Lawrence Berkeley National Laboratory

Recent Work

Title

EXCITATION OF SPECTRA OF MULTIPLY-IONIZED ATOMS BY CAPACITOR DISCHARGES

Permalink

<https://escholarship.org/uc/item/1sr0v6qv>

Authors

Deurzen, Cornelius H.H. Van
Conway, John G.

Publication Date

1973-08-01

Submitted to
Applied Spectroscopy

LBL-1975

Preprint *2*

EXCITATION OF SPECTRA OF MULTIPLY-IONIZED
ATOMS BY CAPACITOR DISCHARGES

Cornelius H.H. Van Deurzen and John G. Conway

August 1973

RECEIVED
LAWRENCE
RADIATION LABORATORY

SEP 19 1973

LIBRARY AND
DOCUMENTS SECTION

Prepared for the U.S. Atomic Energy Commission
under Contract W-7405-ENG-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

LBL-1975
2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Excitation of Spectra of Multiply-Ionized Atoms by Capacitor Discharges *

Cornelius H. H. Van Deurzen[†]

Department of Physics and Lawrence Berkeley Laboratory, University of
California, Berkeley, California 94720

John G. Conway

Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

August 1973

ABSTRACT

Spectra of vanadium have been produced in a vacuum sliding spark and their relative line intensities measured as parameters of the electrical circuit were varied. Intensity maxima of the spectral lines are interpreted as representing excitation energies and have been found to depend in a definitive manner on the power delivered to the source and on the duration of the discharge. The differential equation of the circuit is solved for the charge and energy transfer rates from the capacitor to the source, and two functions of the continuous circuit parameter $\gamma \equiv \frac{C}{L} \left(\frac{R}{2}\right)^2$ are defined which greatly assist in interpreting the effect of the circuit parameters on the excitation in the source. A relationship was found between the excitation in the source and the electrical circuit parameters. By means of this relationship one may obtain a good estimate of the excitation gained in the spark source. It is shown that by exercising careful control over the circuit parameters it is possible to separate spectra of neighbouring ionization stages through either total-pulse or time-resolved observations.

* Work performed under the auspices of the U. S. Atomic Energy Commission.

[†] Taken in part, from the doctoral dissertation submitted to the Graduate Faculty of the University of California, Berkeley, May 1973.

I. INTRODUCTION

Perhaps the most widely used method of generating the spectra of higher ionized atomic species is the discharge of a capacitor across a gap between electrodes of the material to be studied. The degree of atomic ionization in such a discharge depends to some extent on the capacitance, inductance and resistance in the discharge circuit and a method of separating the spectra of the various stages of ionization entails the study and exploitation of this dependence. It is desired to establish a definitive relationship between the excitation observed in a spark discharge and the parameters involved in its production.

A long practiced method of obtaining the spectra of higher ionized atomic states is to use a high voltage spark generator consisting of a rather small capacitor ($< 0.1 \mu\text{f}$) charged to a high voltage ($\geq 10 \text{ kV}$), an inductor, and usually an auxiliary gap to trigger the discharge synchronously with the charging cycle. No external resistance is employed in the discharge circuit because for small capacitors the resistance necessary to change appreciably the character of the discharge dissipates a good amount of energy; less energy is delivered to the light source itself causing a reduction in the intensity of the spectra. The discharge is thus oscillatory and although the degree of excitation is affected to some extent by the variation of inductance, it is not possible to obtain the spectrum of one stage of ionization free of its neighboring stages.

Since 1943 three major developments in this type of spectroscopic unit have arisen in attempts to achieve greater control over the discharge through external parameters. In 1943 Hasler and Dietert¹ developed the idea

that by separating the charge and discharge cycles of the capacitor making each independently controllable, breakdown of the gap can be achieved with a low-power high voltage ignitor circuit and a low-voltage high power capacitor discharged through the gap once it has broken down. Several advantages over the previous sparks are: (1) the amount of energy discharge in each cycle is more reproducible, (2) higher capacitances ($\sim 10 \mu\text{f}$) can be used with the lower voltages ($\sim 1 \text{ kV}$) for a given amount of energy, allowing variation from underdamped through critically damped and overdamped discharges, (3) termination of the discharge depends only on the circuit and gap constants, it is no longer affected by the synchronous rotating gap and (4) lower voltages reduces the broadening and shifting of atomic spectral lines caused by the Stark effect which is particularly important for radiation involving levels with large azimuthal quantum number. In 1950 Vodar and Astoin² suggested introducing an insulating surface between the electrodes to facilitate breakdown of the gap - the sliding spark. The chief advantages are: (1) the voltage necessary for the breakdown of the spark gap is reduced, (2) confining the discharge enhances the spectral line intensity, and (3) it operates with large inductances ($\sim 1000 \mu\text{h}$) which is not possible with vacuum sparks. Spacer impurity spectral lines such as carbon, silicon and oxygen are also produced. The third development in the spark was the introduction of an electronic switching circuit consisting essentially of an ignitron triggered by a mercury thyatron to initiate the discharge.³ This allowed still better control over the reproducibility of the current discharge and is essential for synchronization in the time resolution of spectral line intensities within the current pulse.

The present investigation consists of two chief parts: (1) to determine the excitation of different stages of atomic ionization and investigate the circuit conditions that optimize the variation between these stages when observing the total discharge pulses, and (2) to investigate the behaviour of the ionization stages within a given discharge pulse via the time resolution of its light pulse. The intent is to discuss the basic equations governing the discharge of a capacitor in order to obtain a knowledge of the characteristic times involved as well as of the current and power-per-pulse relations in terms of the circuit parameters, the voltage, and the discharge repetition rate. The results will then be correlated with the experimentally observed intensity variations in a discharge incorporating all three of the above developments.

II. MATHEMATICS OF TRANSIENT DISCHARGES OF CAPACITORS

The general mathematics of transient discharges of capacitors has been developed in many texts and with particular application to the study of spectrochemical sources⁴ but the characteristic times involved and the rate of charge and energy delivery to the source in terms of the circuit parameters are not usually discussed. When a capacitor (C), which at the time ($t = 0$) when the current (i) starts, is triggered to discharge through an inductor (L) and resistance (R), the voltages in the LCR circuit sum to give the differential equation

$$L \frac{di}{dt} + Ri + \frac{q}{C} = 0 \quad (1)$$

where $q(t)$ is the charge on the capacitor. The solution of this equation for the current in the circuit as a function of time is

$$i(t) = \frac{V_o}{R} \left\{ \frac{e^{-\frac{R}{2L} \left(1 - \sqrt{1 - \frac{1}{\gamma}}\right)t} - e^{-\frac{R}{2L} \left(1 + \sqrt{1 - \frac{1}{\gamma}}\right)t}}{\sqrt{1 - \frac{1}{\gamma}}} \right\} \quad (2)$$

where V_o is the negative initial voltage on the capacitor and we introduce $\gamma \equiv \frac{C}{L} \left(\frac{R}{2}\right)^2 \geq 0$ as an appropriate circuit parameter, continuous over the region of possible behaviour of the discharge ($0 \leq \gamma \leq \infty$). Three quite different current flows are possible depending on the value of γ : $\gamma < 1$ underdamped, $\gamma = 1$ critically damped, and $\gamma > 1$ overdamped.

