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LASER EXCITED OPTOGALVANIC TRANSITIONS IN NEON

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Abstract

Laser-excited optogalvanic transitions have been recorded for neon in the near ultraviolet and visible regions of the electromagnetic spectrum and are explained in terms of processes that affect the population of atoms in metastable states. These optogalvanic transitions have been used for direct calibration of laser wavelength so as to facilitate interpretation of laser-induced fluorescence spectra of free radicals.

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 by Penning,[1] who observed that the impedance of a neon discharge tube changes when illuminated by a second neon discharge tube. 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]

Smyth and Schenck[4] have extensively discussed the processes that contribute to ionization discharge and the role of metastable populations in producing secondary ionization, and suggested that the waveform polarity of the OG signals was current-dependent. Erez et al.[5] 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 (as illustrated in Fig. 1) excited within the discharge and at the same time be able to accomplish precise and reliable calibration of laser-induced fluorescence excitation spectra of free radicals.

Experimental

A dye laser (Spectra Physics PDL-3) was pumped by an excimer laser (Impulse 4530GL, Questek) or a Nd:YAG laser (Spectra Physics GCR-11) running at 10 Hz. The output dye beam had a pulse duration of about 15-20 ns and a nominal linewidth in the range 0.07-0.2 cm^{-1}. An uncoated quartz wedge was inserted in the optical path of the primary beam to pick off two weak beam (each about 5% of the primary pulse energy). One of the beams (unfocussed and of typical pulse energy 100 μJ) enters the cathode of a commercial iron-neon hollow cathode lamp as shown in Fig. 2. The second beam traverses a negative lens and illuminates an uncoated, parallel-faced 6 mm thick quartz disk at a small angle of incidence (1-2 deg) which serves as a low-finesse etalon. The interference pattern, generated by the reflection beams from the front and rear surfaces of the disk, is recorded by a photodiode. 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). Temporal evolution of the OG signal was recorded by a digital oscilloscope (Model 9410, LeCroy). The outputs of the boxcar and the photodiode were recorded with a microcomputer-aided data acquisition system. The OG signal and the interference fringes were recorded simultaneously to facilitate calibration of excitation spectra of free radicals. Fig. 3 in turn shows the experimental arrangement used to record the laser excitation spectra of jet-cooled free radicals (such as OH and CH_3O). Free radicals generated by excimer laser photolysis of suitable precursors (e.g. HONO for OH and CH_3ONO for CH_3O) in a supersonic expansion were excited with a frequency-doubled (Spectra Physics GCR-11) Nd:YAG-pumped tunable dye laser (Spectra Physics PDL-3). Fluorescence excitation spectra for the free radicals were recorded by scanning the dye laser wavelength. The signals were accumulated and averaged by a boxcar integrator (Stanford Research Systems Model 250) in conjunction with the microcomputer-assisted data acquisition system. High resolution rotationally-resolved laser-induced fluorescence spectra of the jet-cooled radicals obtained in this manner were accurately calibrated with simultaneously recorded OG neon transitions and etalon fringes, as illustrated in Fig. 4 in case of the OH radical.

Results

In the work reported here, of the 351 OG transitions observed in the 337-598 nm wavelength region, 29 OG transitions that originate from the first excited state of neon have been specifically identified. 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]°2 metastable level, which may have the highest 3s excited state population. This is probably due to the fact that photon excitation from the 3s levels (i.e. $^3P_{0,1,2}$ and $^1P_1$ states) to 3p levels (as indicated in Fig. 1) is subsequently followed by relaxation back to the metastable states, which increases the 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 many cases, the

photoinduced voltage change had both positive and negative components because of 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 takes place 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. On the other hand, collisional ionization from the 3p neon levels can be achieved via energetic electrons and will contribute to enhanced ionization following irradiation, which accounts for the negative voltage component of OG transitions associated with metastable states of neon.

