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DISCLAIMER

LIFETIME OF THE XeII $5s5p^6$ $^2S_{1/2}$ STATE*

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ABSTRACT

Synchrotron radiation affords the possibility of lifetime measurements of excited ionic states following their *selective* excitation. We have used this method to determine the lifetime of the XeII $5s5p^6$ $^2S_{1/2}$ state as 34.4(6) nsec. Multi-configuration Hartree-Fock calculations yield a value of 9.5 nsec, indicating the importance of relativistic effects in such a system.

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Electron-electron correlations in atoms and molecules lie at the frontier of our understanding of the properties of matter. Correlation effects are not only difficult to calculate, requiring computational methods beyond the Hartree-Fock level, but they are also hard to measure, because most spectroscopic parameters are only indirectly sensitive to electron correlation. Electron spectroscopy, on the other hand, provides rather direct insight into correlation effects, because removal of an electron from an N-electron system yields "correlation satellites" in the (N-1) electron system. Of special interest are states of nominal configuration $nsnp^6$ formed by removal of a valence s electron from a closed-shell atom. Excitation of a pair of electrons to configuration of the form $ns^2np^4n'\ell$ costs little in energy: thus a large degree of configuration mixing is expected.

Fluorescence de-excitation of the ionic "$nsnp^6$" state to the ionic ground state, following photoionization, provides further insight into the structure of the nominal $nsnp^6$ state because its lifetime is sensitive to its composition. With the availability of pulsed vacuum ultraviolet synchrotron radiation at the Stanford Synchrotron Radiation Laboratory (SSRL), and the development of a new apparatus that allows spectroscopic studies of gaseous samples above the LiF cutoff, we have undertaken a lifetime measurement of such a state in Xenon.

The XeII $5s5p^6$ $^2S_{1/2}$ state is a particularly desirable candidate for study because it has been the subject of a great deal of recent experimental and theoretical effort and its lifetime has not been previously determined experimentally. Many-body and relativistic effects have been found to play a significant role in this state, as manifested in photoelectron spectroscopy by satellite structure (Süzer and Hush 1977; Adam et al 1978; Gelius 1974) and asymmetry parameter (β) variations (Dehmer and Dill 1976). In order to describe these phenomena adequately, it has been necessary to include both electron correlation and relativistic effects (Johnson and Cheng 1978; Ong and Manson 1977; Wendin 1977). To date, however, only configuration interaction has been incorporated in the calculation of the fluorescent lifetime. The results given below show the need to include relativistic effects in any model used to describe such a system.

The experiments were carried out on the "8° line" at SSRL. The timing characteristics and most of the apparatus have been described previously (Matthias et al 1977). However, in order to extend the usable energy range above the LiF cutoff (11.8 eV), a thin (1500 Å) Al window (Luxel Corp.) was incorporated into the apparatus. This made available radiation in the region 17 eV < $h\nu$ < 35 eV. The Xe sample (99.995%) was introduced through a leak valve to give a nominal chamber pressure of 5 microns. Outgassing from the walls caused the pressure to rise slightly during the experiment. Single photon counting was carried out with an EMR-510G photomultiplier, mounted perpendicular to the synchrotron beam, by the use of standard pulse-counting techniques. The bandpass of the excitation monochromator was set at 2 Å.

The $5s5p^6\ {}^2S_{1/2}$ state is the lowest excited state of XeII (Moore 1958); therefore the only possible fluorescence populates the spin-orbit split ground state of $5s^2 5p^5$, ${}^2P_{3/2}$ (1100 Å) and ${}^2P_{1/2}$ (1244 Å). The threshold for the $5s5p^6\ {}^2S_{1/2}$ falls at 529.6 Å (Moore 1958). At longer wavelengths only a small signal, attributable to residual gases was observed, while at threshold a sharp increase in signal was seen which appeared to decrease slowly at lower wavelengths, in agreement with the photoionization cross section for this state (Gustafsson 1977).

