

Eco-friendly gas mixture candidates for MPGDs

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Abstract. Modern gaseous detectors for detection of particles require F-based gases for optimal performance. Recent regulations demand the use of environmentally unfriendly F-based gases to be limited or banned. In this paper the general review of the potential eco-friendly gas candidate replacements is summarized. Details of the review are given in [1].

1 Introduction

Many currently used refrigerant gases have a great impact on the environment since they either contribute largely to the greenhouse gas effect, or because they tear the ozone layer, or both. In an attempt to protect the environment, regulations preventing the production and use of certain refrigerant gases have been implemented [2]. Gas detectors are wide spread for detection, tracking and triggering of charged particles such as muons in Nuclear and High Energy Physics (HEP). A large part of gas muon detectors used in HEP operates with mixtures containing the regulated refrigerants in applications where excellent time resolution and avalanche operation are necessary. Therefore, actions towards finding new mixtures must be undertaken. Gas Electron Multiplier (GEM) [3] detectors operate in experiments such as CMS (Compact Muon Solenoid) at the LHC (Large Hadron Collider) with an argon/CO₂ mixture [4]. However, for high time resolution applications an argon/CO₂/CF₄ mixture is used [5], where CF₄ has a Global-Warming Potential (GWP) of 7390 [6]. Resistive Plate Counters (RPC) [7] currently operate with a F-based R134a/Isobutane/SF₆ gas mixture, with typical GWP of 1430. Investigations into new gas mixtures have to be performed in order to keep the mixture properties while complying with the regulations. A few industrial refrigerant industrial replacements were proposed [8] as alternatives to R134a. A study of transport properties of currently used gas mixtures in HEP, and an evaluation of transport properties of freon-less gas mixtures, was recently published [9].

2 Gas properties

For a gas mixture to be appropriate in a gas detector, first of all it has to comply with the regulations. Furthermore, its properties must also be appropriate for the specific type of detectors. For example, a gas that is suitable for the RPC detectors may not be fully optimised for the GEM detectors. To better find the appropriate gas for a detector, an understanding of the influence of different parameters is required. This section aims to clarify the most essential parameters for gases.

In order to estimate the impact of a refrigerant on the environment, the effects have to be quantified. Two important effects are the contribution to the greenhouse effect and the depletion of the ozone layer. The first mentioned effect is measured in Global Warming Potential (GWP), and is normalised to the effect of CO₂ (GWP = 1), while the effect on the ozone layer is measured in Ozone Depletion Potential (ODP), normalised to the effect of CCl₃F (ODP = 1). The general properties of selected refrigerant candidates are listed in Table 1. When a particle passes through a medium, energy is transferred from the particle to the surroundings. The energy lost is typically defined as the stopping power expressed as $\frac{1}{\rho} \left(\frac{dE}{dx} \right)$ where ρ denotes the density of the medium, E denotes energy, and x is length. The radiation length X_0 is a characteristic length of a medium. It describes both the mean distance required for a high energy electron to lose all but e⁻¹ of its energy due to bremsstrahlung, and $\frac{7}{9}$ of the mean free path of a e⁺e⁻ produced by a high-energy photon [10]. When an incoming particle passes through a medium, it will eventually interact with the medium and transfer some of its energy to ionize atoms. In this process, a pair consisting of an ionized atom and a free electron is produced. The

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number of ionisations produced by an incoming particle per unit length is denoted by N_p , in units of cm^{-1} . Each produced ion pair will have an initial kinetic energy and can itself produce an ion pair, called secondary ion pair production. In the absence of an electric field, electrons move randomly in all direction having an average thermal energy $\frac{3}{2}kT$. In the presence of an electric field, the electrons start to drift along the field direction with mean drift velocity v_d (the average distance covered by the drift electron per unit time). The average distance an electron travels between ionising collision is called mean free path and its inverse is the number of ionising collision per centimetre (the first Townsend coefficient). This parameter determines the gas gain of the gas.

