OPTOGALVANIC LASER SPECTROSCOPY

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LRAP-5

CONTENTS

1. Introduction

During the last years a number of non-optical detection methods have been developed in laser spectroscopy. Compared to optical detection methods these have the advantage of being free from the potentially strong back-ground associated with stray-light from the laser beam. One of these methods is opto-galvanic (OG) spectroscopy. OG detection registers the increase in discharge current occuring when the ion production in a discharge is enhanced by optical excitation. This effect was observed already in 1928 when Penning irradiated a Ne tube with light from a second Ne discharge (1). The effect was however not subject to more thorough studies before the middle of the seventies. By this time publications on OG spectroscopy in discharges (2) and in flames (3) began to appear from the National Bureau of Standards, USA. The number of publications in the fields has after this risen exponentially.

In this paper the optogalvanic effect has been investigated from three different points of view:

In a Ne-Ba hollow cathod using pulsed laser light.

In a Ne-Ba hollow cathod using a CW laser.

In a discharge column using a CW laser.

The measurements made in this work are mainly qualitative and only qualitative conclusions are drawn.

3. Observation of some optogalvanic features in a Ne-Ba hollow cathode using pulsed laser light

Our first experiments with the optogalvanic effect were performed with a pulsed laser acting on a hollow cathode lamp. First the experimental set up will be described. Then the measurements and the mechanism of Ne ionization will be briefly discussed.

a. Experimental set-up

The experimental set-up is shown in Fig. 1. A nitrogen laser pumping a dye laser was used. The nitrogen laser had a peak power of 200 kW, a pulse length of 8 ns and was operated at a repetition rate of 5 Hz (optimum pressure 60 torr). The light from the nitrogen laser was irradiated on a dye cell in a dye laser of Hänsch design (5), operated without any intra-cavity etalon at a line-width of about 0.1 Å. At the peak of Rhodamine 6 G the output power was some ten kW and the FWHM was 5 ns. The diffraction grating was coupled to a stepping motor and could be continuously scanned yielding a sweep of 1.5 Å/min. or faster.

By using a boxcar integrator with adjustable sample and delay time (Princeton Applied Research Model 162) the optimum sample time for the Ne transition $1s^2 2s^2 2p^5 3s^3P_2$ - $1s^2 2s^2 2p^5 3p^3S_1$ (λ=5881.9 Å) was found to be 5µs with a delay of 0.2µs. In the subsequent measurements a Lambda Physik Model LF 300 boxcar integrator was used. By an adjustment of the internal electronics the fixed sample time of 50µs was changed to 5µs. An amplifier between the hollow cathode and the boxcar integrator was used

mainly for impedance matching. For studying Ne lines a positiv lense was adjusted to make the laser beam fit exactly into the cathode opening. To minimize disturbance from electrical fields the hollow cathode was mounted in a metal box (Appendix A). To eliminate electrical noise from the laser power supply the hollow cathode and the detection equipment was moved into a different room, 10 m away from the laser. The 5 Hz trigging rate was synchronized with the line voltage which practically eliminated the 50 Hz ripple.

b. Measurements and discussion of the results

With this set-up the wavelength interval 5760 Å to 5940 Å was scanned using Rhodamine 6G as a dye. A recording of the corresponding optogalvanic signal is shown in Fig. 2-4. At the used hollow cathode current (11.5 mA) all transitions except λ=5852 Å show an increased current when the laser is tuned to the transition. The lines λ=5852 Å, λ=5882 Å and λ=5945 Å all arise from the lowest configuration ($2p^5 3s$) above the ground level. These three transitions had a very characteristic behaviour compared to the others between higher excited states. If the laser wavelength corresponded to the $2p^5 3s\,^1P_1$ - $2p^5 3p\,^1S_0$ (λ=5852Å) transition the discharge current decreased. This transition was the only one who showed this behaviour and it occured for all currents below 12 mA. The reason for this is probably due to a low probability for ionization by collision for the spherically symmetric $^1S_0$ stage. The sign and the strength of the signal varies completely between hollow cathodes of different designs. Compare e.g. (7-8, 14-17). The two lines λ=5882 Å and λ=5945 Å originate from the metastable $2p^5 3s\,^3P_2$

state and showed extremely strong signals (0,7 V) directly on the oscilloscope. This should be compared with an average signal about 0.02 V for the other transitions.

