OPTOGALVANIC SPECTRA OF NEON AND ARGON

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Abstract

The optogalvanic (OG) spectra of neon and argon in the visible and near ultraviolet (UV) regions were recorded using a pulsed Nd:YAG-pumped tunable dye laser to irradiate either an iron-neon hollow cathode discharge lamp or an iron-neon-argon see-through hollow cathode discharge lamp. Previously unreported OG transitions, especially for argon, were identified and assigned using the J-L coupling scheme. Time-resolved laser optogalvanic (LOG) waveforms of specific neon and argon transitions were analyzed using a promising model of collisional ionization based upon the population distribution of the atomic species in the discharge plasma of a hollow cathode lamp (HCL) found in the literature. With the aid of a non-linear least-squares fit program written in Fortran code, the waveform parameters were determined by fitting a theoretical model to the observed experimental data. Several of these parameters were found proportional to the electron collisional cross sections associated with the states involved in the transition.

Introduction

The optogalvanic effect (OGE) has been used for many years as a sensitive and reliable method of recording calibration spectra when tunable lasers are employed for monitoring species of primary importance to stratospheric photochemistry or tropospheric air quality. Optogalvanic spectroscopic and detection methods are well-established techniques, even though the optogalvanic effect in discharges needs to be understood better. A steady state gas discharge contains a dynamic equilibrium of free electrons and atoms or molecules and their corresponding positive ions distributed over of electronic states and resulting in a well defined impedance and current. A change in the impedance of a discharge or a flame caused by illumination with radiation resonant with an atomic or molecular transition of a species is known as the optogalvanic effect.[1] On resonant absorption of radiation, or due to an optical perturbation, the distribution of the state population of the irradiated species temporarily deviates from equilibrium, resulting in a change in electron and ion densities and the related plasma properties. Optogalvanic spectroscopy in a gas discharge plasma is distinguished from other charged particle detection techniques, such as space-charge limited diodes[2] and gas-filled proportional counters,[3] by the presence of a sustained discharge with an electron gas at a relatively high temperature (0.5 - 10 eV or 5,800 - 116,000 K).[4] Laser Optogalvanic (LOG) spectroscopy is performed by directing a tunable dye laser beam into a plasma (such as the one generated in a hollow cathode discharge lamp).[5] When the wavelength of the laser beam

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coincides with an absorption of a species in the plasma, the rate of ionization of that species changes momentarily due to laser perturbed collisional ionization. The associated impedance change can be detected as a voltage drop across a ballast resistor in the lamp feeding circuit.

Experimental

The in-house designed electrical circuit (see Fig. 1) included a high-voltage power supply (PS) and resistors (R_1) and (R_2), where R_2 was chosen from a variety of resistors ranging from 22 kΩ to 69 kΩ. When the laser pulse was resonantly absorbed by the discharge medium, the voltage across the lamp varied, and the variations were coupled via a 0.05 μF capacitor to a boxcar integrator (BC). The temporal evolution of the signal was recorded by a digital oscilloscope (OSC) and saved onto a floppy disk for further processing and analysis using a personal computer. The discharge current was varied from 0.2 - 3.0 mA and the voltage across the lamp was ~200 V. Extensive laser optogalvanic spectra and waveforms for specific OG transitions were recorded.

