Ionization processes in fluorescent lamps: Evaluation of the Hg chemi-ionization rate coefficients

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Chemi-ionization by two mercury atoms to produce mercury atomic and molecular ions has been considered an important process in fluorescent lamps (FLs) for a quarter of a century. Despite the absence of reliable data, these processes have been included in a number of numerical models to help explain some of the experimental observations. These models have shown that the most important process is the Penning ionization of two Hg metastable atoms $\mathrm{Hg}(6\,^3P_2)+\mathrm{Hg}(6\,^3P_2)\rightarrow \mathrm{Hg}^+ + \mathrm{Hg}(6\,^1S_0)+e$. Although there is no experimental measurement of this cross section, modelers have typically used values implied from measurements of other chemi-ionization cross sections, or values obtained by fitting parameters to numerical models to obtain agreement with experiment. Recent theoretical investigations have indicated that the cross sections for the important processes may not be as large as previously thought. The aim of the present paper is to critically review the historical development of studies of chemi-ionization in fluorescent lamps and to present new experimental evidence which is consistent with the theoretical calculations and contradicts the conclusions from previously published experiments.

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I. INTRODUCTION

Fluorescent lighting, produced by converting ultraviolet radiation from mercury atoms in a gaseous discharge to visible radiation by means of a phosphor, plays a dominant role in the market place. It has been estimated that 80% of the world's artificial light is fluorescent [1]. As lighting companies strive for more efficient lighting, research is directed to developing lamps with operating parameters which differ markedly from the standard operating conditions of the current generation of fluorescent lamps (FLs). In particular, the advent of radio frequency generated light sources has provided the opportunity to dispense with electrodes, which limit the life and efficiency of these lamps. Electrodeless operation also allows these lamps to operate at much higher power densities than conventional FL. These "highly loaded" lamps join a family of electroded lamps, which include compact fluorescent lamps of various configurations, conventional lamps operating at higher currents, and narrow bore FL for backlighting applications.

Plasma models have achieved reasonable success in reproducing many of the observed properties of standard FL [2–7]. However, models have been less successful in describing FL discharges under highly loaded conditions [8,9]. Recent experimental and theoretical investigations [10] suggest that a major cause of the discrepancy is the lack of fundamental data concerning the role of atomic and molecular processes in the FL plasma, particularly the mechanisms leading to the ionization of mercury atoms.

One of the processes considered important in FL discharges has been chemi-ionization due to the interaction of two excited mercury atoms. This mechanism was first proposed for FL discharges by Vriens *et al.* [2] and since then the effect has been included in a number of numerical models [4–7] using the limited experimental [11–13] and theoretical [14] data reported in the literature.

Recently, extensive calculations of chemi-ionization cross sections in Hg [15] have shown these cross sections to be considerably smaller than experimental values previously reported [11–13]. In this paper, we present experimental results which are consistent with the theoretical estimates [15]. In order to resolve these discrepancies, we have included a summary of the most important theoretical results, together with a critical review of previously reported experimental results. In a second paper, we shall demonstrate the importance of all ionization processes on the power balance in fluorescent lamps in the light of these results.

II. BACKGROUND

A. Chemi-ionization between excited levels of mercury

The resonance transition between the $6\,^3P_1$ and $6\,^1S_0$ levels of the mercury atom (wavelength 253.7 nm) is the principal source of radiation in fluorescent lamp discharges. All three levels of the $6\,^3P$ triplet are highly populated in the FL plasma, especially the upper $6\,^3P_2$ state. In standard fluorescent lamps, losses due to recombination of ions and electrons and deactivation of metastable atoms at the wall comprise $\sim$5% of the total electrical energy in the discharge, so most of the excitation energy accumulated in the metastable $6\,^3P_0$ and $6\,^3P_2$ states is released as 253.7 nm radiation. This radiation process can also, in principal, be strongly influenced by collisions between two mercury atoms in $6\,^3P$ levels. In such a collision, the combined excitation energy may be transferred either to one of the colliding atoms, leaving the other in the ground state (energy pooling processes [16]) or into formation of an ion and an electron (chemi-ionization). These two classes of reaction compete with each other, although chemi-ionization is expected to have a larger impact on the FL plasma dynamics. Chemi-ionization has been shown to be a dominant process of nonradiative depopulation of excited atoms in gaseous alkali discharges [17].

