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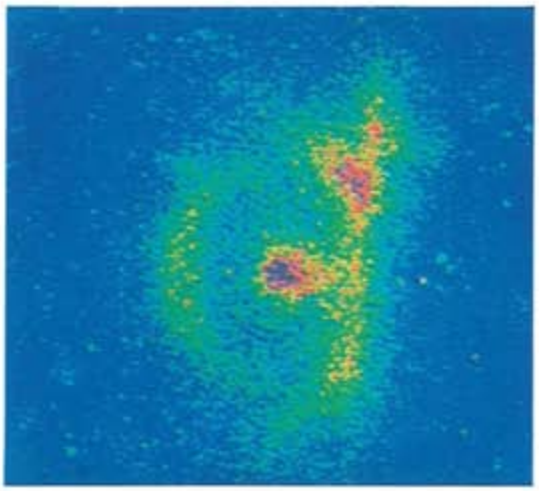

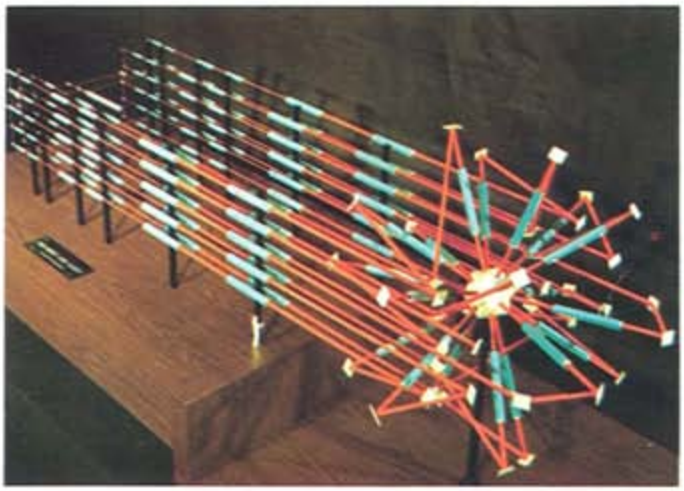

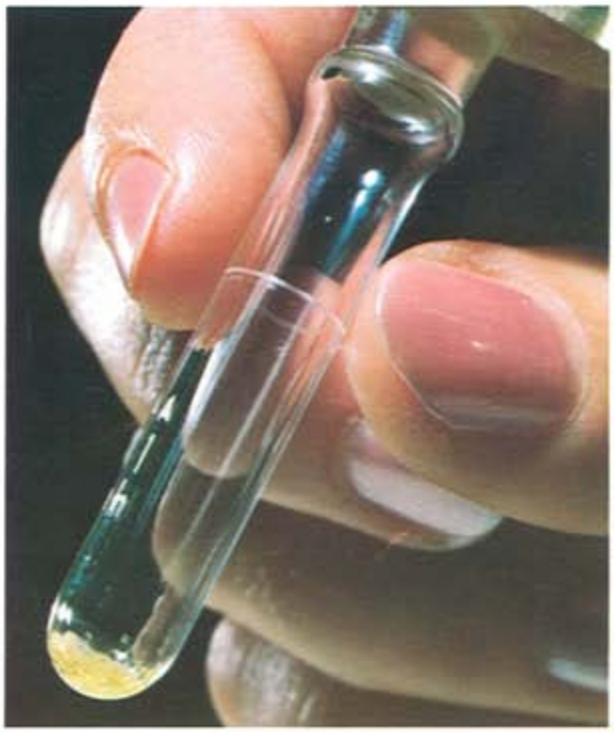

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LLL LASER PROGRAM

Laser excitation spectroscopy, recently applied to uranium enrichment research at LLL, has produced a wealth of new and vitally needed information about the uranium atom and its excited states. Among the data amassed by LLL have been a large number of cross sections, almost a hundred radiative lifetimes, and many level assignments. Rydberg states, never before observed in uranium or any of the actinides, have been measured and cataloged. This work puts a firm experimental base under laser isotope separation, permitting a choice of the laser frequencies most appropriate for practical uranium enrichment.

