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Study of a Calcium Afterglow in a Broida Oven

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PACS.52.80.-s – Electric discharges
PACS.82.20.Rp – Energy distribution and transfer; relaxation

Abstract. — A systematic study of a Broida source producing atomic calcium in ground state \(^1\text{S}\) and first metastable \(^3\text{D}\) and \(^3\text{P}\) states is presented. The relative concentration of the metastables, produced by a DC discharge, is monitored with carrier gas pressure, heating power and discharge current, and it is observed that low values of these parameters are favourable to \(^1\text{D}\) formation. These results are interpreted in terms of relative values of cross section of energy pooling forming the first resonant state \(^1\text{P}\), and the ratio of these cross section is estimated to be \(\sigma(3\text{P}→3\text{P})/\sigma(3\text{D}→3\text{D}) \approx 5 \times 10^{-4}\). Some properties of the source are described, including auto-absorptions of transitions originating from the \(^3\text{P}\) and collisional relaxation of reaction products of Ca with halogenated compounds. An example of utilization of the source for the study of metastable reactivity is presented.

Introduction

Since many years, different types of atomic afterglow: rare gas - helium, neon, argon, Kr, Xe [1–3], and molecular afterglow: oxygen [4], nitrogen [5] have been studied and used for excitation purposes. The afterglow phenomena is due to the presence in the post discharge zone of long lived species, which are used for Penning ionization (rare gas), or energy transfer (rare gas, nitrogen). The most common set-up is the low pressure direct-current (DC) discharge in a cell from which the metastable are extracted by a fast pumping and brought to the reaction zone.

The lowest excited state of the atoms of the second column of the periodic classification is metastable, as it is a triplet \(^3\text{P}\), compared to the \(^1\text{S}\) ground state, and from Ca to Ra, the second state is also metastable, as it is a \(^1\text{D}\). Measured lifetimes decrease from 2.5 milliseconds (calcium) [6] to 29.8 microseconds (barium) [7]. As the energy of these states is low (2.73 eV for Be \(^2\text{P}\), 1.41 eV for Ba \(^5\text{D}\)), they are not used for energy transfer, but are rather introduced as excited partner in reactive collisions. The following experimental set-up are used in that case: effusive beams continuous or pulsed, [8–10], or fast pumped with DC discharge [11].

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must mention that since the apparition of lasers, long lived species have also been produced by
using the large optical power of these sources to populate metastable states by optical pumping
through forbidden transitions.

In order to study Ca reactivity in both $3^1D$ and $4^3P$ states, we have built a similar device
as the one used in rare gas afterglow, and determined the metastable state rate–formation
with different parameters. We are able to control the relative concentration of the two species,
and to observe the reactivity of each one. We give in a first part a detailed description of the
experimental set-up, and results on its control. In a second part we show the importance of
the energy pooling process in this source, and in a third part we give some results obtained on
reactive collision with halogenated compounds and on auto–absorption.

1. Experimental Set-Up

The experimental set-up already mentioned [12] will be described in details: it is similar to
the one used to produce metastable rare gas atoms, with the difference that the cathode has
to be heated to produce metallic vapour, which is extracted by an inert gas, device called a
Broida oven [13].

- Production of the Metal Vapour

A few grams of metal are heated in a small crucible in graphite, or in alumina (more chemically
inert but with a higher calorific capacity) containing. The crucible is surrounded by a tungsten
filament (Balzers) where a current of 150 A, 10 V at the maximum is provided by a stabilized
DC power supply. The thermal insulation is provided by a cylinder of alumina, and the whole
is contained in a vertical stainless steel tube of 10 cm internal diameter, which is water cooled.
The carrier gas enters through the basis and the top is connected to the pump (Fig. 1). Above
the crucible is placed a metallic cone which restrains the gas flow to 2 cm diameter on a short
distance. The reactants arrive through a small tube in the reaction zone 18 cm–20 cm above
the crucible, where windows allow observation, and where a digital thermometer reads the
temperature. The temperature of the crucible was not directly measured, but was estimated
to be a little below 850 °C at its maximum.

The pump, which is protected by charcoal and paper filter against corrosion, is of roots type,
350 m$^3$/h, giving an average velocity for the gas of 25 m/s, measured by a pulsed discharge.
The total volume of the cell is 60 liters, and the pressure measured by a Penning gage placed
at the pump entrance. Typical runs last between 15 to 60 hours, depending on experimental
conditions.

