Cluster formation and uranium photoionization in the afterglow of a pulsed hollow cathode lamp

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Uranium photoionization was observed in the afterglow of pulsed hollow cathode lamps illuminated by a dye laser tuned near the electronic transition around 591.5 nm ($^5L_6^0 - 16\,900\ \mathrm{cm}^{-1}\ ^7M_7$). The photoionization signal was used to monitor the time evolution of the ground state uranium vapor density in the cathode hole. Lifetimes over 1 ms were measured for the uranium vapor; that makes this device attractive for multistep photoionization spectroscopy. The obtained results lead to the conclusion that these long times are due to cluster formation in the afterglow. © *1998 American Institute of Physics.* [S0034-6748(98)04302-0]

I. INTRODUCTION

Hollow cathode lamps are versatile, compact, simple, and reliable tools to provide metal vapor for spectroscopic purposes. They consist basically of hollow cathode electric discharge cells with optical windows. Collisions of discharge ions with the cathode walls can provide a dense vapor of the cathode material. One important application for the hollow cathode lamps is the optogalvanic spectroscopy.[1] We have used this technique in sequential two-photon absorption laser spectroscopy of uranium in previous experiments.[2–4] In multistep photoionization experiments, however, the ionization due to collisions between electrons and highly excited atoms can be more effective than photoionization and conceal it.

Gagné *et al.*[5] showed that, with a pulsed discharge hollow cathode lamp filled with Ar as a gas buffer, it is possible to have uranium vapor with a density of about $10^{13}\ \mathrm{cm}^{-3}$, for about 500 μs after the discharge is turned off. Such arrangement is, therefore, suitable for experiments on multistep photoionization spectroscopy. The undesired ionization due to collisions with electrons can be avoided during the measurements by using a pulsed hollow cathode lamp and performing the measurements in the afterglow.

We have indeed assessed this technique and are presently using it for multistep photoionization spectroscopy. This article describes for the first time experiments of uranium photoionization with pulsed discharge hollow cathode lamps. The photoionization signal was used to measure lifetimes of the uranium vapor generated by sputtering during the discharge. The lamps were driven by an electric circuit that pulsed the discharge and allowed measurement of the current due exclusively to photoionization in the afterglow. The uranium atoms were photoionized by a tunable dye laser, through a well known three-photon absorption sequence. The photoionization signal was measured along the afterglow period, and its time behavior indicated uranium vapor lifetimes of the order of 1 ms. These long lifetimes, however, seem to be too long if one considers the diffusion of single atoms to the cathode walls. They were attributed to higher particle mass and elastic collision cross section, due to the formation of clusters. In additional experiments, an increase of the lifetime with the sputter discharge current indicated an increase of the size of the clusters with the current.

II. EXPERIMENTAL SETUP

The experimental setup is shown in Fig. 1. It consists of hollow cathode lamps, operating in pulsed regime, with a secondary electric circuit that allows electric current measurements during the period in which the electric discharge is off. Each lamp cathode is made of natural metallic uranium, with a 3 mm diam and 9 mm deep cylindrical hole. A drilled mica disk prevents the discharge in the front surface of the cathode. The lamps were filled with 2.7 (Figs. 3 and 4) and 5.9 mbar of Ar as gas buffer and sealed with quartz optical windows.

The electric circuit has two different parts: The first one provides the pulsed electric discharge, and the second one allows ion current measurements in the afterglow. This electric circuit works as follows.

(1) While the switch **H** is off, the discharge voltage is supplied by $\mathbf{S_1}$ to the lamp through the charge resistor $\mathbf{R_1}$. The electric current passes through the resistor $\mathbf{R_1}$, the diode $\mathbf{D_1}$ and the lamp. The Diode $\mathbf{D_2}$ insulates the measuring circuits from the discharge. Uranium vapor is generated inside the cathode hole by sputtering during this period.

(2) When the switch **H** is on, the current supplied by $\mathbf{S_1}$ flows through $\mathbf{R_1}$ and **H** to the ground. Now, the diode $\mathbf{D_1}$ insulates the circuits. The lamp is biased with a positive voltage (smaller than the voltage necessary to sustain the discharge) by the voltage generator $\mathbf{S_2}$. Whenever free charges are generated in the lamp, they are collected by the electrodes, giving rise to current pulses, which are coupled through the capacitor to a Tektronix 7D20 digitizer. The photoionization is made and measured during this period.