Until recently, the spectroscopic information available on the uranium atom consisted primarily of the assignment of a few low-lying states. Experimental difficulties and the extreme complexity of the uranium spectrum discouraged extensive study. Laser isotope separation experiments to find more economical ways to separate the rare uranium-235 from the far more abundant uranium-238 depend on detailed knowledge about favorable excitation levels. Urgently needed were data on radiative lifetimes, branching ratios, autoionization behavior, cross sections, level assignments, and Rydberg states (see explanation on following page). Such data were available only for some of the lighter, more easily studied atoms. Even these data were fragmentary.

In concept, laser excitation spectroscopy is simple. (Figure 20 shows the central components of our spectrometer.) Laser light, because of its extremely uniform frequency, can excite the atoms of one uranium isotope in a vapor and leave the atoms of the other unchanged. A second laser beam further excites the excited atoms, even to the point of ionizing them (again without affecting the other atoms). The ions are then directed through a mass filter and into a charged particle detector. The current collected is a direct measure of the number of ions formed and hence of the cross section of the excited state.

In practice, however, things turn out to be more complicated. An oven capable of providing a beam of atomic uranium is in itself a technical triumph, considering molten uranium's propensity for dissolving everything it touches. The detection system, at least for preliminary experiments, must be highly sensitive and sophisticated.[4] Furthermore, the lasers, in addition to providing light of an extremely uniform frequency, must be tuned to just the right frequency. Excitation is a resonance phenomenon akin to shattering a goblet by singing into it — loudness alone won't do it; it is also necessary to hit exactly the right pitch.

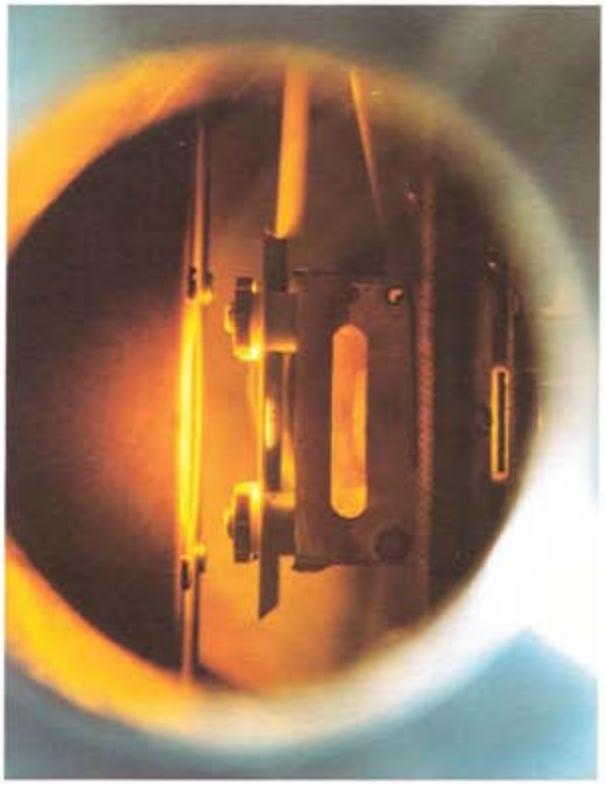

Fig. 20. Experimental apparatus for laser excitation spectroscopy of uranium. The bright area at the left is the exit slit of the uranium vapor oven. Immediately to the right, supported on standoff insulators, is the front of the interaction chamber. Laser beams enter the chamber from the top and sides. The infrared laser beam passes into the chamber through the oblong window. The indistinct rectangular shape at the extreme right is the entrance to the quadrupole mass filter.

