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ABSTRACT

The use of multistep photoionization techniques to measure lifetimes, cross sections, and branching ratios in uranium is described. The measurement of autoionization behavior, the assignment of new levels, and the observation of Rydberg states are also described. Experimental data are presented for all parameters.

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Recent interest in laser separation of uranium isotopes has spurred demand for a wealth of spectroscopic information. Many methods, photophysical and photochemical, are being considered for economic separation schemes and some or all of these methods require data on lifetimes, branching ratios, autoionization behavior, cross sections, new level assignments, and Rydberg states. Fragmentary data on these parameters are available for some of the lighter more easily studied atoms but until recently, the only spectroscopic information available for uranium was the assignment of a modest number of low lying states.[1] The extensive complexity of its spectrum coupled with materials handling difficulties discouraged extensive study. In this paper we report the methods of study and experimental results for a broad range of spectroscopic experiments on atomic uranium.

The apparatus used for these studies is shown in Figure 1. The spectrometer is a crossed beam apparatus where the uranium beam is sequentially stuck by a variety of tunable or fixed frequency lasers. In all cases photoion production is monitored by a channeltron after mass filtering of the atomic beam in a low resolution quadrupole mass spectrometer. The source is a resistively heated tungsten oven loaded with the uranium alloy, URe_2, and operated at approximately 2000°C. The oven is an extremely reliable spectroscopic source and has been operated for periods of hundreds of hours without corrosion. All lasers are pulsed and thyratron triggered. The thyratrons are all switched by a common master oscillator which delivers a 1500 volt trigger pulse to the grid of each thyratron allowing precise temporal control of the lasers. The Hansch type dye lasers are controlled

temporally with a jitter of about 1 nanosecond and the CO_2 oscillator jitter is approximately ±20 nanoseconds in this arrangement. The wavelength standard is an electrodeless discharge lamp of UI_4 in about one torr of argon. Laser wavelengths are monitored through a 3 meter holographic grating monochrometer. The monitoring of photoion product is accomplished through boxcar detection. Temporal adjustment or delay of the various lasers is achieved by switching in delay lines between the master triggering unit and the various laser thyratrons.

We now describe the measurement of spectroscopic properties in uranium. The remainder of the paper will discuss four separate classes of measurements: the assignment of new high lying levels in uranium, the determination of autoionization behaviour, the measurement of lifetimes and excited state-excited state cross sections, and finally, observations and characterization of Rydberg sequences in uranium. All these measurements bear relation to the implementation of multi-step schemes for selective photoionization of uranium isotopes as shown in Figure 2.

The assignment of new levels in uranium is an important area of study prior to the implementation of multi-step schemes in the separation of uranium isotopes. The interest in multi-step schemes is not new and derives from the obvious desire to employ existing, efficient, scalable lasers in any economic separation of isotopes. The handicap here is, of course, the fact that most level assignments in uranium lie between 0-25,000 cm^{-1} and the use of efficient visible lasers requires that levels between 30-35,000 cm^{-1} be accessed in a second step and levels between 49,000-49,900 cm^{-1} be accessed in a third step in a scheme in which, for example, IR irradiation

of this last level is the method of ionization. Since the ground and 620 cm^{-1} levels of uranium are odd parity states of the atom, strong transitions in the stepwise schemes just mentioned will bring the atom to odd parity levels near 35,000 cm^{-1} and subsequently to even parity levels near 49,000 cm^{-1}.

The technique employed in the search and assignment of these levels is that of Dunning and Stebbings.[2] Briefly, in the search for odd parity levels near 35,000 cm^{-1}, a particular even parity level between 15,000-17,000 cm^{-1} is first populated by a pulse from a tunable laser (dye laser one). A second dye laser delayed temporarily from the first laser by typically 10-20 nanoseconds, is next swept in wavelength. As this laser is tuned into resonance with an excited state transition to an odd parity level near 35,000 cm^{-1}, the uranium atom consumes two photons from the beam of the second laser. The first photon raises the atom to the excited odd level and the second photon subsequently ionizes the atom. Thus a display of wavelength of laser two versus photoion production yields the sought for resonances. An important point is that the second laser is normally run at saturation intensities for the bound-bound transitions but is in general not intense enough to saturate the photoionization step unless an autoionizing transition from the excited state is utilized. It is known that the uranium ionization spectrum is heavily dominated by autoionization and that cross sections for photoionization vary by about two orders of magnitude. Thus photoion peak heights in this type of experiment in uranium are generally indicative of the transition probability of only the last step of the photoionization sequence. This is confirmed by the observation that peak

heights are linear in their power dependence upon second laser intensity and become quadratic only when the laser is attenuated to intensity levels of approximately a kwatt/cm^2. A further remark is that by employing this technique from varying even parity levels of differing J values near 16,000 cm^{-1} and by imposing electric dipole selection rules, the levels discovered may also have J quantum numbers attached to them. An illustration of this principle is given in Figure 3 and Figure 4 is a table of a few previously unassigned high lying odd parity levels which have been identified via this technique. Hundreds of new levels have been cataloged by this method. We wish to emphasize a few additional points regarding stepwise techniques in actinide spectroscopy. When applying this method to the search for new states in heavy atoms, due to the enormous density of levels, many chance coincidences are evident in the spectrum. For example, the scan laser itself (laser two) may give rise to three photon ionization of the ground state or thermally excited states of the atom without aid from laser one. Such coincidence processes may be differentiated from noncoincident stepwise effects by the obvious expedient of noting the effect of removal of various lasers from the photoion spectrum. Also, it should be noted that an obvious extension of stepwise excitation techniques allows additional probing and assignment of levels just beneath the continuum in uranium. A final point is that this method is quite simple to apply and the results are unambiguous. Without question it is a simple and rapid method for the sorting and assignment of the complex atomic spectra of lanthanides and actinides.

