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WINTER COLLEGE ON

ATOMIC AND MOLECULAR PHYSICS

(9 March - 3 April 1987)

OPTOGALVANIC AND IONIZATION SPECTROSCOPY

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THE MECHANISM OF THE OPTOGALVANIC EFFECT

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PROCEEDINGS OF THE 6th GENERAL CONFERENCE OF THE EUROPEAN PHYSICAL SOCIETY

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VOLUME 1

27-31 AUGUST 1984,
PRAGUE - CZECHOSLOVAKIA

1. Introduction

The optogalvanic effect (OG) in ionized atomic and molecular gases is based on the change in the electrical impedance of low power gas discharges when irradiated with monochromatic light corresponding to transitions of the atomic and molecular species present in the discharge. In this phenomenon, which may be defined as the bulk photoelectric effect of feebly ionized gases, the ionization degree of the atomic and molecular species changes as a consequence of the resonant light absorption and the perturbation in the population distribution of the excited levels. The phenomenon was observed firstly a long time ago when in a neon lamp, submitted to the resonant light emitted by another lamp, a change in the discharge current was detected /1/. However extensive investigation of the OG effect started as soon as the tunable lasers became available. Making use of these lasers sources the electrical impedance changes could be detected even when minor species contained in the discharge were illuminated on weakly allowed transitions. Moreover spectacular results, as the swith-off of a discharge under illumination of a strongly absorbing species, could be also detected. New possibilities have been opened by this effect for the high resolution atomic and molecular spectroscopy, the analytical chemistry, the plasma diagnostics, the laser calibration and frequency locking, and so on, as discussed in a recent Colloquium specifically devoted to investigate this phenomenon and its applications /2/.

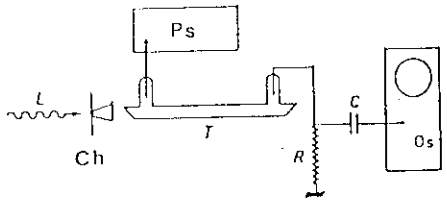

Fig. 1 Typical apparatus for the OG detection: L laser, Ch chopper, T discharge tube, Ps power supply, R ballast resistor, C condenser, Os oscilloscope

A simple apparatus for observing the OG effect is schematically represented in Fig 1. Light from a c.w. laser propagates into a glass tube where a discharge is maintained through a ballast resistor and a d.c. power supply (either a constant voltage supply or a constant current one). The laser light is mechanically chopped and by means of a capacitor C any modulation introduced into the discharge by the light absorption may be detected directly on the Y axis of a scope. The phase-sensitive detection of the current modulation provides a larger sensitivity in the observation of the OG effect. If pulsed laser sources are used in the excitation, a boxcar detector gives the time evolution of the OG signal and additional information on the phenomenon is obtained. Irradiation in different parts of normal glow and hollow cathode discharges has been studied. Furthermore the OG effect has been applied to flames and furnaces to investigate the combustion and the high temperature systems. The detection sensitivity is limited by the noise in the background ionization. It has been found that very quiet background ionization is obtained if the discharge is properly cleaned up through repetitive high-vacuum pumping and discharge running.

A technique closely related to the OG effect is the thermoionic diode, where the ionization of a vapour contained in the diode is used to control the space-charged-limited current flowing between the anode and the cathode /3/. Very large changes in the electrical impedance of the diode may be obtained under resonant light ilumination owing to an amplification in the collected current produced by the space-charge-limited operation. However in the glow discharges the atoms and the molecules collide with electrons having a large kinetic energy, so that the highly excited levels have a population large enough to provide OG signals.

2. Phenomena

The simplest mechanism producing an OG signal is a direct laser ionization of the atoms or molecule, and in this context the technique may be classified as a photcionization process. Pulsed lasers are typically employed and for instance high sensitivity was realized in the detection of hydrogen atoms in plasmas and flames /4/. However most OG investigations are based on a weak c.w. laser excitation so that the multiphoton ionization has a very low probability of occurring. Even if the OG effect with c.w. excitation has been observed on a large variety of atomic and molecular systms, a precise knowledge of the mechanisms leading to a change in the current is restricted to a very limited number of cases.