Chemi-ionization due to collisions between two $6\,^3P$ mercury atoms may proceed through one of the following channels:

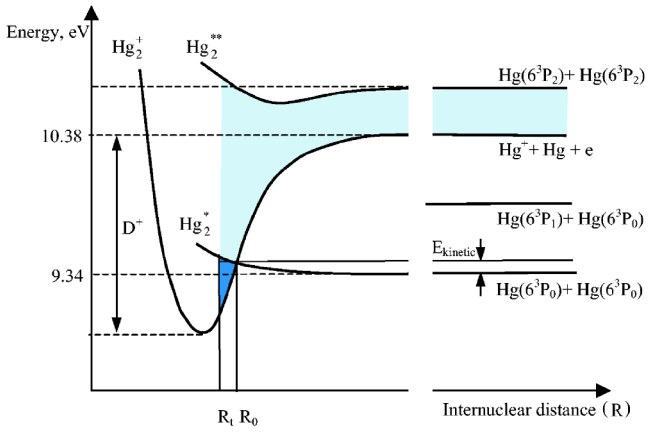

FIG. 1. (Color online.) Dynamics of chemi-ionization in collisions of $6\,^3P$ mercury atoms. Based on data from Cohen *et al.* [15].

$$\text{Hg}(6\,^3P_i) + \text{Hg}(6\,^3P_j) \rightarrow \begin{cases} \text{Hg}_2^+ + e, & (1) \\ \text{Hg}^+ + \text{Hg} + e, & (2) \\ \text{Hg}^+ + \text{Hg}^-, & (3) \end{cases}$$

where $i,j=0$, 1, or 2, subject to conservation of total energy in the reaction. Reaction (1) is usually called associative ionization (AI), (2) is Penning (or Penning-like) ionization (PI), and (3) is ion pair formation. The third channel should not play a role in the FL plasma, since the electron affinity for the mercury atom is low and the negative ion quickly decays, in effect reducing ion pair formation to PI.

In the classical interpretation, a collision between two excited mercury atoms can be represented by the motion of the colliding system along the interaction potential of the colliding atoms (see Fig. 1). Whether AI or PI can occur depends on the energy levels of the excited atoms participating in a collision. For each pair of colliding atoms, the result is determined by the relative positions on the molecular potential for the neutral quasimolecule formed by the colliding atoms and that of the molecular ion, and by the distance between the colliding particles where the ionizing transition takes place. In the AI case, the asymptotic energy of the entrance curve lies below the asymptotic energy for the molecular ion curve, i.e., the ionization potential, as shown in Fig. 1.

During a collision, the system $\text{Hg}(6\,^3P_i)+\text{Hg}(6\,^3P_j)$ travels along the entrance potential curve forming an excited unstable molecule Hg_2^* at small internuclear distances. In the case of a symmetric collision of two $6\,^3P_0$ atoms or in a collision involving $6\,^3P_1$ and $6\,^3P_0$ atoms

$$\text{Hg}(6\,^3P_0) + \text{Hg}(6\,^3P_1) \rightarrow \text{Hg}_2^+ + e^-, \quad (4)$$

$$\text{Hg}(6\,^3P_0) + \text{Hg}(6\,^3P_0) \rightarrow \text{Hg}_2^+ + e^-. \quad (5)$$

Reactions (4) and (5) can only occur when the internuclear distance is between R_0 (the distance at which the potential of the quasimolecule Hg_2^{**} is equal to the potential of the molecular ion) and the turning point R_t. For reaction (5), this corresponds to the darker shadowed area in Fig. 1. Reaction (5) is allowed by the energy conservation law if the depth of the potential well (or dissociation energy) of Hg_2^+, $D^+ > 1.04$ eV (see Fig. 1). Linn *et al.* [18] reported a value of $D^+=1.4$ eV, obtained from a photoionization study of Hg_2^+.

For reactions involving two $6\,^3P_2$ atoms, both AI and PI are possible, since the ionizing transition of the quasimolecule Hg_2^{**} (see Fig. 1) is allowed at any internuclear distance exceeding the turning point R_t. This is illustrated for the case of two colliding $6\,^3P_2$ atoms by the lighter shadowed area in Fig. 1. It is important to note that such reactions may result in the formation of either a molecular or an atomic ion, the excess of energy being transferred to the electron. For the PI reaction

$$\text{Hg}(6\,^3P_2) + \text{Hg}(6\,^3P_2) \rightarrow \text{Hg}^+ + \text{Hg} + e^-. \quad (6)$$

Experimental measurements of rate coefficient for process (4) have been reported by Tan and von Engel [11] and Majetich *et al.* [13] and for process (5) by Sepman *et al.* [12]. Theoretical estimates of cross sections reactions (4)–(6) were recently reported by Cohen *et al.* [15], in which the calculated cross sections were considerably smaller than those inferred from the experiments. There have been no experimental measurements of process (6) to date, although values have been deduced by Vriens [2] from the experimental data for other processes and by Sakai *et al.* [14] from a Boltzmann analysis of electron swarm data.

The experimental and theoretical evidence for chemi-ionization obtained to date are reviewed in the following sections. In view of the lack of experimental data for PI [process (6)], the discussion is limited to AI processes.

B. Chemi-ionization experiments in mercury vapors

The formation of charged particles in a mercury vapor cell irradiated with 253.7 nm radiation from a mercury lamp was first observed by Rouse [19] in 1925. Since then, a number of experiments have been designed to measure cross sections of chemi-ionization reactions in mercury cells, using either a mercury lamp with a filter to isolate the 253.7 nm radiation ([11,12]) or a short pulse laser tuned to 253.7 nm ([13,16]).