A characteristic discharge time is the time (t_p) at which the discharge current reaches its peak value i.e. where the charge transfer from the

capacitor through the circuit for a given interval of time is a maximum. The time t_p may be obtained by putting the time derivative of the current equal to zero and solving for t_p ; the peak current $i_p \equiv i(t_p)$ is then obtained by substituting the value of t_p in Eq. (2). The results are:

$$t_p = \sqrt{LC} g(\gamma) \quad (3)$$

$$i_p = \sqrt{\frac{C}{L}} V_o h(\gamma) , \quad (4)$$

where

$$g(\gamma) \equiv \frac{\tanh^{-1} \sqrt{1 - \frac{1}{\gamma}}}{\sqrt{\gamma - 1}} .$$

$$h(\gamma) \equiv \frac{1}{2} \left\{ \frac{e^{-\left(1 - \sqrt{1 - \frac{1}{\gamma}}\right) \frac{\tanh^{-1} \sqrt{1 - \frac{1}{\gamma}}}{\sqrt{1 - \frac{1}{\gamma}}}} - e^{-\left(1 + \sqrt{1 - \frac{1}{\gamma}}\right) \frac{\tanh^{-1} \sqrt{1 - \frac{1}{\gamma}}}{\sqrt{1 - \frac{1}{\gamma}}}}}{\sqrt{\gamma - 1}} \right\} .$$

The functions $g(\gamma)$ and $h(\gamma)$ are monotonic in γ ($0 \leq \gamma \leq \infty$) and have here been introduced to assist in discussing the effect of the circuit parameters. Their behaviour is shown in Fig. 1. Note that both $g(\gamma)$ and $h(\gamma)$ attain their maximum value as $\gamma \rightarrow 0$; they may thus be viewed as factors which degrade the characteristic time (t_p) and the peak current (i_p), respectively, from their maximum values in a pure oscillatory circuit ($R \equiv 0$). For a fixed LC, $g(\gamma)$ determines t_p and will therefore be referred to as the discharge duration function. The function $h(\gamma)$ is a voltage function in the sense that for given

C/L , the effective voltage for determining the peak current is $V_0 h(\gamma)$. Equation (4) may also be written in the energy form

$$Li_p^2 = CV_0^2 h^2(\gamma) \quad (5)$$

The charge and energy transfer rates may be determined as follows. A measure of the amount of charge transported through the circuit by the time the current reaches its peak value is $i_p t_p$ which may be expressed in terms of the initial charge on the capacitor and γ as

$$i_p t_p = CV_0 h(\gamma) g(\gamma) \quad (6)$$

and is a maximum as $\gamma \rightarrow 0$ for fixed CV_0 . A measure of the rate of energy transfer from the capacitor to the circuit containing the spark gap can be obtained by considering the time interval τ_f between the times ($t_{\pm}$) that the current is a given fraction (f) of its peak value. From Eq. (2) and the definition of f , one obtains

$$f \equiv \frac{i(t)}{i(t_p)} = e^{\sqrt{\gamma} g(\gamma)(1-r)} \frac{e^{\theta r} - e^{-\theta r}}{e^{\theta} - e^{-\theta}} \quad (7)$$

where $\theta \equiv R(1 - 1/\gamma)^{1/2} t_p/2L = (\gamma - 1)^{1/2} g(\gamma)$ and r is the double-valued ratio $t_{\pm}/t_p$ for a given current pulse. A measure of the power in any current pulse may thus be expressed as

$$i_p V_0 = \frac{CV_0^2}{\sqrt{LC}} h(\gamma) = \frac{CV_0^2}{\tau_f} h(\gamma) g(\gamma) \frac{\tau_f}{t_p} \quad (8)$$

where in the expression on the right, $\tau_f/t_p \equiv (t_+ - t_-)/t_p \geq 0$ is the solution obtained from Eq. (7) for given γ and f .

Equations (3) - (8) are useful in discussing charge and energy transfer rates in terms of i_p and t_p , for given L , C , R (or γ for fixed C/L) and V_o which together uniquely determine the discharge pulse. The above equations were solved for the range $10^{-4} \leq \gamma \leq 10^3$ and the results for $f = 1/2$ are presented in Fig. 1. In the case $\gamma < 1$, calculations were made for the first current pulse in the oscillatory train; the calculations for following pulses in the train are straight forward. When γ is outside the range plotted in Fig. 1 or when $\gamma \approx 1$, the expressions presented in Fig. 2 for the limits of Eqs. (3) and (4) are applicable. It should be noted that in the limit when the resistance added to the circuit approaches zero, the resistance of the spark gap and the resistance corresponding to r.f. radiation losses are no longer negligible and must be taken into account. For a discussion in the underdamped case see Ref. 4. Consider now the three various current discharges possible.

A. Underdamped Discharge ($\gamma < 1$)

In this case $(1 - 1/\gamma)^{1/2}$ is imaginary and the equations are more appropriately written

$$i(t) = \frac{V_o}{\sqrt{1-\gamma}} \sqrt{\frac{C}{L}} e^{-\sqrt{\frac{\gamma}{LC}} t} \sin\left(\sqrt{\frac{1-\gamma}{LC}} t\right), \quad (9)$$

$g(\gamma) = \tan^{-1}(1/\gamma - 1)^{1/2}/(1 - \gamma)^{1/2}$, and $h(\gamma) = \exp[-\gamma^{1/2} g(\gamma)]$, where the identities $\tanh(ix) = i \tan(x)$ and $\sin[\tan^{-1}(x)] = x/(1 + x^2)^{1/2}$ have been used. When at least one of the three LCR circuit parameters is known for such an oscillatory current discharge, the effective values of the remaining parameter(s) may be determined by measuring the decay ratio (D) of two consecutive current maxima and/or their time separation (Δt). The necessary

equations may be obtained by evaluating Eq. (9) at two consecutive values of $t_p = (LC/1 - \gamma)^{1/2} n(2\pi)$ where n is an integer and taking the ratio of the resulting peak currents. The results are

$$D = e^{-\frac{2\pi}{\sqrt{\frac{1}{\gamma} - 1}}}$$

$$\Delta t = 2\pi\sqrt{LC} \left(\frac{1}{1-\gamma}\right)^{1/2}.$$

Since D and Δt are functions of LC and γ , the solutions of these equations together with one known circuit parameter and V_0 define the discharge pulse. It is of interest to note (Fig. 2) that as γ decreases from unity both t_p and $2(L/C)^{1/2} i_p/V_0$ increase, and when γ approaches zero, t_p approaches one quarter of the period, $2\pi(LC)^{1/2}$, of pure sinusoidal oscillations ($R \equiv 0$) while i_p becomes independent of R . It is in this region that the earlier sparks ($\gamma \rightarrow 0$ through $C \rightarrow 0$) previously discussed were operated and it may now be seen why no external resistance is employed in the high-voltage, small-capacitor spark. In short, when employing a small capacitor, higher energy-dissipating resistances of low inductance are necessary to change appreciably the character of the discharge pulse from oscillatory behaviour ($\gamma < 1$) to critical damping ($\gamma = 1$).

B. Critically Damped Discharge ($\gamma = 1$)

When $\gamma = 1$ Eqs. (2) to (4) are indeterminate. However, by taking appropriate limits, $(1 - 1/\gamma)^{1/2} \rightarrow 0$, or by differentiation the equations can be written

$$i(t) = \frac{V_o}{L} e^{-\frac{t}{\sqrt{LC}}} \quad (10)$$

$g(\gamma) = 1$, $h(\gamma) = 1/e$, and Eq. (7) reduces to $r \exp(1 - r) = f$. Note that the equations in this case depend on but two of the three circuit parameters, for example $t_p = 2L/R = RC/2 = \sqrt{LC}$, and that $\tau_{1/2} = 2.446 t_p$.

