Pressure Dependence of Secondary NIR Scintillation in Ar and Ar/CF_4

M. M. R. Fraga, C. C. Bueno, J. A. C. Gonçalves, F. A. F. Fraga, R. Ferreira Marques, and A. J. P. L. Policarpo

***Abstract*—The variation with charge gain of the total number of photons emitted per electron, in the visible and near-infrared (NIR) regions ($400 < \lambda < 1000$ nm), in Ar/CF_4 mixtures, is investigated for CF_4 concentrations below 15%. Measurements were performed in a uniform field configuration and results are presented for charge gains below 100, under X-ray excitation. The maximum number of photons emitted per drifting electron (0.7 and 0.2 ph/e^- for $Ar + 2\%$ CF_4 and $Ar + 10\%$ CF_4, respectively) is obtained for a charge gain $G \sim 4$. The spectral distribution of the emitted light in Ar/CF_4 mixtures is also analyzed. The pressure dependence (1–4 atm) of the secondary light output, in the visible and near infrared regions is studied as a function of the reduced electric field E/P for pure argon and Ar/CF_4 mixtures. Above the charge multiplication threshold, the maximum number of photons emitted per electron decreases by a factor of about 1.5 when the pressure increases from 1 to 2 atms.**

***Index Terms*—Gas secondary scintillation, light emission, near-infrared (NIR) scintillation, proportional chambers.**

I. Introduction

LIGHT STUDIES regarding the development of an imaging device based on the detection of the secondary scintillation [1] emitted in a gas electron multiplier (GEM) detector [2], operating at normal pressure, have been reported in a previous paper [3]. These studies included total light yield measurements and spectral analyses of the secondary scintillation emitted in a parallel plate chamber and in a spherical field configuration. The results were compared with those obtained with the CCD coupled to a GEM detector. Although the electric field configurations are quite different, a good agreement was obtained in what concerns both the relative number of photons emitted per electron in the different gas mixtures and the spectral distribution of the light emitted. It was shown that in the mixtures under study, the light was emitted mainly in the near-infrared (NIR) region. In particular, in pure argon, the only detected emissions above 450 nm are the NIR Ar I atomic lines resulting from transitions between the atomic states of the $(3p^5\ 4p)$ and $(3p^5\ 4s)$ configurations. The maximum number of NIR photons emitted per drifting electron in a 4.5-mm-wide gas gap, at 1 atmosphere, is approximately equal to one (for a charge gain $G \sim 3$), decreasing slowly with increasing gain. Although this number is considerably lower than the number of photons emitted in identical conditions in the vacuum ultraviolet (VUV) region (by two orders of magnitude, as estimated by theoretical calculations), it is still convenient for an optical readout of the GEM with a standard CCD camera. Furthermore, NIR emissions can be detected in an easier and cheaper way and are not as sensitive to impurities as the VUV ones.

However, the operation of the detector is limited to low charge gains and the high diffusion coefficients make argon inadequate for imaging purposes. The addition of a small amount of CO_2 or CH_4 reduces the diffusion coefficients but it reduces the total light yield as well [3]. Alternatively, the addition of a small amount of CF_4 was considered, since the quenching rates for the emitting Ar I $(3p^5\ 4p)$ atomic states are lower than those measured for CO_2 or CH_4 [4]. Besides, CF_4 is known to be a good photon emitter, with emissions both in the UV and visible spectral regions [5]–[9] and it features high drift velocities and low diffusion coefficients [10]. The possible use of Ar/CF_4 mixtures in gas radiation detectors has been discussed by several authors [10], [11], but no attempt has been made so far to investigate their scintillation properties. Moreover, most of the studies in pure CF_4 refer to low pressure measurements. The present study reports on spectral measurements in Ar/CF_4 mixtures at normal pressure, and the dependence of the total light yield on charge gain and on the reduced electric field E/P is also presented.

In some applications, pressures above 1 atm are needed. Therefore, we studied the influence of pressure on the NIR scintillation yield, in a parallel plate chamber. Results are presented for argon in an attempt to understand the mechanisms involved in the excitation and de-excitation processes. Similar results are presented for $Ar + 2\%$ CF_4.

