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Atomic lifetime measurements obtained by the use of laser ablation and selective excitation spectroscopy

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The combined use of laser ablation and selective excitation spectroscopy is proposed as a new approach to the convenient and accurate measurement of atomic parameters. Measurement of the radiative lifetimes for the three resonance transitions in chromium served as an initial test of the technique. For the transitions at 425.4, 427.5, and 429.0 nm, our measurements indicate lifetimes of 31.2, 32.2, and 31.4 nsec, respectively, with an estimated uncertainty of 1 nsec. These are in good agreement with the values previously obtained by other techniques.

Various experimental techniques have been used in the past to determine radiative lifetimes. Beam-foil spectroscopy (BFS) represents one technique that has been used extensively during the past decade for the measurement of atomic lifetimes in both neutral and ionic species.[1-6] Unfortunately, this approach can suffer from several inherent difficulties, the most serious of which are cascading effects and energy loss uncertainties. Andrä *et al.*[7] and Arnesen *et al.*[8] have attempted to avoid these drawbacks by replacing the foil in beam-foil experiments with an intense laser beam tuned to selectively excite specific atomic states. However, this technique is limited to ions. The more versatile approach of Harde and Guthohrlein[9] avoids this constraint but is consequently vulnerable to the scattering-loss uncertainties. Gornik *et al.*[10] and Kaiser[11] have shown that stepwise excitation of a sodium atomic beam by two pulsed dye lasers can yield lifetime data on levels not optically connected to the ground level. Somewhat similar experiments, using sodium vapor cells rather than low-density atomic beams, have been undertaken by Gallagher *et al.*[12]

The purpose of the present paper is to introduce a new and versatile approach to the measurement of radiative lifetimes and other atomic parameters. Laser ablation and selective excitation spectroscopy is proposed as a convenient and accurate method of undertaking such measurements with materials that are difficult to handle (refractory or highly corrosive). In essence a vaporized (and partly ionized) plume of the material is created by laser ablation of a solid target within a vacuum chamber (or a low density of specific buffer gas). The vapor cloud is then selectively excited by suitably tuned laser radiation and the subsequent enhanced emission studied. Selective excitation spectroscopy was first suggested by Measures.[13]

In the case of radiative lifetime measurements, the elapsed time between the moment of ablation and the time of excitation is made sufficient to ensure that the dense plasma has recombined and expanded into a rarefied, predominantly neutral vapor cloud. An optimized choice of delay will allow the density of the lower level of the excited transition to be high enough to ensure a good signal-to-noise ratio, yet low enough to prevent collisional quenching and self-absorption effects from having an influence on the measurement.

With a shorter delay other kinds of relaxation processes, such as spin exchange on resonance transfer collisions, may be studied. Where the measurements principally involve the ionized state, sustained resonance pumping[14] during the expansion phase might be used to produce an improved degee of ionization. On the other hand, if neutral species are to be studied, careful control of the ablation laser power density and temporal behavior might be used to optimize the neutral content of the plume.

A schematic diagram of our experimental arrangement is presented as Fig. 1. A Q-switched ruby laser (energy typically 10–50 mJ pulse in 30 nsec) was used for ablation and a nitrogen laser pumped dye laser was employed for the selective excitation of the target material. The peak power of the dye laser pulse did not exceed 10 kW and its duration was less than 6 nsec. A chromium target was chosen for our first tests of the system as chromium possesses an energy level structure that was suitable for a series of experiments we wished to undertake. A fraction of the laser-induced fluorescence emanating from the vapor cloud was captured by a lens, then passed through a ruby laser blocking filter before being spectrally filtered and monitored by a photomultiplier tube (RCA C31034).