- Formation of Metastables

The discharge is produced by applying to the tungsten filament a negative voltage relative
to the ground, which is connected to the cell. This is similar to the production of rare gas
afterglow, but in this case the DC power supply used for heating has to be isolated from the
ground by a transformer. A DC power supply stabilized (300 V, 200 mA max.) is used,
through a 810 Ω ballast resistor. The atoms in metastable states are seen by the colour of
their emission, blue for the $3^1D$ at 457 nm red for the $4^3P$ at 657 nm, due to the $3^1D\rightarrow 4^1S$
and the $4^3P\rightarrow 4^1S$ transitions respectively. The light collected by a lens is sent on a Bausch &
Lomb monochromator of 0.5 m focal length, with slits varying around 0.3 mm, and equipped
with an EMI 9558QB photomultiplier. Signal are sent to a microcomputer for recording and
analysis. The transitions $3^P \rightarrow 1^S$ and $1^D \rightarrow 1^S$ being forbidden, the natural width of the lines
is small, and as the Doppler and the collision broadening are much smaller than the apparatus
function, intensities are measured by their maxima. The Ca ground state $4^1S$ concentration is
Fig. 1. — Experimental set-up used for the study of the calcium atom afterglow.

determined by weighting and the metastables by comparison of their emission with a tungsten calibrated lamp (see below).

We describe first the behaviour of the discharge itself which is formed between the crucible and the metallic cone, and will then study the afterglow by observing the effects of physical parameters on the rate of formation of the metastables.

1.1. Study of the Discharge. — The discharge produces metastables when the values of the three parameters, pressure, heating and discharge current, vary inside determined intervals: the pressure has to be sufficiently high to carry metallic vapour and maintain the discharge on, but not too high otherwise it cools the crucible; the heating power high enough to produce metallic vapour, but not too high otherwise the discharge is quenched; the discharge current high enough to produce metastables, but the ratio of these depends strongly on its value (see below).

1.1.1. Variation of the Pressure. — The pressure which is measured is due to helium: the partial pressure of Ca is too low to be read by the gage, and the metal deposes on the walls.
Fig. 2. — Temperature variation (°C) in the observation zone, as a function of helium pressure (Torr), for a heating power of 328 W.

In the Figure 2 is shown the variation of the temperature with the pressure $P_{\text{He}}$ for a heating power $P = 330$ W. The choice of this value will be justified below. As already said, the favourable effect of He as carrier gas is thwarted by the cooling effect, as can be seen by the saturation from a value of pressure of about 8 Torr. It should be mentioned also that the pump cannot run at pressure higher than 20 Torr.

1.1.2. Variation of the Heating Power. — The heating power has been varied from 200 W to 450 W, and the effect on the metastable production yield is described below. The main observation is that at too low heating the discharge does not start, and at too high heating it is quenched, except in special conditions where pressure is very high. As the Ca vapour pressure increases from $\simeq 0.1$ Torr at 700 °C to $\simeq 1$ Torr at 820 °C (the melting point is 850 °C), and to $\simeq 10$ Torr at 980 °C, the sensitivity of the discharge regime with the temperature is not surprising, but difficult to quantify. Below is shown the variation of the relative production of the metastable states with the heating power.

1.1.3. Variation of the Voltage. — The power supply has a regulation for voltage $V$ or current $i$. We have studied the variation of the voltage $V'$ between the crucible and the ground (obtained by subtracting the voltage drop in the load resistor: $V' = V - R_i$), with the current $i$, for a heating power of 330 W. The results displayed in the Figure 3 show that $V'$ decreases slowly with $i$. In the "luminous regime" of a hollow cathode, this effect is attributed to the increase of the cathode surface with the current circulation, which implies a decrease of the impedance of the system. This is observed here by the drop of the impedance from $\simeq 1.5$ kΩ to 0.155 Ω in the experimental conditions, when the current varies from 25 mA to 200 mA. A systematic study of this variation with the heating power was not made.

1.2. Study of the Afterglow. — We have simultaneously studied the variation of the intensities of the emissions at 657 nm, 457 nm, and 423 nm which correspond to the transitions $4^3P \rightarrow 4^1S$, $3^1D \rightarrow 4^1S$ and $4^3P \rightarrow 4^1S$ respectively, with the three parameters $P_{\text{He}}$, $P$ and $i$. The transition $3^3P \rightarrow 1S$ being much more intense than the transition $1^3D \rightarrow 1S$, neutral filters (SCHOTT NG11) were used in order to get an attenuation of the first without modification of
Fig. 3. — Variation of the voltage $V'$ in the discharge cell with the discharge current, for a heating power of 328 W. The curve represents an average on 4 measurements, the straight line is a least square fitting.

the luminous flux entering the monochromator. To obtain the concentration of the metastables, we have corrected the signal by the wavelength PM sensitivity: the ratio of the quantum yield of the S 20 photocathode $S = S^{(1D)}/S^{(1P)}$, was estimated as 3.86 from published curves. No correction was used for grating and mirror spectral responses.

