Uranium photoionization spectroscopy in a pulsed hollow cathode lamp

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Abstract

The hollow cathode lamp is a powerful tool that allows the study of one or two photons absorption in U atoms through the optogalvanic spectroscopy. However, the observation of the third photon absorption, that usually leads to photoionization, is screened either by collisions with the buffer gas or, mainly, by collisions with electrons in the electric discharge. We performed a series of experiments to verify if it is possible to observe photoionization of U atoms in the afterglow of a pulsed hollow cathode lamp, i.e., pulsing a hollow cathode lamp and trying to observe photoionization signals after the electric discharge is off. The basic experimental setup consists on a conventional hollow U cathode lamp attached to a circuit that allows both the pulsed operation and the monitoring of electric currents in the period when the electric discharge is off. Using a very well known two-photons photoionization sequence (5915 and 6051 Å) it was possible to observe photoionization signal in the afterglow period. Using the photoionization signal to monitor the ground state U vapor density, it was verified that the U vapor can last more than 1 ms after the electric discharge is off in the cathode region. There are indications that this long U vapor lifetime is due to clusters formation. Measurements of the time that the U vapor remains in the cathode region indicated that about 17% of the ground state U is photoionized in every laser shot (the two lasers fired simultaneously).

Introduction.

The hollow cathode lamp is a very versatile, compact, simple and reliable tool to provide metal vapor for spectroscopic purposes. It basically consists on a hollow cathode electric discharge cell with optical windows to allow the passage of light either from the discharge to the outside or from an external light source into the discharge region. The collisions of discharge ions

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with cathode walls can provide a dense vapor of the cathode material that absorbs and, once excited in the discharge, emits light with the cathode material characteristic spectrum. In this way, the hollow cathode lamp can be used as a spectroscopic source [1,2]. However, the most common use for the hollow cathode lamp is in the optogalvanic spectroscopy [3]. The absorption of light from some external source by some species in the discharge changes the plasma impedance, determining a voltage or current fluctuation, the optogalvanic effect. By monitoring this voltage or current fluctuation one can detect light absorption and indeed the hollow cathode lamp has been used for single and double photon absorption spectroscopy. For three photons absorption, however, collisions with electrons and with gas buffer can conceal transitions departing from highly excited states or induce decaying departing from excited states. So, the optogalvanic spectroscopy in hollow cathodes is inconvenient for multi-step photoionization spectroscopy. The effect of collisions with electrons could be avoided with the elimination of the electric discharge effects in the measurements. This can be done by pulsing the hollow cathode lamp discharge and monitoring charge creation after the discharge is turned off (in the afterglow). Gagné and collaborators showed that, with a pulsed lamp with hollow cathode made of uranium and using Ar as the gas buffer, it is possible to have U vapor with a density of about 10^{13} cm^{-3} for more than one millisecond after the discharge is turned off [4].

The objective of this work is to verify the possibility of uranium photoionization spectroscopy studies using a hollow cathode lamp. To avoid the screening of the photoionization signal by the electric discharge, we used a pulsed hollow cathode lamp to generate the U vapor and performed the photoionization experiments in the period that the discharge is turned off. To confirm this idea and to assess the experimental apparatus, we produced ions in the afterglow using a well known two-photons photoionization scheme for U, using dye lasers pumped by copper vapor lasers. We observed that photoionization signals are easily monitored and that the U vapor remains for more than 1 ms in the cathode region after the discharge is turned off.

The experimental setup.

The experimental setup is diagrammed in Fig. 1. The hollow cathode lamp operates in the pulsed regime, with an secondary electric circuit that allows electric current measurements during the period that the electric discharge is off. The lamp cathode is made of metallic uranium, with a 3 mm

diameter and 9 mm deep cylindrical hole; a drilled mica disk prevents the discharge in the front surface of the cathode; the lamp is filled with 2.5 torr of argon as gas buffer and sealed with a quartz optical window.

The electric circuit has two different parts: the first assures the pulsed electric discharge and the second allows ion current measurements. This electric circuit works as follows:

1. While the switch **H** is off, the voltage supply S_1 maintains the electric discharge on the lamp with the electric current limited by the resistor R_1. So, the electric current passes through the resistor R_1, the diode D_1 and the lamp. The Diode D_2 insulates the measuring circuit from the discharge. During this cycle uranium vapor is generated by sputtering.
2. When the switch **H** is on, the current due to the voltage supply S_1 flows through the switch **H** and the left side of the diode D_1 is grounded. Now, the diode D_1 insulates the independent circuits. The lamp is biased with a positive voltage, by the voltage supply S_2 and, if there are any free charges in the lamp, they are collected on the electrodes, generating a current pulse that is coupled through the capacitor and measured by a TEKTRONIX 7D20 digitizer. The photoionization experiment is performed during this period.