In order to condense most of the dye laser output into the spectral bandwidth of interest, a beam expander-grating system (as described by Hänsch,[15] but exclusive of polarizer and etalons) was em-

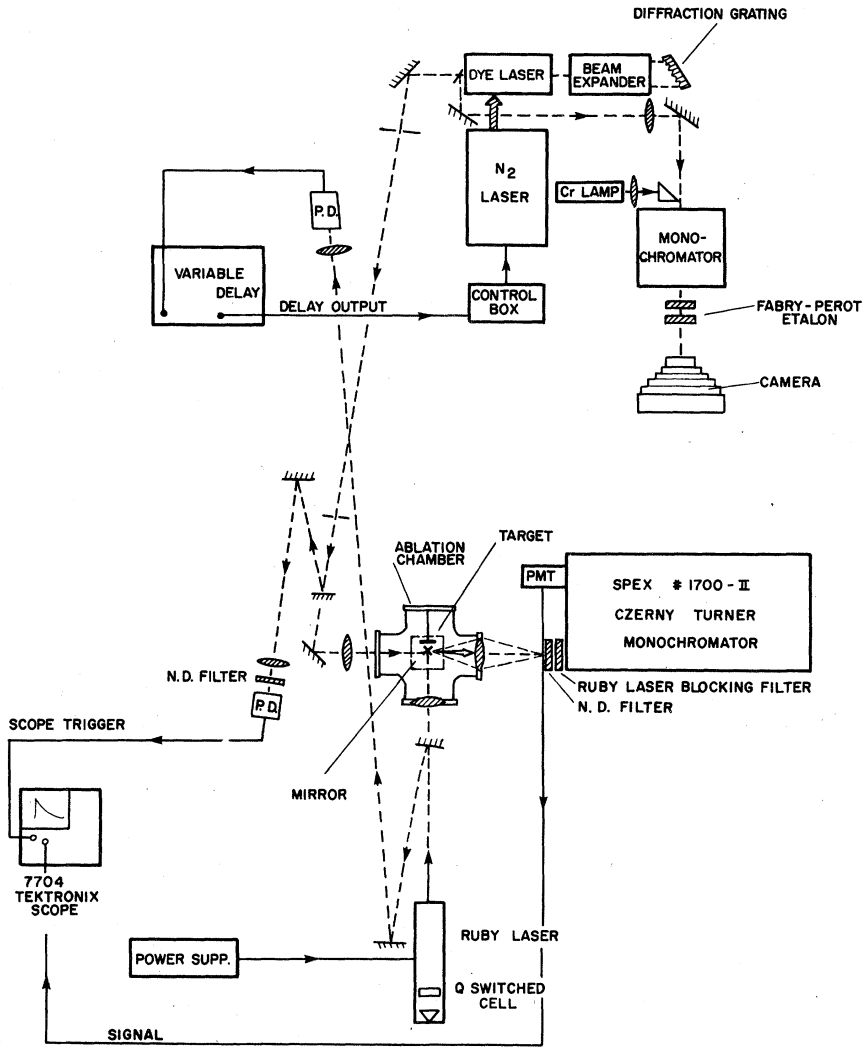

FIG. 1. Schematic of experimental arrangement.

ployed. The spectral overlap between the dye laser pulse and the line being excited was checked by splitting off a small fraction of the dye laser output and passing it through a Fabry-Perot interferometer and comparing the subsequent interferrometric ring system with that produced with the prefiltered light of an appropriate resonance lamp. In order to control the delay between the ablation event and the excitation of the metal vapor, the nitrogen laser was fired by a pulse from a Tektronix 556 oscilloscope which provided a variable delay with respect to a trigger pulse from a photodiode that was exposed to a small fraction of the ruby laser output.

The ruby laser beam, the dye laser beam, and the axis of observation were designed to be mutually orthogonal. The dye laser beam and the observation axis intersected 5 mm in front of the target. The (5×1 mm) entrance slit of the Czerny Turner monochromator (Spex No. 1700 II) was fo-

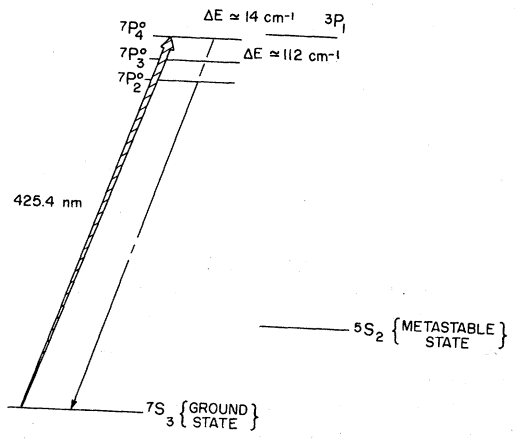

FIG. 2. Partial energy level diagram for chromium I.