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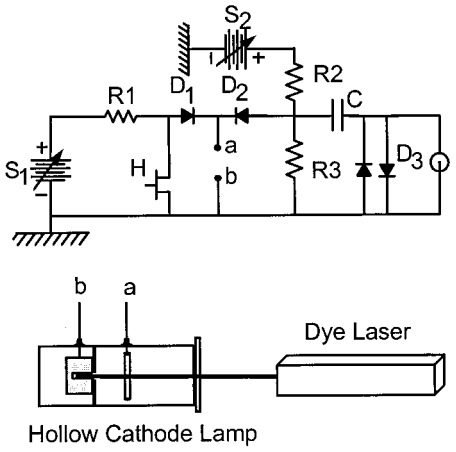

FIG. 1. Experimental setup and electric circuit. $R_1=2\,\mathrm{k}\Omega$, $R_2=1\,\mathrm{M}\Omega$, $R_3=10\,\mathrm{M}\Omega$, S_1 (0–400 V), S_2 (0–400 V), H (IRF 730), D_1 and D_2 (SK4F1/01), coupling capacitor C (1.8 nF), clipping diodes D_3 (1N4007).

The excitation and photoionization of the uranium atoms were provided by a pulsed dye laser, pumped by a copper vapor laser operating at a pulse rate of 5000 pps. The dye laser had about 0.03 cm^{-1} (0.001 nm) linewidth and a pulse duration of 40 ns. It was first tuned to $\lambda=591.539$ nm (resonant with the $^5L_6^0-16\,900.386\ \mathrm{cm}^{-1}\ ^7M_7$ transition of uranium). With a detuning of about 0.1 cm^{-1} (0.003 nm) relative to the center of this single-photon resonance, a two-photon absorption occurs between the ground state and the 33 801.03 cm^{-1} level,[2,6] followed by photoionization through a further single-photon absorption. This photoionization path, shown in Fig. 2, has been observed, with a resolution of about 0.03 cm^{-1}, in previous experiments, with the uranium vapor generated by e-beam in a vacuum chamber.[2,3]

A sample signal of the copper vapor laser driving circuit was used to trigger a Tektronix pulse generator model PG502. The pulse generator trigged the switch **H** (HexFet), setting the alternate discharge and measuring periods in several units of the laser repetition period ($\tau=200\ \mu$s). Most of the measurements were performed with the discharge 400 μs on and 2.2 ms off, allowing, in this way, the observation of 10 laser pulses in the afterglow.

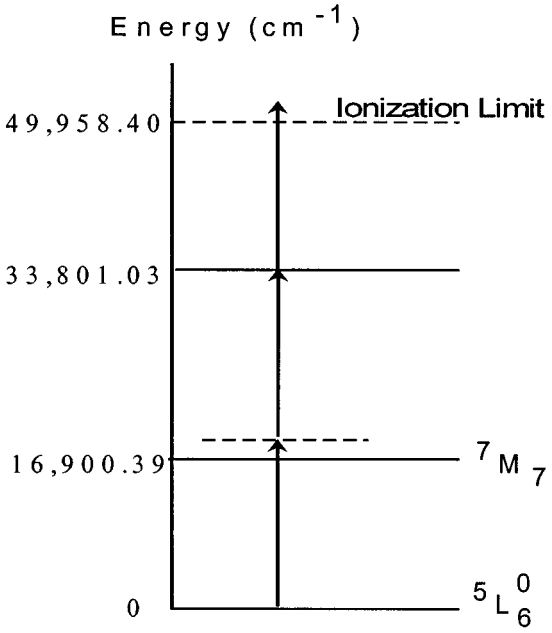

FIG. 2. Diagram of the photoionization path with $\lambda\approx591.5$ Å. There is a detuning of about 0.1 cm^{-1} relative to the one-photon resonance.

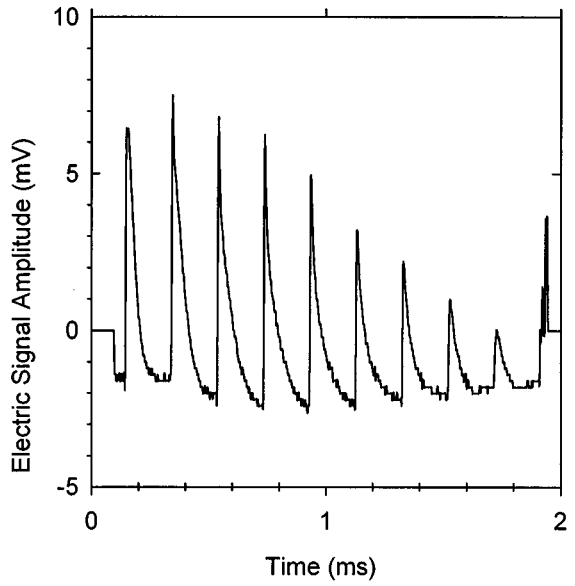

FIG. 3. Typical electric signal in the afterglow period of the lamp with 2.7 mbar Ar pressure, showing nine peaks due to photoionization.