A picture of the λ=5882 Å signal is found in Fig. 5. This is the transition $2p^5 3s\,^3P_2$ - $2p^5 3p\,^3S_1$. From $2p^5 3p\,^3S_1$ the electrons can either return to the metastable states ^3P_o or $^3P_2$ or via $^3P_1$ return to the ground state. That is if the atom does not get ionized by collision. When the atom at first gets excited there is a competition between radiative decay and ionization by collision. This is in correspondance with the observation that at lower discharge currents the signals get weaker. This means that the collisions between Ne and e^- get less frequent and more atoms decay by radiation. The length of the positive period of the signal should then depend on the lifetime in the excited state, the collision rate, the ionization probability and the transit time in the hollow cathode. After a while the number of Ne^+ atoms that absorb an electron exceed the number of atoms that get ionized by collisions and the signal turns to be negative. For the higher transitions there is a correspondance between the signal strength and the pulse length. When the signal strength increases with a factor three the pulse length increases around a factor two. This is a reasonable result. The more Ne atoms the longer time it should take until all of them have absorbed an electron. The uncertainity in these measurements is large since the data are only estimations from the signal on the oscilloscope. Qualitative conclusions can, however, be drawn from the material.

In Fig. 6 the result from a scan with higher speed on the paper recorder is shown. On the vertical scale the position of the signal on the paper in mm is given and on the horisontal scale its wavelength according to (6) is indicated. The observations can with high accuracy be fitted to a smooth curve. This is however not straight line since the scanning speed is wavelength dependent.

4. Observation in a Ne-Ba hollow cathode using a CW laser

This section will contain a description of the behaviour of the resonance line $6s^2\ ^1S_0 - 6s\ 6p\ ^1P_1$ (λ=5535 Å) in Ba as a function of the discharge current and laser intensity. Some exploitations of the optogalvanic effect in hollow cathodes will also be mentioned.

The experimental set-up shown in Fig. 7 was used. The argon ion laser was operated in green and in the dye laser rhodamine 110 was used. A Princeton Applied Research HR-8 lock-in amplifier, operated at a chopping frequency of 125 Hz was employed. From Fig. 8 it can be seen that both the signal from photoionization and the effect from the excitation of the Ba line are approximately proportional to the number of photons. The collisional ionization due to the Ba line excitation rises somewhat faster though. This is probably due to the fact that this signal also contains a term proportional to the square of the excited Ba- concentration rising from the reaction $Ba^* + Ba^* \rightarrow Ba^+ + e^-$ where Ba^* is the excited Ba-atom. In Fig. 9 the same parameters are shown as a function of the discharge current.

For currents between 3.0 and 5.5 mA the hollow cathode burns very irregularly and no signals could be obtained through the background noise. Between 5.5 and 11.5 mA the λ=5535 signal is proportional to the number of photons and the constant of proportionality has a value close to unity. The background decreases slightly with increasing current. This might depend on the fact that the effective lifetime for the Ba^+ and Ne^+ ions decrease. For