A typical decay curve, taken at 526 Å, is shown in Fig. 1. A least squares fit of the data yields a lifetime of 34.4(6) nsec. The analogous level in KrII ($4s4p^6$) was determined by Irwin et al (1976), using beam-foil excitation, to have a lifetime of 0.33(4) nsec, while the $3s3p^6$ state in ArII was measured by Lawrence (1969) with electron impact excitation to have a lifetime of 4.8(1) nsec.

Multi-configuration Hartree-Fock calculations by Hansen (1977) yield a lifetime for the XeII $5s5p^6(^2S_{1/2})$ level of 9.5 nsec. The apparent discrepancy with the experimental value of 34.4 nsec is probably a result of the non-relativistic treatment of the ionic state wavefunctions. In this calculation the ^2S excited state wavefunction was approximated by the mixing of the $5s5p^6(^2S)$ (61%) and $5s^2 5p^4(^1D)5d(^2S)$ (39%) states. This treatment ignores the admixtures of other configurations of even parity and the same J (=½) which would result by the inclusion of relativistic effects. Recently XeII energy level calculations by El Sherbini and Zaki (1978) show an additional 4% mixing of the $5s^2 5p^4 5d(^4P)$ state, and the photoemission work of Adam et al (1978), Süzer and Hush (1978), and Gelius (1974) show several weak satellite lines associated with the $(5s)^{-1}$ hole state attributable to the $5s^2 5p^4 ns(^2P, ^4P)$ and the $5s^2 5p^4 nd(^2P, ^4P, ^4D)$ configurations. These terms can only be correlated to the ^2S hole state through spin-orbit coupling. In addition, the contributions to the transition moment from the two configurations used by Hansen largely cancelled each other. Hence, the small admixtures of other states could lead to a substantial change in the calculated lifetime.

Hansen's results for the analogous states in KrII and ArII are 6.6 nsec and 5.0 nsec respectively. These are set out, with the experimental values, in Table I. The agreement with the experimental result for ArII is quite good, indicating that relativistic effects are less important in this case, as expected. For KrII, the experiment has recently been repeated using beam foil spectroscopy and although the results are not yet conclusive, they do cast some doubt on the earlier measurements (Kernahan 1978).

In summary, we have made the first measurement of the lifetime of the XeII $(5s5p^6)\,{}^2S_{\frac{1}{2}}$ state and found it to be 34.4(6) nsec. The difference between this and Hansen's MCHF result indicate the need for a more sophisticated, multi-configuration, Dirac-Fock calculation. In the future we hope to utilize synchrotron radiation to unambiguously determine the lifetimes of the analogous states in Kr and Ar.

TABLE I. Calculated and experimental lifetimes for the $ns\,np^6$ state in ArII (n=3), KrII (n=4), and XeII (n=5).

Ion	Calculated[a]	Measured	Method
ArII	5.0	4.8(1)[b]	Pulsed electron impact
KrII	6.6	0.33(4)[c]	Beam-foil excitation
XeII	9.5	34.4(6)[d]	Pulsed-photon impact

[a]Hansen (1977)

[b]Lawrence (1969)

[c]Irwin et al (1976)