This has been the crux of the laser isotope separation problem for uranium. This atom, because of its massive nucleus and swarm of electrons, has many thousands of excited states. Most are unsuitable for laser isotope separation because of their small cross section (low probability of excitation), short radiative lifetime, or hyperfine splitting (fragmentation into several closely related energy levels). Small cross sections reduce the overall efficiency by wasting photons. Short radiative lifetimes waste excited atoms by allowing some of them to revert to the ground state before ionization. Hyperfine splitting reduces the

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RYDBERG AND OTHER EXCITED STATES

In normal unexcited atoms, electrons circle the nucleus in stable orbits. In the uranium atom, for example, the nucleus is surrounded by an "atmosphere" of 92 electrons orbiting out to about 3×10^{-8} cm. The scale is very small: if uranium atoms were placed side by side, one for each U.S. citizen, the line would stretch only about 12 cm.

Excited states are simply enlarged unstable orbits that electrons can be forced to take. Only certain of such enlarged orbits, rigidly defined by complex physical processes, are allowed. For complex atoms, however, this number can be quite large: many hundreds or thousands in the case of uranium. It takes energy to raise an electron into one of these excited-state orbits, and, because the orbits are fixed, the required energy is also precisely defined. This energy can be supplied in various forms – e.g., thermal heating or bombardment with charged particles – but an efficient source is radiation (light). The energy of each photon of light depends only on its frequency (reciprocal of wavelength); wavelengths are among the most precisely measurable of all physical quantities. Monochromatic laser light is an especially efficient source of excitation energy because of its extremely narrow band of wavelengths.

An electron in an excited state does not stay there for long. Soon – usually within a few nanoseconds – it drops back into a lower state or all the way to the ground state, giving back in the process the energy originally required to raise it to the excited state. Usually this energy is released in the form of light. The radiative lifetime of a state is a measure of the mean time an electron will stay in that state before dropping back to another.

There is a limit to the amount of energy an atom can absorb without damage. Beyond a certain level (the ionization limit), the excited electron escapes, leaving the atom ionized. However, there are states in which atoms that have absorbed enough energy for ionization "forget" to lose an electron until later. These states, which decay by ejecting an electron instead of by emitting light, are called autoionization levels.

As suggested above, electrons may take more than one path in returning to the ground state. The chances of going one way or the other are known as branching ratios. Also, some orbits are harder to reach than others; this is viewed as the size of the target presented by each state and is measured as its cross section.

Of particular interest to our work are the Rydberg states: highly excited states of unusual stability (lifetimes of several microseconds). An atom in a Rydberg state has a single electron orbiting a thousand times farther out than usual. In a uranium atom, this is analogous to having one electron within easy reach of the second baseman while the rest of the atom – nucleus plus first 91 electrons – is a baseball resting on home plate. Such states have been observed before in other atoms but never in one so heavy as uranium. An atom in a Rydberg state is particularly susceptible to ionization or chemical reaction. Either might be used to separate excited from neutral atoms.

It should be pointed out that traditional optical spectroscopy deals not with the excited states themselves but with a jumble of light photons of different wavelengths from many electrons jumping between different orbits. Each wavelength precisely defines the energy difference between two states; it neither identifies the states nor locates them with respect to the ground state. The virtue of laser excitation spectroscopy is that it furnishes precisely known energy packets and starts from a known energy state. It therefore enormously simplifies the task of assigning energy levels to the different excited states.

separation efficiency by making it impossible to excite – at a single wavelength – more than a fraction of the uranium-235 atoms present. The success of the laser isotope separation effort has hinged on finding, among these hundreds of excited states, a set of suitable levels that are appropriately spaced (excitable in stair-step fashion with available lasers), easy to excite, relatively stable, and above all sharp (not split by hyperfine effects).

Experimental Techniques

The multibeam laser excitation spectrometer has proved to be a probe of matchless versatility for investigating the energy levels of the uranium atom. Sweeping the frequency of the second laser makes it cover a known portion of the atom's energy spectrum. The detection system, synchronized with the laser's sweep, reads out directly the amount of ionization produced at any excited state within that sweep, thus indicating the cross section. Three or more lasers can be used to further subdivide the energy steps.