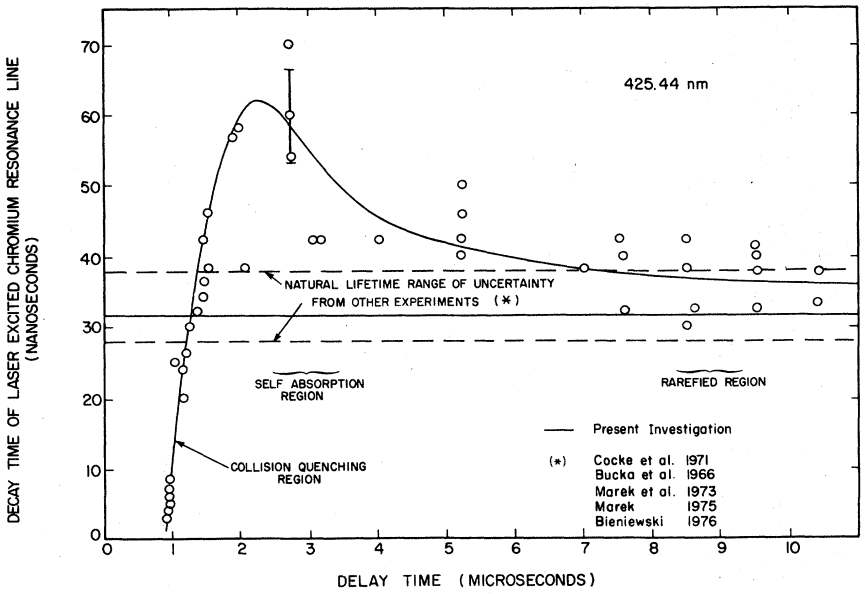

FIG. 3. Variation of enhanced emission decay time at 425.44 nm with delay time for a laser ablated chromium plume (region of observation is about 5 mm in front of target).

cused onto this region of intersection. The signal from the PMT (photomultiplier tube) was displayed on a Tektronix 7704 oscilloscope and photographed, the oscilloscope being triggered by a signal from another photodiode that was positioned to intercept part of the dye laser beam. A Tektronix 4051 calculator with a 4662 Interactive digital plotter was used to digitize and analyze the decay curves recorded from the oscilloscope.

The energy levels and transitions of interest in the case of chromium are shown in Fig. 2. The present report is concerned with the measurement of the lifetimes of the three resonance levels $^7P_2^o$, $^7P_3^o$, and $^7P_4^o$ by laser excitation of the three lines at 428.97, 427.48 and 425.44 nm, respectively. When laser excitation was performed within 10 μsec from the moment of ablation several processes, including collisional quenching and self-absorption, acted to distort the measurement of the radiative lifetime. This is illustrated for the case of the 425.44 nm chromium resonance line in Fig. 3.

For elapsed times of less than 2 μsec it is evident that collision quenching plays the dominant role, while self-absorption has the greatest influence in the 2–10 μsec interval. The steepness of the curve in the collision-dominated region suggests a sudden decrease of the free-electron density (the most likely collision quenching constituent) due to rapid recombination and expansion of the metal vapor plasma. An equally rapid decline in the background recombination continuum emission was observed during this interval and is consistent with this model. As the recombination proceeds there is a buildup of the ground-state population so that once the influence of collision quenching is weakened, the effects of self-absorption appear to dominate the lifetime of the resonance levels. Eventually, expansion of the plume overrides the cascade creation of ground-state atoms and the density drops to the point where self-absorption effects are negligible.