The concentration of metastables $^{1D}$, $^{[1D]}$, is correlated to the intensity of the signal by:

$$I^{(1D)} = K \times [^{1D}] \times A^{(1D)}$$

where $I$ is the intensity of the signal, $K$ represents all the geometric parameters involved in the measurements, it was measured and is of course the same for the two species. A similar formula holds for the $^{3P}$ state and $A$ is the Einstein coefficient: $(A = 1/\tau)$ where $\tau$ is the radiative lifetime.

The radiative lifetime of $^{1P}$ has been taken as $\tau^{(1P)} = 5$ ns [14]. The radiative lifetimes of the metastable states vary from different publications [15], as shown in the Table I. One can see that, although the variation of $\tau^{(3P)}$ is between 25% and 30% around the average value 340 $\mu$s, the variation of $\tau^{(1D)}$ from 1.1 ms to 25 ms, represents a factor of $\approx 24$. A discussion about these variations is given in the reference [16], where the authors mention the possibility for the $^{1D}$ state to radiate to the two $^{3P}$ and $^{3P}$ states, which could explain that the Einstein coefficient $A$ (taken as 40 s$^{-1}$) could be different of the measured lifetime of the $^{1D}$--$^{1S}$ transition. In our case, we have rather used the value of $A$, and these discrepancies, which will affect the precision of some of our results as shown below in study of the energy pooling, do not affect the following approximations:

The observed zone is only 1 cm high, and as the gas velocity is 25 m/s, different measurements are made for the three atomic states: on this distance, $I^{(1D)}$ is constant, $I^{(3P)}$ is attenuated by 0.6 and the measured intensity is averaged (see below, Sect. 3.1). Atoms in the state $^{4P}$ are formed by energy pooling (EP) from $^{3P}$--$^{3P}$, $^{1D}$--$^{1D}$, and $^{3P}$--$^{1D}$ collisions, and the variation of the intensity of the line at 423 nm with vertical distance is not exponential. In the following description, the intensities will be converted into concentrations by using the formula (1).

1.2.1. Variation of the Concentrations with the Pressure. — The variation of the concentrations with helium pressure is shown in the Figure 4. One can observe that the $^{1D}$ emission reaches a
Table I. — Radiative lifetimes of the $^3\text{D}$ and $^3\text{P}$ states of Ca.

<table>
<thead>
<tr>
<th>Lifetime</th>
<th>$\tau(^1\text{D})$ (ms)</th>
<th>$\tau(^3\text{P})$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[15a]</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>[15b]</td>
<td></td>
<td>440 (*)</td>
</tr>
<tr>
<td>[15c]</td>
<td>12.3</td>
<td>256</td>
</tr>
<tr>
<td>[15d]; [15e]</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>[15f]</td>
<td>(**)</td>
<td>340</td>
</tr>
</tbody>
</table>

(*) In the reference [15b], the authors mention that this value is itself an average on three already published results, whose references are given therein.

(**) In this reference, the authors give $A = 40 \text{ s}^{-1}$ instead of $\tau(^1\text{D})$ (see text in the “Study of the afterglow”).

![Graph](image)

Fig. 4. — Variation of the concentration of the metastable states $^1\text{D}$ and $^3\text{P}$ with helium pressure, for a heating power of 315 W, a discharge current of 75 mA, a discharge voltage of 84 V, and a vertical aperture of the monochromator slit of 0.3 mm.

maximum around $p = 5$ Torr, although the maximum occurs near $p = 12$ Torr for the $^3\text{P}$. This observation is general: the values of the parameters for which the $^1\text{D}$ emission is maximum are always lower than the corresponding values for the $^3\text{P}$ emission.

1.2.2. Variation of the Concentrations with the Heating Power. — In the Figure 5a is displayed the variation of the $^1\text{D}$ concentration with the heating power, for different values of the discharge current $I$, at a constant pressure $P_{\text{He}} = 3.5$ Torr. A maximum is observed for $P = 315–325$ W. In the Figure 5b is displayed the same for the $^3\text{P}$. The maximum is shifted toward the value $P = 350$ W.