Figure 21 diagrams two possible excitation schemes. Scheme (a) excites the uranium atom beyond the ionization limit with three visible dye lasers.

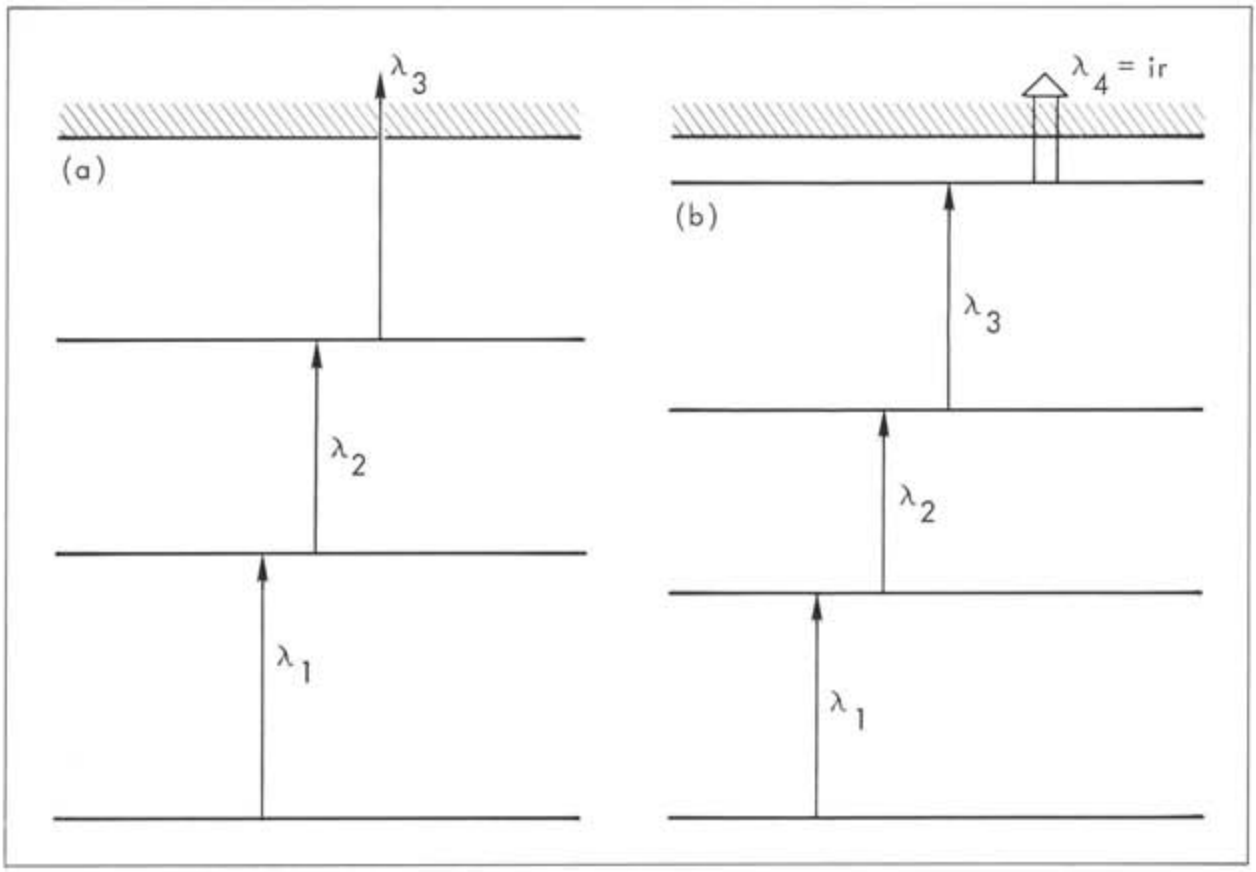

Fig. 21. Multiphoton ionization schemes for uranium vapor: a) three visible-wavelength dye lasers; b) three visible-wavelength dye lasers plus infrared CO_2 laser ionization.