The scatter in our observations shown in Fig. 3 can be attributed to density nonuniformities within the plume and fluctuations in the energy output of our Q-switched ruby laser. This scatter in the lifetime measurements diminishes considerably for delays greater than about 15 μsec as the vapor cloud seems to lose its memory of the details of the ablation event. The radiative lifetime measurements reported in this paper were all undertaken

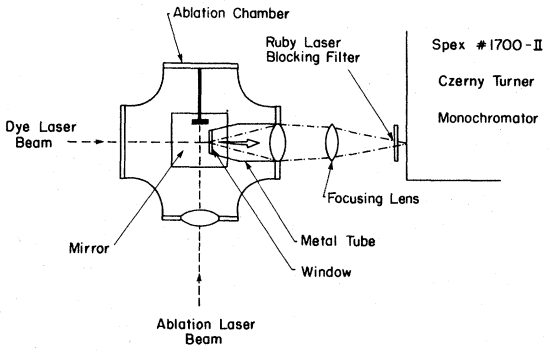

FIG. 4. Collection optics configuration used for radiative lifetime measurements.

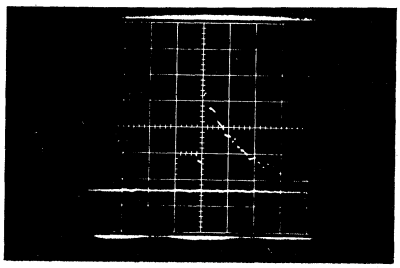

FIG. 5. Example of observed emission at 425.4 nm. (0.1 V per major division, vertical; 20 nsec per major division, horizontal.)

for elapsed times between 20 and 50 μsec and so arise from observations involving a rarefied vapor cloud. To further minimize the effect of radiation trapping for purposes of the present work, the photon path length through the metal vapor was reduced from 14 cm to 2.5 mm by installing the exit window for the receiving optics on the end of a metal tube which projected into the vacuum chamber (see Fig. 4). Under these circumstances, the observed lifetime is expected to converge to the true radiative lifetime for the excited state. An example of the observed emission is shown in Fig. 5. Because of our slow system ($f/7$), the shot-noise contribution to our photomultiplier output is considerable and so the data from many such photos were accumulated for each of the three lines. Figures 6, 7, and 8 reveal the resulting averaged ln(intensity) versus time plots for the tails of the waveforms. A least-squares fit was used to evaluate the best straight line through the points. The corresponding radiative lifetimes derived from the slope of these lines are presented in Table I. The uncertainty of 1 nsec assigned to the lifetimes was based on the calibration accuracy of the oscilloscope and on tests of the manual digitizing process used on the photographs. It is worth pointing out that a considerable improvement in the quality of the data could be achieved with an improved optical design and that the experimental uncertainty could be further reduced by using a transient digitizer.

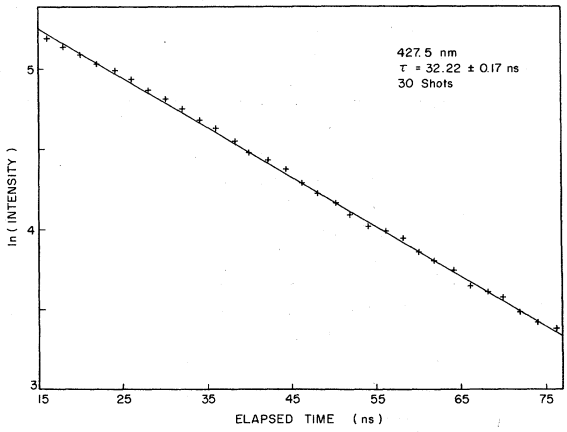

FIG. 7. Least-square fit of ln(intensity) vs elapsed time from moment of dye laser excitation, for the 427.48 nm chromium I resonance line.