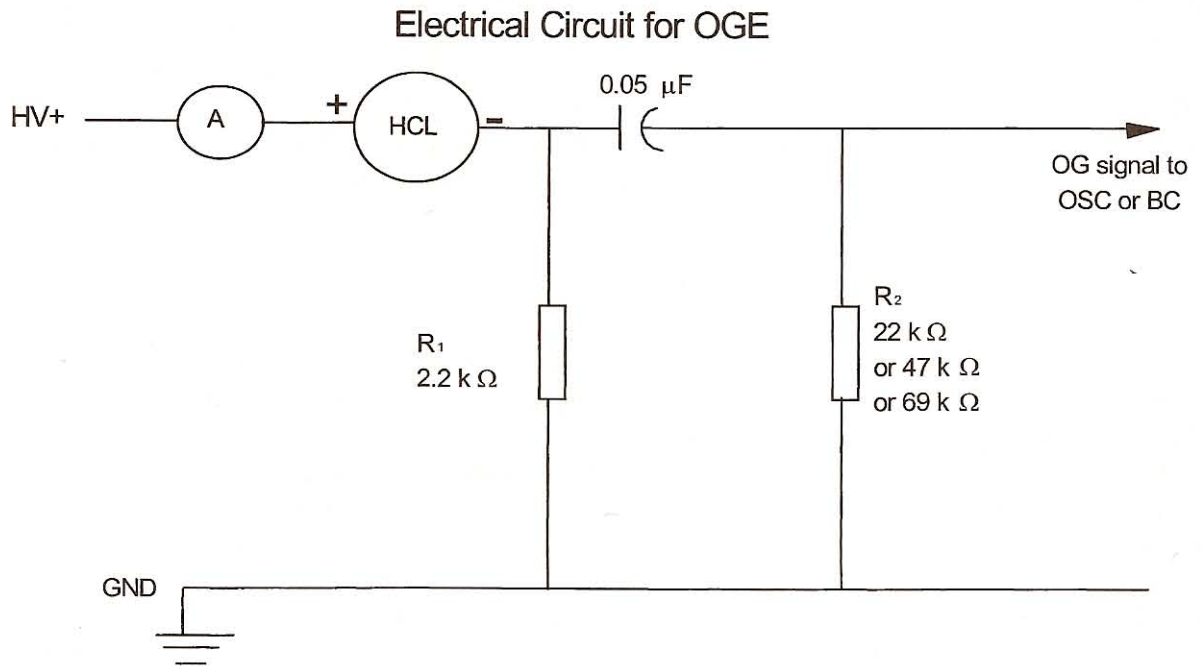

Fig. 1. In-house electrical circuit for the optogalvanic effect showing the power supply, hollowcathode lamp (HCL) and the OG signal output that can be viewed on an oscilloscope (OSC) and recorded with a boxcar (BC).

Commercial hollow cathode lamps (HCLs) have long been used for OG applications. They are relatively inexpensive (when not already present in the spectroscopic laboratory), their electrical noise is fairly low - at the level of shot noise[6,7]. Specific elements can be incorporated into the

cathode, where free atoms of the element may be liberated by cathodic sputtering. The design of hollow cathode lamps can be incompatible with some OG applications. The cathode, which is a cylinder closed at one end, presents a problem. This design does not allow two counter-propagating beams in the cathodic region, a characteristic feature of the sub-Doppler saturation technique. Moreover, at the shortest wavelengths, photoelectric emission produced by the laser striking the cathodic surface, gives an unwanted background. A hollow cathode specifically designed for OG spectroscopy usually provides a clear optical path through the cathode. The neon HCL used in our work was a traditional one with the closed cylinder cathode; however, the argon lamp was a see-through hollow cathode lamp (a laser galvatron) with ends inclined at an angle of 10°- 20° so as to eliminate reflections that might lead to laser interference (see Fig. 2).