II. Experimental Setup

The spectral analyses of the light emitted were performed in a spherical field configuration. A detailed description of the experimental setup is given in [3]. The gas chamber is coupled through a Spectrosil A window to an Applied Photophysics monochromator, mod. 7300, equipped with a 1200-g/mm grating blazed at 500 nm. The light analyzed by the monochromator is detected by a RCA C31034A photomultiplier that covers the region between 185 and 930 nm. The photomultiplier is cooled down to $-20\,^{\circ}C$ and is operated in single photon counting mode.

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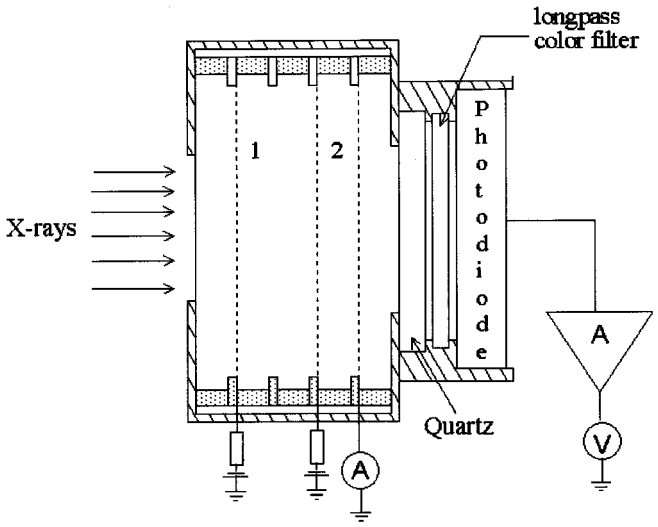


Fig. 1. Schematic view of the PPC. Regions 1 and 2 are the detection and amplification gaps, respectively.

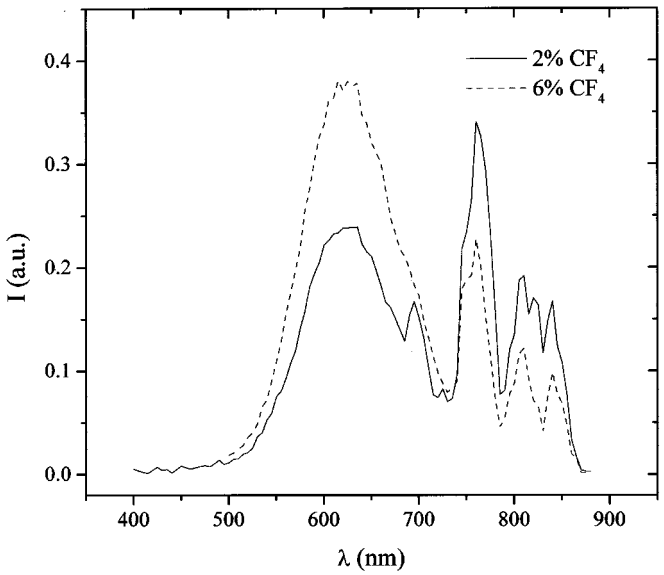


Fig. 2. Emission spectra of Ar/CF_4 mixtures recorded under α particle excitation, at normal pressure, for a charge gain $G \sim 30 (\Delta\lambda = 24$ nm).

The total light yield measurements were performed in a parallel plate chamber (PPC). The experimental setup is represented in Fig. 1. The PPC consists of three parallel stainless steel cross wire meshes (with 80% optical transparency) that define a detection region and an amplification gap. Light is collected through a fused silica window and detected by a UDT planar-diffused silicon photodiode (PIN-25DP) which feeds a linear amplifier. The conversion of the photo current into number of photons striking the photodiode per second is made using the photo sensitivity curve supplied by the manufacturer. Long-pass color glass filters are used to select the lower wavelength cutoff.

X-ray photons from an X-ray generator are used as excitation source. The tube is operated at 10 kV, with a copper target. The electron drift current is measured with a Keithley 414 S picoammeter.