Many refrigerants may constitute a danger for the user and its environment. The greatest dangers involved are the flammability and toxicity. The Health Material Hazardous Material Information System (HMIS), rates Health/Flammability/ and Physical hazards from 0 (low) to 4 (high). Some refrigerants are incompatible with certain materials, and can either react violently, or have long term effect. Some refrigerants may even produce toxic decomposition and/or polymerisation.

3 Estimation of Gas Parameters

Quantities such as the minimum ionization energy can be found if the stopping power is known. An approximate expression for moderately relativistic particles in the momentum region $0.1 \leq \gamma\beta \leq 1000$ can be found using the Bethe-Bloch equation, given by

$$\frac{1}{\rho} \left(\frac{dE}{dx} \right) = K Z^2 \frac{Z}{A} \frac{1}{\beta^2} \left(\frac{1}{2} \ln \frac{2m_e c^2 \beta^2 \gamma^2 T_{\max}}{I^2} - \beta^2 - \frac{\delta(\beta\gamma)}{2} \right) \quad (1)$$

Where $\left(\frac{dE}{dx} \right)$ is the mean energy loss per length, ρ denotes the density of the medium, I is the mean excitation energy and $\delta(\beta\gamma)$ is the density effect correction function to ionization energy loss. K is a constant given by $4\pi N_A r_e^2 m_e c^2 r^2$ and T_{\max} is the maximum energy transfer in a single collision, given by

$$T_{\max} = \frac{2m_e c^2 \beta^2 \gamma^2}{1 + \frac{2\gamma m_e}{M} + (m_e/M)^2} \quad (2)$$

where M is the mass of the incoming particle. The radiation length X_0 of an atom can be found by [10],

$$X_0 = \frac{716.405(\text{cm}^{-2} \text{mol})A}{Z^2(L_{\text{rad}} - f(z)) + ZL'_{\text{rad}}} \quad (3)$$

Table 1 describes the important parameters of some refrigerants. An approximate correlation between primary ionization and atom number has been found based on experimental data by [11]

$$N_p = 3.996 \left(\frac{Z_m}{Z^{0.4}} \right) - 0.025 \left(\frac{Z_m}{Z^{0.4}} \right) \text{cm}^{-1} \quad (4)$$

The above expression holds at normal temperature and pressure (NTP) (1atm, 20°C). For different pressure and

Table 1: Minimum ionization energy, energy loss, radiation length and number of primary ion pair creation for the considered refrigerants.

Name	I [eV]	$\left(\frac{1}{\rho} \frac{dE}{dx} \right)$ [MeV $\frac{\text{cm}^2}{\text{g}}$]	X_0 [$\frac{\text{g}}{\text{cm}^2}$]	N_p [cm^{-1}]
R32	89.3602	1.80973	35.4581	49.2
R7146	127.401	1.67833	28.6027	92.0
R600a	47.848	2.24057	45.2260	81.0
R1234yf	91.9674	1.7734	35.8204	89.5
R152a	78.1889	1.88706	37.0969	67.1
R1234ze	91.9674	1.7734	35.8204	89.5
R115	116.695	1.69178	29.2197	98.4
R1233zd	106.689	1.73915	29.7636	105
R290	47.0151	2.26184	45.3725	65.2
R1311	271.737	1.42486	11.5399	272
R134a	95.0294	1.76439	35.1542	81.6
R14	107.127	1.69909	33.9905	63.6
R123	125.275	1.69722	25.5416	98.4
R143a	87.8152	1.8126	35.8928	74.8
R744	88.7429	1.81124	36.1954	37.2
R23	99.9508	1.7402	34.5214	56.9
R116	105.075	1.70566	34.2947	93.3
RC318	101.578	1.71721	34.8435	123
R218	104.13	1.70873	34.439	117

temperature, the number scales with the density. This value should only be taken as a rough estimation though. This formula has proven to work best for hydrocarbons and worst for molecules consisting mainly of fluorine, differing as much as 30% from the experimental value for CF_4 .