Tan and von Engel [11] performed the earliest quantitative measurement of chemi-ionization in mercury, reporting a thermally averaged cross section of $\sigma_{10}=4.6\times10^{-14}$ cm^2 for reaction (4). They used a mercury vapor cell containing two square electrodes of area 16 cm^2 separated by a gap of 4.3 cm and placed symmetrically with respect to a quartz window. On irradiating the vapor through the window with resonant radiation from a mercury lamp, a current between the electrodes was observed and measured. The current was attributed to AI between $\text{Hg}(6\,^3P_1)$ and $\text{Hg}(6\,^3P_0)$ atoms and the cross section was deduced by assuming that the observed current $i_{AI}=ek_{10}n_0n_1V$, where $k_{10}=\sigma_{10}v_{10}$ is the rate coefficient for reaction (4), σ_{10} is the cross section, v_{10} is the mean relative velocity of the atoms, n_0 and n_1 are the concentrations of the participating species, and V is the volume between the electrodes.

The steady state concentrations n_0 and n_1 were estimated by measuring the resonance radiation flux at the window and using a system of particle balance equations for the $6\,^1S_0$,

$6\,^3P_0$, and $6\,^1P_0$ mercury levels. In order to perform this calculation, it is necessary to know the ratio $\eta=\tau_{\text{eff}}/\tau$, where τ_{eff} is the effective lifetime of the $6\,^3P_1$ resonance level due to radiation trapping and τ is the natural lifetime of the resonance level. Tan and von Engel used a constant value of $\eta=2$, which is a gross underestimate for the range of vapor pressures used. Using the formula of Lawler and Curry [20], with mercury density divided by 5 to allow for the presence of five isotopes of natural mercury, the value of η is found to be between 100 and 1000. The value used by Tan and von Engel therefore greatly underestimates the densities of the participating atomic species and consequently leads to a significant overestimate of the cross section.

Tan and von Engel did not provide enough information to make quantitative *a postieri* calculations of concentrations n_0 and n_1 since the spatially averaged densities of the $6\,^3P_1$ and $6\,^3P_0$ atoms in such an optically thick medium strongly depend on the geometry of the cell, which is not sufficiently described in the paper. Further, it is not clear which of the atomic levels was responsible for the current, since the results may also be accounted for by collisions between two $\text{Hg}(6\,^3P_0)$ atoms [reaction (5)] or two $\text{Hg}(6\,^3P_1)$ atoms

$$\text{Hg}(6\,^3P_1)+\text{Hg}(6\,^3P_1)\rightarrow \text{Hg}_2^+ + e^-, \tag{7}$$

or combinations of these processes.

Sepman *et al.* [12] performed a similar experiment to that of Tan and von Engel, but overcame the major limitations of the earlier experiment. As in Tan and von Engel's experiment, the vapor in a mercury cell was irradiated by the resonant radiation (253.7 nm) filtered from a mercury discharge lamp, but the mercury vapor pressure was maintained below 10 mTorr, by controlling the temperature of the cold spot in the cell. The chemi-ionization current in the mercury cell was measured using a pair of planar electrodes and the concentrations of $\text{Hg}(6\,^3P_1)$ and $\text{Hg}(6\,^3P_0)$ were obtained by absorption measurements of the $6\,^3P\rightarrow 6\,^3D$ transition lines.

The current between the electrodes was not detected until nitrogen at a pressure of at least 0.05 Torr was added to the vapor cell. The energy deficit between $6\,^3P_1$ and $6\,^3P_0$ levels of mercury ($\Delta E=0.218$ eV) is almost exactly equal to the vibrational quantum energy of the nitrogen molecule, which facilitates the effective energy transfer from $6\,^3P_1$ to $6\,^3P_0$ mercury atoms in collisions with nitrogen molecules. The fact that no chemi-ionization current was observed in the experiment without adding nitrogen to the cell suggests that the $6\,^3P_0$ state is involved in the production of charged particles, through reactions (4) and (5).

In an effort to determine the dominant reaction contributing to the chemi-ionization current, Sepman *et al.* fitted the experimentally observed dependence of the current on nitrogen gas pressure to two model functions, one assuming chemi-ionization solely due to reaction (4) and the other solely due to reaction (5). At low nitrogen pressure, one would expect a linear dependence of the current on nitrogen pressure for reaction (4) and a quadratic dependence for reaction (5), with both results converging at sufficiently high nitrogen pressures. The experimental dependence appears to be nonlinear at low nitrogen pressures, suggesting that reaction (5) is an important contributor to the observed current. The reported data, however, does not seem sufficient to conclude that reaction (4) did not contribute to the chemi-ionization current in this experiment. Experiments do, however, provide strong evidence for chemi-ionization involving binary collisions of $6\,^3P_0$ atoms and the reported rate coefficient should be regarded as an upper estimate of the chemi-ionization rate due to reaction (5).