Our results for the three levels are seen to compare favorably with those of Marek and Richter,[16] Marek,[17] and Bieniewski.[18] In the case of $^7P_4^o$ level, slight discrepancies on the mean values between our present result and those of Cocke *et al.*[19] and Bucka *et al.*[20] are observed. However, they are within experimental uncertainty quoted by the two authors.

Our future plans include the use of two-wave-

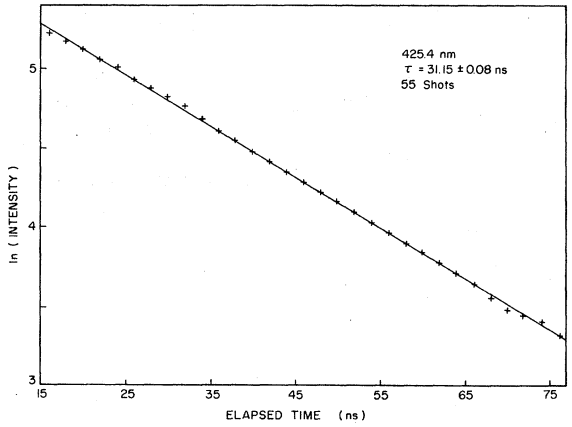

FIG. 6. Least-square fit of ln(intensity) vs elapsed time from moment of dye laser excitation, for the 425.44 nm chromium I resonance line.

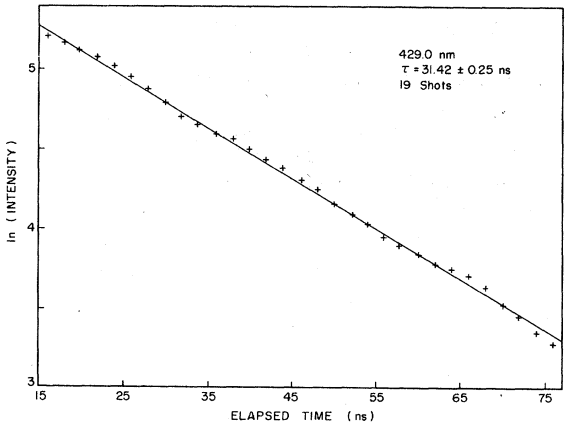

FIG. 8. Least-square fit of ln(intensity) vs elapsed time from moment of dye laser excitation, for the 428.97 nm chromium I resonance line.

TABLE I. Radiative lifetimes (in nsec) for chromium resonance levels.

Authors	$^7P_4^o - {}^7S_3$ 425.44 nm	$^7P_3^o - {}^7S_3$ 427.48 nm	$^7P_2^o - {}^7S_3$ 428.97 nm
Present work [a]	31.15 ± 0.08 [a]	32.22 ± 0.17	31.42 ± 0.25
Marek, Richter [b]	31.4 ± 2.9	32.6 ± 2.6	30.5 ± 1.5
Marek, Richter [c]	31.8 ± 2.5	...	...
Bieniewski [d]	32.9 ± 2.4	33.4 ± 2.5	33.4 ± 2.5
Cocke *et al.* [e]	35^{+3}_{-5}	...	...
Bucka *et al.* [f]	33.4 ± 5	...	...

[a] Uncertainty shown refers to standard deviation associated with statistical data. However, the overall instrumental inaccuracy is unlikely to exceed 2%, which would give a figure of ±1 nsec for the uncertainty.

[b] Reference 16.

[c] Reference 17.

[d] Reference 18.

[e] Reference 19.

[f] Reference 20.

length stepwise excitation in order to measure the lifetime of levels not optically connected to the ground level and the extension of these lifetime measurements to other materials. We have also initiated a preliminary study to test the possibility of undertaking the measurement of collision rates and thereby collision cross sections under certain circumstances.

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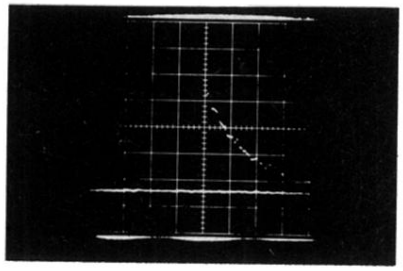

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