A Electric field in the ionization volume

Space charge effects stemming from the presence of slowly-drifting ions can modify the electric field, leading to charge losses due to enhanced charge recombination, or to imperfect electron collection at the anode. For the conditions of our measurements, where the ionization is highly uniform and the external electric field has been established to be uniform within the ionization region, the calculation performed in [34] can be used to assess the situation. In this case, the impact of space charge may be characterized with a single dimensionless parameter α :

$$\alpha = \frac{D}{E_0} \sqrt{\frac{K}{\epsilon \mu}}$$
(A.1)

Here *D* is the conversion gap (0.75 cm), $E_0 = V/D$ is the nominal electric field in the absence of space charge, *V* the voltage drop between anode and cathode, $\epsilon \simeq \epsilon_0$ the electric permittivity of the medium, μ the positive-ion mobility and *K* the rate of creation of electron-ion pairs per unit volume. The latter (in units of [μ C/s/cm³]) was determined at high electric fields, in conditions of full charge-collection.

Using this α parameter the electric field distortion caused by the ions at any location x in the chamber may be calculated simply by evaluation of the following formula [34]:

$$E = \frac{\alpha E_0}{D} \sqrt{x^2 + \left(\frac{DE_{anode}}{\alpha E_0}\right)^2}$$
(A.2)

Before doing that, however, the quantity E_{anode}/E_0 must be obtained by the numerical integration of the aforementioned equation to the whole detector size.

In expression A.1, the input mobilities are obtained in the following way: in argon, the main drifting ions were assumed to be Ar⁺ and their mobility taken from [32]. In the case of Ar/CF₄ mixtures and pure CF₄, CF₃⁺ ions were considered instead and their mobility taken from direct measurements in [33]. CF₃⁺ ions are produced as a byproduct of dissociation/decay of CF₄^{+,*} states [44], or through charge-transfer reactions with CF₄ [33]:

$$Ar^{+} + CF_{4} \xrightarrow{k_{0}} CF_{3}^{+} + Ar + F$$
(A.3)

The electric field h as a numerical dependence on α , that c and b e computed following [34]. As the maximum variations take place close to the anode and cathode, we chose these two cases for representation in Fig. 11, with the experimental conditions corresponding to full charge-collection overlaid (crosses). Based on these results, the field distortions associated to space charge effects are shown to be minimal: values are typically at the ~5%-level or below, with a maximum field distortion of ~15%.

B Charge recombination

Electron-ion and ion-ion recombination, either geminal [64], columnar [65] or volume [66] can reduce the collected charge, so it is important to exclude these during measurements. On general grounds, given the relatively low pressures and X-ray energies, the main contribution to charge recombination is expected to come from the volume, and so being associated to the setup geometry and not to the particle type. Therefore any charge recombination present in the system would render



Supplementary Figure 1. Electric field distortion near the cathode and anode as a function of the α parameter (blue/orange lines). The positions corresponding to the cathode and the anode (x = D and x = 0) are used in the evaluation of equation A.2. Pairs of experimental values obtained in conditions of full charge-collection are overlaid, for all pressures, mixtures and tube intensities employed in this work (crosses).

the interpretation of the results problematic and must be avoided. During the measurements, the electric field was increased, for any given gas mixture and pressure, up to the point where full charge-collection could be guaranteed, within less than 5% variation relative to the flat-top (see Fig. 2-left for the case of pure CF₄). This already assures that all charge is being collected, except perhaps for stray electrons from diffusion, fringe fields or space charge, effects that are expected to be below 5-10% level as per the discussions in previous sections. The good correlation between ionization rate and tube intensity across all the ionization densities considered (Fig. 2-right) confirms the negligible presence of charge recombination.