C. Overdamped Discharge ($\gamma > 1$)

The equations are perhaps most appropriately written in the form (2) to (7). From Fig. 2 note that as γ increases from unity to large values, the time at which the peak current is a maximum decreases and approaches zero (except when $\gamma \rightarrow \infty$ through $C \rightarrow \infty$ in which case t_p increases linearly with C , as expected because $C \rightarrow \infty$ implies large energies available and the current never reaches its peak value). In this limit of γ , Ri_p/V_o increases from $2/e$ at $\gamma = 1$, to unity (Ohm's Law) as $\gamma \rightarrow \infty$; while the rate of energy transfer approaches a constant value (Fig. 1). This is the case that approaches the continuous d.c. arc type of source across which a nearly constant voltage is maintained and pulse discharge duration is sufficiently long for the discharge to achieve thermal equilibrium. In the case of electrode contact the voltage may be varied for the conducting metal and Ohm's Law is obeyed.

III. EXPERIMENTAL DETAILS

To excite and separate the spectra of multiply-ionized atoms, the light source used was a vacuum sliding spark connected in a series LCR circuit with a trigger unit.

A. Light Source

As originally used by Vodar and Astoin,² their arrangement in vacuum consisted of a carbon rod, along which the produced spark slides, provided with two ring electrodes connected to a (0.03-0.1 μ f) capacitor charged to 30 kV. They reported spectra similar to ordinary sparks but with additional carbon lines present. The idea was further developed by Bockasten⁵ who used cylindrical electrodes of the material studied and replaced the carbon rod with an axially-bored porcelain disk provided with a small (1 mm) radial viewing slit towards the spectrograph. In this manner a great gain in intensity was obtained since all the sparks occurred in the bore hole rather than along the outside of a cylinder. To trigger the discharge Bockasten inserted in series an auxiliary spark gap in air, consisting of two brass spheres whose distance apart determined the desired voltage. The spark voltage was between 6-15 kV with a capacitor of 0.3 μ f, triggered 6-8 times per second. The inductance was varied to obtain different degrees of oscillatory discharges.

The light source used in this experiment is similar to the one used at the Johns Hopkins University^{3,6} and the National Bureau of Standards^{7,8} and is a somewhat modified version of the one used by Bockasten. The vacuum chamber consists of a glass envelope in the shape of two cylindrical glass

tubings crossed at their centre (Fig. 3). The two vertical ends are kovar-to-metal seals through which the water-cooled electrodes are inserted and O-ring sealed. The right end of the horizontal tubing fits, through a ball-joint connection, to a pump outlet and an O-ring sealed window holder; the left end is a glass window for alignment and visual observation. The pump system consists of a rotary roughing pump and an oil diffusion pump with which operating pressures of about 5×10^{-6} mm of Hg are maintained. The quartz spacer between the electrodes, instead of being a flat disk which necessitates smooth fitting of the electrodes to the disk to prevent part of the discharge occurring outside the disk, has a recessed bore hole through which the spark passes. It is provided with a horizontal viewport, centered between the electrodes. The spacing between the electrodes is a quarter of an inch. At pressures above about 10^{-4} mm of Hg occasional electrical flash-over occurred between the electrodes and the brass window holder, some five inches apart. The horizontal windows should not be closer to the central electrodes than about five inches to prevent excessive sputter deposition from the sparking which decreases their light transmission.

B. Electrical Circuit

The circuit is basically a series LCR circuit (heavy lines Fig. 4) with the light source and a trigger unit connected in series. Inductance coils were made from copper wire (1.02-2.05 mm dia.) coated with an insulating varnish and consist of the values 13, 36, 133, 312, and 593 μ h. Capacitor values ranged from 1 μ f to 36 μ f. Two types of negligible-inductance ($< 0.5 \mu$ h) resistance were used: for high peak currents several carbon pile

compression rheostats were coupled in series as needed, while for lower peak currents (< 100 amp) two doubly-wound wire rheostats of up to 100 ohms each were added. With this arrangement the external resistance in the circuit could be varied from a fraction of an ohm to 240 ohms. The trigger unit used originally was a rotating spark gap of variable frequency (typically operated at 5-30 times/sec) but this was soon abandoned in favour of an electronic switching unit which gave better stability and improved the suppression of undesirable current ends.

The electronic switching unit is similar to the one used at Johns Hopkins University³ and consists of an ignitron (GL-7171) used as a switching tube which in turn is triggered by a mercury vapour thyatron (FG-105). A modification is that the thyatron is not controlled by the voltage on the capacitor but is itself triggered by a rotating sector wheel which at the same time may serve as a time-selection window when observing the light intensity versus time within a current pulse. The rotating sector wheel consists of an aluminum disk (20 cm dia.) into which have been cut, at a radius of 7.5 cm and at 90° from each other, four slits 3/4 inches in length radially and 0.005, 0.010, 0.020, and 0.050 inches wide azimuthally. When rotated on the axis of a synchronous motor at 3600 revolutions per minute, the result is four time windows i.e. when placed in front of the spectrograph slit, the sector slits will pass light into the spectrograph for 4.5, 9, 18 and 45 μ sec.

The trigger and synchronization units were obtained from this rotating sector wheel as follows. At 60° before a given sector slit reaches the top vertical position of its cycle, it passes between a small light and a photo-diode. The resulting signal is amplified to diode-transistor-logic level

(0-5 volts) and transmitted (1) to a pulse width discriminator (2) to a counter and (3) through a fixed delay (2.8 msec) plus a variable delay (± 300 μ sec). The pulse width discriminator selects the desired slit while the scalar demands a coincidence between the number of times the selected slit has passed the photo-diode and the externally preassigned discharge repetition rate. When the coincidence occurs the signal, appropriately delayed and once more amplified to 50 volts, is transmitted to trigger the thyatron which fires the ignitron, thereby discharging the capacitor and firing the light source at the time (within the variable delay) that the chosen sector slit is passing in front of the spectrograph slit.

For the time resolution of the light pulse the time location of the window in relation to the current pulse was determined as follows. A fiber optics light guide, of $\frac{1}{4}$ " diameter and 12" long which transmits wavelengths between 400 and 2000 nm, was placed inside the spectrograph at 1 m from the entrance slit. The light guide intercepts approximately 4% of the light entering the spectrograph which is transmitted to a photomultiplier (1P28) and the resulting signal displayed on the dual beam oscilloscope, synchronously triggered with the spark discharge. With the built-in variable time delay between the time at which the sector slit is passing in front of the spectrograph slit and the firing of the discharge, the light pulse could be translated across the coincident slits in intervals of the window duration.

C. Mode of Operation

Electrical isolation of the power supply and the LCR circuit was ensured by placing an LR filter (200 mh, 750 ohm power resistor) between the

two. This may easily be checked by means of the relation $\tau_{1/2} = 2.446 t_p$ at critical damping. For a given LCR circuit and source, a lower limit on the initial voltage on the capacitor is set by the minimum voltage necessary to operate the source, while the upper limit is set by the power supply delivery and the discharge repetition rate. The discharge repetition rate of firing the source is itself limited; the upper limit ($\sim 40/\text{sec}$) is determined by the desire to prevent spacer heat and glow or by the power supply, while a lower limit is set by the time elapse that can be tolerated to accumulate a record of the spectra.