Scheme (b) uses an infrared laser to provide the final ionizing increment.

Using two or more dye lasers for excitation and an infrared CO_2 laser for the final ionization step offers many experimental advantages. Only highly excited atoms can be ionized by infrared radiation. If the infrared beam is powerful enough, it will ionize every excited atom it strikes regardless of excitation level. In this mode the ionization current depends only on the cross sections of the various levels excited by the sweep laser. Table 2 lists a few of the cross sections measured in this way.

Table 2. Cross sections for excited state transitions in uranium (peak absorption at 2100°C) from an initial excited state at 16 505 cm^{-1}

Wavelength, nm	Final state, cm^{-1}	$\sigma_{2100°C}$, cm^2
601.39	33 129	1.2×10^{-14}
601.79	33 118	0.61×10^{-14}
602.60	33 096	1.1×10^{-14}
603.06	33 083	1.8×10^{-14}
609.79	32 900	2.4×10^{-14}
612.38	32 831	0.97×10^{-14}
615.25	32 755	0.70×10^{-14}

Also, plotting the intensity of ionization vs the time delay between the last excitation laser pulse and the infrared laser pulse gives a measure of the lifetime of the excited state under observation. Figure 22 is such a plot for a representative energy state with a lifetime of 70 ns. The excellent fit between the experimental points and the straight line indicates the precision of the technique. Table 3 lists a few of the many lifetimes so measured.

Similarly, when the spectrum is cluttered, shortlived states can be eliminated from observation simply by delaying the infrared laser pulse about 100 ns. The shortlived states vanish, leaving only the hardy,

Table 3. Experimentally measured lifetimes in uranium

Excitation sequence, nm	Term energy, cm^{-1}	Parity	Lifetime, ns
605.6	16 505.8	even	329 ± 10
378.1	27 060.8	even	235 ± 20
575.8	17 361.9	even	210 ± 50
605.6 + 595.1	33 303.6	odd	400 ± 50
605.6 + 614.0	32 787.7	odd	145 ± 30
605.6 + 610.3	32 885.6	odd	50 ± 10
605.6 + 603.1	33 083.3	odd	490 ± 50
605.6 + 600.6 + 598.2	49 861.1	even	70 ± 20
605.6 + 609.8 + 597.1	49 642.1	even	40 ± 5
605.6 + 603.1 + 593.3	49 931.8	even	210 ± 30
605.6 + 603.1 + 596.3	49 847.5	even	505 ± 25
Rydberg sequences	n ~15-20	even	av ~250
Rydberg sequences	n ~40-50	even	>2 000

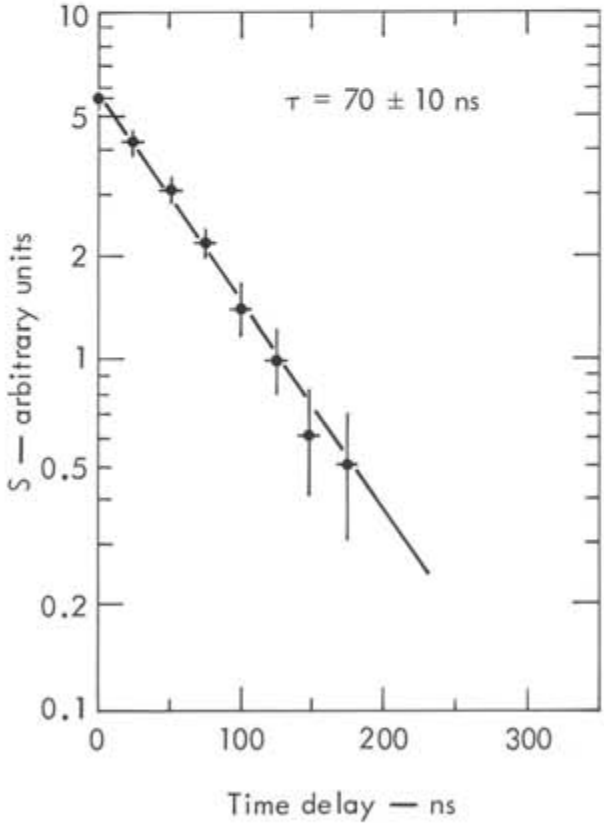

Fig. 22. Lifetime of a uranium level at 49 883.0 cm^{-1}, reached by excitation with lasers tuned to 605.6, 609.8, and 589.1 nm.