To show the differences of the behaviour of the two states, we have plot in the Figure 6 the variation of the ratio of the intensities of the two emissions at 457 nm and 657 nm, which is proportional to $R = \frac{[^1\text{D}]}{[^3\text{P}]}$, with $P$. As it is mentioned above it appears clearly that low heating and low current are favourable to the formation of $^1\text{D}$ relative to $^3\text{P}$. 
1.2.3. **Variation of the Concentrations with the Current.** — The variation of the concentration \(^{1}\text{D}\) with the current is displayed in the Figure 7a, for different heating powers \(P\). Two types of variation are observed: or \(^{1}\text{D}\) is insensitive to \(P\), or it is saturated for \(P = 315\) W and \(P = 345\) W. In the Figure 7b are shown similar results for the \(^{3}\text{P}\) state: the same variation is observed, but with no saturation effect at 345 W. It looks as \(^{3}\text{P}\) could be increased with current, which we have checked by using a more powerful power supply. Another way to present these results is to plot the dependence of \(R\) with \(I\), for different values of \(P\), which is shown in the Figure 8. One can see that above 315 W, \(R\) is independent of \(P\). The general observation made from these results, namely that low values of physical parameters are favourable to \(^{1}\text{D}\) with respect to \(^{3}\text{P}\), will be tentatively explained by the EP mechanism: EP involving collisions between \(^{1}\text{D}\) is much more efficient than those involving \(^{3}\text{P}\); when values of physical parameters are increased, \(^{1}\text{D}\) increases, but is more efficiently quenched by EP than \(^{3}\text{P}\).
Fig. 6. — Variation of the $[^1\text{D}]/[^3\text{P}]$ concentration ratio with the heating power for different values of the discharge current, at a helium pressure of 5 Torr.

Fig. 7. — a) Variation of $[^1\text{D}]$ concentration with discharge current, for different values of heating power, at a helium pressure of 5 Torr. b) Variation of $[^3\text{P}]$ concentration with discharge current for different values of heating power, at a helium pressure of 5 Torr.
1.2.4. Measurement of Metastable Absolute Concentration. — We have found experimental conditions where, at high pressure and at high heating power (415 W and 10 Torr), we have measured the absolute concentration of the $^43P$ state by using a calibrated lamp. This tungsten lamp (ORIEL N°6332) is calibrated with reference to the model 6315 FEL 1000W approved by the NIST for spectral irradiance standard, and was used in the following way: placed at 50 cm from the entrance slit of the monochromator, the signal given by the lamp was recorded, and the surface area of the spectra on 1 nm bandwidth was compared with the signal of the $^43P$ emission at 657 nm taken in the same geometrical conditions, with suitable attenuation filters to ensure the linearity of the PM response. Measurement of the solid angle and use of the velocity of the gas give the density of the $^43P$ state.

We have found $[43P] = 2.05 \times 10^{15}$ atoms/m$^3$, and $[31D] = 2 \times 10^{13}$ atoms/m$^3$. The Ca ground state concentration in the afterglow zone was estimated by gravity to be $\approx 2.7 \times 10^{10}$/m$^3$, which gives a ratio $[43P]/[41S] \approx 4 \times 10^{-4}$, with an uncertainty of ±20%, and a ratio $[31D]/[43P] \approx 0.01$.

To conclude, we have given in this first part experimental evidence that the two metastable states $31D$ and $43P$ of the calcium atom formed in an afterglow present a different behaviour with respect to the physical parameters controlling the discharge: helium pressure, heating power, discharge current. Before giving an interpretation of the results, we first present the general processes involved in the formation and in the annihilation of the metastable states.

2. Kinetics

We introduce in this part the discussion of the results, by setting up the different mechanisms involved in the formation of the metastable states in the discharge and in the afterglow.

* The formation of the metastables in the discharge region (DR) is due to the following processes.

a) Formation of superexcited (relative to metastables) states Ca** and ions Ca⁺ by electronic impact:

$$Ca + e + \Delta E \rightarrow Ca^{**} + e$$  \hspace{1cm} (2)
$$e + \Delta E + Ca \rightarrow Ca^+ + e$$  \hspace{1cm} (3)
Fig. 9. — a) Variation of the intensity of the $4^3P - 4^1S$ emission with the intensity of the discharge current. b) Variation of the intensity of the $3^1D - 4^1S$ emission with the intensity of the discharge current.