The voltage on the capacitor and the current through the circuit were monitored on a dual-beam oscilloscope by means of which i_p , t_p , $\tau_{1/2}$, and the total pulse length were readily reproducible for a given combination of L , C , R , V_0 , and the discharge repetition rate. Critical damping could be achieved by adjusting the resistance while the source was in operation until the ends of the voltage and current pulses on the oscilloscope appeared sharp resulting in $\tau_{1/2}/t_p = 2.45$. Because there exists a lower limit on V_0 , below which the spark gap will not operate, it is necessary to operate the source in the over-damped case in order to achieve lower peak currents (< 100 amperes). In general, the source will operate if $(C/L)^{1/2} V_0 = i_p/h(\gamma) \geq K$ where $K \approx 200$ amperes for the present source as determined from pulses obtained with V_0 near the minimum voltage at which the source barely operates stably. This confirms the well known phenomenon that for a given electrical circuit the voltage across a source gap is nearly independent of current, i.e. the voltage at which the source barely operates is nearly constant for fixed circuit parameters, source geometry and electrode material. For constant

$\gamma (\approx 0.5)$ with various values of L , C , and R , and for the minimum voltage at which the source barely operates, it was found that $CV_o/i_p \tau_{1/2}$ is approximately constant, Eq. (8). Peak currents as low as 20 amperes may be achieved without difficulty, but for still lower currents the source fires intermittently unless L is made smaller and R correspondingly larger. No attempt was made to overcome this intermittent firing by introducing a carrier gas as this would probably result in electrical flash-over between the electrodes and the metallic parts of the present source. Furthermore, since it was found that in this source there is no great difference in atomic ionization between 10 and 20 amperes and because the first and second stages of ionization are produced with better line quality (smaller Stark effect, etc.) in other sources, no advantage was to be gained by investigating these lower currents with respect to the separation of higher ionized atomic states. The oscillatory case was not examined as it is known³ that critically damped discharges are superior for the separation of ionization stages when observing total pulses. This is evident from the results obtained by Strasheim and Blum¹⁰ who reported that the radiated spectra of neutral aluminum and Al^{1+} follow the frequency of the discharge and that the intensity of the ionized line decays faster in the consecutive pulses of the oscillatory train. The ignitron in the circuit prevents oscillation which was utilized to achieve higher peak currents for a given power; the external resistance was decreased to obtain underdamping while the ignitron prevented undershoot. In this manner the first current pulse of a slightly underdamped discharge could be investigated.

In an effort to maintain source conditions as constant as possible, the electrode surfaces were machined flat and the spacer bore hole cleaned

every time a spectrographic plate was exposed. To start the spark a pencil line was made along the bore of the quartz spacer. For wear on the electrodes as a function of the inductance and capacitance see Ref. 10.

D. Observations

In the light of the foregoing discussion and previous experience gained from separating the spectrum of Sc III from lower ionization stages,¹¹ observations were made on vanadium spectra in an effort to correlate the excitation observed in the discharge of a vacuum sliding spark and the parameters involved in its production.

The light emission of the spark, using vanadium metal electrodes (99.7% pure), was observed by means of a 3.4 m focal length, Ebert-mount spectrograph from 2300-4800Å in air (grating: 600 lines/mm, 5.2Å/mm dispersion, 5000Å blaze). The spectra were recorded on Kodak spectroscopic plates (1-0) with the repetition rate set at 15/sec. Each plate was also exposed to a Tungsten-Halogen lamp, reproducible through constant voltage and photo-multiplier monitoring, for appropriately stepped times in order to monitor plate variations and determine plate emulsion calibration curves. Measurements were made on the intensities of representative and convenient lines listed in Table I, and the relative intensities read from each plate's calibration curve. Light pulses were observed as total time-integrated pulses with selected pulses being time resolved.

Total-pulse observations were first made with a constant capacitance of 24 μ f, inductances of 13, 36, 133, 312, and 593 μ h, and resistances adjusted to obtain $\tau_{1/2}/t_p = 1.60$ ($\gamma = 0.08$) and overdamping. At each of

the five inductances and voltage was varied over its range. The constant-time exposures (400 pulses) were made on one photographic plate. Table II lists the circuit parameter values of the discharge pulses investigated, which have been numbered for easy reference. The quantities γ , $g(\gamma)$, and $h(\gamma)$ were obtained from Fig. 1 using the observed ratios $\tau_{1/2}/t_p$ rather than $t_p/(LC)^{1/2}$ which is more subject to residual inductance and capacitance. The observations are presented in graphical form in Fig. 5 where the relative intensities of lines listed in Table I are plotted versus peak current for the five different inductance values. Total-pulse observations were also made with a constant inductance of 13 μh , capacitor values ranging from 1 μf to 32 μf , resistances adjusted to obtain $\tau_{1/2}/t_p = 2.0$ ($\gamma = 0.45$), and constant voltage $V_0 = 2000$ volts. The relative line intensities are plotted versus capacitance in Fig. 6.

To investigate the behaviour of the ionization stages versus time within a given discharge pulse, light pulses were time resolved by use of the rotating sector wheel. With the 9- μsec window, observations were made at 10 μsec intervals on the pulses marked t_r (time resolved) in Table II. Photographic plate exposure times were constant at 4000 pulses. Three plates sufficed to obtain the results of the seven pulses, each plate representing a fixed value of L , C , and R . Relative intensities of the lines of different stages of ionization versus time within the current pulses are shown in Figs. 7, 8, and 9.

IV. RESULTS

Consider first the time resolution observations presented in Figs. 7, 8, and 9 which display several interesting phenomena. The first of these figures shows the relative intensities of the lines versus time within the current envelope of pulse 20. Three lines of each ionization stage present are shown to display their common behaviour. In Figs. 8 and 9 relative intensities are plotted versus time within three different current envelopes at constant L, C, and R; pulses 12, 14, 16 and pulses 5, 7, and 9, respectively. The intensity of the highest ionization stage present is a maximum at t_p , in accord with the results reported for the case of underdamping by Strasheim and Blum.¹⁰ The intensity-time profiles of the lower ionization stages generally consist of two peaks separated by an intensity-minimum valley, the duration of which depends on the current pulse length¹⁸ and the stage of ionization. Both the intensity profile of the higher ionization stages and the intensity valley of the lower stages broaden as the peak current is increased. It appears that as the peak current is increased for fixed L, C, and R the line intensities of the higher ionization stages are increased at the expense of the lower stage excitations and consecutively higher stages begin to appear at t_p . The topmost graphs in Figs. 8 and 9 show the variation of intensity ratios at t_p versus peak current at constant L, C, and R. Comparing relative intensities or intensity ratios it is clear that higher peak currents gain higher excitation energies i.e. higher charge transport through the source within a time interval results in the excitation of higher ionized atomic states during that time interval.

Turning now to the total-pulse observations, consider Fig. 5. As the peak current (or V_0) is increased for fixed values of L, C, and R, higher stages of ionization ($\geq V^{2+}$) are excited at some definite peak current and their line intensities increase with peak current. Sufficiently strong lines of the doubly ionized stage may be present at lower peak currents, for example, the strongest lines of Sc III were observed in a 10-ampere peak current discharge. The singly ionized stage is more favourably excited in the over-damped discharge but remains present at the higher peak currents. Separation of stage ionizations by increasing the peak current for fixed values of L, C, and R, appears difficult as no useful intensity reversal of a given ionization stage is obtained within the limits of the present power supply.