III. EXPERIMENTAL RESULTS

A typical photoionization signal in the afterglow of a pulsed lamp with 2.7 mbar Ar pressure, coupled by the capacitor to a Tektronix 7D20 digitizer, is shown in Fig. 3, where one can see the current peaks due to the laser pulses. It is clearly a resonant effect, vanishing with laser detuning. The amplitude of the peaks does not depend on the bias voltage, from 6 V (minimum of the $\mathbf{S_2}$ power supply) up to 40 V.

Figure 4 shows the time evolution of this sequence of photoionization peaks in the afterglow period. This time behavior is similar to that one observed by Gagné *et al.*[5] when measuring the absorption of a continuous wave dye laser beam in a pulsed hollow cathode lamp. In that work the initial signal increase, soon after the discharge is turned off, was attributed to the return to the ground state of the atoms which, during the discharge, were excited by electron or ion impact, or by optical pumping. During all the afterglow period, on the other hand, diffusion to the wall decreases the uranium population in all states (neutral or ionized, excited or in the ground state). So, the uranium ground state population in the afterglow starts in an initial value established during the discharge, increases until a peak value and then decreases with a time comparable to the diffusion time.

Figure 5 shows the time evolution of such a sequence of photoionization peaks in a lamp with 5.9 mbar Ar pressure. Figure 5 shows only the peaks occurring after the maximum, in order to investigate the time behavior of the vapor in the

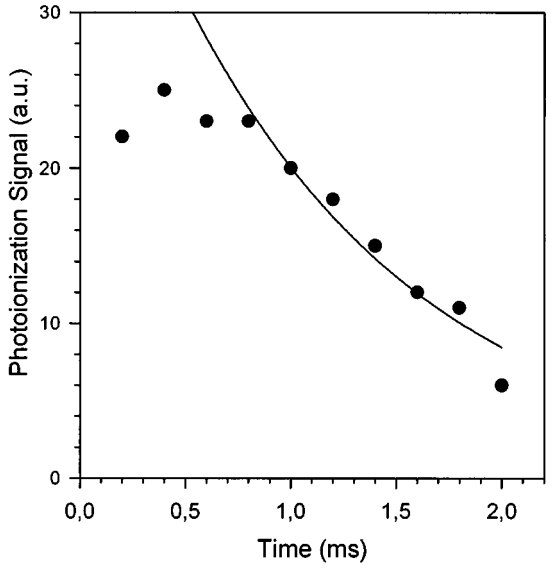

FIG. 4. Time evolution of the peaks shown in Fig. 3.

tail of the curve. This signal was next fed into a boxcar averager, with an aperture of 200 ns centered on the fourth peak (850 μs after the discharge is turned off), in order to measure its amplitude. The amplitude of the photoionization signal was then measured as function of the laser input power. These measurements intended to state the saturation characteristics of the photoionization process. Figure 6 shows the photoionization signal amplitude against laser power. The dots indicate the measured values and the curve is a fitting to a curve similar to a homogeneously broadened saturation curve ($y \propto 1-1/(1+P/P_s)$. This expression is valid only for the absorption of continuous wave beams by a two level system, while the processes we are studying are transient, multilevel phenomena. Anyway, we fitted this expression to the experimental values just to have rough figures for the saturation. The fitting shows a saturation power of about 3 mW. The photoionization measurements shown in Fig. 5 were made with 35 mW of laser power. This power

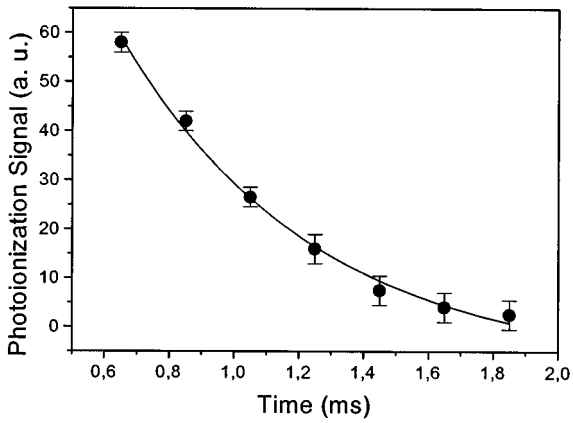

FIG. 5. Time decay of the photoionization signal in the afterglow of the lamp with 5.9 mbar Ar pressure. The dots indicate average of 64 measurements for each photoionization peak and the line indicates an exponential fitting to the last six experimental points.