$\Delta E$ is the electron kinetic energy,

$$\text{He}^* + \text{Ca} \rightarrow \text{Ca}^{++} + \text{He} + e \quad (\text{Penning ionization})$$  \hspace{1cm} (4)

followed by
• desexcitation by radiative cascades towards metastables

$$\text{Ca}^{**} \rightarrow \text{Ca}^+$$  \hspace{1cm} (5)

• radiative recombination

$$\text{Ca}^+ + e \rightarrow \text{Ca}^{**} \rightarrow \text{Ca}^+.$$

(6)
**Fig. 10.** — Variation of the intensity of the $4^3P-4^1S$ emission with the intensity of the $3^1D-4^1S$ emission.

b) Direct formation by electronic excitation

$$\text{Ca} + e + \Delta E \rightarrow \text{Ca}^{\neq} + e.$$  \hfill (7)

* The disappearance of the metastables in the discharge is due to the following processes.

a) Radiative desexcitation

$$\text{Ca}^{\neq} \rightarrow \text{Ca} + h\nu.$$  \hfill (8)

b) “Energy-pooling” (EP)

$$\text{Ca}^{(3)P} + \text{Ca}^{(3)P} \rightarrow \text{Ca}^{(1)P} + \text{Ca} + \Delta E$$  \hfill (9a)

$$\text{Ca}^{(1)D} + \text{Ca}^{(1)D} \rightarrow \text{Ca}^{(1)P} + \text{Ca} + \Delta E$$  \hfill (9b)

$$\text{Ca}^{(3)P} + \text{Ca}^{(1)P} \rightarrow \text{Ca}^{(1)P} + \text{Ca} + \Delta E$$  \hfill (9c)

$$\text{Ca}^{*} + \text{Ca}^{*} \rightarrow \text{Ca} + \text{Ca}^{**} \rightarrow \text{Ca} + \text{Ca}$$  \hfill (9d)

$\text{Ca}^{\#}$ represents the states $1^1D$ or $3^1P$.

c) Collisional desexcitations

$$\text{Ca}^{\neq} + \text{Ca} \rightarrow \text{Ca} + \text{Ca}$$  \hfill (10)

$$\text{Ca}^{\neq} + e \rightarrow \text{Ca} + e$$  \hfill (11)

collisions with helium are much less efficient.

* In the afterglow region (AG), there is no formation of metastables and the quenching of the metastables are due to processes (8) to (10). The reactions (9a–9c) give directly the $4^1P$ state, which implies that the atoms formed have a high kinetic energy: $\Delta E$ varies from 0.86 eV, 2.91 eV, and 1.69 eV from (9a–9c), which could be measured by Doppler effect on the resonance line $4^1P-4^1S$ at 423 nm. The reaction (9d) forms super–excited states which cascade to $4^1P$; in that case the energy resonance condition can be almost matched. These
states are observed in our case, as they were by Husain et al. [17] (see below), but with small intensities.

We must mention here that the radiative relaxation of the singlets can lead either to the \( 3^1D \), or to the fundamental \( 4^1S \), although the radiative relaxation of the triplets leads only to the \( 4^3P \). The reaction (10) does not exist for the triplet manifold:

\[
Ca^{**} \longrightarrow Ca + h\nu. \tag{12}
\]

This difference is fundamental as it accounts for the difference between the concentrations of the two metastables: it represents indeed a "leak" in the formation, and in the concentration, of atoms in the \( 1^1D \) state.

In order to explain the observations reported above on the variation of the \( 1^1D \) and of the \( 3^3P \) concentrations with the three parameters \( R_{He}, P, I \), the following assumptions are made:

- cross sections for formation of the two states (processes (2–7)) are of the same order of magnitude;
- EP is much more efficient for \( 1^1D \) than for \( 3^3P \): \( k_{bb}(1^1D) \gg k_{bb}(3^3P) \). This assumption is verified experimentally (see below), and in reference [17];
- the collisional desexcitations (processes (10, 11)) will be neglected.

We give now results and interpretation based on the "energy–pooling" process.

3. Energy Pooling

The following data were obtained under the same conditions as above: \( p \approx 8 \text{ Torr}, P \approx 400 \text{ W} \). The consumption of calcium is high and the run cannot last very long, but signals are strong and stable, which enabled us to carry on a reproducible quantitative analysis of the energy pooling phenomena.

3.1. \([3^3P]\) and \([1^1D]\) Variations. — As mentioned above, the two \( 3^1D \) and \( 4^3P \) states can produce by collision higher excited states (reactions (9a) and (9b)), which populate by radiative cascade the \( 4^1P \) and \( 4^3P \) states. As in reference [17], we have observed some of the cascading processes, and we have studied the intensity dependence of the transition \( 4^1P \rightarrow 4^1S \) (desexcitation of the \( 4^1P \)) with current, with \([3^3P]\), and with \([1^1D]\).