Argon N50 and $CF_4 (> 99.9\%)$ from Air Liquide, were used. The gases may flow continuously, at atmospheric pressure, through calibrated flowmeters and the detector, or may be admitted into the chamber and kept in a closed circuit without further purification. In this case, the chamber is evacuated with a diffusion pump before filling.

III. Light Emissions in Ar/CF_4 Mixtures

A. Emission Spectra

The emission spectra were measured at normal pressure, under α particle excitation for a charge gain $G \sim 30$ in a scintillation counter with a spherical anode. The data were not corrected for the transmission of the mirrors and diffraction grating of the monochromator. The quantum efficiency of the photocathode of the photomultiplier is almost constant for the wavelength region between 200 and 900 nm. A long-pass color glass filter, with a wavelength cutoff (specified at 50% internal transmittance) of 435 nm, was placed between the chamber and the monochromator to avoid 2nd order diffraction effects. The emission spectra of $Ar + 2\%\ CF_4$ and $Ar + 6\%\ CF_4$, recorded with a resolution of 24 nm, are shown in Fig. 2. Between 690 and 900 nm, one can identify the Ar I atomic lines, while between 500 and 700 nm a molecular continuum is observed. This emission was further studied with an improved resolution but no structure was found. It was attributed to the $CF_3{}^*$ radical [8]. Since the spectra were recorded with equal widths of the entrance and exit slits, a comparison between the intensities of atomic lines and the molecular continuum is not direct. Taking into account the large width of the monochromator slits, we estimate that, for these low CF_4 concentrations, the dominant emissions are still the Ar I atomic lines. The decrease of the Ar I atomic line intensities is followed by an increase of the $CF_3{}^*$ emission, resulting in a lower total light output. Intense molecular continua peaking in the UV region and extending up to 500 nm have been reported for pure CF_4 [7], but their presence could not be checked for using the present setup.

B. Total Light Yields in a PPC

Measurements of total light yields in given wavelength regions were performed for several concentrations of CF_4. The total number of photons emitted, per drifting electron, is given by

$$\frac{N_{\rm ph}}{\rm e^-} = \frac{I_{\rm ph}}{\rm I_e \cdot Q \cdot T \cdot \frac{\Delta\Omega}{4\pi}} \tag{1}$$

where

- $I_{\rm ph}$ photocurrent;
- $I_{\rm e}$ electron drift current;
- Q mean quantum efficiency of the photodiode over the wavelength region from 500 to 900 nm [3];
- T optical transparency of the grids;
- $\Delta\Omega$ solid angle subtended by the photodiode.

Data are shown in Fig. 3 as a function of the charge gain. The overall uncertainty on the total number of photons emitted per electron, due to solid angle, quantum efficiency of the photodiode and statistics of the measurement, is estimated to be less than 20%.

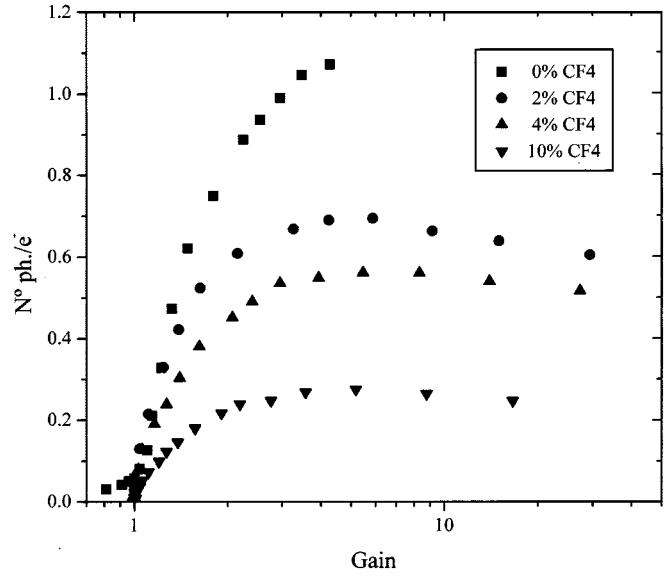


Fig. 3. Total number of photons emitted per drifting electron as a function of the charge gain for different Ar/CF_4 mixtures.

