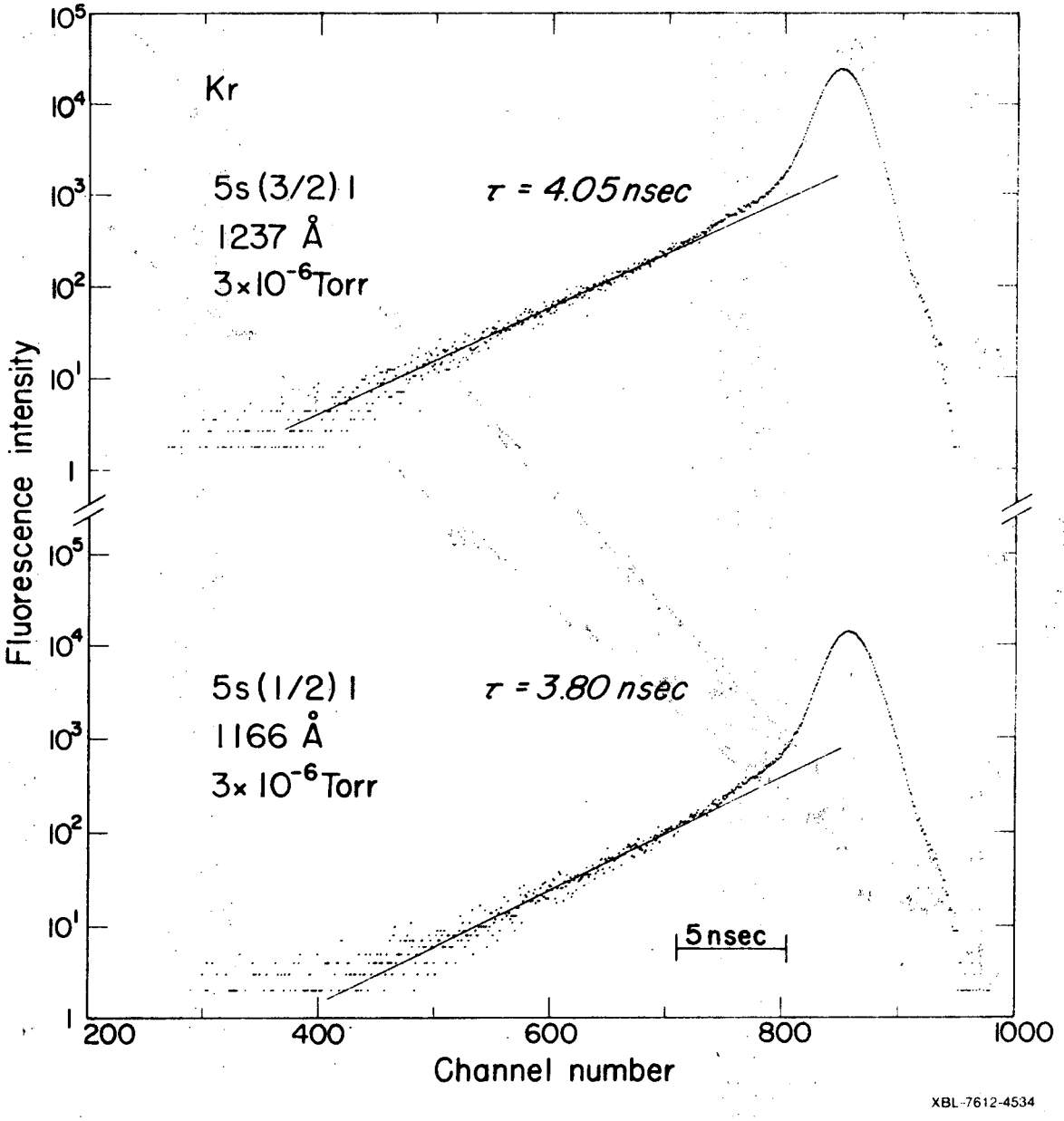
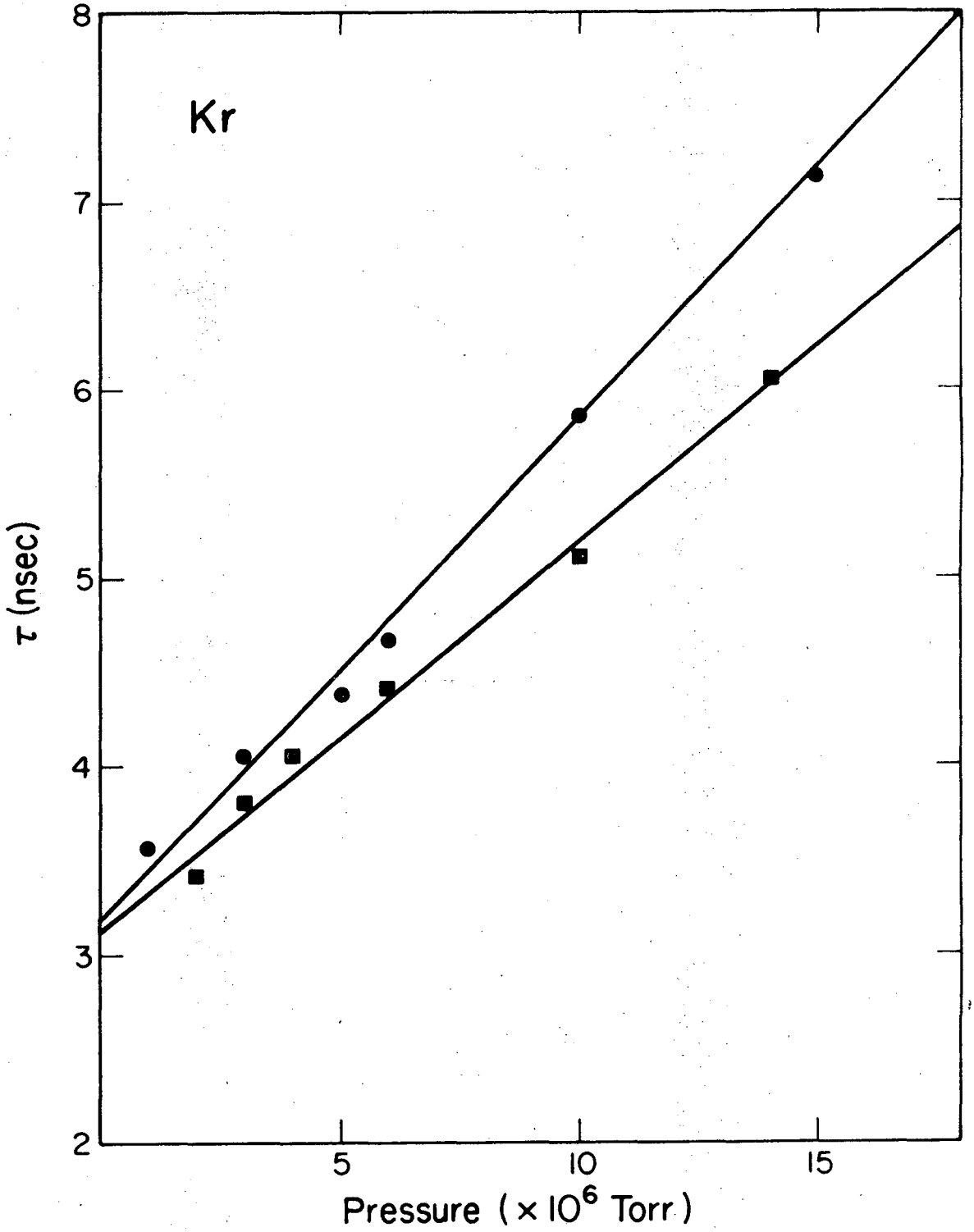