The kinetics of the main mechanisms involved in the EP process can be summarized by the following equations:

\[
\begin{align*}
\frac{d[3^3P]}{dt} & = \{S_3 - A_3[3^3P] - k_{bb}[3^3P][1^1D] + k_{bc}[3^3P][1^1D]\} \cdot dt \\
\frac{d[1^1D]}{dt} & = \{S_1 - A_1[1^1D] - k_{bb}[1^1D]^2 - k_{bc}[3^3P][1^1D]\} \cdot dt \\
\frac{d[1^3P]}{dt} & = \{S_p + k_{bb}[3^3P]^2 + k_{bb}[1^1D]^2 + k_{bc}[3^3P][1^1D] - A[3^3P]\} \cdot dt
\end{align*}
\tag{13}
\tag{14}
\tag{15}
\]

\( A_3, A_1 \) and \( A \) are the Einstein coefficients of \( 3^3P, 1^1D, \) and \( 1^3P \) respectively, \( S_3, S_1 \) and \( S_p \) represent the term sources of \( 3^3P, 1^1D \) and \( 1^3P \) respectively. \( S_3 \) and \( S_1 \) represent the sum of the processes (2–7), and are \( \neq 0 \) in the DR only. \( S_p \) is neglected in the AG (see below).

As the observed zone is only 1 cm high, and as the gas velocity is 25 m/s, different measurements are made for the three atomic states on this distance: \( I(1^1D) \) is constant; \( I(3^3P) \) is attenuated by \( \approx 0.6 \) and the measured intensity \( I(3^3P) \) is the averaged value

\[
I(3^3P) = (t_0^{-1}) \int_0^t I_0 \exp(-t/t_0) dt
\]
with \( t_0 = 4 \times 10^{-3} \) s. The measured intensity \( I^{(3)P} \) is 0.6 the intensity \( I_0 \) at the lower part of the observed zone if we take into account the radiative decay of the \( 3P \) state. One can estimate that both \( I^{(1)D} \) and \( I^{(3)P} \) are roughly constant along the observation zone. That implies that the same approximation can be made to \( I^{(1)P} \), as the lifetime of \( 1P \) is very short, if the EP is the only source of this state (see below).

If we use the reactions (2-4, 6) to get an estimation of the term \( S_1 \) and \( S_3 \), we obtain the equation (13), similar to a Lindemann mechanism [18],

\[
I^{(3)P} = \frac{k_1 \cdot k_3 \cdot [Ca] \cdot [e]}{(k_{-3} \cdot [e] + k_3)}
\]

and a similar equation for the \( I^{(1)D} \) variation, where \([e]\) represents the current intensity \( i \). The variation of \([3P]\) and \([1D]\), monitored by the variation of \( I^{(3)P-1S}) \) and \( I^{(1)D-1S}) \) with the discharge current, are displayed in the Figures 9a and 9b. In the equations (13) and (14), the terms \( S_3 \) and \( S_1 \) are dependent on \( i \). One can see that for \( i < 100 \) mA and for \( i < 30 \) mA for \( 3P \) and \( 1D \) respectively, the variation is linear, which shows that \( k_{-2} \) (and the deactivation process) is larger for \( 1D \) than for \( 3P \).

3.2. [1P] Variation. — The population of the \( 41P \) state, which is followed by the observation of the transition \( 41S-41P \) at 423 nm, can be attributed to two phenomena: the EP and the absorption, by ground state atoms present in the afterglow zone, of resonance radiation coming from the discharge, which is represented by \( S_P \). However, this second mechanism would have produced very strong self-absorption of the line, which was not observed at all, and more, the \( 1P-1S \) transition is not observed when the discharge being on, there is no emission at 457 nm and at 657 nm. So we neglect the term \( S_P \). The following observations of the dependence of the 423 nm emission with the \( 43P \) and with the \( 31D \) concentration show that the EP is the main mechanism of the \( 41P \) state presence in the afterglow. It must be mentioned that both discharge production and EP mechanism are included in this analysis, as the afterglow is the only observed zone.

We have plot in the Figure 10 the observed relation between \( A_3[3P] \) and \( A_1[1D] \), which can be fit roughly by two linear functions. The first fit with a slope of 1150 gives by using the correcting factor of 3.86 for PM sensitivity, the ratio \( R \) of the concentrations \([3P]/[1D]\). This value depends of course on the values of \( \tau^{(1)D} \) and \( \tau^{(3)P} \).