4 Molecules and their optimized geometries

The freon gases we have been interested in are R134a (CH_2FCF_3), R152a ($\text{C}_2\text{H}_4\text{F}_2$), HFO1234ze (CFHCHCF_3), HFO1234yf ($\text{CH}_2\text{CF}_2\text{CF}_3$), CF_3I and HFO1233zd (CHClCF_3). Meanwhile we choose R12(CCl_2F_2) to be the standard freon gas model. CH_4 and CF_4 are the molecules we used to make a comparison between the results calculated by using the quantum chemistry calculation tool NWC_{HEM} and experimental results, in order to check the reliability of NWC_{HEM} . Figure 1 shows the optimized ground state geometries of gas molecules, where the green balls stand for carbon atoms, the grey balls stand for hydrogen atoms, the indigo balls stand for fluorine atoms, the brown balls stand for chlorine atoms, and purple ball for iodine. Figure 2 shows the highest occupied molecular orbitals (HOMO) of gas molecules.

5 Calculation of the absorption spectrum

The excitation energy of a molecule is one of the fundamental properties of molecular interactions one can get

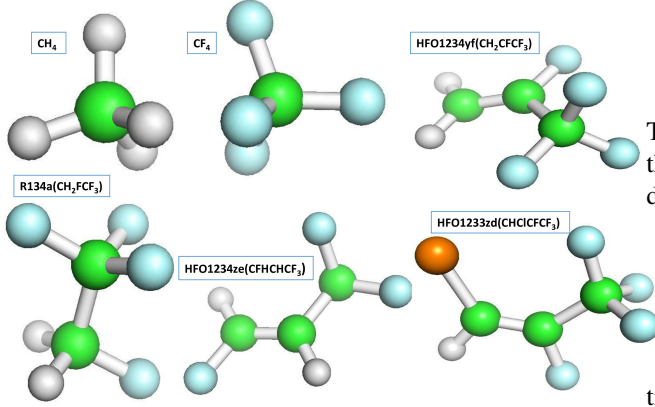


Figure 1: Optimized ground state geometries of gas molecules.

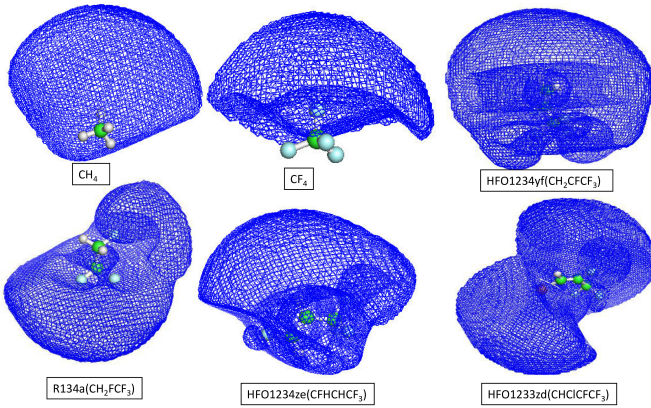


Figure 2: Highest Occupied Molecular Orbitals (HOMO) of gas molecules.

from experiment. To study these properties, we used the framework introduced in Ref.[12] to simulate the time-dependent response of molecules under external fields using quantum chemical calculations. The framework implemented is the Real-Time Time-Dependent Density Functional Theory (RT-TDDFT) [13] method within the NWCHEM, making it capable of doing the simulation beyond small perturbation from the ground state. In our case, we are mostly interested in low excitations of small molecules. We therefore adopt the procedure as described in Section 3 of the reference [12]. The choice of the external field is a δ -function-like electric field “kick”.