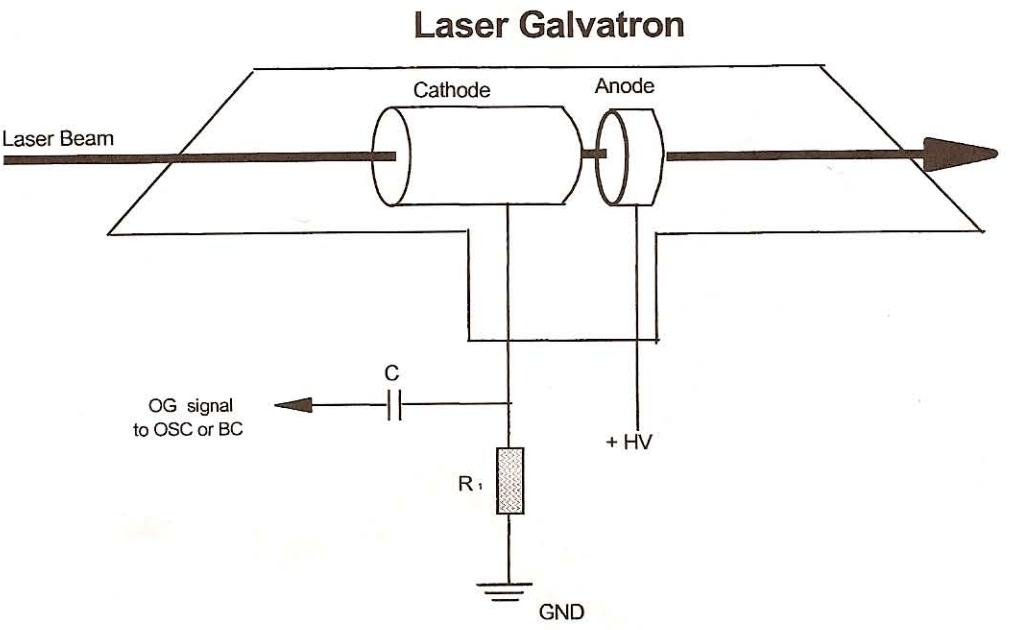

Fig. 2. The argon laser galvatron, a see-through hollow cathode lamp, used to produce the argon OG signal.

Results and Discussion

One might think that all of the parameters in a DC plasma would be time-independent, which is not the case. Although the electrons and ions are in dynamic equilibrium as a whole, it is an average result of many detailed interactions. If a small section of the plasma is perturbed from neutrality for any reason, then there occur large restoring forces trying to restore charge neutrality. Due to the large mass difference between ions and electrons, it will be the electrons that first respond to the restoring forces, followed by the ions. The restoring forces are proportional to the displacement, which is the condition required for oscillations.[8]

In the case of our argon laser galvatron, oscillations became evident even before OG transitions were tuned in, so our group dubbed these oscillations *the ringing effect.* Oscillations became intense enough so as to interfere with the optogalvanic signal within certain current ranges. We recorded the oscillations and estimated their frequency to be ~40 kHz. Fig. 3 illustrates how interference from these oscillations depended upon current. This graph depicts the resonance peak

of Ar 320.366 nm plus the interference from the oscillations, within the current range 1.2 - 2.4 mA.

Other transitions that were analyzed in the present investigation involved more than two energy levels. For some of the waveforms studied, up to three exponential decay terms were used to fit the OG signal. The Fortran program used fits up to twelve parameters involving five different energy levels. The analysis of the time-resolved OG waveforms provided quantitative information about the prominent physical processes in a discharge plasma described earlier. Analyses of signals produced at different currents aided in the understanding and determination of the effective decay rates of the states involved in the OG transitions and to thereby determine their effective lifetimes, along with values of parameters related to electron collisional ionization cross sections.