Assuming that reaction (5) was solely responsible for the observed chemi-ionization current in their experiments, Sepman *et al.* deduced a value of the rate coefficient for this reaction of $k_{00}=4\times10^{-10}$ cm^3 s^{-1} ($T=295$ *K*) which corresponds to a thermally averaged cross-section of $\sigma_{00}=2.8\times10^{-14}$ cm^2. The derivation accounted for symmetry of the collision, i.e., they assumed that the chemi-ionization current in their experiment, caused by binary collisions of $6\,^3P_0$ is $I_{AI}=\frac{1}{2}e\sigma_{00}\nu_{01}n_0^2V$.

Another chemi-ionization experiment in a mercury vapor cell was conducted Majetich *et al.* [13]. In contrast with earlier experiments by Tan and von Engel and Sepman *et al.*, the vapor in this experiment was excited by a short (few nanosecond) pulse from a Nd:YAG-pumped dye laser tuned to the $6\,^1S-6\,^3P_1$, transition (253.4 nm) and the temporal behavior of the current between two planar electrodes was analyzed. Majetich *et al.* reported a rate coefficient for reaction (4) of $k_{10}=2.5\times10^{-8}$ cm^3 s^{-1} ($T=298$ K) which was subsequently corrected to $k_{10}=2\times10^{-10}$ cm^3 s^{-1} (see Ref. [15]). The latter corresponds to a thermally averaged cross-section of $\sigma_{10}=1.4\times10^{-14}$ cm^2.

C. Theoretical estimates of chemi-ionization cross sections

Any analysis or theoretical treatment of chemi-ionization dynamics requires that the appropriate potential curves are known with high accuracy, as well as the probability of transition between the terms of the quasimolecule and the molecular ion. The ionization probability, the so-called electronic width of the quasimolecular term, may be calculated based on a particular interaction model. Rigorous theoretical treatments of chemi-ionization are described in Ref. [17], but possibly due to their extreme complexity, no attempt has been made to calculate cross sections for AI and PI in collisions of mercury $6\,^3P$ atoms until recently [15].

Cohen *et al.* [15] used a semiclassical representation to obtain potential curves of the form illustrated in Fig. 1. The cross sections were calculated using a black-sphere approximation for the short range interactions (i.e., the ionizing transitions were assumed to occur with unit probability when the potential curve corresponding to the particular collision crosses the molecular ion term, as given in Fig. 1). The results therefore represent upper estimates of the cross sections. The *ab initio* calculations gave a full set of cross sections for chemi-ionization in collisions of $6\,^3P_{0,1,2}$ and $6\,^1P_1$ mercury atoms, for every combination of the colliding partners (see Table I in the paper by Cohen *et al.* [15]), and new data for the dissociation energy of Hg_2^+ which is in a good agreement with latest experimental measurement by Linn *et al.* [18]. The cross sections calculated by Cohen *et al.* for AI involving the $6\,^3P_0$ and $6\,^3P_1$ states are presented in Table I

TABLE I. Published estimates of AI cross sections in Hg: σ_{10}, reaction (4); σ_{00}, reaction (5); σ_{11}, reaction (7).

	σ_{10} (10^{-14} cm^2)	σ_{00} (10^{-14} cm^2)	σ_{11} (10^{-14} cm^2)
Tan and von Engel [11]	4.6		
Sepman *et al.* [12]		2.8	
Majetich *et al.* [13]	1.4		
Cohen *et al.* [15]	<0.3	<0.12	<0.17

along with the earlier reported experimental values.

The theoretical cross sections are considerably lower than the experimentally obtained values. An experiment designed to help resolve these discrepancies is described in the following section.

III. EXPERIMENT

The experiment followed a traditional approach of irradiating a vacuum diode containing mercury vapor with resonant radiation, and observing a current through the diode. As in the study by Majetich *et al.* [13], the vapor was excited using a nanosecond laser pulse tuned to 253.7 nm. The experimental setup (Fig. 2) included a vacuum cell with electrodes, a Nd:YAG-pumped dye laser, and chemi-ionization current measurement electronics. All parts were controlled by a host computer.

A mode-locked Nd:YAG laser, a product of Quantel International, model YG471, was used to excite the dye laser. The fundamental wavelength of the Nd:YAG laser (1064 nm) was multiplied by a third-harmonic generator (two KD*P crystals) to obtain 355 nm radiation required for pumping a Coumarin 500 dye. Another crystal (BBO) was used to double the dye laser (Molecron Corporation, model DL-II) output producing a radiation of 253.7 nm, the color required for the excitation of mercury atom from the $6\,^1S_0$ ground state to the $6\,^3P_1$ state. A photodiode and calibrated grey filters were used to measure laser output. To increase the excitation volume in the mercury cell, the laser beam was expanded to approximately 1 cm by a telescope. Radiation of 253.7 nm was locked to the corresponding mercury line by directing a part of the radiation into a mercury discharge

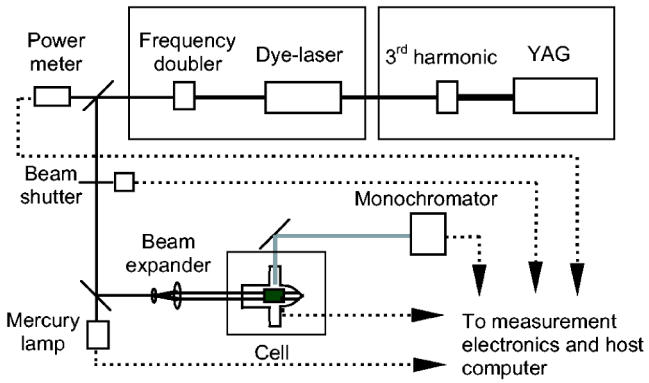

FIG. 2. Schematics of the experimental apparatus.