[d]present work

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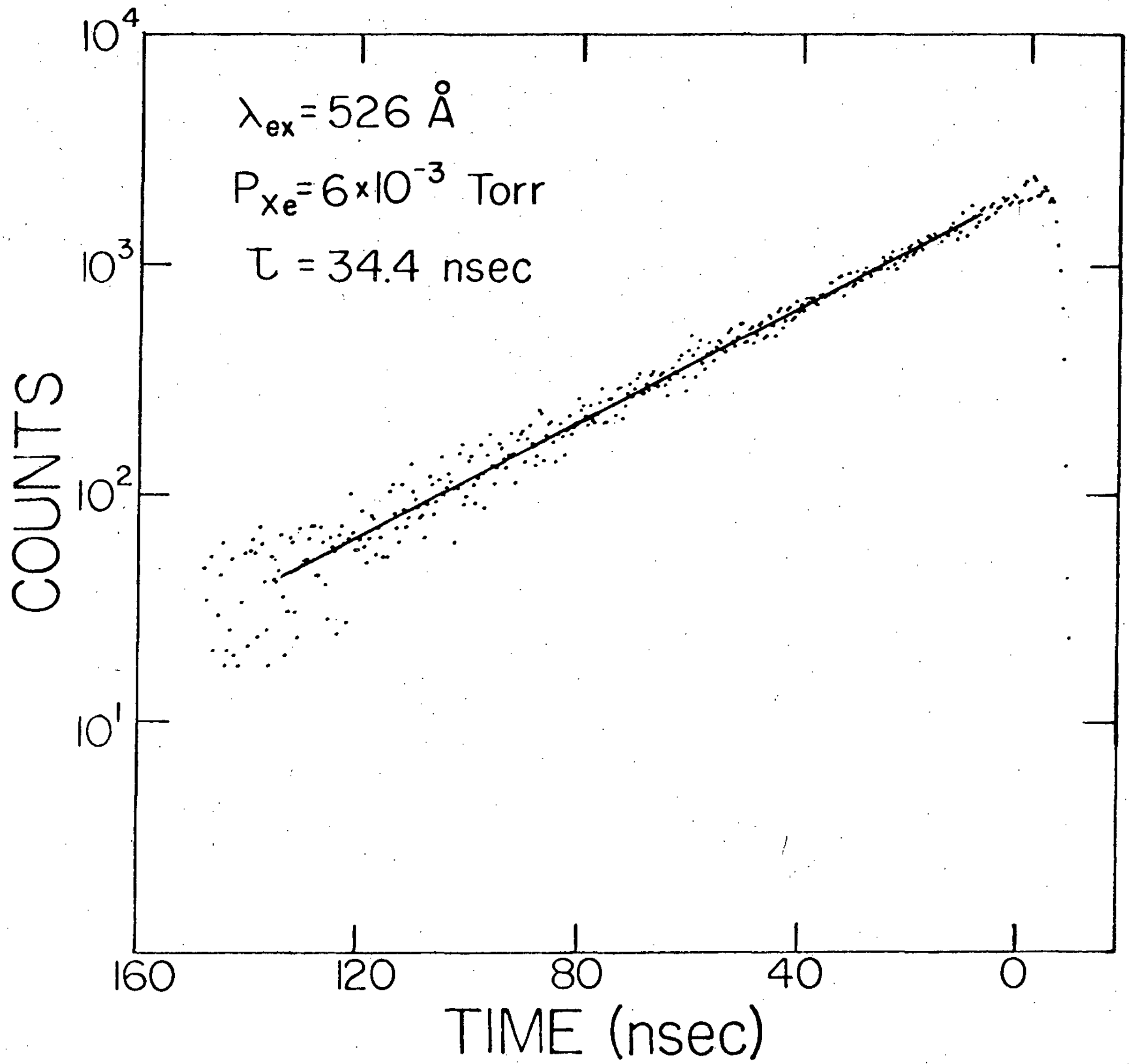
FIGURE CAPTION

Fig. 1. Fluorescence decay curve of XeII $5s5p^6\ ^2S_{1/2}$ fitted with a single exponential.


10⁴
10³
10²
10¹
COUNTS
λex = 526 Å
PXe = 6×10⁻³ Torr
τ = 34.4 nsec
160
120
80
40
0
TIME (nsec)

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Dear Sir:

Enclosed are 2 copies of a manuscript entitled "LIFETIME OF THE XeII $5s5p^6\ ^2S_{\frac{1}{2}}$ STATE", by R. A. Rosenberg, M. G. White, E. D. Poliakoff, G. Thornton, and D. A. Shirley.

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