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POLARITY OF LASER EXCITED OPTOGALVANIC TRANSITIONS IN NEON

Key Words: Optogalvanic effect; Polarity; Metastable population.

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Abstract

Irradiation of a gaseous discharge with a tunable laser produces observable voltage changes at wavelengths that correspond to electronic transitions for species within the discharge. Optogalvanic (OG) transitions of neon have been investigated in the visible and near UV regions by axially irradiating a hollow cathode discharge with an excimer-pumped dye laser. A variety of OG transitions that originate from metastable states have been recorded. A digital oscilloscope was used to record the waveforms of the OG transitions. The polarities of 29 OG transitions recorded

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in the near UV and visible are explained in terms of processes that affect the population of neon atoms in metastable states.

Introduction

In the optogalvanic (OG) effect, an external source of narrowband resonant radiation is used to induce current or voltage changes in a medium within a discharge. The phenomenon was discovered for atoms in 1928 by Penning, who observed that the impedance of a neon discharge tube changes when illuminated by a second neon discharge tube [1]. The net ionization rate of a tube, and therefore its impedance, is affected when electronic transitions are induced in species present in the discharge. The discharge impedance may be either increased or decreased by the resonant absorption of radiation by one or more species in the discharge. Such an impedance change may be detected as a voltage change across the discharge tube. The polarity of the signal voltage may depend upon the lifetime of the energetically lower of the two states involved in the OG transition [2]. The OG effect has been used for a number of purposes, including analytical flame spectroscopy, laser stabilization, plasma diagnostics, atomic spectroscopy, wavelength calibration, bandwidth determinations and molecular spectroscopy [3].

Several authors have reported varied investigations concerning the OG effect. Reddy et al [4] reported the temporal evolution of OG signals in a Hg-argon discharge. Nestor [5] obtained OG spectra of atomic neon and argon for wavelength calibration of tunable lasers. Smyth and Schenck [6] extensively discussed the processes that contribute to ionization in the discharge and the role of metastable populations in producing secondary ionization, and

suggested that the waveform polarity of the OG signals was current -dependent. Suri et al [7] observed relative enhancement of the OG signal of uranium (^{235}U) in the visible. Erez et al [8] presented a phenomenological theory for the OG effect and predicted the dependence of the signal on gas pressure and current. The primary motivation for the current investigation has been to attempt to understand the polarity of observed waveforms of certain OG transitions in terms of the population of neon atoms in metastable states excited in the discharge.

Experimental

A block diagram of the laser OG apparatus is presented in Fig. 1. A commercial hollow cathode lamp filled with neon as the filler gas and iron as the cathode element (Model 303, Perkin Elmer) was employed. The lamp was maintained at a potential difference of 160 V through a current limiting resistor of 22 kΩ, while the discharge current was limited to 1 mA. A dye laser (Spectra Physics PDL-3) was pumped by an excimer laser (Impulse 4530GL, Questek) running at 10 Hz. The output dye beam had a pulse duration of about 20 ns and a nominal linewidth of 0.07 cm^{-1}. About 5% of the primary laser pulse energy axially irradiated the hollow cathode discharge lamp. When the laser pulse was resonantly absorbed by the discharge medium, the voltage across the discharge changed, and these variations were coupled via a 0.05 μF capacitor to a boxcar integrator (Model 520, Stanford Research). The temporal evolution of the OG signal was recorded by a digital oscilloscope (Model 9410, LeCroy).

Results and Discussion

The electronic configuration of the neon ion is $1s^2 2s^2 2p^5$. Since L=1 and S=1/2, J=3/2 or 1/2 for the ionic neon. This gives

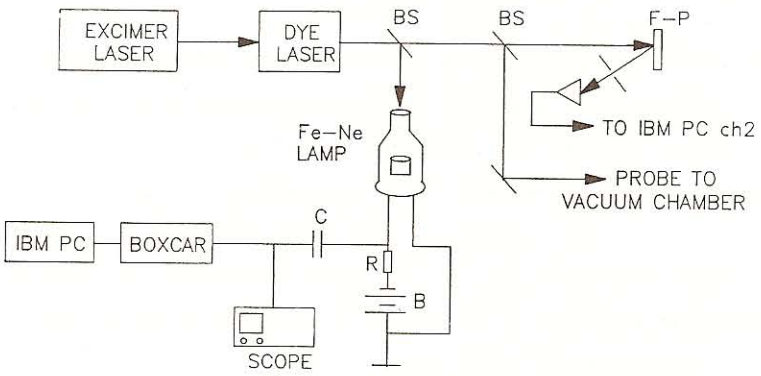

Figure 1 Experimental arrangement for recording laser optogalvanic transitions. **BS**=Beam Splitter, **F-P**=Fabry-Perot Etalon, **C**=Capacitor, **R**=Resistor, **B**=Power Supply.