As we have already noted this technique can also be applied with three (or four or more) lasers to probe the structure of the atom in any region.

Figure 5 illustrates a three laser 4-photon experiment ($\lambda_1 + \lambda_2 + 2\lambda_3$) wherein even parity level structure just below the ionization limit is probed. Two observations are worth noting here. First is the enormous density of states, approximately one every three or four cm^{-1}, and the second is the nearly arbitrary closeness within which they lie near the ionization limit. The states shown in this figure are in general not Rydberg states but are predominately valence states. That is they are low (high) lying states of high (low) lying configurations of the atom. This is confirmed both by measurements of lifetimes of these states and transition probabilities for excitation. As we shall see, most of these states have cross sections for excitation from levels near 35,000 cm^{-1} of about 10^{-14} cm^2 and have lifetimes of about 70 nanoseconds.

Multiphoton techniques can also be used to study the ionization properties of the atom. Such work was presented recently by Janes et al.[3] in the case of two step excitation of the vapor. We present here the determination of autoionization behavior of excited odd parity levels near 35,000 cm^{-1}, that is we illustrate autoionization in a three photon, three step case. In this experiment the first two lasers, separated temporally by about 20 nsec, sequentially bring the atom in a two step process to an odd parity level at 33082.7 cm^{-1} as shown in Figure 5. An important aspect of these experiments is that very high resolution dye lasers are used. The scan shown in Figure 6 utilized lasers of spectral width 0.5 cm^{-1} and Figure 7 shows portions of a scan taken with a combined laser-instrumental width of 0.05 cm^{-1}. These results confirm and extend the observations of Janes that the autoionization times (linewidths) in uranium are exceptionally long (narrow). The autoionization linewidths of typically 0.5 cm^{-1} are

much narrower than the linewidths (1.0-5.0 cm^{-1}) of the lasers used for autoionization studies by earlier workers. This prevented earlier workers from measuring a true peak autoionization absorption cross section as the lasers probed averaged ionization cross sections over a spectral region wider than that of a single autoionizing feature.

By using a laser saturation method we have measured cross sections of a number of autoionizing transitions. As mentioned before, since no quantitative measure of natural widths of autoionizing transitions were made in previous works, the values we report here, up to 3×10^{-17} cm^2, are the first measurements not subjected to the instrumental linewidths limitation. We point out an interesting feature of the ionization spectrum of uranium, that is that the density of autoionizing lines nearly match the density of valence states just below the continuum. Also, the measured value of the ionization potential using the high resolution photoionization technique is 6.189 ± .002 ev which is in good agreement with the value of 6.187 ± .002 ev reported by Janes.[3]

We next discuss the measurement of lifetimes and excited state cross sections in uranium. The technique used to measure lifetimes is precise and rapid. The measurement is accomplished by simply monitoring photoion production yields as a function of delay time between "populating" and "probing" laser beams. Figure 8 shows the results for the measurement of the lifetime of the 16505 cm^{-1} level. The sensitivity of the technique is enhanced by tuning the probe laser to an autoionizing transition to ensure copious quantities of photoion product. Using this method, first used by Janes,[3] the measurement of a lifetime to 10% or better is readily accomplished. Figure 9 tabulates typical lifetimes of levels throughout

the spectrum measured via this technique. Of special interest is the measurement of the lifetimes of states near the continuum. In these measurements a CO_2 laser with a temporal jitter of about 20 nanoseconds is the probing pulse which monitors decay from the stepwise laser populated even parity levels near the continuum. The CO_2 laser is intense enough to saturate the ionization step so that only a small portion of the 150 nsec temporal profile of the laser is actually utilized in the probe step before complete ionization is effected. Also, since boxcar detection is used only the RMS of the ± 20 nsec jitter is carried into uncertainty of the lifetime measurement as born out by the nearly perfect straight line fit in Figure 10 which displays lifetime data taken on a very highly excited level.

Figure 13 shows a Rydberg sequence accessible from the odd parity level at 32,899.3 cm^{-1}. This spectrum was taken using a delayed CO_2 pulse for ionization. It is important to remember that just below the continuum there are copious quantities of valence states living side by side with Rydberg levels. In an experiment in which these states are probed by an ionizing laser which is applied immediately (within 10 or 20 nsec) after the levels are populated, both short lived (approx. 50-75 nsec) valence states and long lived (approx. ten microseconds) Rydberg levels are detected. By the simple expedient of delaying the ionizing CO_2 pulse approximately 0.5 μseconds from the populating pulse, valence states decay away leaving only longer lived Rydberg sequences to be monitored. See Figure 12. This simple trick reduces spectral complexity considerably and permits the observation of the sought for sequences. Equally important, the intense (approx. 1 MWatt/cm^2) IR laser saturates the ionization step from every level whether or not an autoionization peak is struck. This means that

photoion peak heights are indicative only of the efficiency of population of the individual Rydberg members. This enables the experimenter to obtain a Rydberg spectrum which displays the expected weakening of excitation probability as a function of principal quantum number rather than a spectrum where photoion peak intensities offer no clue to the nature of the spectrum. Figure 13 illustrates the manner in which the previously complicated spectrum is cleaned up via the pulse delay technique. By measuring the lifetimes of each Rydberg level to 5-10% and fitting the data to the theoretical n = 3 slope,[4,5] effective principle quantum numbers, n^* where $n^* = n - \Delta$, are confirmed. Such a fit is shown in Figure 11. Obviously, the observation of Rydberg progressions yields an improved measurement of the ionization potential as well.