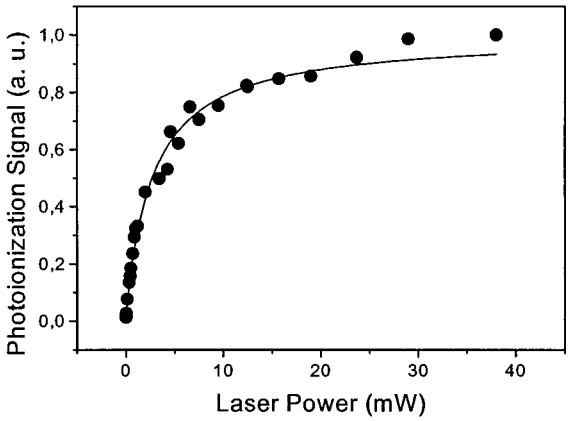

FIG. 6. Photoionization signal vs laser power in the lamp with 5.9 mbar Ar pressure. The dots indicate the values of the fourth photoionization peak after the discharge is turned off, and the line is a fitting with the curve $y \propto 1-1/(1+P/P_s)$, used to indicate the saturation trend.

saturates the photoionization process and assures that the amplitude of the photoionization signal is proportional to the population of the neutral uranium in the ground state at the moment in which the laser pulses occur. The saturated photoionization signal can, therefore, be used to study the time behavior of the neutral uranium density in the afterglow.

IV. URANIUM VAPOR DENSITY AND LIFETIME

Modeling the time behavior of the ground state uranium population is a very difficult task because it demands a detailed knowledge about level populations and transition rates. However, a rough estimate of the vapor lifetime can be obtained by fitting the tail of the experimental data to a decreasing exponential. The best fit for the experimental data in Fig. 5 gives $\tau = 841\ \mu$s. Although this value is in a reasonable agreement with Gagné's results,[5] both seem to be too long for single uranium atom diffusion in Ar.

The diffusion time in a cylindrical cathode hole with length L and radius a can be estimated by[7]

$$\frac{1}{\tau_D} = D\left[\left(\frac{\pi}{L}\right)^2 + \left(\frac{2.405}{a}\right)^2\right], \tag{1}$$

where D is the diffusion coefficient. Considering collisions between hard spheres, the diffusion coefficient is given by

$$D = \frac{2}{3\sqrt{\pi}}\frac{1}{p\sigma}\sqrt{\frac{(k_B T)^3}{m}}, \tag{2}$$

where k_B is the Boltzmann constant, p is the buffer gas (Ar) pressure, m is the uranium mass, and $\sigma = \pi(r_{\mathrm{Ar}} + r_{\mathrm{U}})^2$ is the collision cross section. Here r_i is the atomic radius of the atom i.[7] The temperature T was previously evaluated, by Doppler linewidth measurements for the 591.5 nm line, to be about 1000 K, in typical operation conditions for this experimental apparatus.[8] With Ar pressure of 5.9 mbar, $m = 3.98 \times 10^{-25}$ kg, $r_{\mathrm{Ar}} = 0.88$ Å and $r_{\mathrm{U}} = 1.38$ Å, one obtains $\tau_D \approx 37\ \mu$s, what is much smaller than the vapor lifetime ob-

tained from the experimental data in Fig. 5. A hypothesis to explain this discrepancy is the uranium cluster formation in the hollow cathode discharge.

V. LONG DIFFUSION TIME AND CLUSTER FORMATION

In a recent article, Xenoulis *et al.*[9] presented an intense source of nanoscale metal clusters based on a hollow cathode plasma sputter device, with cathodes made of Cu, Ag, Au, and Ta. The net sputtering rates and the size of the metal clusters as a function of gas pressure, flow velocity, electric current, and cathode geometry were measured. Although uranium was not specifically treated, much of the discussion about the involved physical processes applied to the current experiment. According to Ref. 9, cluster formation of a given metal X starts with X vapor generation due to sputtering, followed by dimer formation, described by

$$X+X+\mathrm{Ar}\rightarrow X_2+\mathrm{Ar},$$

where the Ar atom presence is necessary for momentum and energy conservation. In a supersaturated X_2 vapor, there is nucleation, producing X_n clusters. The maximum net sputtering rates found in that work, for all the different metals, were obtained at Ar pressures near 1 mbar.