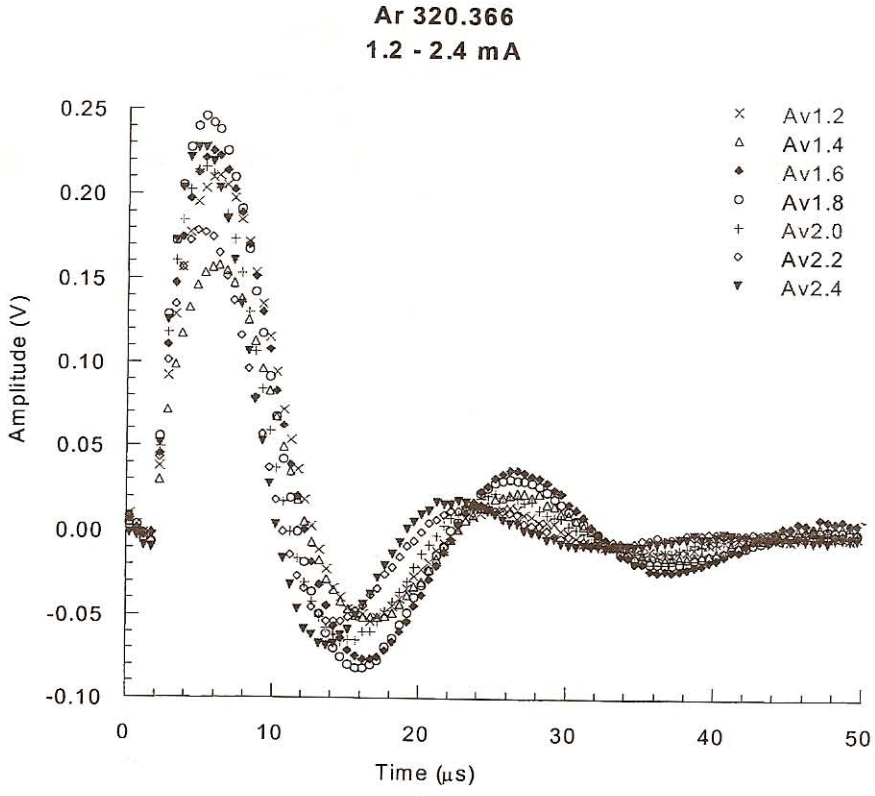

Fig. 3. Averaged OG Signals of Ar 320.366 nm in the laser galvatron within the current range of 1.2 - 2.4 mA and at intervals of 0.2 mA, illustrating the effect of resonance oscillations upon the OG signals.

Fig. 4 displays the waveforms of the argon OG transition Ar 320.366 nm at five different discharge current settings (0.4, 0.6, 0.8. 1.0 and 1.2 mA). The rising peak indicates an increase in the impedance and voltage of the plasma and therefore is a negative OG signal due to a decrease in the discharge current. Higher current settings, produced higher peaks, indicating a greater increase in impedance or ΔV. Higher current settings also produced faster decay rates (see 0.4, 0.6 and 0.8 mA plots). The last curve (1.2mA) shows an example of interference from oscillations caused by electrical resonance in the hollow cathode lamp and the associated circuit. Lee et al.[9] pointed out that HCL's have properties that can lead to such resonance in their negative-resistance region. Interference from these oscillations can render information obtained from the optogalvanic effect inaccurate.