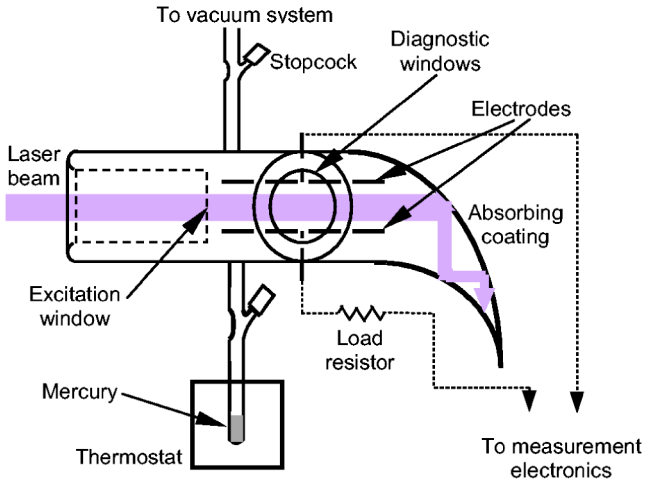

FIG. 3. (Color online.) Mercury cell.

lamp and observing an optogalvanic signal in the lamp current. The same lamp (an Hg-Ar Oriel-model No. 6035 pencil style spectral calibration source) was used to measure the linewidth of the 253.7 radiation. Calibration of the dye laser wavelength dial using a 0.5-m monochromator and tuning the laser wavelength off the maximum of the optogalvanic signal provided the linewidth of the 253.7 nm laser radiation full width of half maximum (FWHM) of 0.20 ± 0.05 nm.

The laser beam entered a cylindrical Pyrex cell through the excitation window and passed through the volume between the electrodes, before being trapped in a carbon-coated horn-shaped cone with negligible reflection back into the electrode area (see Fig. 3). Six-by-four centimeter rectangular electrodes were made from 0.5-mm-thick nickel sheet and separated by a distance of 2 cm. The optical windows were 25 mm in diameter and made from fused silica O12 with 175 nm uv cutoff. A droplet of 99.999% pure mercury was placed into the cold spot, which could be separated from the cell by a stopcock. The temperature of the mercury cold spot was controlled by a thermostat. The cell and the cold spot were preheated at 350 °C under vacuum to eliminate impurities which could potentially depopulate the excited states of mercury during the measurements. The mercury pressure at a given temperature of the cold spot was calculated using the Nesmeianov's tables [21].

Following the irradiation of the cylindrical volume between the electrodes with the 253.7 nm laser light, electrons and ions which were created in chemi-ionization reactions (4) or (5) drift towards the corresponding electrodes. Any resultant current in the external electrical circuit could then be measured using a load resistor. The voltage pulse on the load resistor was amplified, then digitized and stored in a fast memory to be collected by the data acquisition circuit in pauses between the laser pulses. The measurement circuit was calibrated by observing single-electron current pulses from a photomultiplier. The minimal measurable current was found to be 0.25 nA, with temporal resolution of 100 ns.

In most of the experiments, the mercury cell was filled with a buffer gas, nitrogen. As mentioned earlier, collisions between nitrogen molecules and $6\,^3P_1$ mercury atoms facilitate the effective energy transfer from $6\,^3P_1$ to the $6\,^3P_0$