The wavelength position between OG transitions can be determined by counting the interference fringes that were recorded simultaneously with the OG and LIF signals (see Fig. 4). The free spectral range of the etalon can be determined by dividing the wavenumber difference between OG transitions by the total number of fringes present between the two neon transitions. It was possible to calibrate the excitation spectrum of OH via fringe counting and thereby to precise determination of the unknown wavelengths and assignment of the rotationally-resolved transitions as indicated in Fig. 4. Thus, a hollow cathode Fe-Ne discharge tube can be used to calibrate precisely the wavelength scale of tunable dye lasers in the near UV and visible regions of the electromagnetic spectrum.

Acknowledgments

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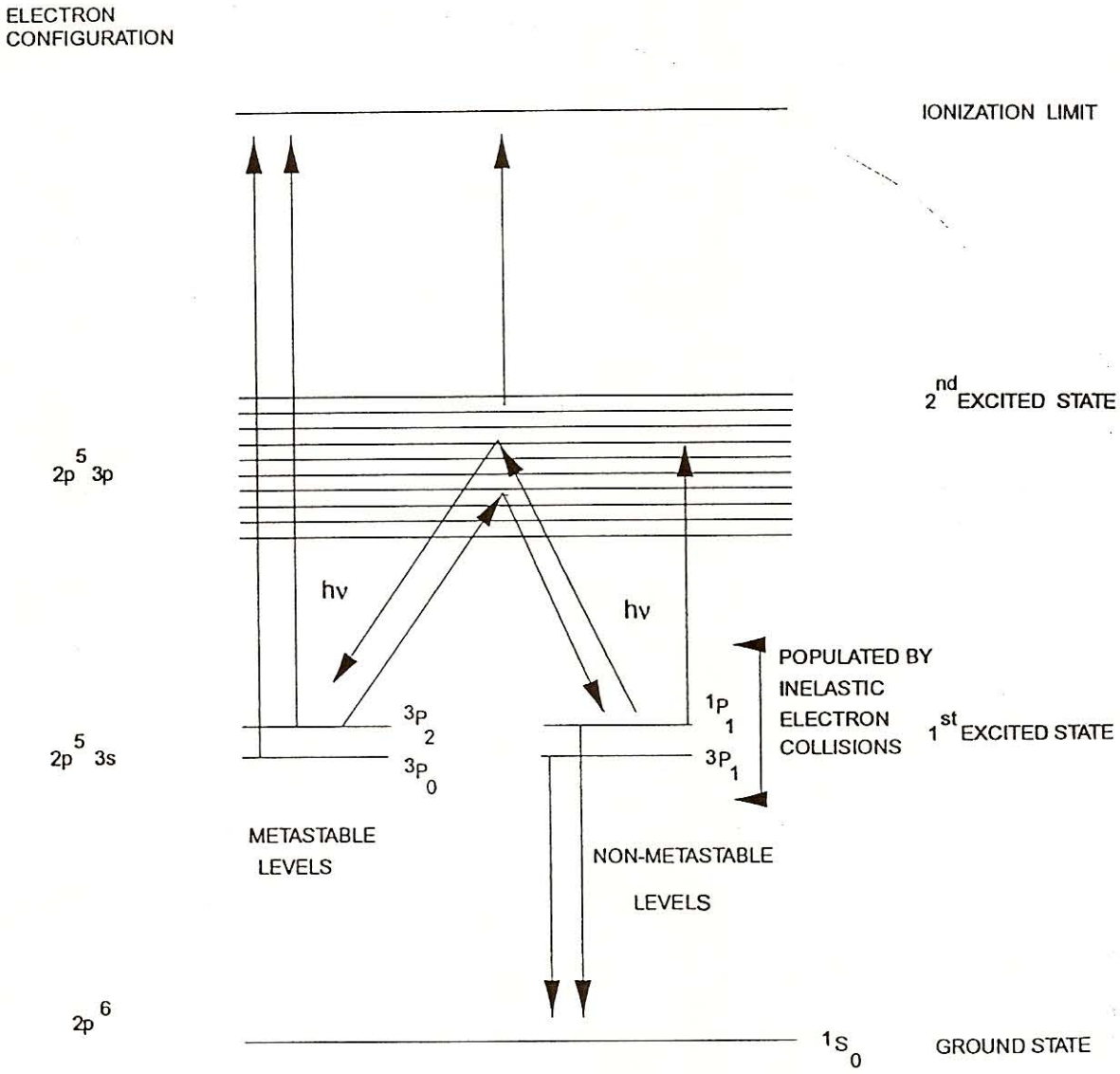

Fig. 1. Energy level schematic explaining the optogalvanic ionization mechanism.