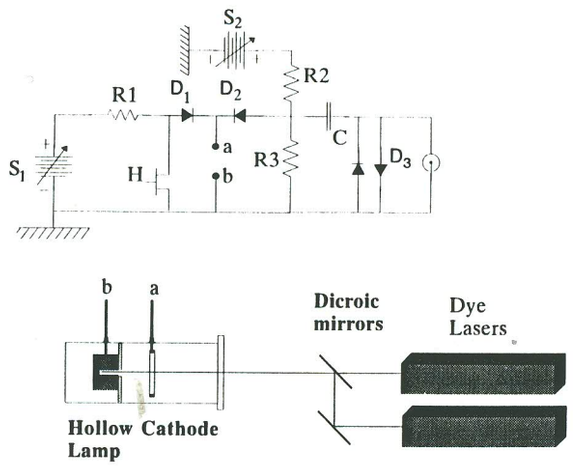

Figure 1. Experimental setup and electric circuit. The circuit values and components characteristics are: R_1 = 2 kΩ, R_2 = 1 MΩ, R_3 = 10 MΩ, S_1 (0-400V), S_2 (0-400V), H (IRF 730), D_1 and D_2 (SK4F1/01), coupling capacitor (1.8 nF), clipping diodes (1N4007). The dye lasers are tuned to 5915 Å and 6051 Å, with a bandwidth of about 1 GHz.

The photoionization was provided by combining the beams of a pair of pulsed dye lasers pumped by copper vapor lasers operating at 5 kHz, one tuned at 5915 Å and the other at 6051 Å. The 5915 Å transition in uranium has a huge absorption cross section ($\sigma \approx 5x10^{-13}$ cm^2) [6] and using only this wavelength it is already possible to obtain single frequency multi-photon photoionization at high beam intensities. In the case of our experimental setup, the combination of these two wavelengths allows two independent paths to photoionization departing from the ground state, as indicated in Fig.2. In the first there is the resonant absorption of λ_1 (exciting U atom from the ground state to the 16,900.39 cm^{-1} level) followed by the resonant absorption of λ_2 (exciting the U atom to the 33,421.02 cm^{-1} level) and, at last, the absorption of either λ_1 or λ_2 promotes the ionization [7] ; in the second path, there is a detuning of about 3.1 GHz in the λ_1 beam such that a two-photons absorption happens between the ground state and the 33,801.03 cm^{-1} level [8], this two-photons absorption is then followed by the absorption of either λ_1 or λ_2 that leads to the ionization. In previous experiments, performed in a vacuum chamber, with the U vapor generated by e-beam heating and using the same lasers used in this work, we observed clearly these two paths of photoionization with a resolution of about 1 GHz [7]. The same experiment was repeated using optogalvanic spectroscopy techniques, in a U hollow cathode lamp, and, due to Doppler broadening, the two different paths were mixed up, where it was only possible to observe a small shoulder in the optogalvanic signal line profile that indicated the presence of these two mechanisms [9]. In the experiments described in this paper, both dye lasers have linewidths of about 1 GHz and the Doppler absorption linewidth for U was measured to be in the same order of magnitude. So, tuning the first laser (λ_1) between the two photoionization paths described above, it is possible to have both processes simultaneously but in independent fashion, because for each process a different part of the laser beam (in the frequency spectrum) is absorbed.

A sample of the copper vapor laser driving circuit was taken to trigger a TEKTRONIX pulse generator model PG 502. The pulse generator then trigged the circuit switch (HexFet) by setting the discharge and measuring periods in units of the laser pulse period (τ = 200 μs). Most of the measurements were performed with the discharge 400 μs on and 2.2 ms off, this way allowing the observation of 10 laser pulses in the afterglow.