In our experiments, hollow cathode lamps filled with 2.7 and 5.9 mbar of Ar as a gas buffer were used to produce uranium vapor. It is reasonable to suppose that uranium clusters were formed in our experiments also. This can explain the very long vapor lifetime observed in Fig. 6. Mass and elastic collision cross sections increase with the formation of clusters, with a consequent increase in the diffusion time. Clusters diffusion time can be estimated using Eqs. (1) and (2), with the clusters mass and collision cross section given by

$$m_n=nXm, \tag{3}$$

$$\sigma_n=\pi(r_{\mathrm{Ar}}+n^{1/3}r_{\mathrm{U}})^2, \tag{4}$$

where n is the number of atoms per cluster. Equation (4) is obtained by supposing a spherical cluster whose volume equals the sum of the n individual atom volumes, i.e., $V_C=(4/3)\pi r_{\mathrm{cluster}}^3=n(4/3)\pi r_{\mathrm{U}}^3$. The actual cluster volume is, of course, still higher than this. With the same parameters used in the previous section, the diffusion time for metallic uranium clusters with n atoms becomes

$$\tau_D=5.6\times 10^{-6}(1+1.57n^{1/3})^2\sqrt{n}. \tag{5}$$

Therefore, diffusion times around 1 ms would imply $n\approx 30$.

We measured the vapor lifetime as a function of the discharge current. According to Xenoulis *et al.*,[9] the higher is the discharge current, the larger is the size of the clusters, as a consequence of the increase in the uranium vapor density. The diffusion time should also, therefore, increase with the discharge current. This is shown in Fig. 7, for a lamp with 5.9 mbar Ar pressure. Using Eq. (5) for the data in Fig. 7, the number of atoms per clusters should range from 8 to 35. The laser light interaction with the clusters, on the other hand, will probably help to dissociate them and, therefore,

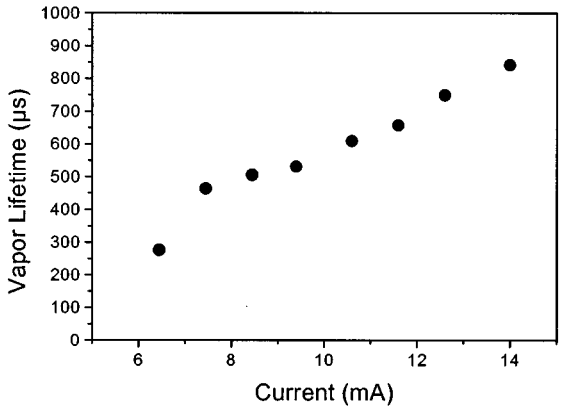

FIG. 7. Photoionization signal decay time vs discharge current in the lamp with 5.9 mbar Ar pressure. The solid line is a linear fitting.

the lifetimes we have measured are a lower limit to the real diffusion time, and the mean size of the clusters is still larger than this. Further experiments, with lower laser intensities, have shown indeed decay times over 2 ms for the vapor. These results are being prepared for another publication.

VI. DISCUSSION

Pulsed hollow cathode lamps were assessed for use in multistep photoionization spectroscopy. For this application, the vapor generated by sputtering during the discharge pulse should remain in the cathode region for a time long enough, after the discharge is turned off, to allow the necessary measurements. A previously known single-color, three-photon path was used to promote photoionization. The power of the used dye laser was high enough to saturate the studied process. Using the saturated photoionization signal to monitor the time behavior of the ground state uranium vapor, lifetimes of the order of 1 ms were observed for the uranium vapor. Such long times are, in principle, very convenient for our purposes, since the laser interpulse period is 200 μs and it is possible to observe several photoionization pulses after the electric discharge is turned off. However, these long times are an indication of cluster formation in the uranium vapor, and this can be deleterious for spectroscopic purposes because of a possible spectral broadening. In an additional experiment performed to evaluate the hypothesis of clusters formation, the measurement of diffusion time as function of the discharge current confirmed what would be expected: The diffusion time increases with electric current, probably due to increase in clusters volume. In a further experiment, to be reported in the future, we have obtained indications that interaction between the laser and the U atoms may induce cluster rupture, shortening the vapor lifetime. Even so, it is possible to make photoionization spectroscopy in the afterglow period. This will be also subject for a future report.

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