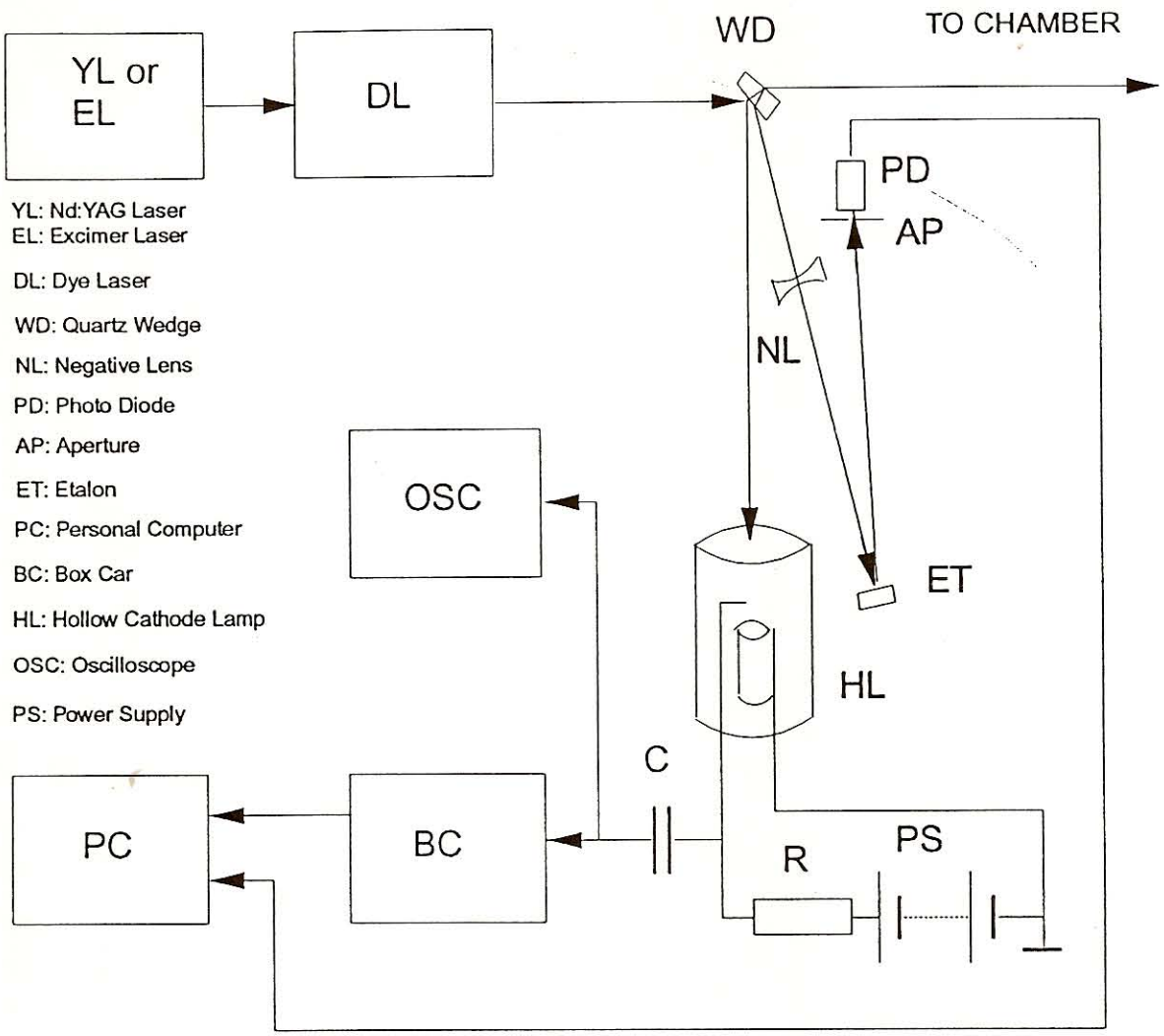

Fig. 2. Experimental arrangement for recording laser optogalvanic transitions of neon.