rise to the terms $^2P^o_{3/2}$ and $^2P^o_{1/2}$ (where the "2" and "o" superscripts represent the multiplicity and parity, respectively). When a 3s electron is added to this configuration, as in $2p(^2P^o_{3/2})3s$, the generated energy levels are designated as 3s[3/2]°2 and 3s[3/2]°1, where the number inside the brackets represents one of the vector sum values of the ionic J value (3/2 or 1/2) and the l value of the added electron (l=0 for an s electron). The number inside the brackets is coupled with the spin of the added electron (s=1/2) to generate the total J value and is stated outside the brackets. A prime is used to identify the levels generated from the J=1/2 of the ionic level. Thus, the first excited state of neon can be represented by four energy levels, namely 3s[3/2]°2, 3s[3/2]°1, 3s'[1/2]°1, and 3s'[1/2]°0 in Racah notation [9]. Two of these levels are metastable with long radiative lifetimes, since they have J=0 and J=2, respectively, and cannot undergo an electric dipole

transition to the ground state with J=0 because of the selection rule ($\Delta J=J'-J=0,\pm1$; excluding 0-0). The remaining two levels are short-lived non-metastable states.

In the absence of an external resonant source, the excited states of neon are populated via collisional excitation in the glow discharge. Thus, all of the transitions in absorption begin from excited electronic energy levels populated by electron-neon collisions within the discharge. Three major processes make important contributions to ionization: direct electron-neon ionization, collisional ionization of metastables by electrons and metastable-metastable collisions [10-13]. The important role of metastable atoms in producing secondary ionization within a gaseous discharge has been well known for some time now. The shape of the observed OG signals may be interpreted in terms of processes which directly affect the concentration of neon atoms in metastable levels. For low discharge currents, the metastable states are significantly populated. When laser radiation is introduced within the discharge medium, neon atoms in metastable states are excited to (3p, 4p,..) levels. The metastable concentration is reduced via radiative decay to short-lived $3s[1/2]^{\circ}1$ and $3s[3/2]^{\circ}1$ states, followed by decay to the ground state (since direct transitions $2p^5 3p \rightarrow 2p^6$ are not allowed due to parity considerations - both states having even parity). Decay of these states results in decreased metastable population, which corresponds to reduced ionization (metastable-metastable collisional processes make an important contribution to the ionization). On the other hand, the absorption transitions from the non-metastable levels enhance the metastable population. Laser-enhanced ionization is generally believed to be the mechanism for the OG effect involving non-

metastable states [10-13]. Ionization of laser-excited atoms in the discharge medium occurs principally through collisions with other excited species or with thermal electrons. Negative voltage changes for transitions that originate in short-lived non-metastable levels, $3s'[1/2]^\circ 1$ and $3s[3/2]^\circ 1$, can be explained in terms of enhanced ionization following irradiation. Radiative decays from the excited 3p to 3s levels occur so as to preferentially populate the metastable levels. Again, collisional ionization by electrons is enhanced for neon atoms excited to 3p levels relative to the $3s'[1/2]^\circ 1$ and $3s[3/2]^\circ 1$ levels, because more electrons have sufficent energy to ionize the atoms. Thus, all of the above effects increase ionization within the discharge, and thereby increase the current and decrease the OG voltage.

In the work reported here, 29 OG transitions that originate from the first excited state [14] of neon have been recorded and are listed in Table I. A majority of these signals (25 of 29) arise due to the $2p^5 3s \rightarrow 2p^5 4p$ transition, while the remaining four are due to the $2p^5 3s \rightarrow 2p^5 3p$ transition. Of these 29 transitions, 7 are categorized strong OG signals (intensity $\geq$ 1 V). All of these strong signals are due to transitions that originate in the metastable states of neon. Of the 7 strong OG signals, all but one originate from the $3s[3/2]^\circ 2$ metastable level, which may have the highest 3s excited state population. This could be due to the fact that photon excitation from the 3s levels (that is, $^3P_{0,1,2}$ and $^1P_1$ states) to 3p levels is subsequently followed by relaxation back to the metastable states and thereby increases metastable population. Relaxation from the 3p levels back to the $^3P_2$ state appears to be favored as compared to relaxation to $^3P_0$. In most cases, the photoinduced voltage change had both positive and negative