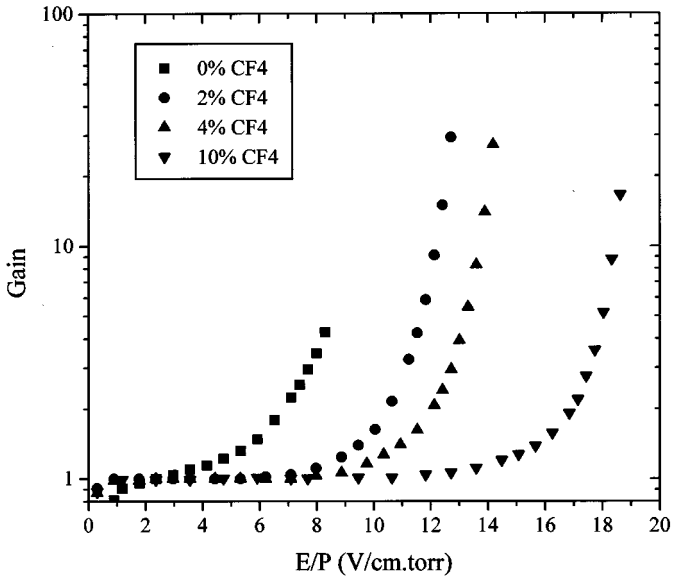


Fig. 4. Variation of the charge gain with the reduced electric field in Ar/CF_4 gas mixtures (gap width $= 4.5$ mm).