In general, the relationship between the line intensity and the excitation energy is complicated by the fact that the line intensity depends on the number of atoms excited to the particular upper state involved in the transition i.e. on the number of atoms released from the electrodes and their distribution over the ionizations stages present during a discharge pulse. The time resolution observations indicate that during a given time interval within the current pulse the line intensities of the higher stages of ionization stages increase at the expense of the lower stages when the peak current is increased. Thus, the number of atoms per unit time contributing to the rate of charge transfer through the source appears to be approximately constant for fixed L, C, and γ (fixed t_p). This is further supported by photographs¹⁰ of electrode wear as a function of L and C with constant γ , which show the highest degree of similarity when the product LC is constant. From the relative line intensities in Fig. 5 at high peak currents, two conclusions

may be drawn. For a given stage of ionization the relative line intensities (1) increase as i_p is increased for fixed L , C , and γ (fixed t_p) and (2) increase when the inductance is increased (increasing t_p) at constant C , γ and i_p . Thus, the line intensities of a given ionization stage increase as either i_p or t_p is increased at constant C and γ . A simple picture of line intensity and excitation energy as a function of the circuit parameters presents itself. Let $i_{\min,s}$ be the minimum rate of charge transfer necessary to produce the highest ionization stage, (s), observed in a discharge pulse. With sample vapour leaving the electrode surface at a constant rate for fixed L and C , the longer pulse duration results in a higher intensity of a time-integrated line exposure i.e. $\tau i_{\min,s}$ increases where τ is the time interval during which $i(t) \geq i_{\min,s}$. From Eq. (6) $i_p t_p = CV_0 h(\gamma) g(\gamma)$, hence for a fixed C the product $i_p t_p$ is governed by both $V_0 h(\gamma)$ and the discharge duration function $g(\gamma)$, increasing with higher voltages or lower values of γ . The departure from this generalized simple picture at low peak currents may be due to the following phenomena. Walters¹⁸ reports that at any fixed electrode displacement the intensity-time profile contains an initial high amplitude spike, whose duration ($< 15 \mu\text{sec}$ for the present source) depends on the electrode gap distance but not on the form of the discharge pulse. This would explain the irregular intensity behaviour at constant-voltage, low peak currents: (1) for sufficiently short pulses the initial intensity spike becomes a significant fraction of the total time-integrated intensities and (2) for long pulses obtained with large L values the initial intensity spike is also dominant for the highest ionization stage present because in the later part of the current pulse after breakdown effects cease to play a major

role, the circuit-parameter controlled charge transfer rate is less effective in exciting the higher ionization stages as will be seen later. Generally then, the relationship between relative intensities and circuit parameters is complicated by the distribution of the atoms among the different ionization stages and in certain cases by breakdown effects. Caution is necessary when trying to relate relative intensities and especially intensity ratios of different ionization stages to the circuit parameters.

Intensity peaks, however, considered as the most favourable excitation of the upper state involved in the emitting transition, may be interpreted as representing excitation energies attained and are directly associated with the circuit parameters. Perhaps the most convenient intensity peaks to be considered first are those obtained when three of the four circuit parameters are held fixed. Relative intensities of the different lines may be read from Fig. 5 as a function of L at constant C , γ , and V_0 . Results are presented in Fig. 10 for $C = 24 \mu\text{f}$, $\gamma = 0.08$ and $V_0 = 850$ volts. Intensity peaks are clearly defined and good separation of ionization stages may be obtained from the spectra at constant C by varying L , adjusting R to achieve constant γ , and maintaining constant V_0 . In this manner the spectra of Sc III and V V in the region $500\text{\AA}$ to $9500\text{\AA}$ were successfully separated from their lower stages of ionization.^{11,17} In the top graph of Fig. 10 excitation energies (Table I) are plotted, at the corresponding intensity peaks, versus $1/L$. For voltages less than 850 volts, the intensity peaks occur at lower L values and are spread further apart. Similar plots at different voltages, although further observations at different L values are necessary to determine the intensity peaks more closely, indicate that sufficiently high excitation energies are

proportional to V_o^δ/L where $\delta \approx 2$, for constant C and γ . The departure from V_o^2/L at low excitation is attributed to breakdown effects, i.e. a certain minimum current is necessary to operate the source.

The power delivered to the source is a quantity more generally applicable to a variety of sources and it is appropriate to investigate its influence on the excitation energy attained in the source. A useful relation between the power in a pulse and $i_p V_o$ may be obtained from Eq. (8). For the cases of present interest in Fig. 5, γ is constant and $i_p V_o$ will serve as a measure of the power per pulse, the proportionality factor between $i_p V_o$ and $CV_o^2/2\tau_{1/2}$ being about three for $\gamma = 0.08$ (Fig. 1). Relative intensities of the different lines may be read from Fig. 5 as a function of L at constant C , γ and $i_p V_o$ with curves of $i_p V_o$ obtained from Table II. This was done for two values of $i_p V_o$ (200 kVA and 340 kVA) and the results are presented in Fig. 11, plotted versus $1/L$. Intensity peaks of the different ionization stages occur, though there appears to be greater mixing of ionization stages at higher L values than the plot at constant voltage. In the central graph of Fig. 11 excitation energies are plotted, at the corresponding intensity peaks, versus $1/L$. With exception of the V IV intensity peak at 200 kVA, all points are rather well defined resulting in two linear, parallel lines of excitation energy versus $1/L$; the curve obtained with the higher value of $i_p V_o$ is shifted to higher excitation energies. Figure 5 further indicates that the intensity peaks (including that of V V) at a higher power would result in a line shifted further to the left. The graphs were obtained at constant C and γ . With breakdown effects appropriately reflected in the product $i_p V_o$, one obtains from the intercept and slope of the two linear curves

$$E_e = (9.67 \times 10^{-3} i_{p_o} V_o)^2 + 2.61 \times 1/L \quad \text{constant } C, \gamma \quad (11)$$

where the excitation energy, E_e , is in electron volts when $i_{p_o} V_o$ is expressed in kVA and L in mh. Equation (11) reproduces both excitation energy versus $1/L$ curves with an error of less than 3%, and may be useful in future investigations of other elements.

The γ dependence of the slope of the E_e versus $1/L$ curve (Eq. (11)) is indicated by Fig. 5 as follows. The relative intensities of V II lines for the pulses numbered 24, 21, and 17 in Table II are 4.1, 4.3, and 5.9, respectively. The corresponding values of L are 593, 312, and 133 μ h, and of γ are 6.3, 6.3, and 10.0. From the topmost graph in Fig. 5 note that the V II line intensity increases with a decrease in γ and a corresponding increase in $i_{p_o} V_o$, at fixed L and C . Therefore, the relative intensity (5.9) observed from pulse 17 ($L = 133 \mu$ h, $\gamma = 10.0$) would increase for a decrease in γ and a corresponding increase in $i_{p_o} V_o$, at the given L and C . Hence, the intensity peak of the V II lines for $\gamma = 6.3$ and $i_{p_o} V_o = 70$ kVA occurs at $L < 133 \mu$ h, resulting in a single data point on the E_e versus $1/L$ plot in Fig. 11 with ordinate 12.3 eV and abscissa not less than $1/L = 7.52 \text{ mh}^{-1}$. Because no negative excitation energies exist by definition the intercept of the E_e versus $1/L$ plot is positive and the slope at constant C is less for $\gamma = 6.3$ than for $\gamma = 0.08$. Relative intensity measurements from exposures made with $C = 24 \mu$ f, $\gamma = 1.2$, $i_{p_o} V_o = 500$ kVA, and using the same inductances as in Fig. 5, showed the relative intensity versus $1/L$ profile of V II to have a slow peak at $1/L \approx 40 \text{ mh}^{-1}$, while the profiles of V III and V IV increased to at least $1/L = 77 \text{ mh}^{-1}$. Thus, the slope of the E_e versus $1/L$ curve is a decreasing function of γ .