Table I

Optogalvanic neon transitions

Wavelength in Air (Å)	Ne Transition	OG Signal Intensity (mV)	Laser Energy (μJ)
3369.9069	3s [1.5]°2 — 4p'[0.5]1	1500	50
3375.6489	3s [1.5]°2 — 4p'[1.5]1	100	55
3417.9031	3s [1.5]°1 — 4p'[1.5]2	700	70
3418.007	3s [1.5]°1 — 4p'[0.5]1	400	60
3423.9120	3s [1.5]°1 — 4p'[1.5]1	200	60
3447.7022	3s [1.5]°2 — 4p [1.5]2	20	45
3450.7641	3s [1.5]°2 — 4p [1.5]1	1300	40
3454.1942	3s [1.5]°1 — 4p [0.5]0	600	20
3460.5235	3s'[0.5]°0 — 4p'[0.5]1	600	25
3464.3385	3s [1.5]°2 — 4p [2.5]2	1000	25
3466.5781	3s'[0.5]°0 — 4p'[1.5]1	1000	30
3472.5706	3s [1.5]°2 — 4p [2.5]3	300	30
3498.0632	3s [1.5]°1 — 4p [1.5]2	150	35
3501.2154	3s [1.5]°1 — 4p [1.5]1	200	35
3510.7207	3s [1.5]°2 — 4p [0.5]1	800	40
3515.1900	3s [1.5]°1 — 4p [2.5]2	150	40
3520.4714	3s'[0.5]°1 — 4p'[0.5]0	50	45
3593.5263	3s'[0.5]°1 — 4p'[1.5]2	25	50
3600.1694	3s'[0.5]°1 — 4p'[1.5]1	15	45
3609.1787	3s'[0.5]°0 — 4p [0.5]1	150	50
3633.6643	3s'[0.5]°1 — 4p [0.5]0	35	80
3682.2421	3s'[0.5]°1 — 4p [1.5]2	25	50
3685.7351	3s'[0.5]°1 — 4p [1.5]1	28	50
3701.2247	3s'[0.5]°1 — 4p [2.5]2	35	70
3754.2148	3s'[0.5]°1 — 4p [0.5]1	18	60
5400.5616	3s [1.5]°1 — 3p'[0.5] 0	500	100
5881.8950	3s [1.5]°2 — 3p'[0.5] 1	3800	90
5944.8342	3s [1.5]°2 — 3p'[1.5] 2	2300	50
5975.5340	3s [1.5]°2 — 3p'[1.5] 1	1300	40

components, which could be explained by the fact that there are two competing processes. Photon excitation from the neon $^3P_2$ and $^3P_0$ metastable states to the higher 3p levels will deplete the neon metastable population, since radiative decay occurs to the $^3P_1$ and $^1P_1$ states followed by decay to the ground state ($^1S_0$). Such a sequence of events accounts for the positive component of the OG signal. Also, collisional ionization from the 3p neon levels can be achieved via energetic electrons. Such a process will contribute towards enhanced ionization following irradiation and accounts for

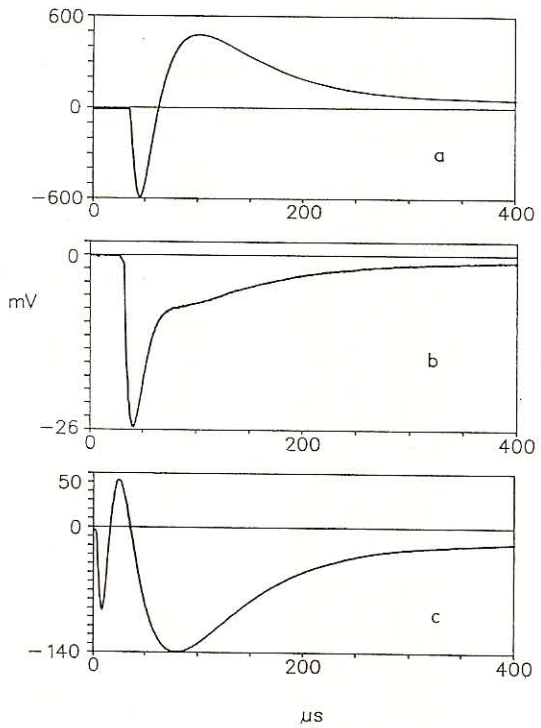

Figure 2 Optogalvanic waveforms recorded with 0.5 mA discharge current and 20 μJ dye laser pulse corresponding to neon transitions at (a) 3510.721 Å (b) 3520.471 Å (c) 3515.190 Å.

the negative voltage component observed for OG transitions from metastable states.