Under the assumption of constant concentrations, we write:

\[
A^{[1P]} = \beta (k_{9a}[3P]^2 + k_{9b}[1D]^2 + k_{9c}[3P][1D]) = I^{(1)P}
\]

(17)

where \( \beta \) represents a coefficient of collection and detection efficiency. This gives the two following equations:

\[
A^{[1P]} = \frac{\beta (k_{9a}(I_3)^2)}{\left(2.94 \times 10^3\right)} + \frac{k_{9c}I_3}{\left(2.94 \times 10^3\right)} + k_{9b}[1D]^2
\]

(18)

\[
A^{[1P]} = \frac{\beta (k_{9b}(I_1)^2)}{(\beta^{584})} + \frac{k_{9c}[3P]I_1}{(\beta^{584})} + k_{9a}[3P]^2
\]

(19)

where \( I_3 \) and \( I_1 \) represent \( I^{(3)P} \) and \( I^{(1)D} \) respectively, and using the transformations:

\[
I^{(1)D} = \frac{\beta \tau^{(1)D}}{\tau^{(3)P)}[1D] \quad I^{(3)P} = \frac{\beta \tau^{(3)P}}{\tau^{(3)P)}[3P].
\]

(20)

In the Figure 11a and 11b are shown the intensity dependence of the \( 41P-41S \) emission on the \( 43P-41S \) and on the \( 31D-41S \) emissions. A fit with a second order polynomial gives \( 0.35 \times 10^{-8} \)
and $8.29 \times 10^{-8}$ for the second order coefficient in the two cases respectively. From equations (18) and (19) the ratio $k_{9a}/k_{9b}$ can be estimated, but again, as for $R$, this ratio depends on the values of $\tau(1\text{D})$ and $\tau(3\text{P})$.

In the Table II are shown the different values of $R$ and $k_{9a}/k_{9b}$ obtained with the published values of the lifetimes from Table I. The value of $A(1\text{D})$ which give the best fit with the absolute measurement of $R$, given above in the study of the afterglow is $A(1\text{D}) = 50 \text{ s}^{-1}$, which gives $k_{9a}/k_{9b} = 4.9 \times 10^{-4}$. That means that the EP is more than four order of magnitude more efficient for the $1\text{D} \rightarrow 1\text{D}$ collisions than for the $3\text{P} \rightarrow 3\text{P}$ collisions, as was mentioned above, and which is consistent with the results of Husain et al. [17].

In conclusion, we have shown that the energy pooling process gives a valuable interpretation of the results given in the first part on the relative variations of the $4\text{P} \rightarrow 4\text{S}$ and $3\text{D} \rightarrow 4\text{S}$ emissions, and we have also estimated the relative efficiency of this process involving both $1\text{D}$ and $3\text{P}$ states.
Fig. 12. — Transition $A^2\Pi - X^2\Sigma$ ($\Delta v = 0$) of CaCl observed with a 1.15 m focal length spectrometer with a 1024 CCD detector (Hamamatsu) when a trace of CHCl$_3$ is added to the afterglow. A spectrum obtained in a beam gas apparatus [20] is shown for comparison.
Fig. 13. — Some atomic lines of Ca obtained when a laser beam at 316.5, 317, and 318 nm is sent in the afterglow, showing strong auto-absorption. The lines are due to the transitions \( 4p^3P - 9s^3S \), \( J \to 0-1, 1-1, 2-1 \), respectively, from UV to Red.

Table II. — Variation of \( k_{9a}/k_{9b} \) and \( R \) with \( \tau(1D) \) (see text).

<table>
<thead>
<tr>
<th>( \tau(1D) ) (ms)</th>
<th>( k_{9a}/k_{9b} )</th>
<th>( R = [1D]/[3P] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>( 1.5 \times 10^{-6} )</td>
<td>( 56 \times 10^{-5} )</td>
</tr>
<tr>
<td>12.3</td>
<td>( 1.9 \times 10^{-4} )</td>
<td>( 63 \times 10^{-4} )</td>
</tr>
<tr>
<td>20.1(*)</td>
<td>( 4.9 \times 10^{-4} )</td>
<td>( 10 \times 10^{-3} )</td>
</tr>
<tr>
<td>25</td>
<td>( 7.6 \times 10^{-4} )</td>
<td>( 13 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

The value of \( \tau(3P) \) has been chosen as 440 \( \mu s \).

(*) This value corresponds to the best fit with the measured value of \( R \) by the independent method described in the measurement of the concentration of the metastables (see text).