For the positive columns of atomic He and Ne discharges accurate analyses of the OG phenomena have been performed /5,6/. In those discharges the lower and upper levels of the transition excited by the laser have a very different ionization rate, so that the electron density, typically 10^{11}-10^{13} cm^{-3}, is modified under the laser irradiation. For instance in a helium discharge, the 5976 A laser excitation from the lower $2\,^1P$ level to the upper $3\,^1D$ level produces a large positive OG signal (e.g. increase in the discharge current) because in the upper level the associative ionization process gives helium molecular ions and electrons and in the lower level it does not. In the neon positive column the metastable $1s_5$, $1s_4$ and $1s_3$ levels at 16.6 eV energy above the ground level are populated by the electron collisions. Furthermore in the electron collisions the neon atoms in those levels may gain the 5 eV energy required to reach the ionization limit. In a laser excitation to the upper 2p levels, the atoms may decay through visible and ultraviolet light emission to the ground level. Thus in the laser absorption the neon atoms have a probability of decaying from the metastable levels to the ground level, and a decrease in the current, i.e. a negative OG signal, results. The record on the bottom of Fig. 2 reports a typical OG spectrum of a neon discharge with the negative OG signal associated to the transitions starting from the metastable levels.

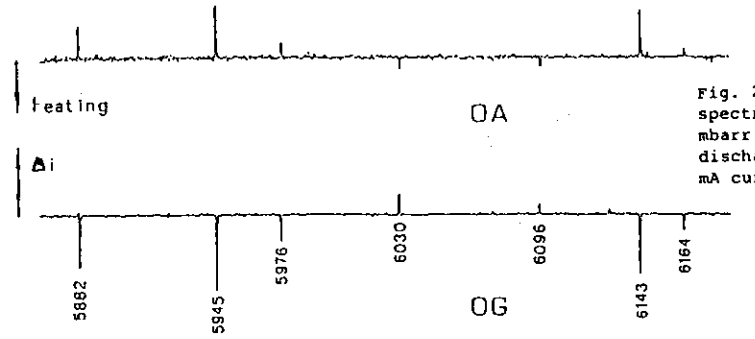

Fig. 2 OA and OG spectra in a 0.7 mbarr neon discharge at 0.6 mA current.

In a discharge the electrons have a kinetic energy distribution described through the electronic temperature T_e. For the rare gas discharges the temperature T_e is typically 10000-20000 ^0K, corresponding to an average 1-2 eV kinetic energy. The electron temperature determines the energy given up by the electrons in the elastic and inelastic collisions with the atoms and ions of the discharge. Thus the ionization and recombination processes depend on the electron temperature. The energy distribution of the atoms is described by the translational energy temperature T_t and by the temperature T_h of the excited state population distribution. In a normal glow discharge both these temperatures are lower than the electron temperature T_e . The translational temperature T_t ,typically in the 300-600 ^0K range, depends on the thermal conduction to the discharge cell walls. In an hollow cathode discharge, where the electron density is larger than in the normal glow, a local thermal equilibrium may be reached with equal electronic, atomic and ionic temperatures.

The electrons reach their equilibrium through the collisions with the atoms and the ions of the discharge. Because in the OG effect the atomic population distribution is modified by the laser radiation, the electron temperature may be affected, and as a consequence also the atomic temperatures may be modified. In effect in an OG experiment in an hollow cathode discharge where uranium atoms were excited, a modification of the atomic temperature under laser irradiation was measured /6/. Because the electron mobility in the negative glow of an hollow cathode discharge depends strongly on the electron temperature, the change in the electron temperature is an efficient mechanims in producing the OG effect in the hollow cathode discharges /7/.