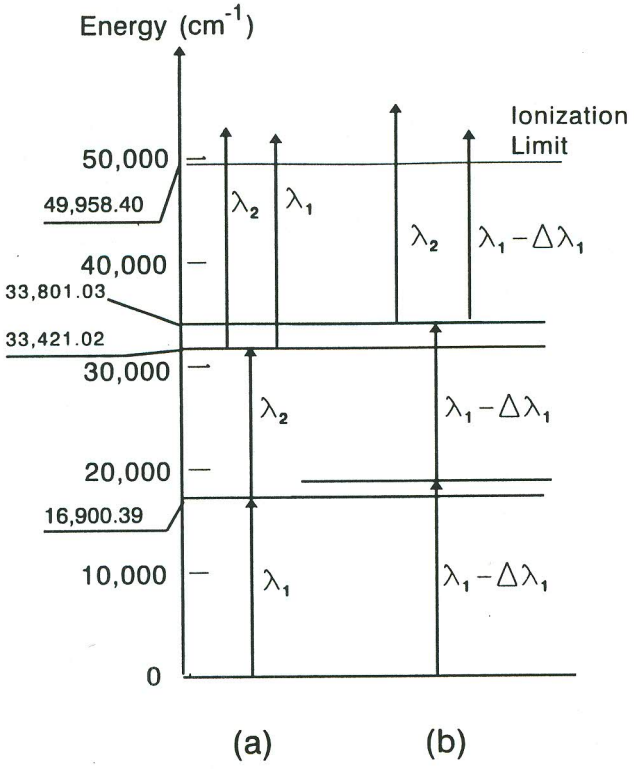

Figure 2. Diagram of the photoionization paths with λ_1 = 5915 Å and λ_2 = 6051 Å. There is a difference of about $\Delta\lambda_1 \approx 3.1$ GHz between the two photoionization paths.

Fig.3 shows the measured electric signal in the afterglow period, using the photoionization scheme described above. The peaks in the electric signal were considered as due to photoionization because:

1. they only appeared when the laser beams illuminate the discharge and it was a resonant effect, vanishing with laser detuning;
2. they did not appear if there were no discharge in the hollow cathode lamp (the S_1 power supply was off), leading to the conclusion that they are due to the presence of U vapor, and not to the Ar gas buffer or to a wall effect contribution (laser ablation, for instance);
3. they did not appear without the bias voltage, so they are due to free charges generated by the lasers.

4. The amplitude of the peaks doesn't vary considerably with the bias voltage, from 6 V (minimum of the S_2 power supply) until 40 V, concluding that the signal was due to electric charges generated by agents other than the bias electric field.

These results confirm that it is possible to observe photoionization in the U vapor generated by a pulsed hollow cathode discharge provided that the photoionization measurements are performed in the afterglow (after the discharge is off). Yet, some other important parameters can be observed in such a simple experiment, as will be seen ahead.

Photoionization signal saturation.

The peak value of the photoionization current signal (that will be called simply *photoionization signal* from now on) was measured for different laser intensities. Two different conditions were considered: a) the beam intensity of the first laser (λ = 5915 Å) was kept constant and the intensity of the second laser (λ = 6051 Å) was varied by using calibrated attenuation filters and b) the first laser beam had the power varied while the second laser remained constant. In both situations, the fixed laser was kept at the maximum available power.
Fig.4 shows the photoionization signal against laser power for the situations described above. During the *discharge-off* period, there are 10 or more photoionization peaks and the photoionization signal shown on Fig. 4 corresponds to the third peak (τ = 600 μs) after the discharge is turned off. The symbols indicate the measured values while the curves are fittings for a Doppler-broadened-absorption curve ($y \alpha 1\text{-}1/(1 + P/P_s)^{1/2}$). This expression is valid only for the absorption of a continuous wave beams by a two level Doppler broadened system and 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 for the case a) gives a saturation power of about 1 mW while the case b) gives 8 mW. Thus, both lasers have power at least ten times higher than necessary to saturate the photoionization process. This leads us to an important conclusion: since the transition from the ground state to the first excited state is resonant and the photoionization signal is saturated, *the amplitude of the photoionization signal is proportional to the population of the neutral uranium in the ground state.*

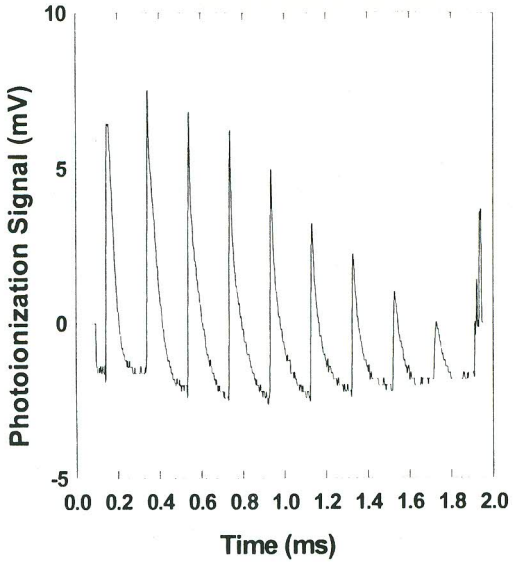

Figure 3. Typical electric signal in the afterglow period, showing 9 peaks due to photoionization