The dependence on capacitance of the relative intensities of different ionization stages is shown in Fig. 6. The increase in intensities with increasing capacitance is most likely due to the combined effects of an increase in the initial charge (CV_0) stored in the capacitor (or increased peak current) and longer discharge duration. In addition, for these pulses the initial rate of current rise (V_0/L) is constant and the electrode evaporation is expected to change with capacitance. The nearly equal intensities for the different ionization stages at low C values may be due to the relative importance of an initial intensity spike¹⁸ in these short ($\lesssim 20 \mu\text{sec}$) discharge pulses. Evidently in this region of capacitance, the relative intensity is nearly linear in C with increased slope for higher stages of ionization which it may be possible to exploit for separation of spectra belonging to different ionization stages. Returning to the relative intensity versus $1/L$ curves, exposures were made for two values of the capacitance (24 μf and 36 μf) with other parameter values: $\gamma = 0.1$, $i_p V_0 = 450 \text{ kVA}$, and the same inductances as in Table II. Comparing a plot of relative intensities versus $1/L$ for 36 μf to that for 24 μf indicates that (1) intensities increase as the capacitance is increased with greater intensity gains for higher ionization stages, and (2) the slope of the E_e versus $1/L$ curve decreases with an increase in capacitance, the behaviour being approximately $1/C$.

It has been noted that Eq. (11) contains breakdown effects whereas the previously observed proportionality for sufficiently high excitation, $E_e \propto V_0^2/L$, does not. Correlation of these two observations implies that at low excitation $V_0 = R i_p / 2\gamma^{1/2} h(\gamma)$ is constant. In the limit $\gamma \rightarrow \infty$,

$R_{ip}/V_o = 2\gamma^{1/2}h(\gamma) \rightarrow 1$ and V_o is the constant operating voltage of a d.c. arc type of source in which only the first and second spectra of an atomic species are excited at low power. The resulting C/L dependence in the first term of Eq. (11) is consistent with the data reported by Schreiber and Fry¹⁹ on the low excitation of iron ($\lesssim 30$ eV) in an underdamped discharge at constant voltage. In addition, the remaining constants in Eq. (11) are in general expected to depend on the source geometry and the electrode sample material.

V. DISCUSSION

Both total-pulse and time-resolution analysis indicate that higher excitation energies are gained with increased power delivered to the source. For a fixed γ , increasing the voltage increases the highest excitation energy gained in a current pulse, while for a fixed peak current increasing the discharge duration increases the time-integrated intensity. To excite higher ionization stages increase the maximum rate of charge transfer determined by $(C/L)^{1/2} V_0 h(\gamma)$, to obtain stronger line intensities increase the discharge duration governed by $(LC)^{1/2} g(\gamma)$ which determines the length of time during which atoms are excited to the upper level of the emitting transition. In both cases this means deliver more energy to the light source and/or decrease L as indicated by Eq. (5). For a fixed energy there exists a trade-off between the highest ionization stage gained and the strength of its line intensity. For ionization stages lower than the highest ionization stage present, increasing the rate of charge transfer depletes the number of atoms excited to those stages during a given time interval for a nearly constant electrode vapourization rate. We discuss now the excitation of the atoms in the discharge and the separation of the spectra belonging to different stages of ionization.

Time resolving the first current pulse of an underdamped discharge achieves excellent separation of the spectra of higher ionization stages. It has been noted that the highest stage of ionization occurs at t_p . This is as expected since the amount of charge transported through the source within a fixed time interval is a maximum at t_p , i.e. the highest stages of ionization enter the discharge at this time. In addition to sample vapour leaving the

electrode surface during the discharge, it was found that the sputtered sample material on the surface of the spacer borehole contributes significantly to the material being excited. As the current is less on either side of t_p , lower ionization stages enter the discharge at times different from t_p . This would explain the observed twin-peaked intensities of the lower ionization stages on both sides of t_p . When the voltage is increased the necessary charge transfer rate to gain a given stage of ionization is achieved before t_p and lasts after t_p , the intensity-time profile of the highest stage present broadens as does the intensity-minimum valley of the lower stages, and higher stages of ionization begin to appear at the time (t_p) when the charge transfer rate is maximum. Using a time-resolution rotating sector with a time window of appropriate duration, we have observed these spectral variations as well as a rather sudden change in the intensity ratio at t_p of the spectra belonging to two consecutive ionization stages (Figs. 8 and 9). The number of pulses required for proper plate exposure remains reasonable.

Consider now low excitation energies. It is well known that spectroscopic sources will not operate below a certain minimum current, i.e. a sufficient number of electrons must be present to give rise to a current, and that no electrical source will excite only the neutral atom. This may be interpreted as saying that there exists a minimum excitation energy, of the order of the first ionization energy of the neutral atom, below which a source will not operate. Thus, there exists a lower threshold $E_e \geq E_{\min} > 0$, the last inequality because no negative ionization energies exist by definition, which represents a horizontal line in the E_e versus $1/L$ plot. This explains the

intermittent firing of the vacuum sliding spark at low currents achieved by overdamping with large values of L , i.e. Eq. (11) approaches zero as γ and/or L approach large values such that E_e is below E_{min} for the electrode element and the source geometry. Similarly it explains why a vacuum spark (low C and γ) will not operate at some fixed voltage for sufficiently large L value. In the limit $\gamma \rightarrow \infty$ and voltages such that the source barely operates stably a d.c. arc type of source results. In this limit the slope of the E_e versus $1/L$ plot decreases and for powers just sufficient to operate the source stably, i.e. for minimum currents, only the radiation of the neutral atom and the single ionized stage is observable. In addition, the intensity peak of the singly ionized stage broadens and moves off to $1/L \rightarrow \infty$, making its detection difficult.

As noted, to gain high excitation energies it is necessary to increase the power delivered to the source or the rate of charge transfer through the source. Both these quantities may be made a maximum, for a given initial charge (CV_0) or energy ($\frac{1}{2} CV_0^2$) stored in the capacitor, by making the resistance and the inductance added to the circuit as small as possible. As R and therefore γ is made small, resulting in a highly underdamped discharge, the slope of the E_e versus $1/L$ curve increases which gains higher stages of ionization but the intensity peaks of neighbouring stages crowd closer together and the lower stages are unduly excited in the consecutive pulses of the decaying oscillatory train, both making stage separation difficult when observing all the light from such a train of pulses. Separation of these high ionization stages, gained in nearly sinusoidal discharges with pulses of high peak current and short duration (small γ and L), may be attained in the following manner. For sufficiently short current pulses the intensities of

the highest ionization stages present tend to dominate (Figs. 9 and 11), so that pulses with high peak current and with t_p not larger than a few microseconds excite mainly a few high ionization stages. These few high ionization stages may be observed by transmitting into the spectrograph only light arising from pulses in the train with nearly the same peak current, for example, by use of a rotating-sector time window of appropriate duration. Alternatively, the spectrum of the highest stage of ionization present near t_p in any one of the current pulses may be observed with a time-window of sufficiently short duration (a fraction of the total pulse duration) and appropriately synchronized with the discharge. Thus, for high values of V_o and fixed C/L with sufficiently small values of γ and L, high stages of ionization are excited which may be separated by simply varying the peak current through voltage variation. For total discharge observations stage separation by means of intensity peaks is difficult by just increasing the peak current (increasing V_o) at fixed L, C, and R (fixed γ). The variation in the second term in Eq. (11) is not utilized, all that occurs is a vertical traversal in the E_e versus $1/L$ plot, exciting more and higher stages of ionization as the power is increased. At best, broad intensity peaks may be obtained by exciting higher stages of ionization at the expense of the lower stages for a constant sample vapourization rate (Fig. 5, $L = 13 \mu h$, V III at $i_p = 900$ amperes).