A similar mechanism based on the modification in the ionic mobility under laser illumination of the discharge operates in the OG molecular effect for electronic transitions of the N_2^+ and CO^+ ions /8/. In these molecular ions the charge exchange cross sections for the collisions of excited state ions are smaller than for the collisions of ground state ions so that a decrease in the discharge current, e.g. a negative OG signal, originates for the resonant laser excitation of the ions. In I_2 where both positive and negative OG signals were observed under the electronic laser excitation, the negative OG signals were interpreted as an increase in the rate of the dissociative attachment when the iodine molecule was excited to an upper electronic level. In the dissociative attachment a negative I^- ion is produced in the electron-iodine molecule collisions. Thus the electron mobility is modified by the laser excitation of the molecules.

The positive signals in the I_2 molecular discharge, as well in other molecular discharges under infrared illumination /11/, were not interpreted through a specific OG mechanism. However in pulsed laser excitation experiments with the irradiation outside the discharge, it was observed that the OG signal appeared delayed with respect to the laser absorption. The delay corresponded to the propagation of a thermal acoustic disturbance through the gas, from the irradiation position to the discharge center. Thus in those discharges the temperature increase may play an important role in producing the OG effect.

3.Optoacoustic investigations

In order to test the influence of the temperature mechanisms on the occurrence of the OG phenomenon some experiments with the simultaneous observation of the OG and optoacoustic (OA) signals were performed /12,13/. In the usual OA detection the laser-induced changes in the pressure and temperature of the sample are detected through a microphone. In the OG apparatus a microphone should be able to detect any laser-induced change in the translational temperature of the atoms or molecules of the discharge. The apparatus of Fig. 1 was modified by inserting a microphone inside the glass tube near the anode of a neon discharge. By sweeping the laser frequency an OA spectrum was observed for the resonant absorption of the neon atoms of the discharge. The top record of Fig. 2 presents such a spectrum, recorded simultaneously with the bottom OG spectrum. The phase sensitive detection of the OA signal did not tell us if the observed signals corresponded to a decrease or increase in the discharge translational temperature. On the contrary in the conventional OA spectroscopy in molecular gases the microphone signal is produced by an increase in the translational temperature, because the absorbed laser energy is converted into the translational energy through the relaxation mechanisms. Thus we performed a conventional OA experiment on a molecular gas in the same OG set-up with the discharge swichted off. From the results of this experiment we deduced that the OA signals observed in the record of Fig. 2 for the transitions starting from the metastable neon levels corresponded to a decrease in the traslational temperature of the discharge. The OG effect may produce either an increase or a decrease of the translational temperature depending on the discharge conditions. If a temperature decrease was observed in the low current record of Fig. 2, at larger currents an increase in the translational temperature of the discharge was observed.

The change in the translational temperature of the atoms contained in the discharge originates from modifications in the discharge energy balance and in the amount of energy dissipated into the gas. The energy entering into the discharge is composed by the laser absorbed power, Q photons per unit time at laser frequency ν , and the electric power P_e . This total input power is dissipated through the radiation emission (visible and ultraviolet photons), the wall energy deposition through the atomic, ionic and electronic diffusions, and the gas temperature increase through the inelastic electron-atom collisions. The gas translational temperature depends also indirectly on the energy deposited at the walls. In presence of the laser radiation the electric input power is modified by the quantity ΔP_e , and the OA signal S_{OA} ,i.e. the change in the translational gas temperature, can be written as:

$$S_{OA} = f_e \Delta P_e + f_L Q h\nu \qquad (1)$$

Here the factors f_e and f_L,containing appropriate dimensional factors, take into account the fractions of the electric and laser power respectively affecting the gas temperature. In atoms the electronic-translational relaxation mechanism is a very inefficient process: most of the absorbed laser power is irradiated out as fluorescent photons, except for the inelastic electron-atom relaxation collisions. An extimate of the rate for these collisional processes as compared to the fluorescent rate gives f_L =0.001. A proper determination of f_e requires a precise description of the energy dissipation channels listed above. Thus the experimental data on the OA signals in neon were qualitatively fitted supposing that in Eq. (1) the contribution of the laser absorbed power to the OA signal was negligible and the f_e factor was nearly unity. A resonable fit of the experimental results was obtained deriving the electric power change from the measuremerts of the OG signal and the electric field in the positive column. The discharge temperature decrease at low currents and the discharge temperature increase at high currents were expained by this simple model /12/. This analysis shows that in an atomic discharge the laser radiation directly controls the input electric power and the temperature changes are produced by the modification in the dissipated electric power.