When a slower, higher resolution scan of the progression shown in Figure 11 is made, the cleaner results shown in Figure 14 are obtained. It is seen that actually two progressions are accessed from the level at 32899.3 cm^{-1}. . tentatively assign the configuration of this level as f^3s^2d which allows even parity sequences of f^3s^2nf and f^3s^2 np to both be accessed as in Figure 15. The doublets observed in Figure 14 can be explained only in this manner and cannot arise from fine structure as the splittings from this effect are many orders of magnitude smaller at these principal quanta. Figure 16 shows the fit of the data to the theoretical Rydberg plot which yields n^*. Figure 17 shows the same plot for the lower n^* members of the f^3s^2 nf series. These sequences converge to the ground state of the ion. Figure 18 shows a region of a Rydberg spectrum in uranium which is perturbed. This sequence is accessed from the odd parity level at 33082.3 cm^{-1}. Perturbations of Rydberg spectra have been known for

years[6] but it is rare to observe these perturbations at such high principal quantum numbers. To our knowledge these are the first observations of Rydberg sequences in an actinide.

Lastly we discuss the measurement of cross sections of excited state-excited state transitions in uranium. A solution of the two level rate equations yields a simple expression for the pumping of an excited state as a function of cross section, level lifetimes, laser intensity, and laser pulse length. By fitting a plot of ion yield as a function of laser intensity to this expression, a cross section is readily obtained. The experiment may be visualized as first a population pulse followed by a transition probe pulse and finally the omnipresent ionization pulse. All pulses are disconnected in time and the two level approximation is therefore valid. The two level solution is:

$$S_{ion} = \frac{1}{2} N_0 \frac{2n_\lambda \sigma\tau}{2n_\lambda \sigma\tau + 1} \left[1 - e^{-\left(2n_\lambda \sigma + \frac{1}{\tau}\right) t_0}\right]$$

Here τ is the measured level lifetime, t_0 the measured pulse length of the saturating laser, n_λ is the photon density, and N_0 is the density of absorbers. N_0 does not have to be measured, of course, as in the final analysis it is absorbed into the experimental detection parameters. The measurement of n_λ is accomplished by taking a saturation curve of the 0-16505 cm^{-1} absorption, whose cross section has been tabulated.[7,8] In effect, all subsequent cross sections are then scaled relative to this cross section which is used to extract the experimental n_λ.

Figure 19 shows a typical set of data for such measurements while Figure 20 gives a table of previously unreported excited state cross sections. We should also mention that this method has been tested by

saturating different transitions from the ground state where cross sections have already been reported. We find excellent agreement with the previously reported values.[7,8]

To summarize stepwise laser photoionization spectroscopy has proven to be a valuable, simple, flexible technique for investigating the spectroscopic properties of heavy atoms. By exercising precise temporal control of sequential laser pulses and tuning the probe laser to autoionizing transitions, spectral simplicity and maximum sensitivity are simultaneously obtained. The technique and variations on its general theme permit measurement of lifetimes, cross sections, and branching ratios. Furthermore the experiments can preferentially monitor Rydberg or valence states and can search out new transitions in the atom and assign them.

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EXPERIMENTAL APPARATUS FOR MULTIWAVELENGTH STEPWISE IONIZATION

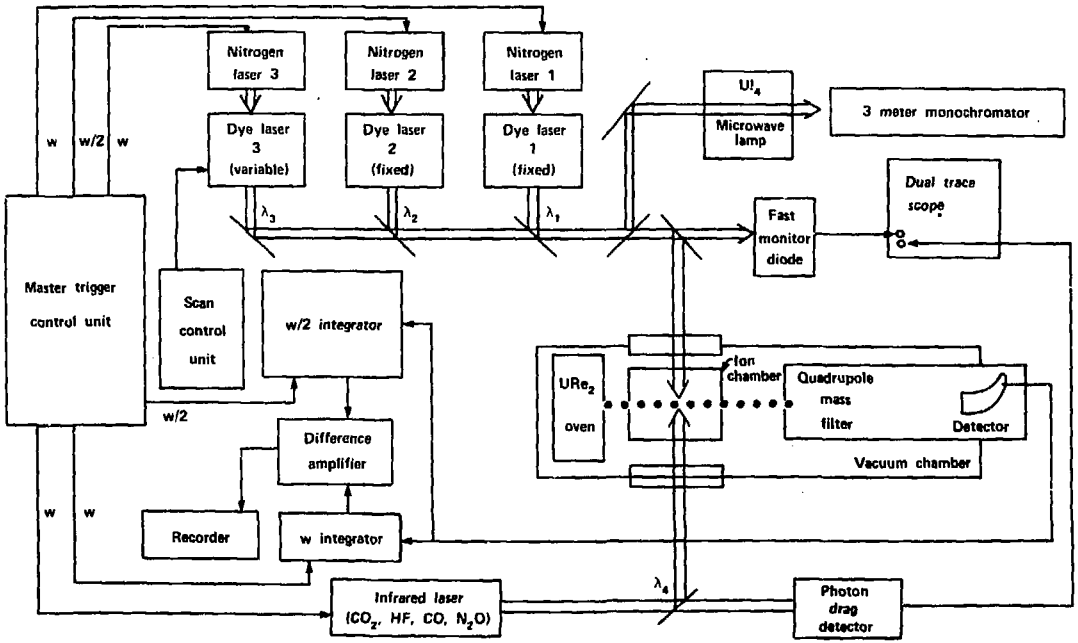
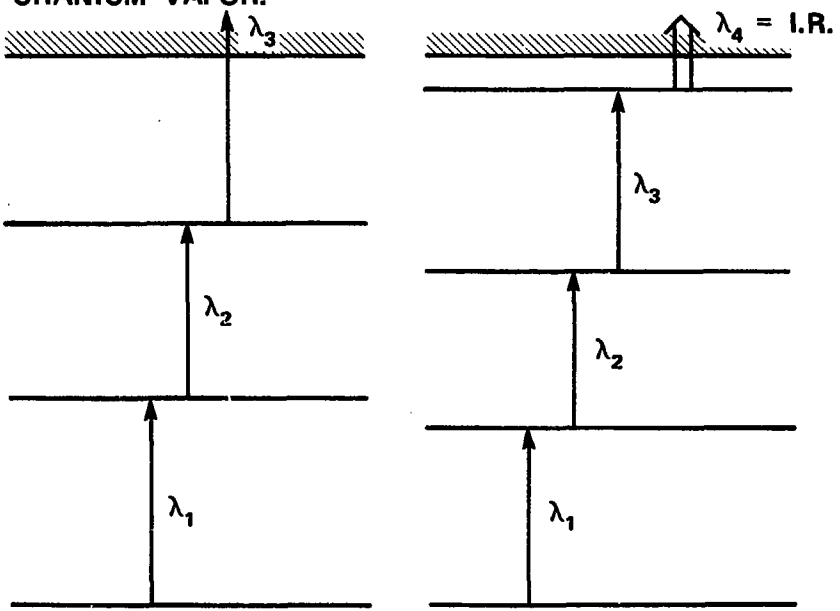