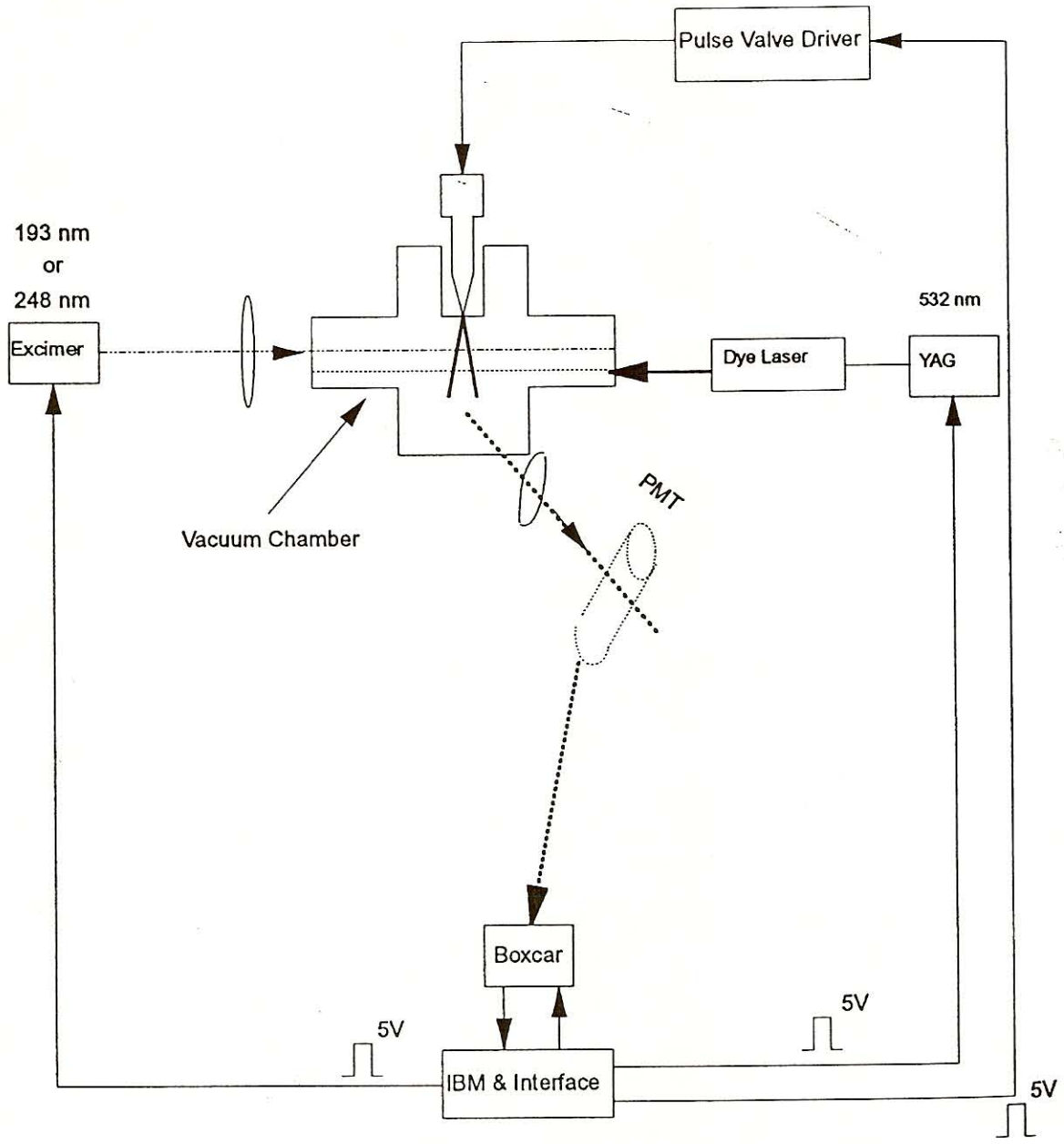

Fig. 3. Experimental arrangement for recording laser excitation spectra of jet-cooled free radicals.