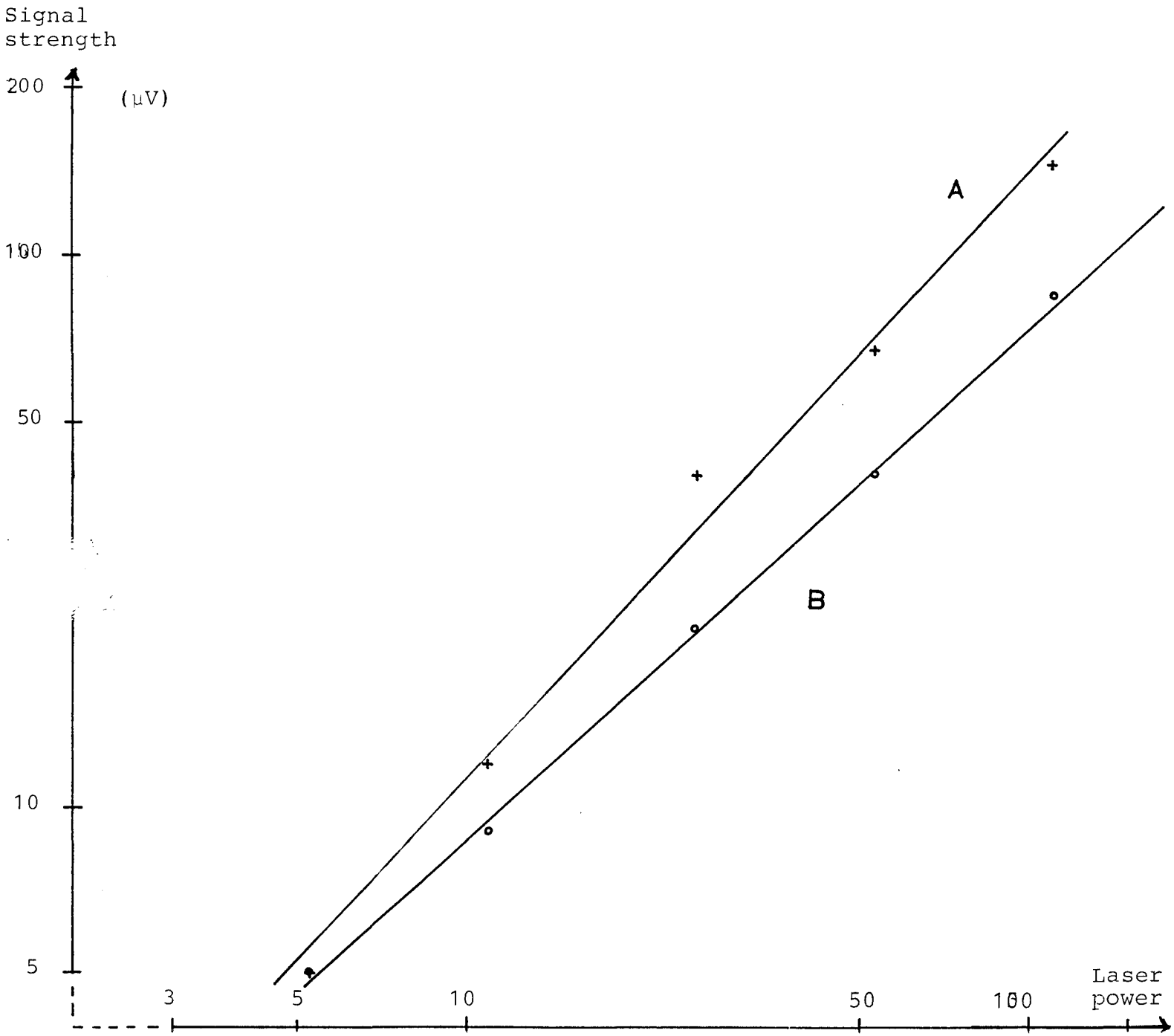


Fig 8

The signal from collisional ionization (A) and photo-ionization (B) as a function of laser power. λ=5535, the first resonance line in Ba.

currents close to the minimum current 1.5 mA the background is about 200 μV which is considerably higher than the actual signal (20 μV). At this current the voltage over the hollow cathode has decreased from around 118 V at 5.5 - 11.5 mA to 100 V. In Fig. 10 the photoionization from a scan over the entire range of Stilbene 3 is shown. A CR 699 ring laser pumped by a CR 3000 K krypton ion laser was used in multi-mode operation. The output power at the peak of Stilbene 3 was 250 mW. An extrapolation in Fig. 8 would give a background of 250 μV. However, in this scan the maximum background is 56 mV. This shows that optogalvanic detection in the blue region might be complicated.

In (4) there is an excellent presentation of the possibilities and methods of optogalvanic spectroscopy. Three possible applications will here be briefly mentioned. As is clear from this work optogalvanic spectroscopy is useful for elucidating collision mechanisms. There are also possibilities to calibrate dye lasers when scanning over long wavelength intervals by using optogalvanic lines from, e.g. a hollow cahtode. Since the signal in optogalvanic spectroscopy is electric, this can be used to lock a dye laser to a specific transition in an easy way by a system for automatic control.

index for air at 4500 Å. This gives a wavelength in air of 4471.5 Å. To find the line one could watch a He lamp through a small spectroscope and tune the Lyot filter of the laser till the laser line overlapped the line from the corresponding transition in the He lamp. (The laser was run in multi-mode operation in the first tests.) After a little scanning around this position the transition was found and could easily be seen on the oscilloscope.