Figure 1

MULTIPHOTON IONIZATION SCHEMES PROPOSED FOR URANIUM VAPOR.



a) Three visible wavelengths
b) Three visible wavelengths plus IR ionization

Figure 2

The Assignment of Quantum
Numbers of Excited States

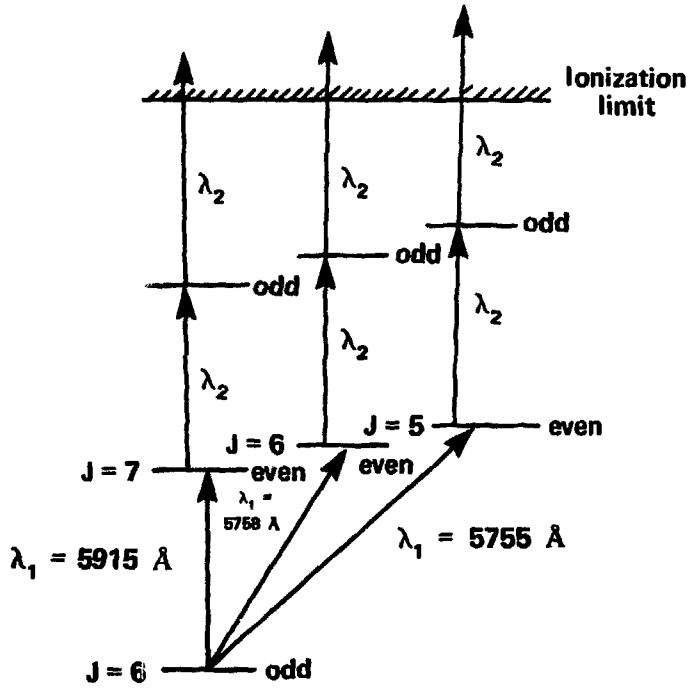


Figure 3

ASSIGNMENT OF EXCITED ODD PARITY STATES IN URANIUM

Level energy	From J = 4 at 17448.2 cm^{-1}	From J = 5 at 16929.7 cm^{-1}	From J = 6 at 17070.5 cm^{-1}	From J = 6 at 16505.8 cm^{-1}	From J = 7 at 15631.8 cm^{-1}	J assignment
33442.8	33442.8	33442.8	33442.8	33442.7	–	5
33500.3	33499.8	33500.5	–	33500.6	–	5
33624.2	–	33624.2	–	–	33624.2	6
33720.5	33720.5	–	33720.8	33720.4	–	5
33742.7	33742.8	33742.7	33742.6	33742.6	–	5
33833.2	–	33833.2	–	–	33833.1	6
33914.4	33914.3	33914.2	33914.7	–	–	5
34003.1	34003.1	–	34003.2	–	–	5
34024.6	34024.6	34024.5	34024.7	–	–	5
34070.5	34070.8	34070.3	34070.5	–	–	5

Figure 4

Even Parity Resonances Near the
Continuum in Uranium Vapor

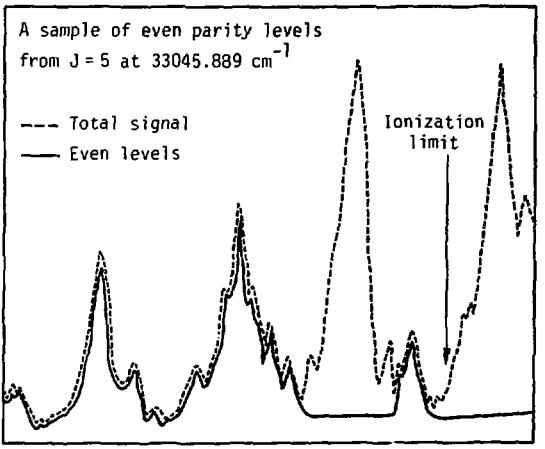
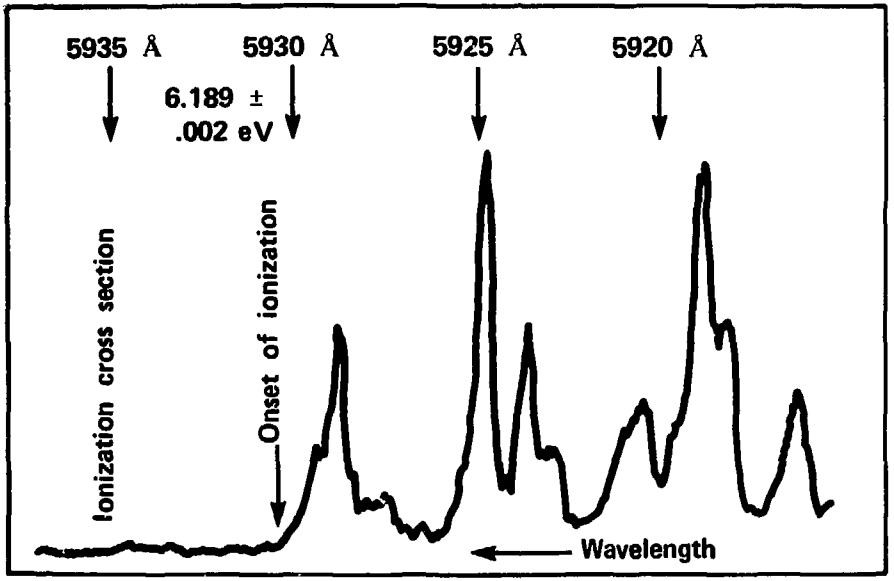