The simultaneous investigations of the OG and OA effectd in molecular CO_2 and NH_3 discharges under irradiation by infrared CO_2 and N_2O lasers were a test of a different molecular behaviour /13/. The experimental observatios were concentrated on the comparison of the time evolution for the OG and OA signals. It resulted that in the CO_2 discharges those signal have an identical time evolution whichever the discharge conditions and the irradiation position. On the contrary in the NH_3 discharges the OG and OA siganls presented a different behaviour. For instance the OG signals for laser irradiation near the cathode resulted negative, and for laser irradiation inside the positive column resulted positive, while the OA signals remained identical. An important difference with the atomic discharges results when the terms of the laser absorbed power and the electric power change appearing in Eq. (1) are evaluated for the infrared absorption of a molecular discharge. In the investigated cases the absorbed laser power resulted very large as compared to the change in the input electric power. Furthermore in a molecular discharge the

absorbed laser power is entirely dissipated through the vibro-translational and roto-translational relaxation processes. Thus the molecular gas temperature produced by the laser absorption is the main mechanism governing the discharge behaviour. The OG signals arise as a consequence of the molecular temperature modifications. However in molecular systems under laser irradiation two different temperatures should be introduced to describe the translational motion and the vibrational population distribution. The increase in both these temperatures produced by the laser absorption produces the OG effect through different processes. In the CO_2 molecular discharges the translational temperature increase affects the discharge current through a change in the elctron mobility. In the NH_3 discharges where OG effects with different signs were observed, both the translational and vibrational temperatures modify the current discharge. For instance the vibrational temperature modifies the electron attachment: because the excited vibrational levels have a larger attachment cross-section, a vibrational excitation produces a negative OG signal. However a more precise knowledge of the molecular discharge processes is required to interpret completely the experimental observations and further measuremens may provide additional information on the molecular plasma diagnostics.

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RESONANCE IONIZATION SPECTROSCOPY

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In the past decade techniques have been developed, in a widespread area of fundamental as well as applied research, for detecting the presence and observing the behavior of single atoms of a given species in a given state of excitation. A method for selective counting at the one-atom level is an outstanding need in the modern analytical studies. Starting with the limit of conventional analytical sensitivity, e.g. 10^8-10^{10} atoms or molecules, as the limiting sensitivity increases (for example 10^4 atoms can be detected) the number of analytical applications also increases. Below 10^4 atoms new features appear; namely the atomic fluctuations begin to be detectable and a whole new class of studies becomes possible. If the sensitivity is increased to the ultimate single atom limit, the possibility of detecting very rare species become feasible.

From its beginning the Resonance Ionization Spectroscopy has been recognized as a method for the ionization of matter which allow an absolute measurement of the number of excited atoms in a specified volume of space, is spectroscopically selective and has one-atom detection sensitivity. Prior to the development of this method for sensitive analytical purposes, similar laser ionization schemes were proposed for the separation of the isotopes.

Several review papers have been published to provide full information on the method and the use of various laser methods for sensitive detection of atoms /1/.

In the Resonance Ionization Spectroscopy multifrequency laser radiation with laser pulses on the order of $1 J/cm^2$ of beam area, is used for resonant selective ionization of atoms, with a quantum yield close to unity. The photoelectron or photoion produced are registered by an appropriate method. An increase in sensitivity and detection limit nearly equal to a single atom is obtained if the recorded current is amplified by operation of a current multiplier, as if the photoionization occurs in a proportional counter, or an electron multiplier is used.