For both pure Ar and pure CF₄, the existence of recombination light at pressures slightly above atmospheric is well documented in case of α -particles [4, 67, 68]: for argon, recombined electron-ion pairs landing in the first p-multiplet yield VUV photons with 100% efficiency; for CF₄ the visible emission is enhanced, yet the detailed pathways are not known. In this latter case, if considering for reference the scintillation yields of pure CF₄ in the 500-800 nm band (796 ph/MeV for α particles [3]) and its W_I value of 34.3 eV/e⁻ [37], the ratio of electrons to photons is about 37. Therefore, even a 2.5% fraction of recombined charge may double the scintillation yields if recombination light would be emitted with 100% probability. It is thus pertinent to study the spectrum of emission for different electric fields and ionization rates. We have chosen for illustration Ar/CF₄ admixed at 95/5 in Fig. 12, but similar conclusions can be drawn for other admixtures. Besides the large independence observed both with electric field and ionization density, an important additional



Supplementary Figure 2. Emission spectra per eV of released energy for Ar/CF_4 admixed at 95/5 and different pressures. Two different electric field conditions are considered: i) zero field and ii) a field sufficient to reach full charge-collection. Top spectra were taken with a tube current of 40 mA while bottom spectra were taken with lower tube currents of 20, 13, 10 and 8 mA, for the same irradiation time.

result is apparent, that has been discussed in the main text in full: wavelength-shifting properties of Ar/CF₄ mixtures are largely pressure-independent, in the range 1-5 bar.

In order to better understand the absence of charge-recombination effects in our measurements it is possible to resort to previous data, e.g, considering measurements done for α -particles in pure CF₄ at 1 bar [3], for which experimental conditions overlap. The authors reported no recombination light at any electric field in that situation. In our setup the ionization is uniform and volume recombination can be expected to be the main source of charge recombination. When comparing with the conditions in [3], it is thus natural to consider an uniform ionization channel too, with the average ionization and spatial extent of an α particle. We take for simplicity the direction along the field, although this assumption is not critical at the fields discussed (diffusion is largely isotropic). Under the prescribed-diffusion approximation [65], ionization density for α particles can be approximated by:

$$\left(\frac{dN}{dV}\right)_{\alpha} = \frac{\varepsilon}{W_I} \frac{n^2}{(\pi R_{\alpha} D_T^2)} \tag{B.1}$$

where $\varepsilon = 5.5$ MeV is the energy of the α particle, R_{α} its range at $P_0 = 1$ bar and D_T the transverse diffusion at $P_0 = 1$ bar for the corresponding field. The *P*-scaling factors are absorbed in the term

 $n = P/P_0$. Considering $R_{\alpha} = 1.6$ cm [69] and $D_T = 55 \text{ µm/}\sqrt{\text{cm}}$ -obtained with Pyboltz for pure CF₄ at 1 bar- and the electric field conditions in [4] (2.2 kV/cm), the average ionization density amounts to ~ 190 pC/cm³. This is 4 times larger than in our 1 bar measurements, and about the maximum levels throughout our work (Fig. 2-right), thus consistent with the fact that no recombination effects are seen in neither case. At 2 bar, where the average ionization density of an α -track in [3] would quadruple the maximum space charge densities explored here, the authors were still able to obtain a recombination-free spectrum upon application of a field of 2.2 kV/cm, comparable to our full-collection field. Conditions corresponding to $P \ge 3-5$ bar, where recombination became severe in [4] (i.e., full charge-collection not being possible even upon application of fields in the few-kV/cm range), would therefore exceed the ionization densities explored here by a factor of up to 25.

C Gas mixing and calibration

Mixtures were prepared by filling at high C F₄ partial pressure in order to increase the precision of the pressure readings, and diluted then in argon down to low concentrations. The system was left for some time until the concentration displayed by the RGA reached a plateau, moment at which the measurements were conducted. As shown in Fig.13, the pressure ratios of the main CF₄ and argon peaks obtained from the RGA reading show a proportional trend with the target CF₄ concentration estimated from the mixing procedure described above, as expected. Systematic uncertainties due to the resolution of the *P*-gauge and dilution procedure, and pure statistical uncertainties, were used to calculate the total uncertainty for each data point. A χ^2 -fit to a proportionality law was used on Fig.13 to derive a corrected value for the concentration, with its uncertainty (see adjacent table). Even if, for clarity, the target concentration has been used throughout the text, the experimentally-determined one with its uncertainties will be used in trend plots.



Supplementary Figure 3. Left: ratio of the partial pressure of CF_4 to argon peaks measured in the RGA during operation, as a function of the target CF_4 concentration. The error bar is estimated from the statistical deviation of measurements performed at different pressures and from systematic uncertainties due to the *P*-gauge resolution and dilution procedure. Right: target and calibrated concentrations, alongside their uncertainties.