Figure 5



Autoionization of uranium from the odd parity level at 33082.7 cm^{-1}

Figure 6

High Resolution Autoionization

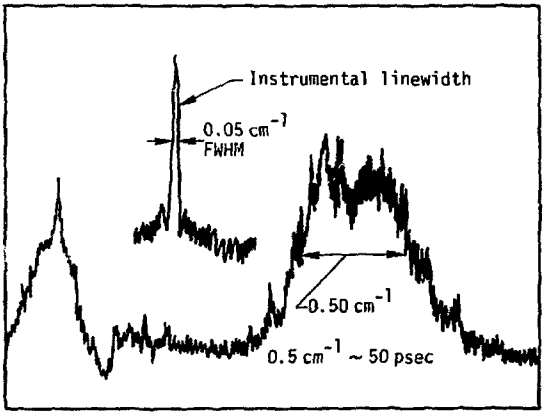


Figure 7

3781 Å TRANSITION FROM 620 cm^{-1}

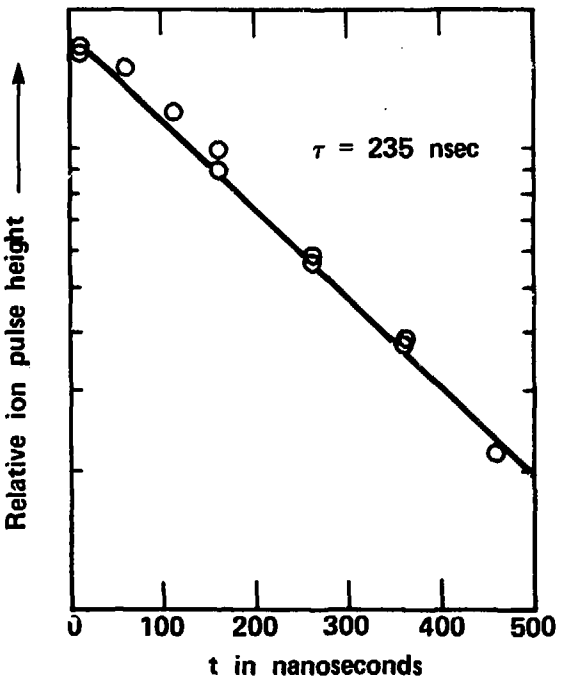


Figure 8

EXPERIMENTALLY MEASURED LIFETIMES IN URANIUM

Excitation sequence (Å)	Term energy (cm^{-1})	Parity	Lifetime (nsec)
6056	16505.8	even	329 ± 10
3781	27060.8	even	235 ± 20
5758	17361.9	even	210 ± 50
6056 + 5951	33303.6	odd	400 ± 50
6056 + 6140	32787.4	odd	145 ± 30
6056 + 6103	32884.6	odd	50 ± 10
6056 + 6031	33082.3	odd	490 ± 50
6056 + 6006 + 5982	49860.1	even	70 ± 20
6056 + 6098 + 5971	49641.1	even	40 ± 5
6056 + 6031 + 5933	49930.8	even	210 ± 30
6056 + 6031 + 5963	49846.5	even	505 ± 25
Rydberg sequences	n ~15-20	even	avg. ~250
Rydberg sequences	n ~40-50	even	>2000

Figure 9

LIFETIME OF EVEN PARITY LEVEL AT T = (6056 + 6098 + 5891 Å)