For making a recording it was necessary to insert the intra-cavity assembly (ICA) and use the electronic control equipment of the ring-laser. When the ICA is inserted it is not possible to make a continuous scan with the Lyot filter since a mode-hop occurs every 10 GHz on the thick etalon. To find the line the Lyot filter was first roughly aligned with help from the Lyot filter curve in the laser manual. The laser wavelength was then determined by the λ-meter and by going from one Fabry-perot resonance to the other on the thin etalon (free spectral range 225 GHz, about 1.1 Å) by adjusting the Lyot filter followed by off-setting the thin etalon. The transition fell into the manual scan region of 30 GHz. 30 GHz corresponds at this wavelength to 0.2 Å. A scan over the line is shown in Fig. 12. Without any special efforts a signal of 0.6 V with a signal to noise ratio of about 30:1 could be obtained directly on the oscilloscope. The input light power to the tube then was about 20 mW.

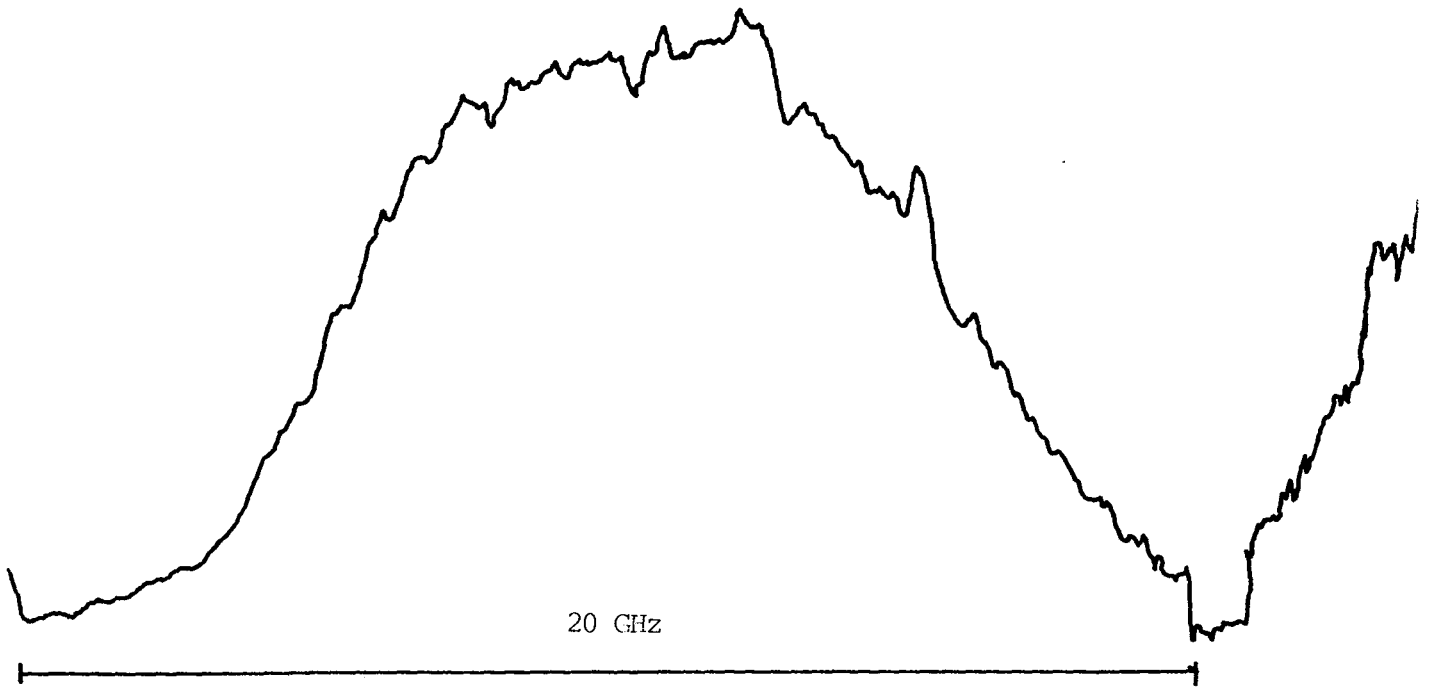
b. The Doppler-free transition

In order to obtian a Doppler-free spectrum it is necessary to have a laser of very sharp frequency, i.e. a single-mode laser.