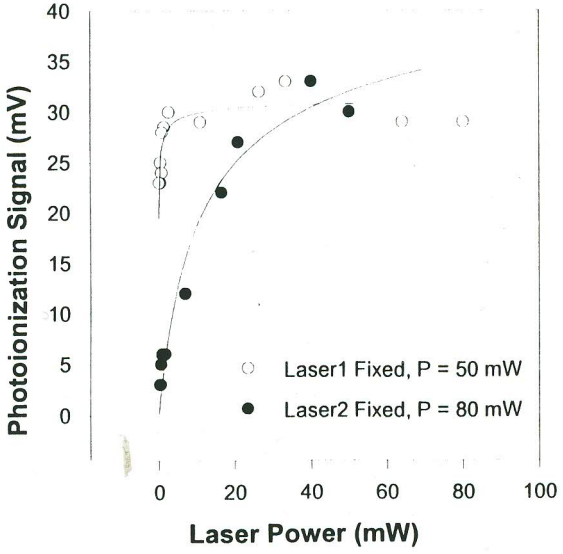

Figure 4. Photoionization signal versus laser power: a) laser 1 fixed at 50 mW and laser 2 variable power; b) laser 2 fixed at 80 mW, laser 1 variable power. The symbols indicate the peak value of the third photoionization signal after the discharge is turned off; the solid lines are hand fittings just used to indicate the saturation trend.

U vapor density and lifetime.

Fig.5 shows the photoionization signal time evolution in the afterglow for: a-) hollow cathode lamp illuminated only by laser 1 and b-) by laser 1 and laser 2 simultaneously. This temporal behavior (that corresponds to the time evolution of the ground state U vapor density) is similar to that one observed by Gagné et all. [4] for the absorption in a pulsed U hollow cathode lamp with Ar gas buffer. This behavior was explained by the authors as follows: after the discharge is turned off and the plasma vanishes, there is a fraction of the U vapor in excited and ionized states that, while relaxing, increases the ground state population of neutral U; at the same time, diffusion to the wall decreases the U population in all states (neutral or ionized, excited or in the ground state). So, the U ground state population in the afterglow, departs from an initial value established during the discharge, increase up to a peak value and then decreases with time comparable to the diffusion time. The ground state U population temporal behavior, and consequently the photoionization signal temporal behavior, are very difficult to be modeled and this demands a detailed study about species population and rates. However, if the main loss term is the diffusion to the walls then the vanishing time (time that the U population vanishes) can be obtained fitting the tail of the curve to an exponential. The best fit for the experimental data in Fig.5 gives τ = 1.25 ms, for the hollow cathode lamp illuminated only by laser 1, and τ = 0.91 ms, for the hollow cathode lamp illuminated by lasers 1 and 2 simultaneously.

The diffusion time can be roughly estimated considering elastic collisions between hard spheres [10], as

$$\tau_D = \frac{z^2}{2D} \qquad (1)$$

where z is the diffusion length, taken for simplicity as the cathode hole radius, and D is the diffusion coefficient, given by

$$D = \frac{2}{3\sqrt{\pi}} \frac{1}{p\sigma_0} \sqrt{\frac{(k_B T)^3}{m}} \qquad (2)$$