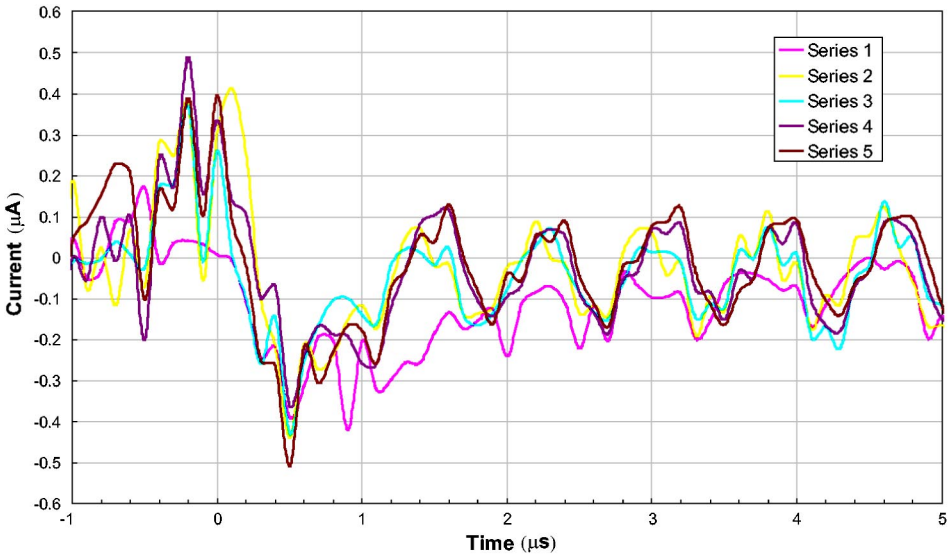

FIG. 4. (Color online.) Current signal. Mercury and nitrogen pressures are 2.5 mTorr and 2.56 Torr, respectively. Applied electric field is 27.5 V cm^{-1}

metastable level of the mercury atom. In the reported experiments, high purity nitrogen gas was obtained by thermally decomposing a small amount of sodium azide (NaN_3), which was placed inside the vacuum system in advance and thoroughly decontaminated by pumping out gaseous admixtures.

Chemi-ionization measurements were carried out in the following range of parameters: nitrogen pressure from 0.5 to 8 Torr, the electrode bias voltage from 1 to 350 V, and the value of the load resistor from 1 kΩ to 1 MΩ. The mercury cell was kept at room temperature and the temperature of the cold spot with a mercury droplet was varied between 0 °C and the room temperature.

IV. RESULTS

In our experiments we were unable to detect any current between the electrodes which could be attributed to charged particles formed in the cell under the influence of the 253.7 nm radiation. Figure 4 shows the results of five independent series of measurements, carried out at nitrogen gas pressure of 2.56 Torr in the mercury cell at a cold spot temperature of 30 °C. Each series is an average of 150 differential signals and each differential signal represents the difference between a two consecutive current measurements, with the beam shutter open and closed, respectively. The measurement series were repeated at nitrogen pressures of 5.5 and 8.2 Torr resulting in similar current dependencies.

It can be seen from Fig. 4 that all five measurement series provided roughly the same results. Following the start of the laser pulse ($t=0$), the current exhibited a bipolar disturbance ranging between −400 and 400 nA, returning to the preirradiation level of noise of ±150 nA approximately 1.5 μs later. The disturbance is most likely caused by electromagnetic influence on the measurement circuits from the YAG-laser power supply, rather than by motion of electrical charges between the electrodes.

The magnitude and duration of chemi-ionization current is determined by the number of charged particles created by the irradiation and by their travel time to the electrodes. Since the duration of the laser pulse (~7 ns) is much smaller than the time it takes for a mercury atom to move between the electrodes, it is safe to assume that the excitation of $6\,^3P_1$ atoms is instantaneous. The temporal evolution of the $6\,^3P_1$ and $6\,^3P_0$ atoms is then determined by the processes of energy transfer between $6\,^3P_1$ and $6\,^3P_0$ levels in collisions with nitrogen molecules, radiative decay (for $6\,^3P_1$) and diffusion (for $6\,^3P_0$): $n_1(t)=n_1(0)e^{-(1/\tau_{\text{eff}}+1/\tau_{N_2})t}$ and $n_0(t)=n_1(0)(1+\tau_{N_2}/\tau_{\text{eff}})^{-1}(1-e^{-(1/\tau_{\text{eff}}+1/\tau_{N_2})t})e^{-t/\tau_d}$. Here $\tau_{N_2}=1/(k_{N_2}n_{N_2})$, where n_{N_2} is the concentration of nitrogen molecules and k_{N_2} is the rate coefficient of energy transfer from $6\,^3P_1$ to $6\,^3P_0$ mercury atoms in collisions with nitrogen molecules, and τ_d is the diffusion time for $6\,^3P_0$ atoms. The losses due to chemi-ionization and energy transfer from $6\,^3P_1$ to $6\,^3P_0$ atoms are neglected. The rate of electron and ion production due to chemi-ionization is $dn_e/dt=dn_i/dt=k_{lm}n_l(t)n_m(t)$, where the subscripts $(l,m=0,1)$ indicate either $6\,^3P_0$ or $6\,^3P_1$ state. The total electron current between the electrodes is then

$$I(t)=\int_{(d-w)/2}^{(d+w)/2} I_x(t)\frac{A}{d}dx, \tag{8}$$

where d and w are the distance between the electrodes and the width of the laser beam, respectively (see Fig. 5), A is the laser beam projection area to the electrode ($A=wL$, L is the electrode length) and the current from the elementary layer $[x,\ x+dx]$ is given by $I_x(t)=\int_c^t ev_e k_{lm}n_l(\xi)n_m(\xi)d\xi$. Here v_e is the electron drift velocity and

$$c=\begin{cases} t-\dfrac{x}{v_e} & \text{for} \quad t\geqslant\dfrac{x}{v_e}, \\ 0 & \text{for} \quad t<\dfrac{x}{v_e}. \end{cases}$$