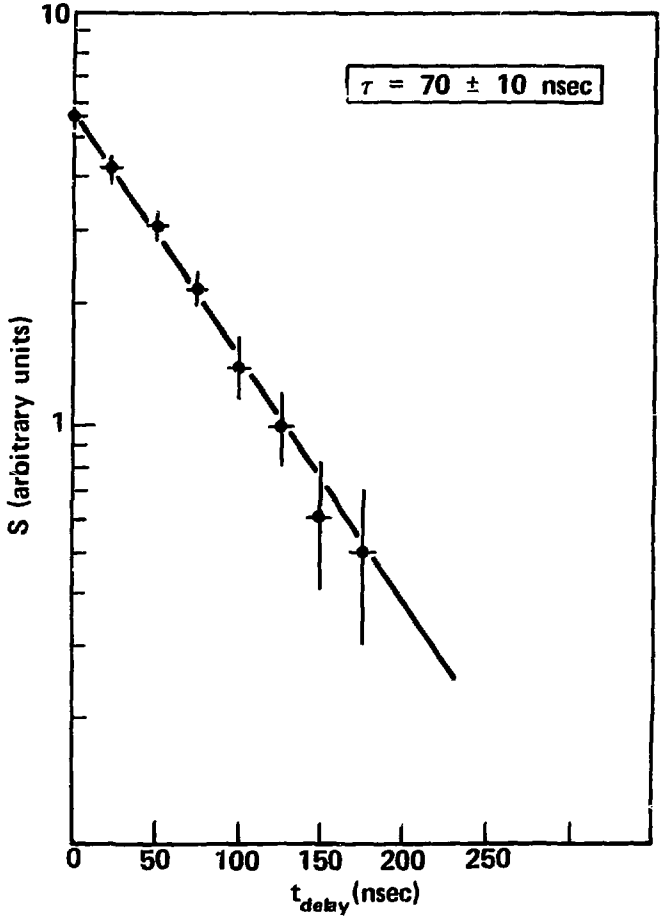


Figure 10

QUANTUM NUMBER DEPENDENCE (n) OF LIFETIMES OF RYDBERG MEMBERS

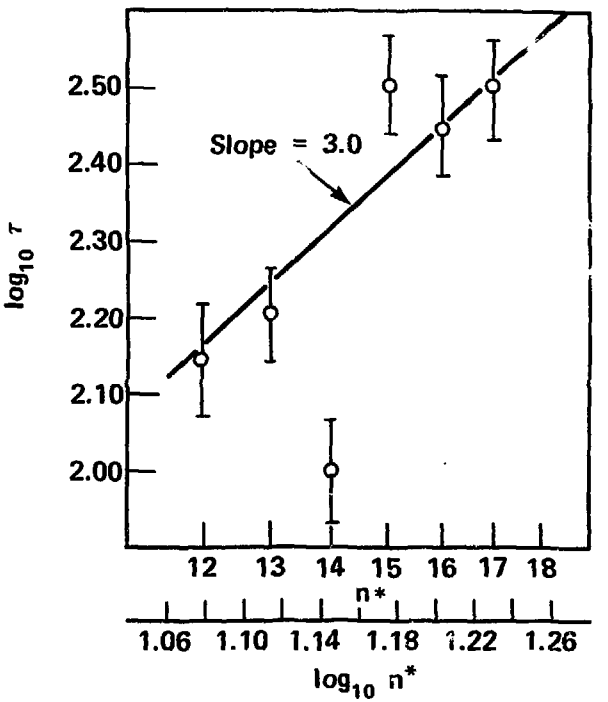
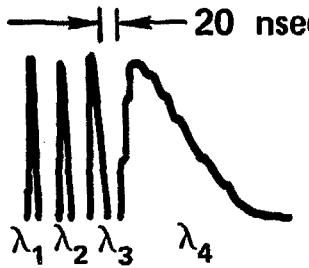
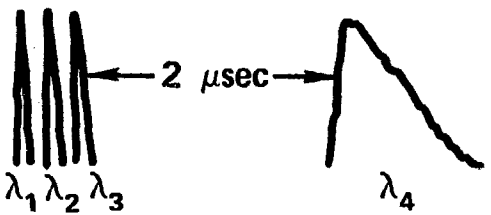