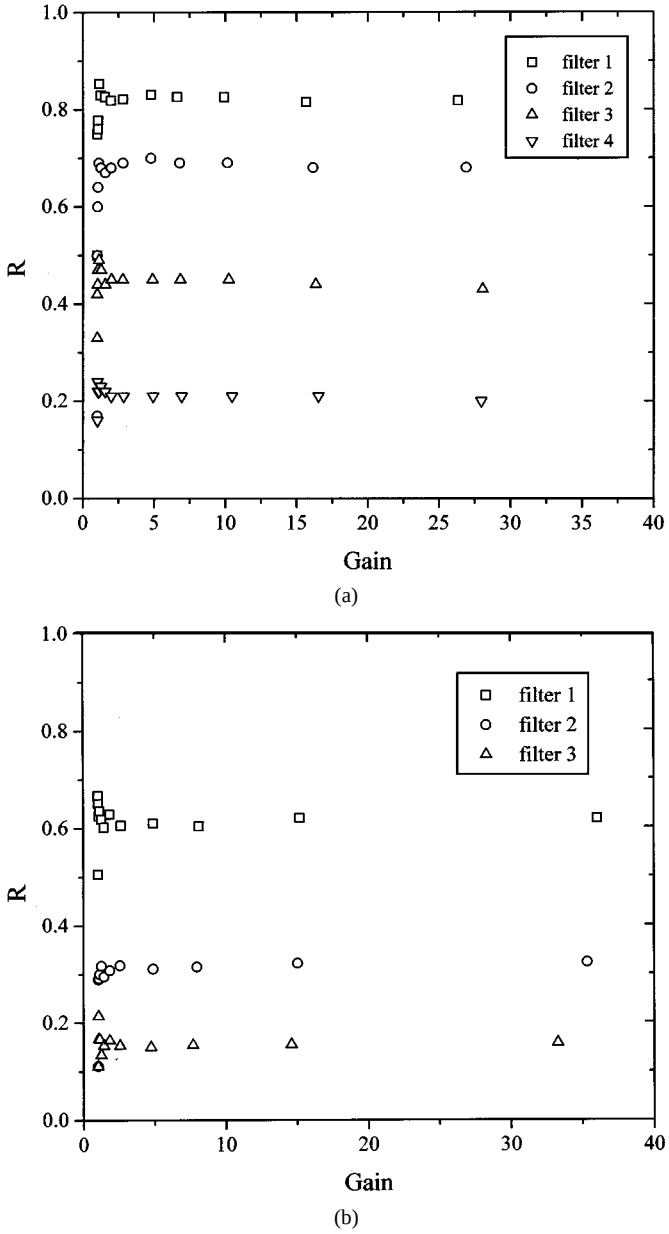


Fig. 5. Ratio between the total light yield with and without long-pass color glass filter as a function of the charge gain for: (a) $Ar + 2\%$ CF_4 and (b) $Ar + 10\%$ CF_4. The limits of stop-band (specified at 0.01% internal transmittance) of filters 1, 2, 3 and 4 are at 580, 640, 640 and 700 nm, respectively, and the corresponding cutoff positions (specified at 50% internal transmittance) are at 630, 695, 780, and 850 nm, respectively.

The increase of CF_4 concentration results in a decrease of the total light yield. However, this decrease is not so severe as in Ar/CO_2 or Ar/CH_4 mixtures. Below the charge multiplication threshold, the secondary scintillation is absent or very faint. For higher electric fields, the number of photons emitted per electron is expected to decrease slowly with increasing charge gain. Concentrations of CF_4 above 15% could not be investigated with the present setup, because the reduced electric field threshold for charge multiplication increases with increasing CF_4 concentration (see Fig. 4) and exceeds the maximum value of E/P allowed by the design of our chamber.

Measurements of the total number of photons emitted per electron were also performed with long-pass color glass filters placed between the photodiode and the chamber window. Results shown in Fig. 5 indicate that, for $Ar + 2\%$ CF_4, the scintillation is emitted mainly above 695 nm, i.e., the dominant emissions are the Ar I atomic lines. Comparing with the data obtained in pure argon [3], we conclude that the scintillation yield due to CF_4 is approximately 20% of the total light output. In $Ar + 10\%$ CF_4 the main contribution to the total number of photons emitted comes from the dissociation products of CF_4. From these results we cannot infer that there are emissions in the UV. The origin of UV emissions (with a first appearance potential around 21 eV) is not well established but they seem to result from the radiative de-excitation of molecular excited states of positive ions (CF_4^+ or CF_3^+) [7], [12]. Therefore, under the low electric fields used in the present work, we expect the probability of producing such emitting ionic states to be very low.

In wire chambers or in microstructure based detectors, the electric fields in the multiplication region are considerably higher and these emissions may then be important. Results obtained with a GEM coupled to a standard CCD [13] show that a considerable amount of light is emitted even for high concentrations of CF_4, but its spectral distribution is not known.

IV. Pressure Dependence of NIR Scintillation

A. Argon

The pressure dependence of the secondary scintillation of argon was measured in a PPC as a function of the reduced electric field. The argon NIR scintillation is due to transitions between atomic states of the $(3p^5\ 4p)$ and $(3p^5\ 4s)$ configurations. The excitation and de-excitation mechanisms of these states have been subject of several studies, most of them performed at very low pressures and in the absence of an applied electric field [14]–[16]. As discussed in a previous work [17], we consider the emitting states as a single one that can de-excite either radiatively or by two body collisions with argon atoms or molecules of impurities in their ground states. In the absence of quenching by impurities, the de-excitation rate is given by $\gamma = 1/\tau + k_Q P$, where τ is the radiative lifetime $(\sim\ 28$ ns), $k_Q\ (\sim 6 \times 10^5$ torr$^{-1} \cdot$ s$^{-1})$ is the intermultiplet rate constant for the deactivation by argon ground state atoms [4], [16], and P is the pressure (torr). Assuming a stationary regime, the number of photons emitted is proportional to $n_{\rm exc}/\gamma$, $n_{\rm exc}$ being the total number of excitations, including cascading contributions from higher-lying states. In the absence of charge multiplication, the total number of excitations is given by $\alpha_{\rm exc}.\Delta x$, where $\alpha_{\rm exc}$ represents the effective excitation coefficient $(\propto P)$ and Δx is the gap width. The total light yield should then be almost independent of the pressure. For E/P values above charge multiplication threshold, the total number of excitations per electron is given by