The chemi-ionization currents due to reactions (4), (5), or (7) which would have maximum values of 400 nA [for reactions (4) and (7)] and 150 nA [for reaction (5)], calculated numerically using Eq. (8), are given in Fig. 6. The current

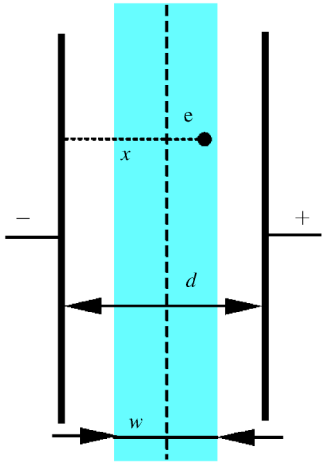

FIG. 5. (Color online.) Schematics of electron motion between the electrodes. Shadowed area represents laser beam.

maxima were chosen equal to the noise level observed in the experiment, see Fig. 4. The effective cross sections inferred from these calculations represent the upper limit estimates (see Table II).

In these calculations, the following parameters of the problem have been used: $L=5$ cm, $w=1$ cm, $n_{N_2}=8.2\times10^{16}$ cm^{-3}, $k_{N_2}=3.0\times10^{-12}$ cm^3 s^{-1} [12], $\tau_{\text{eff}}=1.5\times10^{-6}$ s [22], $\tau_d=5.9\times10^{-3}$ s [23], $v_e=4.6\times10^6$ cm s^{-1} [24], and the mean relative velocity of mercury atoms was found to be $v=2/\pi(2kT/\mu)^{1/2}=1.4\times10^4$ cm s^{-1}. Estimation of the initial concentration of $6\,^3P_1$ atoms produced in the volume by the laser pulse is one of the most important and difficult tasks in chemi-ionization experiments. At the temperature of mercury cold spot 30 °C, the absorption coefficient in the center of the 253.7 line is 85cm^{-1} and the light is fully absorbed in 2 mm of its travel path inside the cell. The excitation between the electrodes occurs on the far wings of the absorption profile. Based on this assumption, we estimated the spatially averaged initial density of $6\,^3P_1$ atoms in our experiment to be $n_1(0)=10^{12}$ cm^{-3}. The same value was initially obtained by Majetich *et al.* through spectroscopic observations [25]; however, in the calculation of the chemi-ionization rate coefficient, they used the saturated concentration of 3×10^{13} cm^{-3} [13].

TABLE II. Upper limits for AI cross sections in Hg obtained in the present study. Terminology as in Table I.

	σ_{10} (10^{-14} cm^2)	σ_{00} (10^{-14} cm^2)	σ_{11} (10^{-14} cm^2)
Present study	<0.1	<0.07	<0.02

V. DISCUSSION

Excitation of mercury vapor with nanosecond laser pulses does not seem to be particularly useful for chemi-ionization experiments in mercury. At high mercury densities, laser excitation leads to a strongly nonuniform distribution of the excited mercury atoms in the volume. Due to the quadratic dependence of the chemi-ionization output on the excited state concentrations, the accurate prediction of the rate coefficients is only possible if this distribution is well defined, which is not a straightforward theoretical or experimental task. However, since τ_{eff} at low mercury pressures is small, such excitation would not result in significant concentrations of $6\,^3P_0$ mercury atoms and chemi-ionization electrons, because most of the $6\,^3P_1$ atoms, instantaneously excited by a laser pulse, would decay radiatively before they have a chance to collide with another atom.

Majetich *et al.* [13] observed a maximum in the current some 2 μs after the laser pulse, followed by an exponential decay with a characteristic time of 22 μs (see line 1 in Fig. 7). This current cannot be explained by collisions involving $6\,^3P_1$ mercury atoms (see Fig. 6). It is also unlikely that this current is due to binary collisions of $6\,^3P_0$ atoms [reaction (7)] since this assumption leads to an unrealistically high value for the chemi-ionization rate coefficient.

A possible explanation for the electron current observed in the experiments by Majetich *et al.* is the photoelectric-effect at the cathode. In that experiment, the laser beam

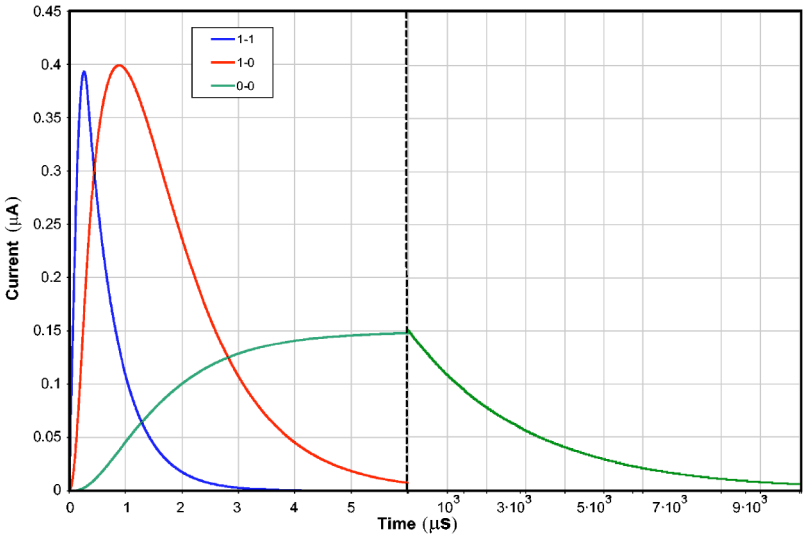

FIG. 6. (Color online.) Model chemi-ionization current signals for different types of collisions.