Consider an atomic level with an energy $E=h\nu$. Suppose there is a higher level $E'=h\nu'$, where $\nu'-\nu=\nu_0$. In Fig. 13 a the number of atoms as a function of v_x (the velocity in the x-direction) can be seen for the upper and lower level. If a laser with a frequency $\nu_1=\nu_0+\Delta\nu$ is irradiated along the $\hat{x}$-direction only those atoms with a certain velocity in the $\hat{x}$-direction get excited. It can easily be shown that the relation between the atomic velocity component in the direction of the propagation of the light (v) and the offset frequency ($\Delta\nu$) is $v=c\frac{\Delta\nu}{\nu_0}$. Around 5000 Å with $\Delta\nu$=1 GHz this gives v = 500 m/s. The population in the lower level will when the laser interacts with the media look as depicted in Fig. 13 b. If the laser beam is chopped with a frequency $f_1=\frac{\omega_1}{2\pi}$ it will in a discharge be possible to detect an optogalvanic signal on this frequency. Now, if there is a beam with the same frequency propagating through the discharge in the opposite direction, this beam will interact with atoms with a velocity v_x'. The population in the two levels will then look as depicted in Fig. 13 c. This second beam is chopped with a frequency $f_2=\frac{\omega_2}{2\pi}$. It is now possible to detect a signal on both the frequencies f_1 and f_2. If the beams overlap a special case will occur when the laser frequency is at the line center ($\nu_1=\nu_0$). Both beams will then interact with the same atoms (those with $v_x=0$). It will then but only then arise signals on the frequencies f_1+f_2 and f_1-f_2 (see appendix F). These signals then are Doppler-free and that broadening only depends on the natural linewidth and the linewidth of the laser.

The experimental set-up is showed in Fig 15. The construction of the 800 Hz chopper is described in Appendix B. The construction of the mixer and the filters is described in Appendix C and Appendix D, respectively. The set-up is very similar to the one described in (11). However, there are some differences, e.g. the 50 kΩ resistor between the HeNe tube and the capacitor. This was inserted since the discharge turned out to be very sensitive to capacitive load. Since the Doppler-free signal is proportional to the square of the laser intensity it is advantageous to focus the beams as is indicated in Fig. 11.

In these last measurements we noticed that on the sum frequency there appeared a Doppler-broadened signal of about 50 mV directly on the oscilloscope. The Doppler-free signals could not be resolved with any significance, Fig. 16. This effect can be explained as follows. If the laser has the frequency $\nu_1 = \nu_0 + \Delta\nu$ a group of atoms with a certain velocity will be excited to 4^3D. 4^3D in He, however, lies close enough to the ionization-limit to be ionized by a λ=4472 Å photon from the other laser-beam. Unfortunately this process does not select atoms with a certain velocity and furthermore, since every ionization creates a free electron this process gives a large contribution to the optogalvanic signal since it in optogalvanic spectroscopy is the creation of free electrons that is detected. From this observation it can be concluded that optogalvanic spectroscopy in general cannot be very favourable if energetic photons have to be used.