4. Applications

We give in the third part some examples of uses of the source

4.1. CaCl Chemiluminescence. — The reactivity of Ca with halogenated compounds has been largely investigated (see for example Ref. [16] and Ref. therein). When Ca is in an excited state, the product formed by the reaction can be in an electronic excited state, which desexcites to the fundamental with emission of fluorescence: it is a chemiluminescent reaction. Up to now, these fluorescences in the case of CaCl, CaBr, CaI have been recorded with low resolution, due to the weakness of the signal; indeed, these data were obtained in molecular beams, and the yield of the chemiluminescent channel has been estimated to a few % of the total reaction exit channels [19]. We show in the Figure 12 as an illustration of the high quality of the source a spectrum of the \( A^2\Pi - X^2\Sigma \) transition of CaCl obtained by adding to the afterglow in the observation zone a trace of CHCl3. The detection apparatus is an OMA made with a 1.15 m focal length spectrometer (SOPRA), equipped with a 1024 CCD.
Fig. 14. — Comparison between a laser induced fluorescence spectrum of the MgCl $A^2\Pi - X^2\Sigma^+$ transition taken in a beam–gas apparatus [22], and taken in the Broida source [11]. a) Laser excitation spectrum of MgCl ($X^2\Sigma^+$) formed in the Mg($^1\Sigma$) + Cl$_2$ reaction under single-collision conditions (beam–gas). b) Laser excitation spectrum of MgCl ($X^2\Sigma^+$) formed in the Mg($^1\Sigma$) + Cl$_2$ reaction under multiple-collisions conditions (Broida oven).

detector (from Hamamatsu). The two $A^2\Pi_{1/2}$ and $A^2\Pi_{3/2}$ components of the transition are well-separated, and we were able by simulation to determine the rotational and the vibrational temperature of the population of the $A^2\Pi$ upper state, assuming a Boltzmann distribution. A comparison with a spectrum obtained in a beam gas apparatus [20] is shown.

4.2. AUTOABSORPTION. — We have observed very strong autoabsorption on some atomic lines when a laser beam sent in the afterglow is scanned at wavelengths 316.5, 317, and 318 nm, corresponding to the transitions $4p^3P-9s^3S \rightarrow 0-1$, 1-1, and 2-1 respectively. The Figure 13 shows these three lines. We have observed other Ca lines, but only some are autoabsorbed, although all involve the metastable $4^3P$ as lower state. An analysis of the line profile can give an estimation of the atomic density, as is made in hollow cathode observations [21]. That implies that this source could be very useful for atomic spectroscopic studies of high excited states.

4.3. COLLISIONAL RELAXATION. — The problem which arises from experiments made in a Broida oven for the study of reactions dynamics is the determination of the influence of the
Fig. 15. — Variation of the lifetime of the $A^2\Pi - X^2\Sigma^+$ transition of CaI with He pressure [23]. The extrapolation at zero pressure gives $\tau(A^2\Pi_{1/2}) = 42.9 \pm 2$ ns and $\tau(A^2\Pi_{3/2}) = 43.9 \pm 2.1$ ns.

relaxation processes in such systems. Indeed molecular beams has been developed to detect the primary event of what is called “single collision” conditions, where the products of the reactive collision are analyzed before any relaxation process. We can show by the following results that rotational relaxation occurs, essentially due to the carrier gas helium, but that vibrational relaxation is relatively inefficient.

In the Figure 14 are presented two spectra of the transition $A^2\Pi - X^2\Sigma^+$ of MgCl, one recorded on “single collision” conditions in a beam–gas apparatus [11], the other taken in a Broida oven [22], both recorded by using the laser excitation technique. Although these results were obtained by using magnesium atom instead of calcium, the conclusions are similar: one can see by comparing the values of the rotational and vibrational temperatures, estimated by simulation, that — the first one is rotationally more “hot” than the second, which is therefore “relaxed” — the first and the second have similar “vibrational temperatures”, which means that collisional vibrational relaxation is negligible in the Broida oven apparatus.

The effect of collisional relaxation can be seen in the Figure 15 where the variation of the lifetime of the CaBr $A^2\Pi - X^2\Sigma^+$, $(0 - 0)$ transition with pressure is presented [23], using the same laser excitation technique. One can see that collisional relaxation affects the measurements, and extrapolation to zero pressure is necessary.

Conclusion

In conclusion, we have described a source of calcium metastable states which is well–controlled and very useful, for the high density of excited states produced and for its stability. We have shown that the relative and absolute concentrations of the two metastable states of Ca, namely the $3^1D$ and $4^3P$, can be varied by acting on some physical parameters (He pressure, power heating, discharge intensity), and have estimated the radiative lifetime of $3^1D$ state. We have shown some applications for molecular dynamics and estimated importance of the collisional relaxation processes. This source can to be used for studies on the reactivity of excited atomic states, as well as for spectroscopic studies of high atomic excited states. We have to emphasize
that this source has the advantage to be "clean", in the meaning that, as the distance between the discharge and the reaction zone is large, its avoids the presence of ions or hot electrons in the observation zone, which is not always the case with the supersonic beams or the ablation laser techniques.

References