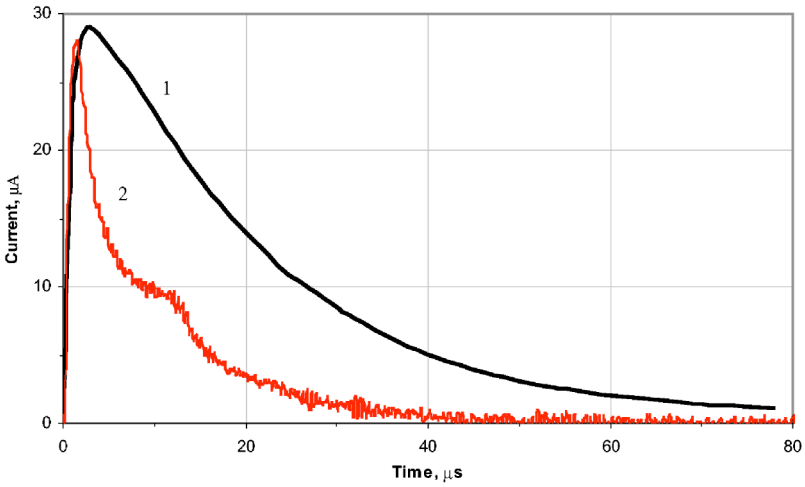

FIG. 7. (Color online.) Chemi-ionization current reported by Majetich *et al.* [13] (1) and photoionization current obtained in present study by illuminating the cathode with laser radiation (2, enlarged five times). The electrode gap, nitrogen pressure, and bias voltage were 1.2 cm, 5 Torr, 150 V and 2 cm, 0.6 Torr, 235 V, respectively.

passed through a cylindrical cell fitted with two windows at the ends. In contrast to the cell configuration used in the present work (Fig. 3), this would result in the significant reflection of radiation from the second window, a fraction of which would arrive at the cathode resulting in a photoelectric emission of electrons. The high bias voltage used by Majetich *et al.* ($E/p > 20$ V/cm Torr) most probably leads to a prebreakdown regime of electron propagation between the electrodes, with formation of scattered avalanches. We tested this assumption by intentionally directing the lased beam at the cathode, and obtained current pulses consistent with those observed by Majetich *et al.* In a further experiment, we detuned the laser wavelength away from the mercury line of 253.7 nm and obtained similar current pulses. Figure 7 gives a comparison of typical current signals obtained in the present experiment with those obtained by Majetich *et al.* The shape of the photocurrent signal in the two experiments is similar, the differences in signal magnitude and decay time probably resulting from differences in the cathode luminance and nitrogen pressure used in these experiments. We therefore conclude that the current measured by Majetich *et al.* was not due to chemi-ionization.

VI. CONCLUSIONS

We have shown that experiments to measure cross sections for chemi-ionization reactions between mercury atoms are difficult both to implement and to interpret. For reasons discussed in the text, we believe that the experiments to measure chemi-ionization currents performed to date have been unable to conclusively identify the atomic processes involved or to determine definitive values for these cross sections.

In the absence of reliable experimental data, the calculations by Cohen *et al.* [15] provide a unique source of cross sections for reactions chemi-ionization between excited Hg atoms. They represent an attempt to show the relative importance of all relevant interactions between the lower levels of excited Hg atoms. In particular, the conclusion that chemi-ionization processes are of associative, rather than Penning type, even when the latter is energetically allowed, will have a profound influence on numerical modeling of FL discharges.

The *ab initio* calculations by Cohen *et al.* [15] show a substantial cross section for reactions between two $6\,^3P_1$ atoms, which has never been confirmed experimentally. There is a clear need for a new, definitive experiment to resolve the above issues. Such an experiment should be based on the continuous, rather then pulsed, excitation of the mercury atoms either in a low mercury pressure cell or in a cross-beam apparatus, and on direct measurement of the excited state and change particle densities in the experimental volume.

Finally, chemi-ionization processes are not the only interatomic reactions which may play a role in the physics of FL. Energy pooling, in which two mercury atoms in particular excited states interact to produce atoms in different atomic states may influence both the radiation and ionization balance in these discharges. Experimental observation of these processes is even more challenging, but use of a similar model to that of Cohen *et al.* could provide valuable insight for modeling FL.

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