Figure 11

PREFERENTIAL DETECTION OF RYDBERG SEQUENCES



Rydberg and valence states



Rydberg states only

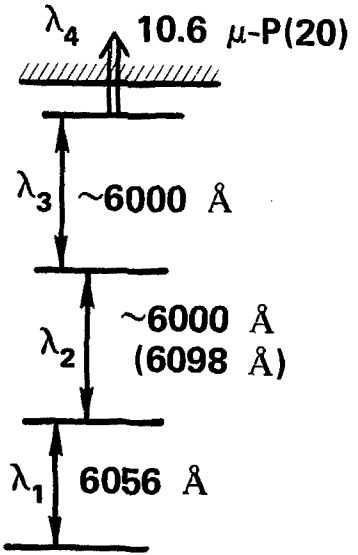


Figure 12

PREFERENTIAL OBSERVATION OF RYDBERG STATES IN URANIUM FROM 32899.3 cm^{-1}

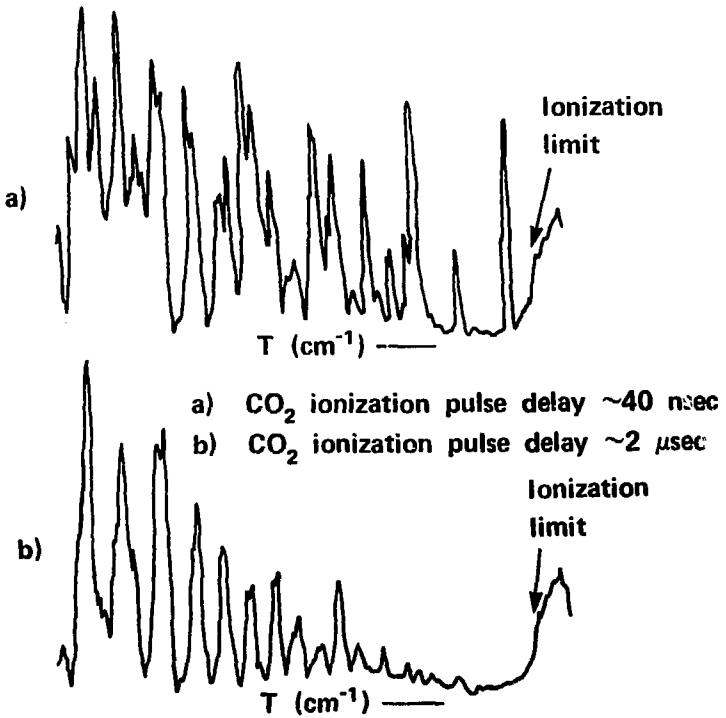


Figure 13

RYDBERG PROGRESSIONS ORIGINATING FROM 32899.3 cm^{-1}

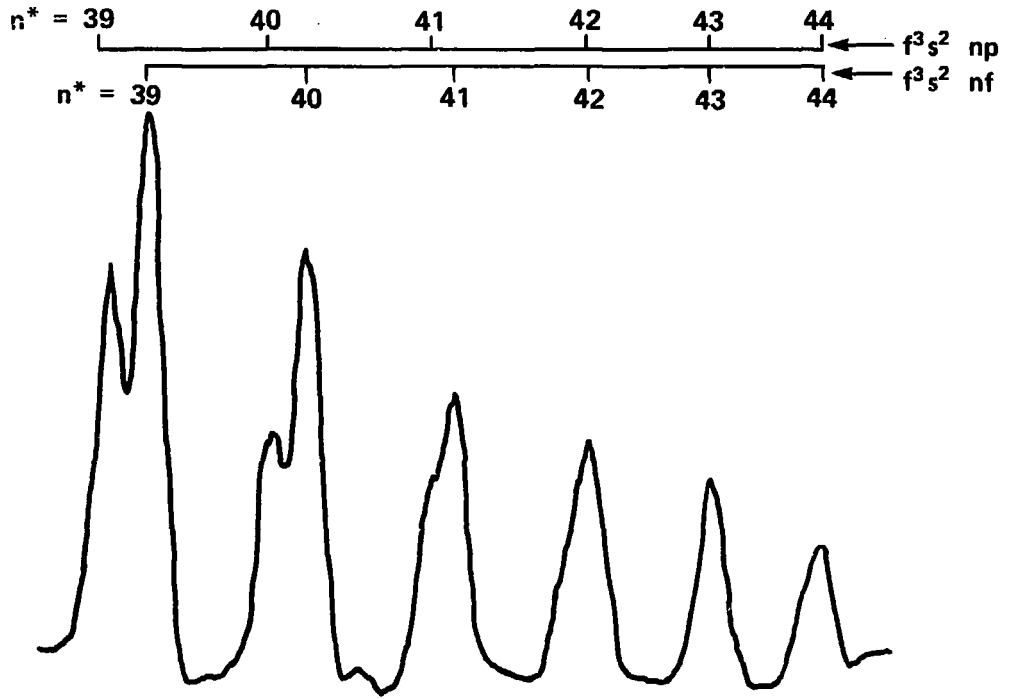


Figure 14

TENTATIVE CONFIGURATION ASSIGNMENTS FOR OBSERVATION OF RYDBERG PROGRESSIONS IN URANIUM

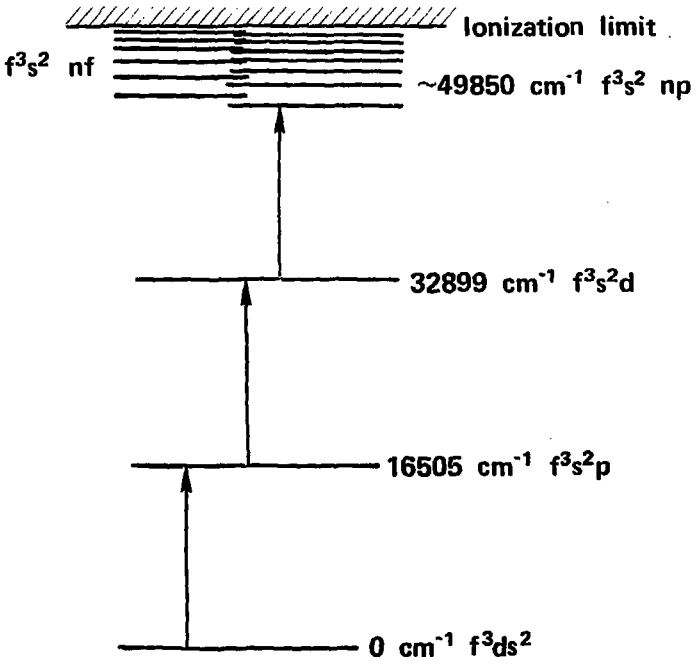


Figure 15

RYDBERG SEQUENCE OBSERVED FROM 32899.3 cm^{-1}

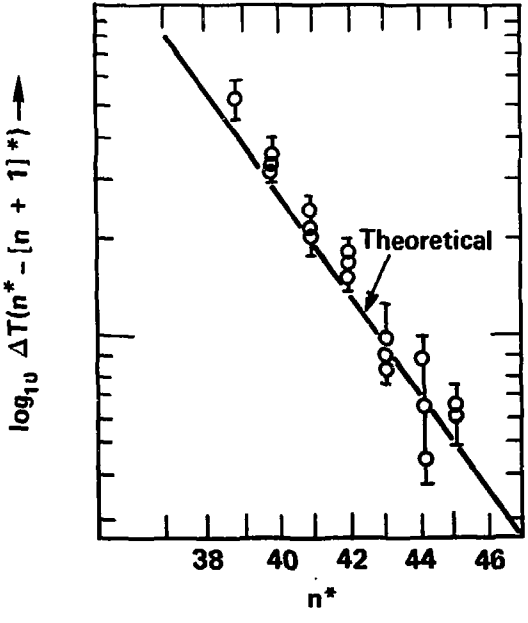


Figure 16

LOW PRINCIPLE QUANTUM RYDBERG PROGRESSIONS ORIGINATING FROM 32899.3 cm^{-1}

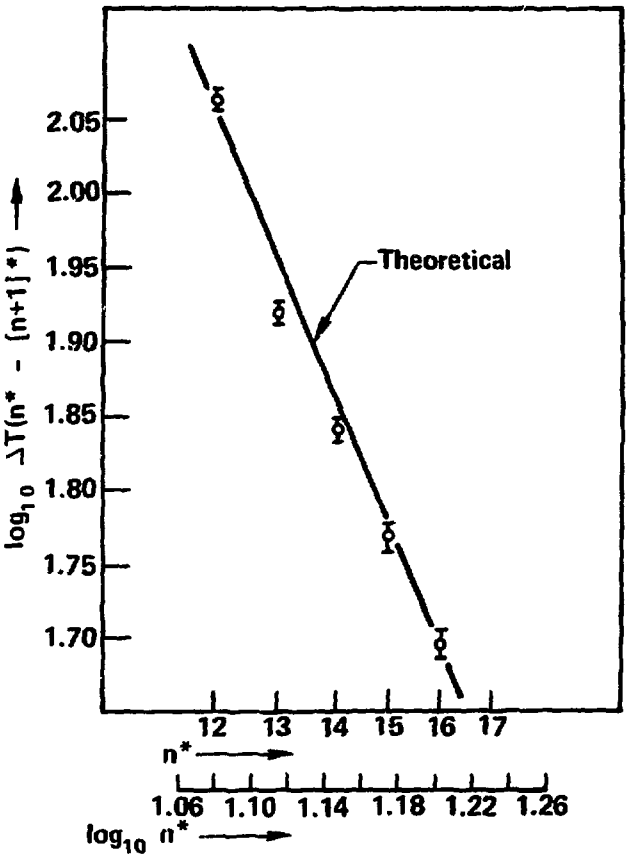


Figure 17