Separation of stages when observing total-pulse, time-integrated intensities may be effected by varying the discharge duration while maintaining constant voltage. In addition to C and L the γ dependence of the slope of the E_e versus l/L curve may be exploited to improve stage separation. This slope is a decreasing function of γ , i.e. the intensity peaks in the l/L plot are spread further apart ($\gamma \rightarrow \infty$, improved separation) or brought closer together ($\gamma \rightarrow 0$, worse separation) for fixed C and power. However, at fixed power the former means a decrease in the maximum excitation attained in the discharge, while the latter gains higher excitation. Thus, there exists a trade off between stage of excitation attainable and the ability to separate their spectra. Without time resolving underdamped discharges, indeed the optimum exists at critical damping ($\gamma = 1$) where high stages are best separable. For fixed CV_0 , overdamping reduces the stage attainable while underdamping introduces an unduly amount of lower stages of ionization in the consecutive pulses of the oscillatory train.

In summary, a relationship has been found between the excitation in the source and the electrical circuit parameters that may be expressed and discussed in terms of the capacitance, the inductance, the initial voltage on the capacitor, two known functions of the continuous circuit parameter γ one of which is directly associated with the discharge duration and the other directly to the peak current through the source, and two constants which in general depend on the source geometry and the electrode sample material. No such direct relationship could be ascertained between the intensities of the spectral lines and the electrical circuit parameters, because in general the line intensity depends on the distribution of the sample-vapour atoms among

the different stages of ionization present in the light source. Separation of the spectra of higher ionized atomic states was obtained by two different methods. The first method consisted of analyzing the total light pulse while varying the inductance and resistance, with constant capacitance, γ , and constant initial voltage on the capacitor. The second method, superior to the first in separating higher ionization stages, consisted of time-resolving the light pulse while varying the initial voltage on the capacitor with constant inductance, capacitance, and resistance. Other variations of the circuit parameters may be employed to attain different degrees of excitation and separation of ionization stages. The equations developed and found have here been applied to the excitation and separation of spectra of multiply-ionized atoms. In addition, these equations should be of use in spectrochemical analysis where quantitative application of the specification of spark source parameters and their correlation with spectral character is of basic importance.

ACKNOWLEDGEMENTS

The authors wish to thank Professor Sumner P. Davis of the Physics Department at the University of California, Berkeley for his interest in this work. We also thank George V. Shalimoff of the Lawrence Berkeley Laboratory for his aid in the laboratory.

REFERENCES

- (1) M. F. Hasler and H. W. Dietert, J. Opt. Soc. Am. 33, 218 (1943).
- (2) B. Vodar and N. Astoin, Nature 166, 1029 (1950).
- (3) G. H. Dieke, H. M. Crosswhite, and B. Dunn, J. Opt. Soc. Am. 51, 820 (1961).
- (4) C. H. Corliss, Spectrochimica Acta 5, 378 (1953).
- (5) K. Bockasten, Ark. Fys. 9, 457 (1955).
- (6) Wm. R. Callahan, J. Opt. Soc. Am. 53, 695 (1963).
- (7) J. Sugar, J. Opt. Soc. Am. 53, 831 (1963).
- (8) J. Reader, G. L. Epstein, and J. O. Ekberg, J. Opt. Soc. Am. 62, 273 (1972).
- (9) The light source is a modification of the original design kindly supplied to us by Drs. V. Kaufman, J. Reader, and G. L. Epstein of the National Bureau of Standards, Washington, D. C.
- (10) A. Strasheim and F. Blum, Spectrochimica Acta 26, 694 (1971).
- (11) C. H. H. Van Deurzen, J. G. Conway, and S. P. Davis, J. Opt. Soc. Am. 63, 158 (1973).
- (12) C. E. Moore, An Ultraviolet Multiplet Table, 1, Natl. Bur. Std. (U.S.) circ. No. 488 (U. S. Government Printing Office, Washington, D. C. 1950).
- (13) C. E. Moore, A Multiplet Table of Astrophysical Interest, Nat. Stand. Ref. Data Ser., Natl. Bur. Std. (U.S.) 40 (1972).
- (14) L. Iglesias, An. Real Soc. Esp. Fis. y Quim (Madrid) [A] 58, 191 (1962).
- (15) L. Iglesias y R. Velasco, An. Real Soc. Esp. Fis. y Quim (Madrid) [A] 54, 83 (1958).
- (16) L. Iglesias, J. Research Natl. Bur. Std. 72A, 295 (1968).
- (17) C. H. H. Van Deurzen, Ph.D. Thesis, Lawrence Berkeley Laboratory Report LBL-1657 (1973).
- (18) J. P. Walters, Applied Spectroscopy 26, 25 (1972).
- (19) T. P. Schreiber and D. L. Fry, Spectrochimica Acta 13, 104 (1958).

TABLE I. Vanadium Lines Selected for Intensity Measurements.

	Wavelengths (Å)	Transition	Reference	Excitation energy ^a (electron volts)
V II	2924.017	$a^5F_5 - z^5F_5^o$	12	11.4
V II	3257.893	$c^3P_1 - y^3D_2^o$	13	13.0
V II	3263.33	$b^3G_4 - z^3H_4^o$	13	12.6
V III	3107.817	$c^2D_{5/2} - z^2F_{7/2}^o$	14	32.4
V III	3350.211		15	≥ 25.1
V III	3351.56		15	≥ 25.1
V IV	3294.259	$3d(4d^3P_2 - 5p^3P_2^o)$	16	82.7
V IV	3295.501	$3d(5p^3F_2^o - 5d^3F_2)$	16	86.2
V IV	3328.527	$3d(5p^3F_4^o - 5d^3F_4)$	16	86.3
V IV	3333.986	$3d(4d^3P_2 - 5p^3P_1^o)$	16	82.6
V IV	3334.79	$3d(4d^1G_4 - 5p^1F_3^o)$	16	82.7
V V	2774.998	$5p^2P_{3/2}^o - 5d^2D_{5/2}$	17	145.6

^aThe excitation energy is defined as the total energy necessary to excite a neutral atom in its ground state to the upper state of the transition emitting the radiation.

TABLE II. Circuit Parameter Values of Discharge Pulses Investigated.

Pulse No.	Observed							From FIG. 1		
	Circuit Parameters (C = 24 μ f)			Current Pulse						
	L (μ h)	V _o (volts)	R ^a (Ω)	i _p (amp)	t _p	$\tau_{1/2}$ (μ sec)	d ^b	γ	g(γ)	h(γ)
1	13	340	<1	150	35	56	96	0.08	1.34	0.68
2	13	540	<1	300	35	56	96	0.08	1.34	0.68
3	13	670	<1	400	35	56	96	0.08	1.34	0.68
4	13	830	<1	500	35	56	96	0.08	1.34	0.68
5(tr) ^c	13	900	<1	600	35	56	96	0.08	1.34	0.68
6	13	990	<1	700	35	56	96	0.08	1.34	0.68
7(tr)	13	1140	<1	800	35	56	96	0.08	1.34	0.68
8	13	1220	<1	900	35	56	96	0.08	1.34	0.68
9(tr)	13	1350	<1	1000	35	56	96	0.08	1.34	0.68
10	36	350	1	150	48	77	115	0.08	1.34	0.68
11	36	580	1	300	48	77	115	0.08	1.34	0.68
12(tr)	36	700	1	400	48	77	115	0.08	1.34	0.68
13	36	840	1	500	48	77	115	0.08	1.34	0.68
14(tr)	36	930	1	600	48	77	115	0.08	1.34	0.68
15	36	1060	1	700	48	77	115	0.08	1.34	0.68
16(tr)	36	1210	1	800	48	77	115	0.08	1.34	0.68