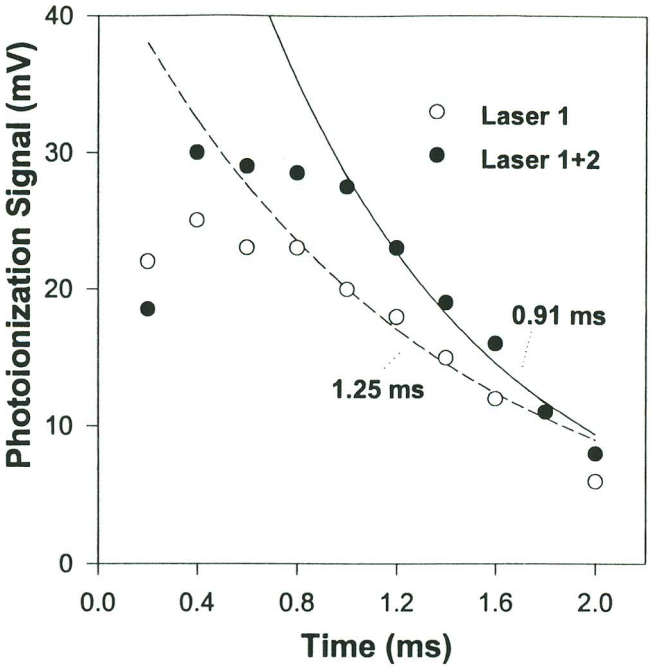

Figure 5. Photoionization signal time evolution in the afterglow. The symbols indicate the peak value of every photoionization signal, the lines indicate the exponentials fitted to the last 6 experimental points.

where p is the buffer gas (Ar) pressure, $\sigma_o = \pi(r_{Ar} + r_U)^2$ is the elastic collision cross section, with r_i being the atomic radius of the ith atom, and m is the U atomic mass. The temperature T was previously evaluated, by Doppler bandwidth measurement for the 5915 Å line, to be about 1000 K, in typical operation condition[11] . With Ar pressure of 2.5 torr, τ_D = 62 μs, which is much smaller than the vanishing time obtained from the experimental data in Fig.5.

Babin and Gagné [5] presented a device that produces U atomic beam using a pulsed hollow cathode lamp. The metal vapor that is produced inside the cathode hole is dragged outside the discharge regions by flowing the buffer gas through an orifice in the cathode. They observed that the fluorescence spectral profile of the atomic beam decreases in amplitude and increases in linewidth, becoming blurred, with the buffer gas (Ar) pressure, indicating a *"probable cloud formation in the output orifice "* [5]. We go a little bit further, we supposed that there is clusters formation in the U hollow cathode discharge. If there is such clusters formation, the particle mass and elastic collisional cross section will increase and, consequently, there will be an increase in the diffusion time,

as it can be seen in (1) and (2). The first observable photoionization pulse comes 200 μs after the discharge is off, much later the single-atom U vapor had already diffused to the walls. So, the metal vapor that still remains in the cathode hole is made of particles heavier than single U atoms: clusters probably.

Fig.6 demonstrates the dependence of the vanishing time with electric current and this can be another evidence of clusters formation: the vanishing time increases with the electric current. The first explanation that comes in mind is that increasing the electric current there will be an increase in temperature, what changes the diffusion time, according to Eqs. 1 and 2. However, the temperature increase should *decrease* the relaxation time, and what is observed is exactly the contrary. So, there must be another dominant mechanism. A hypothesis to explain this behavior is that with the electric current increase, denser U vapor is generated [14], increasing the probability of heavier clusters formation, with consequent increase in the diffusion time.

U vapor loss, ion extraction and amount of photoionized U.

Fig.7 shows that the U vapor vanishing time decreases with the bias voltage, which can be understood as an indication that there is, besides the diffusion to wall, another loss channel: photoionization followed by ion extraction due to the applied electric field (bias). Part of the ions generated by photoionization recombines with electrons in the plasma, returning to the ground state, and part of the ions are extracted by the applied electric field. Increasing the bias voltage, the efficiency of ion extraction increases [12,13], or rather, the U vapor loss rate increases. If this assumption is true, then the U vapor vanishing time must also depend on the amount of ground state U that is photoionized, since the photoionization acts now as a loss channel. Going back to Fig.4, one can see exactly this: the photoionization signal amplitude is larger and vanishing time is shorter when the hollow cathode is illuminated by lasers 1 and 2 simultaneously ($\tau = 1.25$ ms), when compared to the signals obtained only with laser 1 ($\tau = 0.91$ ms). So, the photoionization is, for our experimental conditions, an important loss mechanism for the ground state U vapor.