$$E(t) = k \cdot \exp\left[\frac{-(t-t_0)^2}{2\omega^2}\right] \hat{d} \quad (5)$$

where t_0 is the centre of pulse, ω is the pulse width, which has dimensions of time, $\hat{d} = \hat{x}, \hat{y}, \hat{z}$ is the polarization of the pulse, and k is the maximum field strength. The system is then evolved in time, and the dipole moment can be calculated with respect to the added dipole coupling term

$$V_{\mu\nu}^{\text{app}}(t) = -D_{\mu\nu} \cdot E(t) \quad (6)$$

where D is the transition dipole tensor of the system. Then we Fourier transform the dipole signals to construct the complex polarizability tensor $\alpha_{ij}(\omega)$, and finally the dipole absorption spectrum is

$$S(\omega) = \frac{1}{3} \text{Tr}[\sigma(\omega)] = \frac{4\pi\omega}{3c} \text{Tr}[\text{Im}[\alpha_{ij}(\omega)]] \quad (7)$$

We first validate our calculation of the lowest excitation energy of CH_4 as given in the paper [12]. With the same basis set (6-311G) and functional (B3LYP), our calculation gives 11.16 eV excitation energy, which is consistent with the 11.13 eV in the paper. The small difference can come from minor uncertainty sources like the choice of time separation in the simulation. We further checked the dependence of our result on the wave function basis sets and the density functional. The dependence of basis sets is found to be much smaller than the functional one.

6 Calculation of the vertical ionization energy and the electron affinity

The vertical ionization energy and the electron affinity are another two important parameters closely related to experiments. In the case of small molecules, there is a simple way to do the estimation. The Koopman's theorem states that at in closed-shell Hartree-Fock (HF) theory, the negative value of the Highest Occupied Molecular Orbital (HOMO) energy is a good approximation of to the experimental ionization energy (IE). Similarly, it also suggests that the electron affinity (EA) is equal to the negative of the Lowest Unoccupied Molecular Orbital (LUMO) energy. However, the EA part of the prediction is in general not reliable because of the large effect of orbital relaxation on the LUMO eigenvalue [14] [15].

For the electron affinity calculation, we calculated the LUMO with two methods. The Hartree-Fock method, computes the closed-shell Restricted Hartree-Fock (RHF) wave functions, and the Density Functional Theory (DFT), computes the closed shell densities and Kohn-Sham orbitals in the Generalized Gradient Approximation.

7 Estimation of the first Townsend parameter

Following Ref. [16], we express the dependance of the first Townsend parameter α as a function of the reduced electric field $\frac{E}{p}$, and $\frac{\alpha}{p} = A \exp\left[\frac{-Bp}{E}\right]$. The reference [16] shows that the first Townsend coefficient at high reduced electric field depends almost entirely on the mean free path of the electrons. The mean free path, which is defined as $\lambda_m = \frac{1}{n\sigma}$. where n is the number of atoms per unit volume and σ is the total cross section for electron collision with atoms, can be calculated if the environment of gas molecule is provided. For real gases, we cannot take the

free path lengths as a constant and the ionization cross section is only a fraction of the total cross section. In that case the estimation needs to be modified and use the following equation:

$$\alpha(r) = A_p \cdot \exp\left(\frac{-Bp}{E(r)}\right) \left(1 - \exp\left(\frac{-I_0 n \sigma}{eE(r)}\right)\right) + n \sigma_i \cdot \exp\left(\frac{-I_0 n \sigma}{eE(r)}\right) \quad (8)$$

Numerous measurements of the Townsend coefficients are available for standard gas mixtures, such as those reviewed in [17].

8 Conclusions

Currently used F-based gases in HEP gas detectors are being phased out by industry and will be replaced by ecofriendly substitute gases. In this paper we have presented a survey of F-based eco-friendly gases properties like physical properties, materials compatibility and other parameters of interest for their use in HEP detectors. Important parameters have been computed following different approaches ranging from parametrizations to quantum chemical calculations: number of primary pairs, vertical ionization energy and the electron affinity. Statistical methods to compute amplification parameters of the ionization shower production such as the Townsend coefficients were discussed. Promising candidates (such as HFO1234ze, HFO1234yf, CF₃I and HFO1233zd) with lower GWP/ODP, suitable physical parameters, low or null flammability are identified for further experimental studies focused on both particles detection efficiency and materials compatibility.

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