The method of the stepwise atomic ionization by laser radiation is best suited to selectively ionize atoms (or molecules). In this method the atoms are excited by laser radiation to an intermediate state in one or several steps and then the excited atoms are photoionized. Since the process of atomic excitation to intermediate levels is resonant, moderate intensities of laser radiation are necessary to saturate appropriate transitions, i.e. to excite effectively the atoms. The saturation condition is particularly critical for the last quantum transition from an intermediate

state to the ionization continuum. There are three basic methods shown in Fig 1 which are suited to ionize atoms from the last intermediate state. *Non-resonant photoionisation:* in this method the excited atom is ionized by an additional laser pulse or a laser pulse used in one of the resonant excitation steps. Such nonresonant photoionization is characterized by relatively low cross sections $\sigma_{ion} = 10^{-17} - 10^{-19}$ cm^2, compared to the cross sections of the resonant excitation of intermediate levels $\sigma_{exc} = 10^{-11} - 10^{-14}$ cm^2. *Ionisation by electric field:* in this method the atom is excited from an intermediate state to a Rydberg (high-lying) rate and then is ionized by an electric field. The Rydberg atoms have an unique ability of being ionized rather easily in an electric field irrespective of their type. It is very convenient to act on the atom by an electric field pulse after the laser pulse is over. In this case the process of atomic excitation is not complicated by Stark shift and splitting of the last high-lying level. *Excitation of an Autoionizing State:* A possibility to increase the cross section of atomic photoionization is excitation to an autoionizing state at the last step. For multielectron atoms such states may be sufficiently narrow and the cross section of such an autoionization transition may exceed that of nonresonant ionization by several orders.

If we investigate the resonant ionization through nonresonant photoionization in a simple two photon scheme as that depicted in Fig. 1, we suppose that a pulsed laser provides a constant flux equal F during its pulse width T , so that the total laser fluence is ϕ=FT, in resonance with the transition from the ground state 0 to the first excited state 1, If γ is the rate of spontaneous emission from the state 1, β is the rate of destruction of state 1 due to all the collision processes, and σ_{ion} is the ionization cross section, the saturation of the ionization, i.e. each atom which was in the volume of laser excitation before the laser pulse is converted to an ion pair during the laser pulse, is obtained if:

$$\sigma_{ion} F >> \gamma + \beta; \qquad \sigma_{ion} \phi >> 1$$

Five different schemes involving different laser have been proposed to selectively ionize each element in the periodic table. The schemes are reported in Fig. 2.

Most of the early work reported on one-atom detection has involved the detection of single electrons created by a laser in a proportional counter. However the proportional counters require gases of selected properties for their operation, as argon and methane in appropriate relative pressures. Other particle detectors are available which can be used to count individual charged particle (electrons, negative ions or positive ions) with nearly 100% efficiency, and they work at pressures below 10^{-5} Torr. Positive ion detectors eliminate the noise problems associated with the phctoelectrons produced by the laser interactions with window materials. In fact in an experiment on the selective detection of the Xe atoms a simple version of a quadrupole mass filter was used /2/, and later work has made use of a time of flight mass spectrometer /3/.

The final detection sensitivity of this scheme as well of other schemes using the selective laser excitation of atoms has enabled to count one cesium atom in a $10^{-9}/cm^3$ background of argon and methane /4/ and small numbers (100-1000) of rare gas atoms of any selected isotope in isotopic background of up to 10^{15} /5/.

The application of the method to molecular spectroscopy is more difficult, because the molecules usually spread into many different vibrational and rotational sublevels, which cannot collectively be excited with one laser source. The combination of supersonic molecular beam to a multiphoton ionization process has allowed to detect with high sensitivity alkali aggregates /6/.

A practical application of the resonance ionization spectroscopy was made by using laser beams in proportional counters to detect Na impurity atoms in electronics grade Si /7/. The combination of tunable dye lasers and time-of-flight mass spectroscpy has been used for the identification and characterization of the labile molecules like organometallics used in the Metal Organic Chemical Vapor Deposition or the Laser Chemical Vapor Deposition /8/.