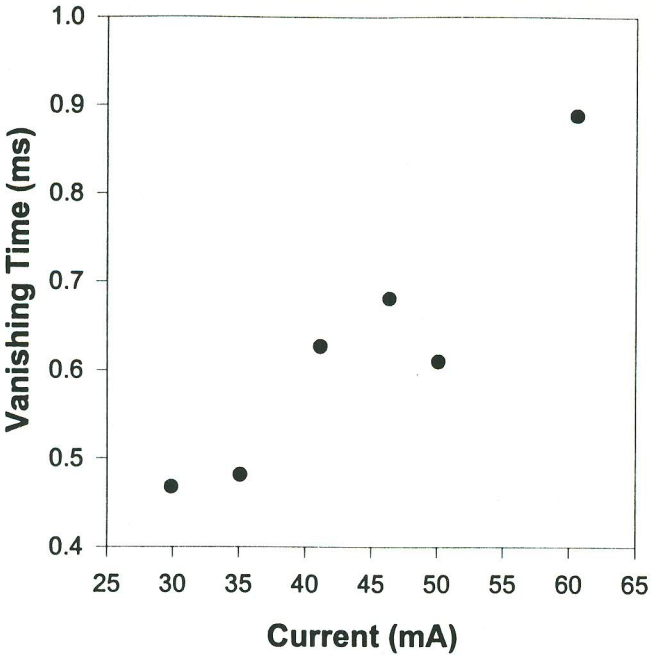

Figure 6. Photoionization vanishing time versus electric current. This behavior indicates the time the U vapor remains in the hollow cathode region.

With the data shown in Fig.4 it is also possible to estimate an important magnitude for photoionization experiments: the amount of U that is photoionized by every laser pulse. Let's assume that the ground state U vapor vanishing mechanism has three contributions, diffusion to the walls, photoionization only by laser 1 and photoionization by laser 1+2, and that these processes can be described by a decreasing exponential with an effective vanishing time given by

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_D} + \frac{1}{\tau_1} + \frac{1}{\tau_2}$$

where τ_D is the diffusion time, τ_1 is due to the photoionization caused by the laser 1 and τ_2 is due to the contribution of the laser 2 on the photoionization (laser 1 plus laser 2 mechanism). From the values presented in Fig.5 we can obtain $\tau_2 = 3.3$ ms. Considering the time interval between two consecutive laser pulses of 200 μs, one has that every "laser 2" pulse contributes with the photoionization about 5% of the total ground state U population. Since the photoionization signal is proportional to the amount of photoionized U, the ratio

between the photoionization signal for the "laser 1+2" case and for the "laser 1" case must be equal to the ratio of photoionized neutral U in each case.

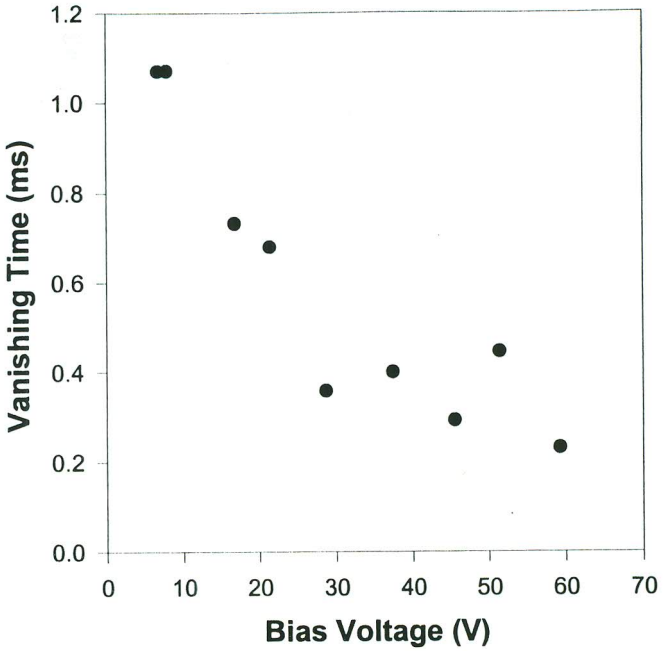

Figure 7. Photoionization vanishing time versus S2 power supply voltage (bias voltage).

So, in the experimental conditions presented in this paper, the combination of the lasers 1 and 2 provides the photoionization of about 17% of the total ground state U vapor.

Conclusions.

A pulsed hollow cathode lamp was evaluated with the aim of being used in photoionization spectroscopy. A known sequence of laser wavelengths was used to promote photoionization and to evaluate the lamp behavior. It was observed that it is possible to have U vapor for about 1 ms after the discharge is turned off which is very convenient for our purposes. The long life of the vapor was attributed to clusters formation which is deleterious, because it decreases the cross sections and broadens the spectral profile. Some indirect evidences of clusters formation are obtained with the experiments. With the experimental results we obtained, it was also possible to estimate that the setup used is able to

provide the photoionization of about 17% of the ground state U vapor. Three-photons photoionization spectroscopy will be the continuation of this work.

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