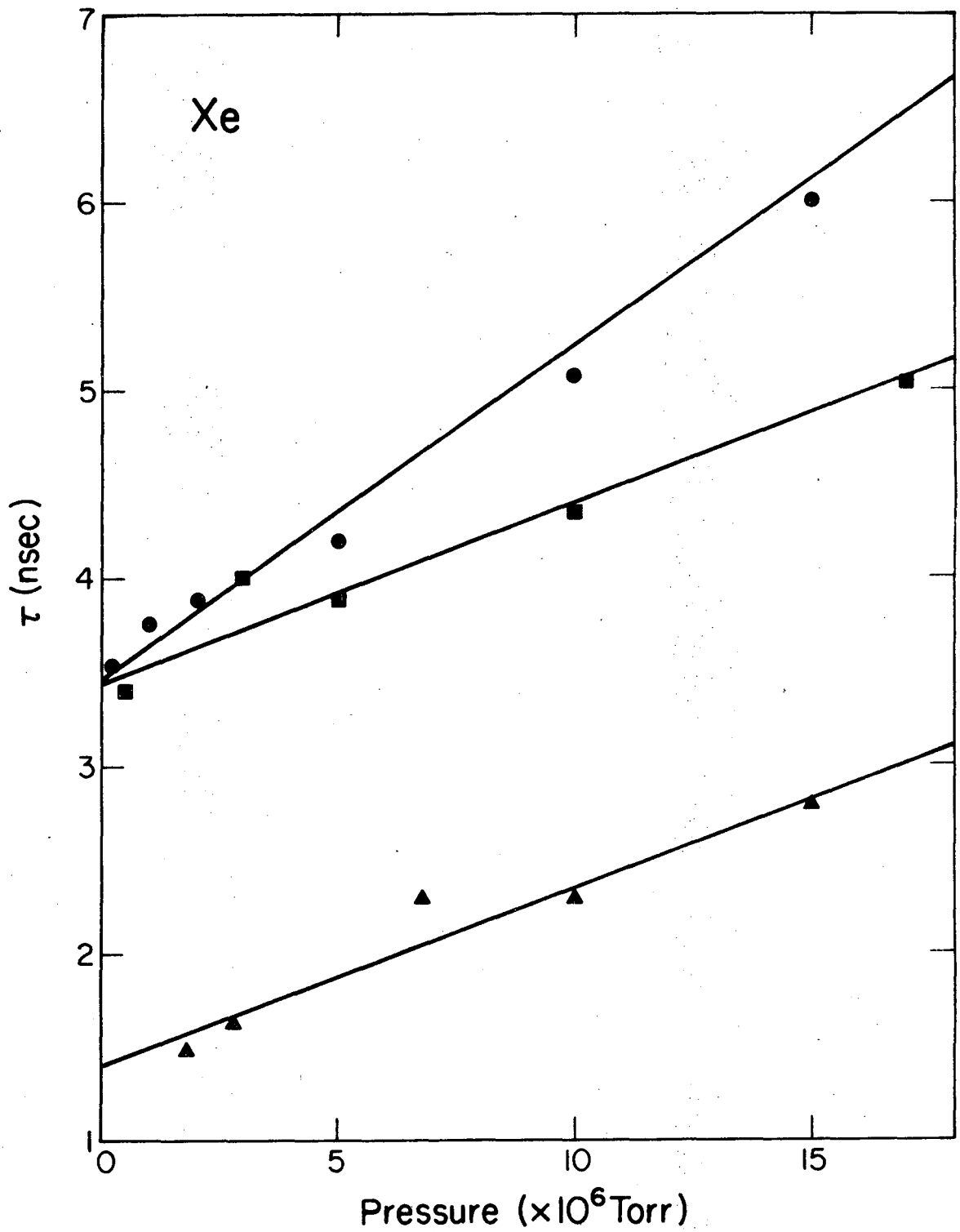


Fig. 2



XBL-7612-4529

Fig. 3



XBL-7612-4532

Fig. 4

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720