$$n'_{\rm exc} = \frac{\alpha_{\rm exc}}{\alpha_i}\left(1 - {\rm e}^{-\alpha_i \Delta x}\right) \tag{2}$$

where α_i is the first Townsend ionization coefficient. For $Gss \gg 1$, $n'_{\rm exc}\ (\approx \alpha_{\rm exc}/\alpha_i)$ is only function of the reduced electric field E/P and the total number of photons emitted per electron is expected to decrease with increasing pressure. For the low charge gain region, $n'_{\rm exc}$ depends both on E/P and P, the total number of photons emitted per electron being mainly determined by the decay constant γ. We calculated the variation of $n'_{\rm exc}$ and $n'_{\rm exc}/\gamma$ with both the reduced electric field and with the gain, and we compared the results with the experimental data shown in Figs. 6 and 7. We concluded that: i) both the thresholds for charge multiplication and excitation of the atomic emitting levels (Ar$(3'p^5\ 4p)$ and Ar$(3p^5\ 4p')$ occur for E/P values lower than expected from theoretical calculations; ii) below charge multiplication threshold and for very low charge gains $(G < 1.2)$, the number of photons emitted per electron increases linearly with pressure (Fig. 7), in contradiction with theoretical predictions; iii) for higher E/P values, the maximum number of photons emitted per electron tends to decrease with increasing pressure and is shifted toward lower values of E/P, as expected. However, the decrease of the number of photons emitted per electron with increasing pressure is larger then expected, assuming the decay rates given above. In order to reproduce the experimental data, a deactivation rate $k_1 \sim 700$ Torr$^{-2} \cdot$ s^{-1}, due to three-body collisions, has to be introduced, the total decay rate being given then by $\gamma = 1/\tau + k_Q P + k_1 P^2$.

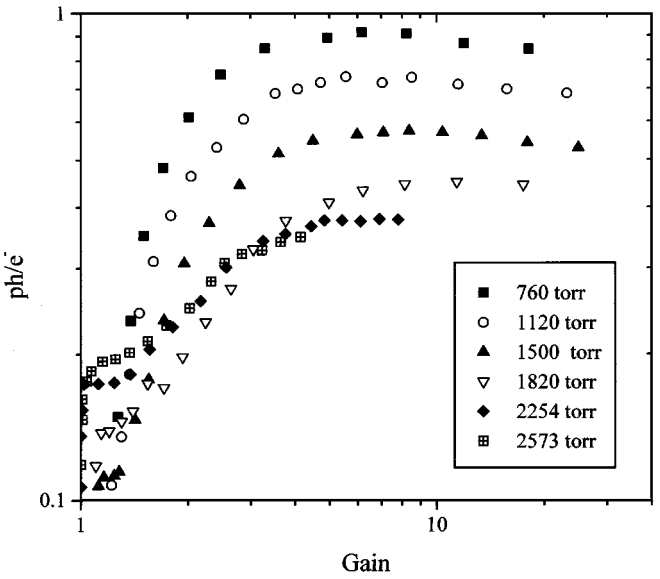


Fig. 6. Total number of photons per electron emitted in argon as a function of the charge gain, for several pressures (gap width $= 4$ mm).

One of the reasons that may account for the disagreement between experimental and theoretical data is the contamination of the gas by impurities. A decrease of the total light output with time followed by a shift toward lower E/P values of the gain versus E/P curve was observed. For low E/P, the experimental values of the reduced ionization coefficients (α_i/P) are well above the theoretical ones, suggesting an effective Penning ionization process, but they do not depend on pressure.