In the laser ionization experiment ions and electrons are produced through the laser absorptions and are collected by an external field. The electron and ion densities, hence the collection efficiency, depend on the balance between the production and loss mechanisms. The diffusion to the walls, the recombination and attachment processes are the main loss channels. We have investigated these loss rates by monitoring how the buffer gas collisions modify the ionization rate in a experiment on cesium atoms involving the two photon excitation via the resonant 7P states /9,10/. In fact if a π light illumination is used, an alignment in the excited 7P state is produced and the alignment is destroyed in the relaxation through the collisions. The dependences of the ionization signal on the buffer gas pressure provides a measurement of the disalignment cross section. In the experiment it resulted that the ionization signal was greatly affected by the recombination and attachment processes, so that the analysis of the experimental results was based on

the ratio R of the ionization signal via the $7P_{3/2}$ and $7P_{1/2}$ states. In a separate experiment the modification in the laser produced initial density of electrons and ions because of the diffusion, attachment and recombination processes was monitored. The electron and ion densities produced by the laser excitation at the initial time t=0 of the laser pulse, evolved in an electric field-free regime until at time t an electric field was applied at two electrodes and the remaining charges were collected.

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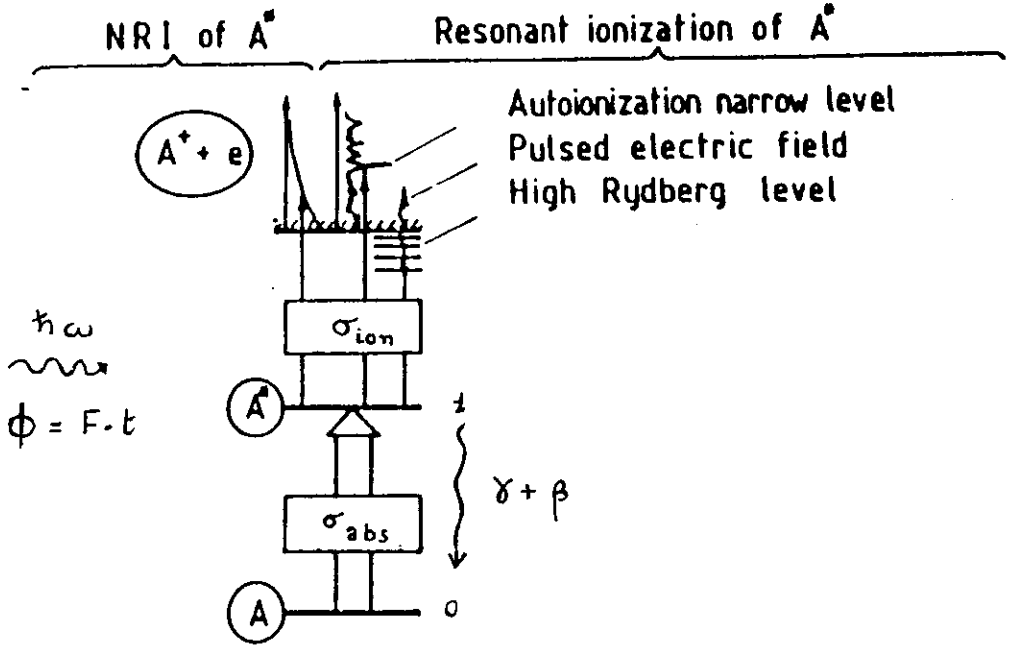

Fig. 1

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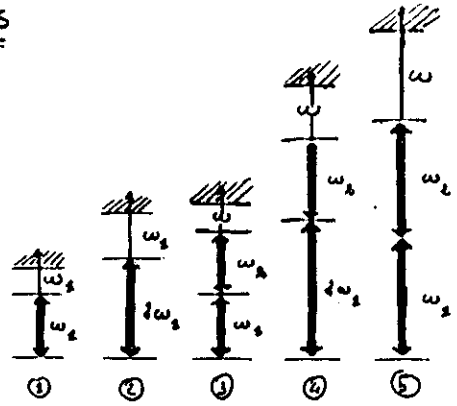

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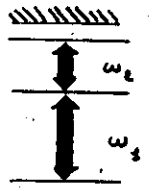

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$A + \omega_1 + \omega_2 + A \rightarrow A_2^+ + e^-$

$A + \omega_1 + \omega_2 + B \rightarrow A^+ + B + e^-$

$A + \omega_1 + \omega_2 + B \rightarrow AB^+ + e^-$

$A + \omega_1 + \omega_2 + M \rightarrow A + M^+ + e^-$

Fig. 2