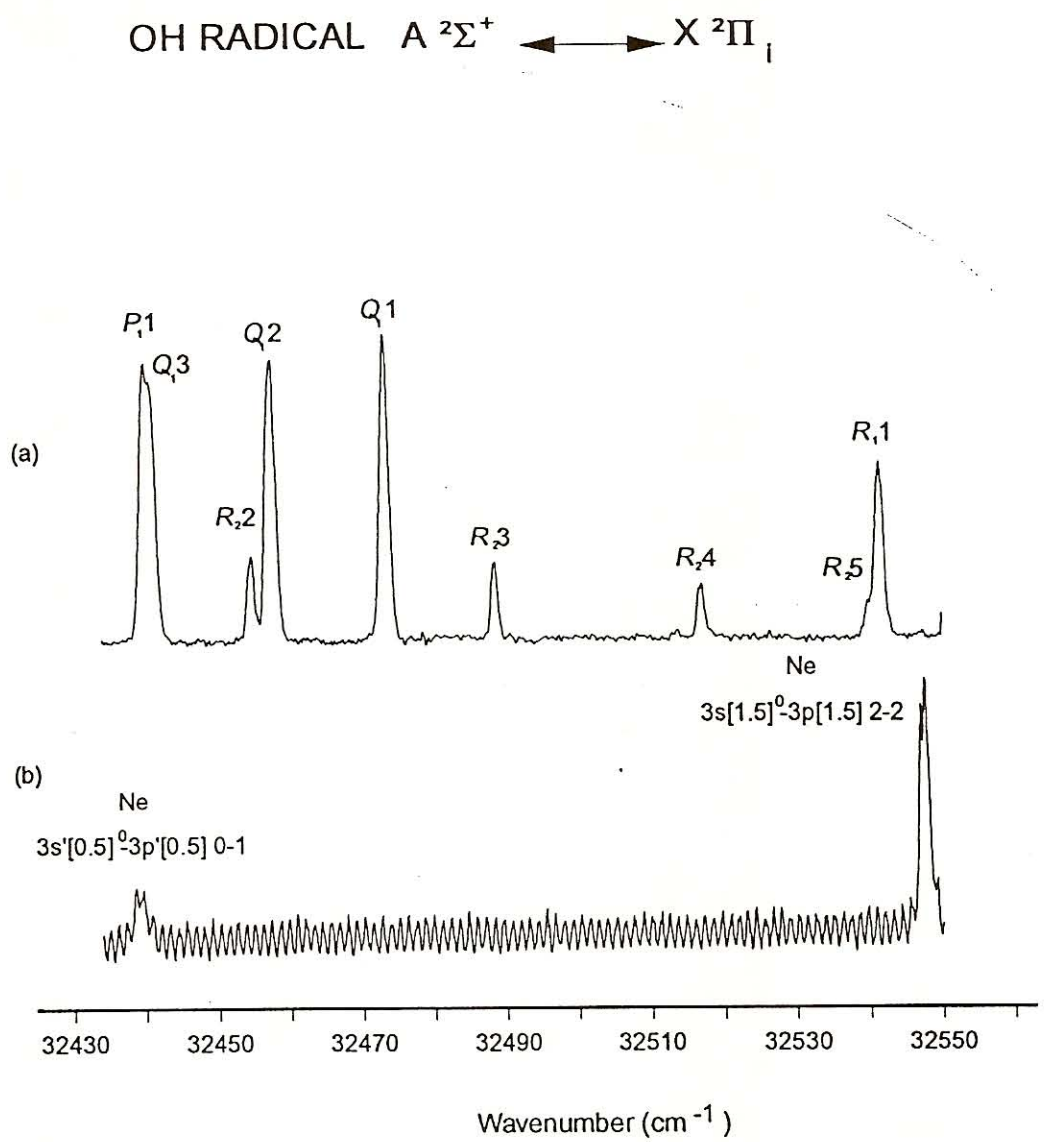

Fig. 4. (a) Rotational transitions of the A $^2\Sigma^+ \leftrightarrow$ X $^2\Pi_i$ (0,0) band of the OH radical. (b) Identified neon transitions and etalon fringes used for OG calibration of spectrum (a).