PERTURBATION OF THE RYDBERG PROGRESSION OBSERVED FROM 33,082.3 cm^{-1}

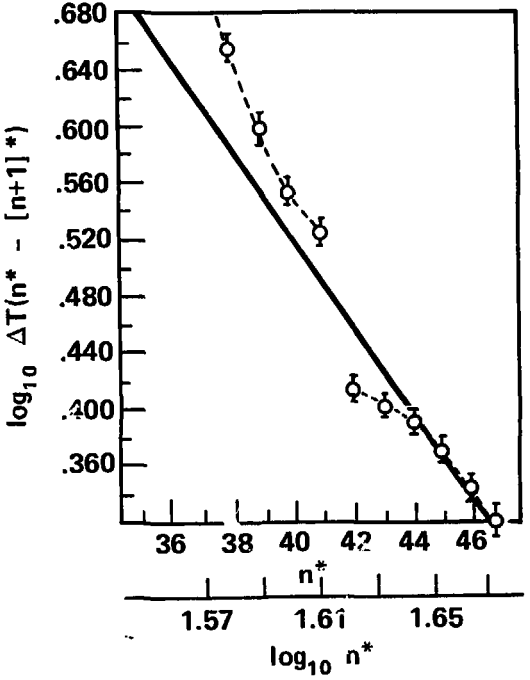


Figure 18

SATURATION OF THE EXCITED STATE TRANSITION FROM 16505.8 cm^{-1} → 33150.6 cm^{-1}

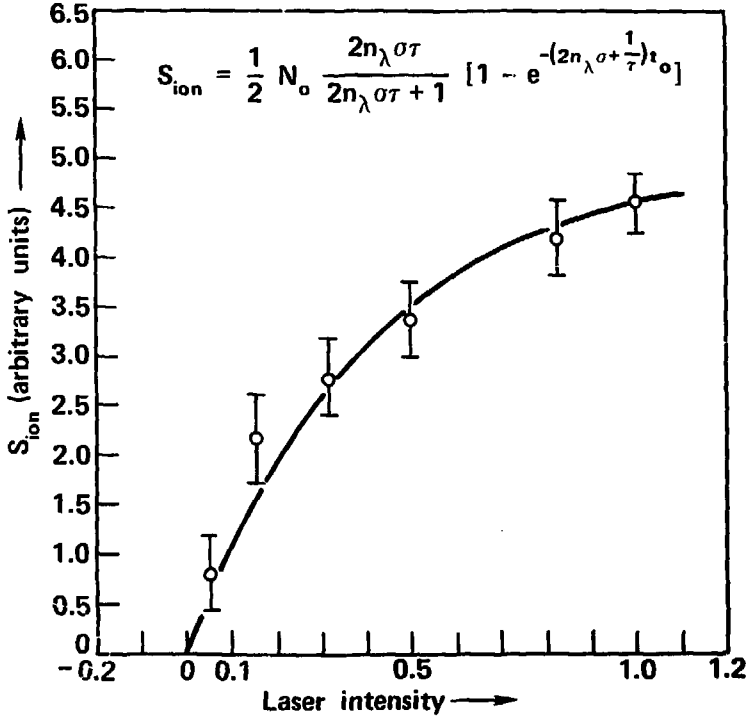


Figure 19

CROSS SECTIONS FOR EXCITED STATE TRANSITIONS IN URANIUM (PEAK ABSORPTION AT 2000°C)

Initial state	Wavelength	Final state	$\sigma_{2000°C}$
16505 cm^{-1}	6014.2	33129 cm^{-1}	1.2×10^{-14} cm^2
16505 cm^{-1}	6018.3	33118 cm^{-1}	$.85 \times 10^{-14}$ cm^2
16505 cm^{-1}	6026.3	33095 cm^{-1}	1.7×10^{-14} cm^2
16505 cm^{-1}	6031.0	33082 cm^{-1}	3.5×10^{-14} cm^2
16505 cm^{-1}	6098.3	32899 cm^{-1}	3.1×10^{-14} cm^2
16505 cm^{-1}	6123.9	32831 cm^{-1}	1.7×10^{-14} cm^2
16505 cm^{-1}	6152.9	32754 cm^{-1}	$.59 \times 10^{-14}$ cm^2

Figure 20