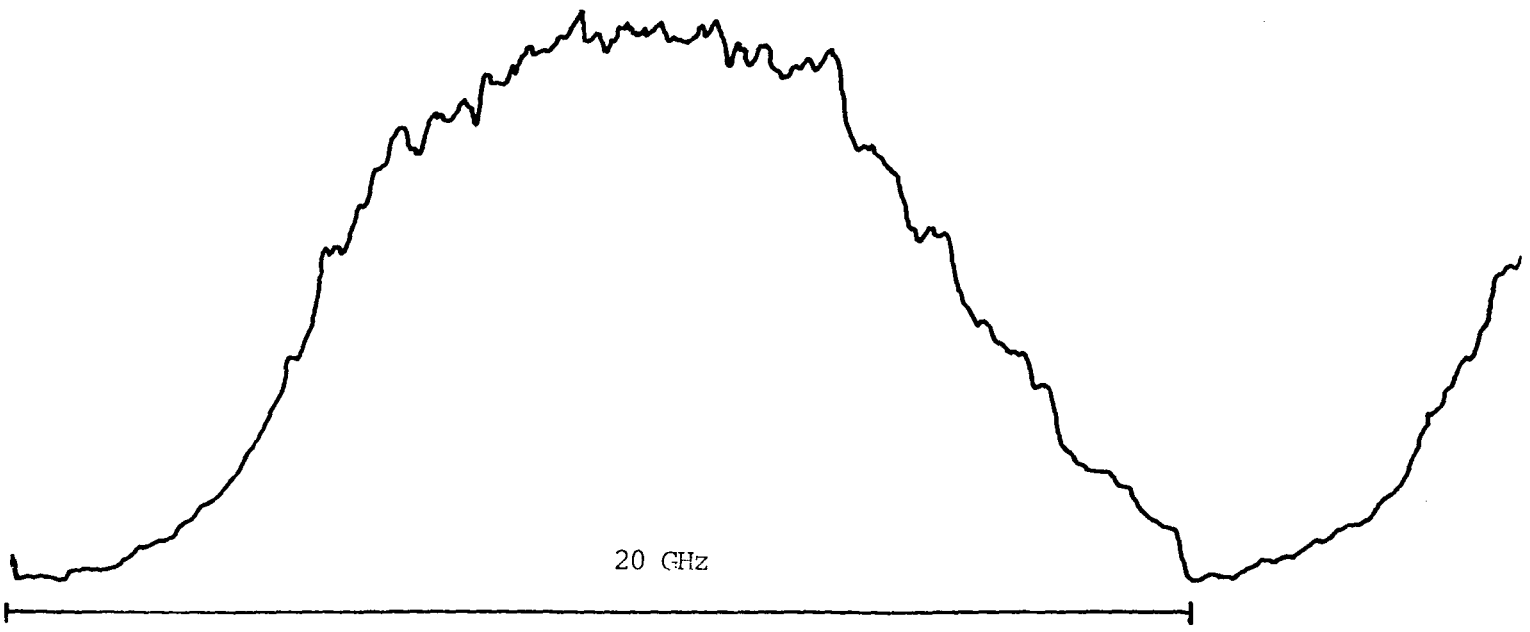


Fig 16
Optogalvanic signal from the 2p ^{3}P - 4d ^{3}D transition in He obtained at detection on the sum frequency (850+125 Hz) of the choppers.

Appendix C

In order to get the sum (or difference) frequency of the reference signals from the two choppers a mixer was built. This had as its main element a μA 796 modulator/demodulator circuit. This was completed with the components shown in Fig. C1. The output $+V_0$ from this circuit was then connected to a resonance circuit (Fig. C2) to chose (depending on the position of the switch) the sum or the difference frequency. This construction with a passive bandpass filter showed however not to be very favourable. The desired signal could be selected with better precision by using a tunable active bandpass filter described in Appendix D. In Fig. C3 the front panel of the mixer is shown.

Appendix D

Since the Doppler-broadened signal was very strong it migth be advantageous to suppress these frequencies with respect to the sum and difference frequencies. Especially since overload occurred in the lock in the amplifier if the composite signal exceeded the selected intensity more than 1000 times. In Fig. D1 lowpass-, highpass- and bandpass-filters taken from (12) are shown. In the bandpass construction the R_2 resistor was exchanged against a T - network with R_x=2.48 KΩ. The operational amplifiers are of type μA 741. A tunable bandpass filter from 100 Hz to 2000 Hz was also constructed by inserting two 47 K potentiometers instead of R_5 and R_6. By lowering R_x the Q value could be increased to around 50 before the filter became instable.

Appendix F

A brief explanation of how a signal can arise on the sum and difference frequency will be given in this appendix.

$N_0(V_x)$ is the number of atoms with velocity V_x in the x-direction that are in the lower state when the laser beam is blocked.

I_0 is the laser intensity. It is supposed that if there are two laser beams travelling in opposite directions both have intensitiy I_0.

$\frac{\omega}{2\pi} = f$ is the chopping frequency.

$A = \frac{1}{\tau}$ is the transition probability.

$N_u(v_x', t)$ is the number of atoms in the upper state with a velocity v_x' in the x-direction at the time t.

Now consider Fig. 13b. Suppose that the laser is chopped with a frequency f_1

$$\frac{dN_u(v_x',t)}{dt} = (N_0(v_x)-N_u(v_x',t))\mathcal{L}I_0\sin(\omega t) - N_u(v_x',t)\mathcal{L}I_0\sin(\omega t) - AN_u(v_x',t) \quad . \quad . \quad A$$

The chopped laser intensity is described as $I_0\sin(\omega t)$ (this is however not entirely correct, see Appendix G).

It is here also assumed that when the laser is blocked

$N_0(v_x) >> N_u(v_x')$

The first term in Eqv. (A) comes from absorbtion, the second from stimulated emission and the third from spontaneous

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