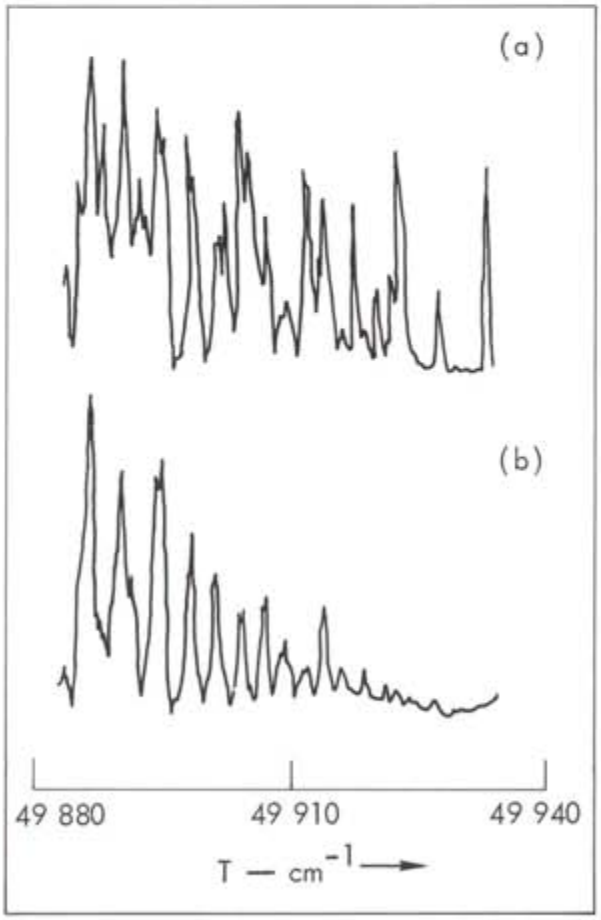

Fig. 23. Preferential observation of uranium Rydberg states reached from a level at 32 899.8 cm^{-1}: a) infrared ionization pulse delayed 40 ns; b) infrared ionization pulse delayed 2000 ns.

longlived survivors. Figure 23 shows this process, with before and after spectra that display Rydberg states never before observed in any actinide.

Applications

Finding a way to excite the Rydberg levels of uranium and other heavy atoms has implications far beyond the isotope separation program. For example, excited atoms might serve as efficient detectors of infrared and other long-wavelength radiation. Such detectors could open up a whole new field of astronomy, as happened with the introduction of radio detectors and x-ray detectors. Photographic emulsions, conventional astronomy's favorite recording medium, are all but blind to infrared radiation.

Furthermore, the isotope separation applications of this work need not stop with uranium. The method is perfectly general and can be applied to other elements or sets of isotopes. Boron, for example, has long been used as a neutron "sponge" in nuclear reactors, shielding against neutrons and regulating the reaction itself. Its value in these applications comes entirely from its less-abundant isotope boron-10, which has a large cross section for neutron capture and produces only nonradioactive end-products. An economical isotope separation process would lead to more efficient shielding and more compact control-rod assemblies.

The major impact of this work, however, is likely to be in uranium enrichment. Demands of the rapidly expanding nuclear power industry will exceed the capacity of the present gaseous diffusion uranium-enrichment facilities in the 1980's. Unless better means are found, we will be encountering enormous construction costs and daily operating expenses for new gaseous diffusion plants well before the year 2000.

Key Words: uranium isotopes; laser isotope separation; spectroscopy; cross sections; radiative lifetimes; Rydberg states; excitation.