(continued)

TABLE II (continued)

Pulse No.	Observed							From FIG. 1		
	Circuit Parameters (C = 24 μ f)			Current Pulse						
	L (μ h)	V _o (volts)	R ^a (Ω)	i _p (amp)	t _p (μ sec)	$\tau_{1/2}$ (μ sec)	d ^b	γ	g(γ)	h(γ)
17	133	900	20*	50	35	300	750	10.0	0.60	0.15
18	133	490	1.5	150	83	133	190	0.08	1.34	0.68
19	133	670	1.5	300	83	133	190	0.08	1.34	0.68
20(tr)	133	850	1.5	400	83	133	190	0.08	1.34	0.68
21	312	1400	30*	50	65	380	700	6.30	0.68	0.18
22	312	780	2	150	125	200	300	0.08	1.34	0.68
23	312	1360	2	300	125	200	300	0.08	1.34	0.68
24	593	1460	30*	50	65	380	1100	6.30	0.68	0.18
25	593	1590	15*	100	110	330	600	1.06	0.92	0.32
26	593	1280	3	200	160	255	400	0.08	1.34	0.68

^aAdded resistance values are approximate only; * = overdamped.

^bTotal time duration of current pulse.

^cPulses marked (tr) were time resolved.

FIGURE CAPTIONS

Fig. 1. Behaviour of functions associated with characterization of capacitor discharges, Eqs. (3) to (8). The curves may be used for graphical determination of γ , $g(\gamma)$, $h(\gamma)$ and i_p from given values of t_p , $\tau_{1/2}$, C , and V_o . In the underdamped case curves are for the first current pulse.

Fig. 2. Limits of t_p and Ri_p/V_o in capacitor discharges. ^aSinusoidal as $R \rightarrow 0$, ^bCurrent never peaks as $C \rightarrow \infty$ implies infinite energy available, ^cOpen circuit never starts, ^dOhm's Law.

Fig. 3. Sliding spark light source. See Ref. 9.

Fig. 4. Schematic of the electrical circuit used to excite spectra of multiply-ionized atoms.

Fig. 5. Relative line intensities of vanadium spectra (V II - V V) versus peak current. $C = 24 \mu f$, $\gamma = 0.08$ except $\blacktriangle$ = overdamped; for additional circuit parameter values see Table II.

Fig. 6. Relative line intensities of vanadium spectra (V II - V V) versus capacitance. $L = 13 \mu h$, $\gamma = 0.1$, $V_o = 2000$ volts.

Fig. 7. Characteristic vanadium intensity-time profiles.
 $C = 24 \mu f$, $\gamma = 0.08$, $L = 133 \mu h$.

Fig. 8. Characteristic vanadium intensity-time profiles.
 $C = 24 \mu f$, $\gamma = 0.08$, $L = 36 \mu h$.

Fig. 9. Characteristic vanadium intensity-time profiles.
 $C = 24 \mu f$, $\gamma = 0.08$, $L = 13 \mu h$.

Fig. 10. Relative line intensities and excitation energies versus $1/L$.
 $C = 24 \mu f$, $\gamma = 0.08$, $V_o = 850$ volts.

Fig. 11. Relative line intensities and excitation energies versus $1/L$.
 $C = 24 \mu f$, $\gamma = 0.08$, $i_p V_o = 200$ kVA and 340 kVA.

XBL 738-3838

Fig. 1. Behaviour of functions associated with characterization of capacitor discharges, Eqs. (3) to (8). The curves may be used for graphical determination of γ , $g(\gamma)$, $h(\gamma)$ and i_p from given values of t_p , $\tau_{1/2}$, C , and V_0 . In the underdamped case curves are for the first current pulse.

	$\gamma < 1$ Underdamped	$\gamma = 1$ Critical	$\gamma > 1$ Overdamped			
	$0 < \gamma$		$\gamma \rightarrow \infty$			$\gamma \rightarrow 1$
	$L \rightarrow \infty \quad C \rightarrow 0 \quad R \rightarrow 0$		$L \rightarrow 0$	$C \rightarrow \infty$	$R \rightarrow \infty$	
$t_p =$	$\frac{\pi}{2} \sqrt{LC} \left(1 - \frac{2}{\pi} \sqrt{\gamma} + \dots \right)^a$	$\sqrt{LC}$	$\sqrt{\frac{LC}{\gamma}} \left(\frac{1}{2 - \frac{1}{\gamma}} \right) \rightarrow 0$	$\sqrt{\gamma LC} = \frac{RC}{2} \rightarrow \infty^b$	$\sqrt{\frac{LC}{\gamma}} = \frac{2L}{R} \rightarrow 0^c$	$\sqrt{\frac{LC}{\gamma}} \left[1 - \frac{1}{3} \left(\frac{1}{\gamma} - 1 \right) + \dots \right]$
$\frac{Ri_p}{V_0} =$	$R \sqrt{\frac{C}{L}} \left(1 - \frac{\pi}{2} \sqrt{\gamma} + \dots \right)$	$\frac{2}{e}$	$\frac{1 - \sqrt{1 - \frac{1}{\gamma}}}{1 + \sqrt{1 - \frac{1}{\gamma}}} \frac{e}{\sqrt{1 - \frac{1}{\gamma}}} \rightarrow 1^d$			$\frac{2}{e} \sqrt{\gamma} \left[1 + \frac{1}{3} \left(\frac{1}{\gamma} - 1 \right) + \dots \right]$

XBL 734-441

Fig. 2. Limits of t_p and Ri_p/V_0 in capacitor discharges. ^aSinusoidal as $R \rightarrow 0$, ^bCurrent never peaks as $C \rightarrow \infty$ implies infinite energy available, ^cOpen circuit never starts, ^dOhm's Law.

XBL734 - 2609

Fig. 3. Sliding spark light source. See Ref. 9.

XBL734-2606

Fig. 4. Schematic of the electrical circuit used to excite spectra of multiply-ionized atoms.

XBL734-2594

Fig. 5. Relative line intensities of vanadium spectra (V II - V V) versus peak current. $C = 24 \mu f$, $\gamma = 0.08$ except $\blacktriangle$ = overdamped; for additional circuit parameter values see Table II.

Fig. 6. Relative line intensities of vanadium spectra (V II - V V) versus capacitance. $L = 13 \mu\text{h}$, $\gamma = 0.1$, $V_0 = 2000$ volts.

XBL734-2595

Fig. 7. Characteristic vanadium intensity-time profiles.
 $C = 24 \mu\text{f}$, $\gamma = 0.08$, $L = 133 \mu\text{h}$.

Fig. 8. Characteristic vanadium intensity-time profiles.

$C = 24 \mu\text{F}$, $\gamma = 0.08$, $L = 36 \mu\text{H}$.

XBL 734-2597

Fig. 9. Characteristic vanadium intensity-time profiles.

 $C = 24 \mu\text{f}$, $\gamma = 0.08$, $L = 13 \mu\text{h}$.

XBL 734-2598

Fig. 10. Relative line intensities and excitation energies versus $1/L$.
 $C = 24 \mu f$, $\gamma = 0.08$, $V_0 = 850$ volts.

Fig. 11. Relative line intensities and excitation energies versus $1/L$.

$C = 24 \mu\text{f}$, $\gamma = 0.08$, $i_p V_0 = 200$ kVA and 340 kVA.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720