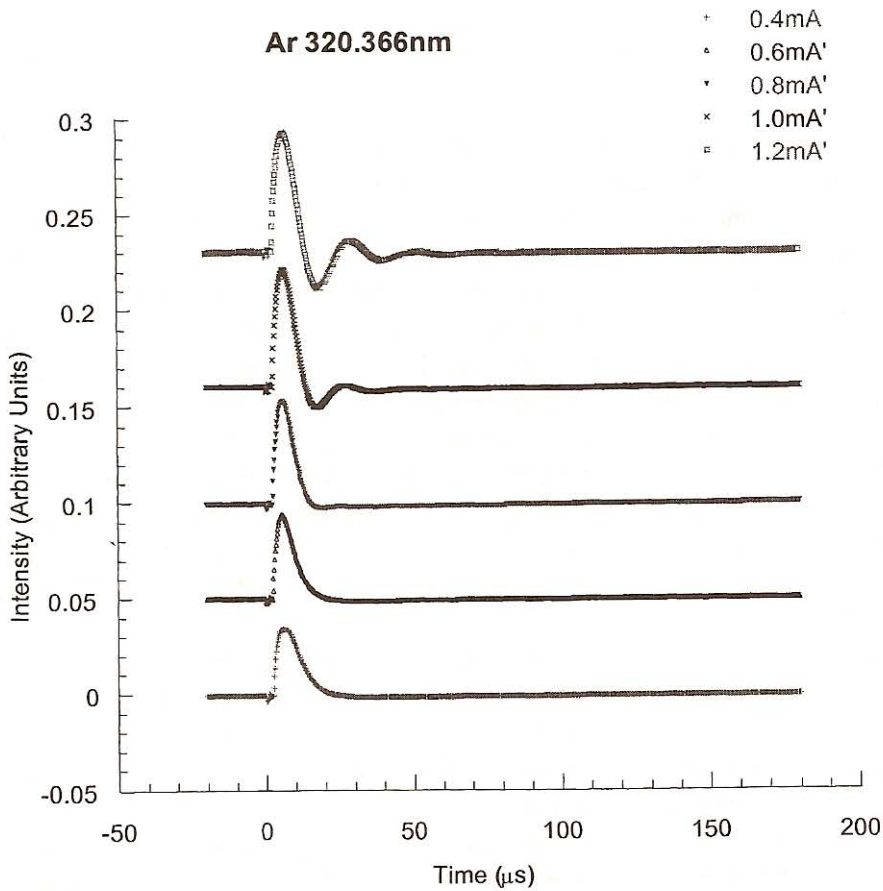

Fig. 4. Argon OG waveform at 320.366 nm showing the changes in the waveform as the discharge current increases.

Table 1. Illustrative Optogalvanic Spectral Lines of Ar-Fe and OH Rotational Laser-Induced Fluorescence (LIF) Lines

λ_{air}(in Å)	λ_{vac}(in Å)	ν_{vac}(in cm^{-1})
$a_0 = 3113.36508(49)$, $a_1 = -.166658(31) \times 10^{-2}$ (least-square fit coefficients)		
3109.9636(18)	3110.8657(18)	32145.392(19)
3110.2752(18)	3111.1775(18)	32142.171(19)
3110.6636(18)	3111.5659(18)	32138.159(19)
3111.7918(18)	3112.6944(18)	32126.507(18)

3111.8118(18)	3112.7145(18)	32126.301(18)
3112.1801(18)	3113.0826(18)	32126.507(18)
3113.0784(17)	3113.9814(17)	32138.159(19)
3114.0484(17)	3114.9516(17)	32142.171(19)
3114.1500(17)	3115.0532(17)	32145.392(19)

The optogalvanic effect (OGE) gives rise to efficient, sensitive, and economical spectroscopic and detection methods. OGE complements other optical techniques, such as traditional absorption and fluorescence spectroscopy and optoacoustic spectroscopy. It is intrinsically more sensitive than absorption spectroscopy; since the OGE is based upon a signal whose background is zero, while absorption spectroscopy records a small variation superimposed on a large signal. When compared to laser-induced fluorescence (LIF), the OGE has the advantage of not being affected either by the background signal due to the discharge luminosity or by the scattering of the excitation signal. This last is particularly important when the fluorescence must be detected at the same wavelengths as the absorbed radiation.

Zalewski et al.[10] reported changes in voltage ratios for OG signals of up to 10% and Smyth et al.[11] reported changes of 2%. The optogalvanic impedance changes in the present study were calculated in terms of current ($\Delta I/I$) and they were < 2.0 %. This small current change still produced many detectable OG waveforms large enough to be analyzed, lending support to the premise that the optogalvanic effect is highly sensitive.

High efficiency of detection and collection of charges, rather than photons, is the basis of the greater sensitivity of optogalvanic spectroscopy. Based on this point of view, the OGE may be compared to resonance ionization spectroscopy (RIS), where starting from neutral atomic or molecular species, ionizations are induced by resonance multiphoton absorption and the created electron-ion pairs are collected by electrodes.

A glow discharge is an inexpensive way to obtain large densities of excited states in volatile elements, especially those involving metastable states. Gaseous states of refractory elements are easily produced in hollow cathode lamps by sputtering. Rydberg states can also be studied by the OG technique, since these can be reached by exciting radiative transitions starting from metastable levels that are well populated in discharges, particularly in the noble gases.

Acknowledgments

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