The above explanation is consistent with the pulse shape of the OG signals recorded by the digital oscilloscope. Figure 2(a) shows the OG signal waveform for a distinct transition at wavelength 3510.721 Å (in air) and corresponds to the neon

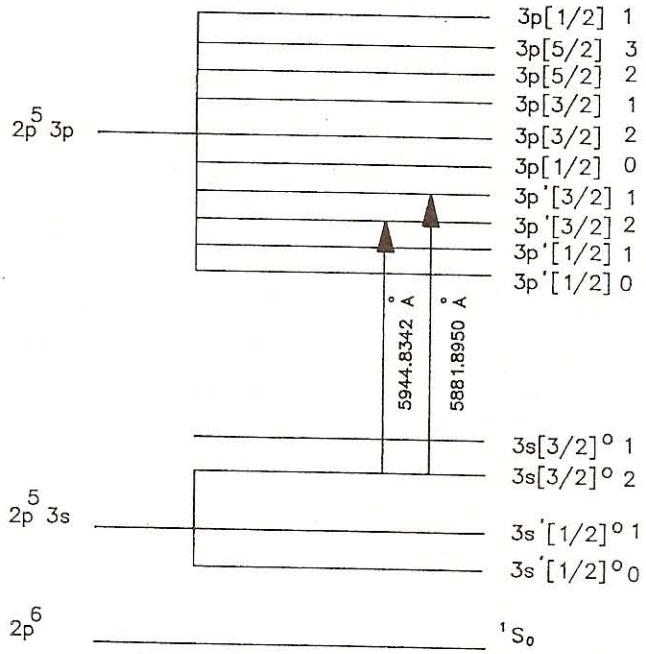

Figure 3 Schematic energy level diagram (not to scale) showing two strong optogalvanic transitions (at 5881.8950 Å and 5944.8342 Å) originating from the same metastable level 3s[3/2]°2.

transition 3s[1.5]°2 - 4p[0.5]1. The pulse shape observed had an initial negative peak; the signal then rose to the base line and became positive with a long tail (the slow positive voltage component exhibited by many of these transitions most likely arises from a two-step radiative decay [3p → 3s($^3P_1$), followed by 3s($^1P_1$) → $^1S_0$)] [6]. Figure 2(b) shows the OG signal waveform at 3520.471 Å for the transition 3s'[0.5]°1 - 4p'[0.5]0 involving the non-metastable first excited state of neon. In agreement with the above

argument, the pulse shape is observed to be entirely negative. Figure 2(c) shows the neon transition 3s[1.5]°1 - 4p[2.5]2 at 3515.190 Å. The OG signal associated with this transition (Fig. 2(c)) (involving the non-metastable level) is nearly inverted compared to that from the metastable one (Fig. 2(a)). The OG transitions from (3s) metastable states to 3p levels are generally more intense than those to 4p levels. There is one strong transition, namely 3s'[1/2]°0 - 4p'[3/2]1, that originates from the lower metastable level 3s'[1/2]°0. The two strongest OG transitions for neon (tabulated in Table I), namely 3s[3/2]°2 - 3p'[3/2]1 and 3s[3/2]°2 - 3p'[3/2]2, occur at 5881.8950 Å and 5944.8342 Å (see Fig. 3), respectively, and like the majority of transitions cited earlier arise from the 3s[3/2]°2 metastable level.

Conclusions

In summary, oscilloscope traces have revealed that the OG signals arising due to excitation from metastable neon levels exhibit waveforms that are negative (corresponding to increased ionization current) and subsequently become positive (owing to decreased ionization current); whereas the OG signals from short-lived non-metastable levels are either entirely negative or inverted in nature compared to those from metastable levels. The observed OG signals, in conjunction with simultaneously recorded etalon fringes, have made possible accurate calibration of rotationally-resolved laser excitation spectra of jet-cooled free radicals of environmental and atmospheric significance.

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