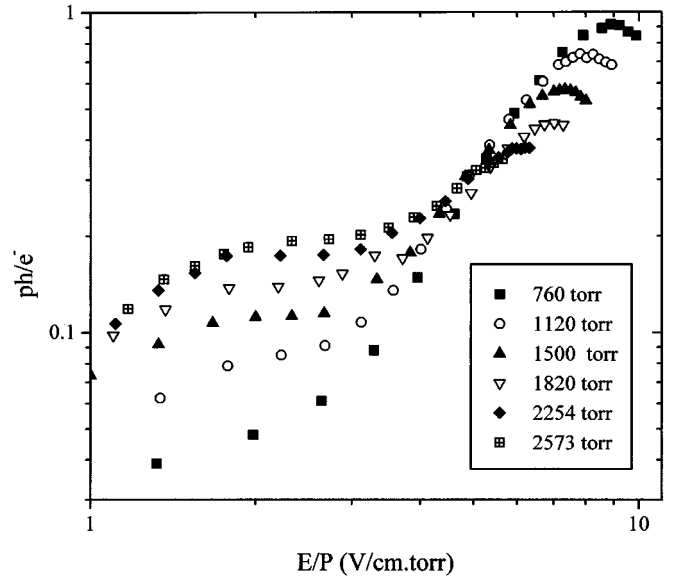
The spectral distribution of the scintillation at 3 atm was measured with the long-pass color glass filters. Results are gathered in Fig. 8. For low E/P values, emissions below 690 nm, probably due to impurities, are important, while for higher values they are negligible. Similar results are also obtained at normal pressure.

Total light yields above 650 nm (to exclude emissions from impurity molecules), normalized to the electron drift current, were also measured as a function of gas pressure and exhibit a behavior similar to the one described above and shown in Fig. 7. The role of impurities in the light production mechanisms is not clear and deserves further investigation.

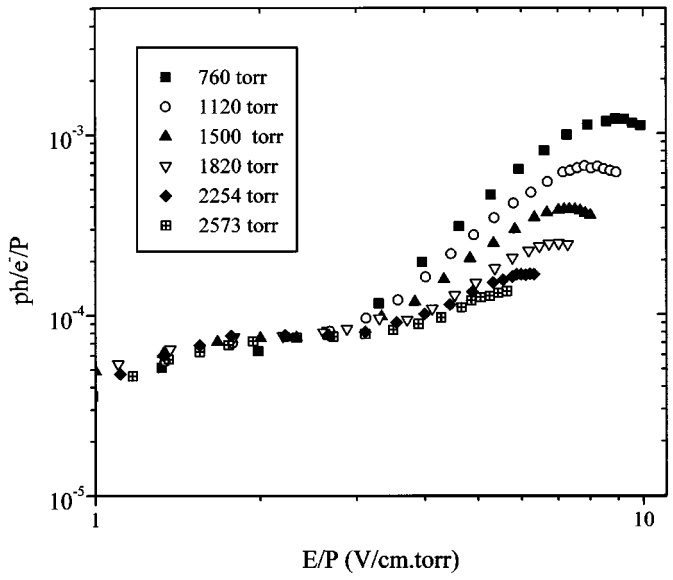
B. Ar/CF_4 Mixtures

The dependence of the secondary scintillation for Ar + 2% CF_4 on the pressure is represented in Fig. 9. As in the case of argon, there is a decrease of the number of photons emitted per electron with increasing pressure. Theoretical predictions of the total light output are more difficult in Ar/CF_4 mixtures because, together with the argon atomic lines, we also observe molecular emissions of CF_3 that cannot be quantified.

As in argon, the impurities also affect the total light output of the Ar/CF_4 mixtures.



(a)



(b)

Fig. 7. (a) Number of photons emitted per drifting electron, in argon, as a function of the reduced electric field. (b) Number of photons emitted per drifting electron and per unit pressure as a function of the reduced electric field (gap width = 4 mm).

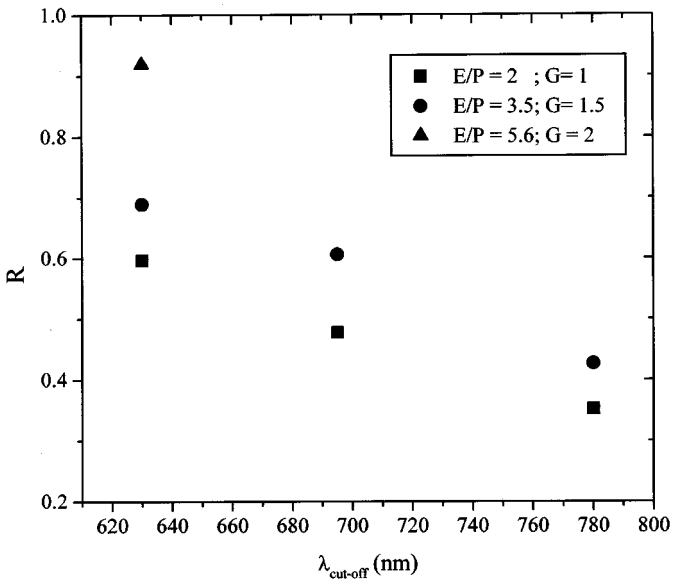


Fig. 8. Ratio between the total light yield with and without long-pass color glass filters as a function of their cutoff positions (specified at 50% internal transmittance) in argon (3 atm), for different E/P values. E/P values are given in $\mathrm{V/cm \cdot torr}$ and the corresponding charge gains are also indicated.

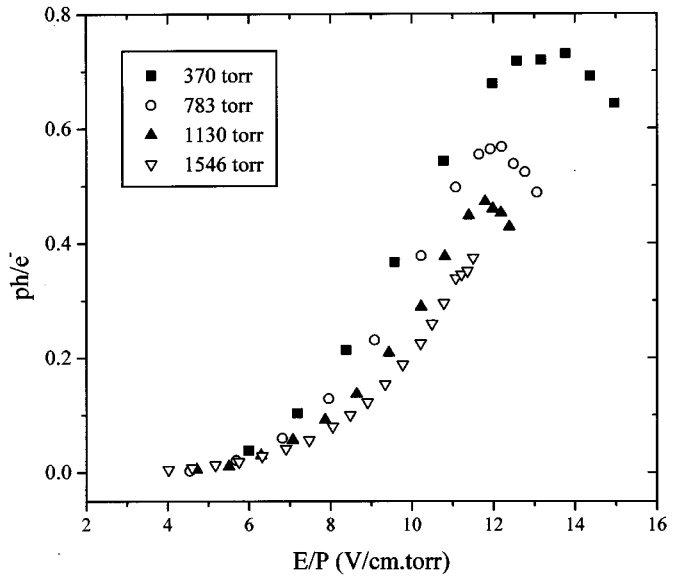


Fig. 9. Number of photons per electron emitted in $\mathrm{Ar} + 2\%\ \mathrm{CF_4}$ as a function of the reduced electric field, for several gas pressures (gap width = 4.5 mm).

V. Conclusion

For $\mathrm{Ar/CF_4}$ mixtures, the emission spectra between 500–900 nm consist of the argon atomic lines, resulting from transitions between the atomic states of the $(3p^5\ 4p)$ and $(3p^5\ 4s)$ configurations, and a molecular continuum attributed to the CF_3 radical. The atomic line intensities decrease with increasing concentration of CF_4, while the intensity of the molecular continuum increases. The total number of photons emitted per drifting electron, in the visible and near-infrared regions, has a maximum value of 0.7 and 0.2 $\mathrm{ph/e^-}$ for $\mathrm{Ar}+2\%\ \mathrm{CF_4}$ and $\mathrm{Ar}+10\%\ \mathrm{CF_4}$, respectively, while in pure argon this number is about 1 $\mathrm{ph/e^-}$. These figures are of practical interest for applications like GEM based imaging devices.

The addition of a third gas component, such as Ne or He is being considered. The study of the scintillation properties of $\mathrm{He/CF_4}$ and $\mathrm{Xe/CF_4}$ are also underway.

It was also shown that the decrease in the scintillation yield with increasing pressure is not severe. The maximum number of photons emitted per drifting electron is shifted toward lower values of the reduced electric field and, in argon, it decreases by a factor of 2.5 when the pressure increases from 1 to 3 atms. This decrease is mainly due to the deactivation of the emitting levels by two-body collisions with argon and impurity molecules in their ground states. However, the quenching by impurity molecules is much less important than the quenching

of the precursor states of the VUV emissions. In "pure" argon, a de-excitation mechanism by three-body collisions also seems to contribute to the total decay rate.

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