

## Candidates to replace R-12 as a radiator gas in Cherenkov detectors<sup>☆</sup>

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### ABSTRACT

Dichlorodifluoromethane (R-12) has been widely used as a radiator gas in pressure threshold Cherenkov detectors for high-energy particle physics. However, that compound is becoming unavailable due to the Montreal Protocol. To find a replacement with suitably high refractive index, we use a combination of theory and experiment to examine the polarizability and refractivity of several non-ozone-depleting compounds. Our measurements show that the fourth-generation refrigerants R-1234yf (2,3,3,3-tetrafluoropropene) and R-1234ze(E) (*trans*-1,3,3,3-tetrafluoropropene) have sufficient refractivity to replace R-12 in this application. If the slight flammability of these compounds is a problem, two nonflammable alternatives are R-218 (octafluoropropane), which has a high Global Warming Potential, and R-131i (trifluoroiodomethane), which has low Ozone Depletion Potential and Global Warming Potential but may not be sufficiently inert.

### 1. Introduction

The Cherenkov effect is often exploited in particle physics experiments. When a charged particle moves through a medium faster than the speed of light in that medium, photons are emitted. The most common detectors based on this effect are pressure threshold detectors, in which the presence or absence of Cherenkov radiation upon variation of gas pressure (and thus refractive index) is used to “tag” the type of particle (proton, pion, etc.) [1,2]. For particle beams of high momenta (hundreds of GeV/c), for example the secondary beams in the East and North Area of the CERN PS and SPS accelerators [3], common gases such as helium or CO<sub>2</sub> can be used.

However, when the beam particles have low momenta (a few GeV/c or less), such as in CERN’s future Neutrino Platform Facility [4], a radiator gas of high refractive index is required. R-12 (dichlorodifluoromethane) has been used in low-momentum threshold Cherenkov detectors; Ref. [2] is an early example of this technology. However, the high Ozone Depletion Potential (ODP) of R-12 has led to its phase-out under the Montreal Protocol [5]. It is therefore necessary to find a replacement with similar refractivity but zero ODP.

In many refrigeration applications, such as automobile air conditioning, R-12 was replaced in the 1990s by R-134a (1,1,1,2-tetrafluoroethane), which has similar thermodynamic properties but zero ODP. This led Charitonidis et al. [6] to examine R-134a as a radiator gas in an experiment with a low-energy hadron beam. Their results suggested that the refractivity of R-134a was lower than that of R-12 by

roughly 30%, which would limit its ability to identify low-momentum particles.

Here, we use physical principles to identify candidates to replace R-12 in these detectors. The key principle is the relationship between the refractive index  $n$  and the molecular electronic polarizability  $\alpha$ , as given by the extended Lorentz-Lorenz equation:

$$\frac{n^2-1}{n^2+2} = \rho \left( \frac{4\pi}{3} N_A \alpha + B_R \rho \right) = \rho (A_R + B_R \rho), \quad (1)$$

where  $N_A$  is Avogadro’s number and  $\rho$  is the molar density. The  $A_R$  term is dominant; the refractive virial term  $B_R$ , representing the effect of interactions between pairs of molecules, is negligible except in highly precise work such as the measurements reported here. While Eq. (1) requires  $n$  and  $\alpha$  to be measured at the same wavelength, for our purpose the dispersion across the visible spectrum and into the near-UV, where Cherenkov detectors typically operate, should not be significant (these gases are transparent in the visible region). Eq. (1) shows that searching for compounds of high refractive index is equivalent to searching for molecules of high polarizability.

In this work, we identify candidate compounds and estimate their polarizabilities with both structure-based correlations and density functional theory (DFT) quantum computations. We then report refractivity measurements for two compounds lacking experimental data. Ultimately, we identify four viable candidates and discuss the tradeoffs among them.

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## 2. Identification of candidate compounds

The first criterion for a compound is that its molecular electronic polarizability be similar to, or greater than, that of R-12. Hohm [7] examined available data and recommended the electronic polarizability  $6.35 \times 10^{-24} \text{ cm}^3$  for R-12. Chlorinated gases such as R-12 have relatively large polarizabilities because of their many electrons. If we avoid ozone-depleting chlorinated compounds, increasing the polarizability requires molecules with a larger number of atoms lighter than chlorine (carbon, fluorine, etc.), or possibly molecules with a heavier atom such as bromine or iodine (which are, however, also ozone-depleting). However, such molecules may not be sufficiently volatile, as discussed below.

The Global Warming Potential (GWP) is also significant. Many third-generation refrigerants, such as R-134a, are being replaced in applications because of their high GWP. Current international agreements mandate a reduction of high-GWP compounds, but not a complete phase-out [5,8]. Use of these compounds in research will likely be feasible for the foreseeable future, but all else being equal it would be better to avoid molecules with a high GWP.

Additional factors include toxicity, flammability, and availability. These may vary in importance depending on the application. In some cases, safety considerations may dictate that no flammability is acceptable, while in other cases compounds that are slightly flammable may be allowed. A “slightly flammable” classification is defined by ASHRAE [9] and ISO [10] as a flame propagation speed below 10 cm/s.

A vital criterion is that the compound must remain a gas in the operating range of the detector. The efficiency of threshold Cherenkov detectors is lost if the gas liquefies (since the high-density fluid will scatter or absorb all the beam particles), and they are usually operated at pressures up to roughly 0.3 MPa. This means that the equilibrium vapor pressure of the compound should be significantly above 0.3 MPa at the temperature of operation. As a measure of volatility, we use the vapor pressure at 20 °C. For R-12, this is 0.566 MPa as computed by the reference equation of state (EOS) of Marx et al. [11] implemented in NIST’s REFPROP database [12]. Therefore, any compound with vapor pressure similar to or greater than that of R-12 should be sufficiently volatile. Table 1 shows the vapor pressures computed from the best available component-specific EOS [11,13–17] for compounds considered in this work.

Based on these criteria, we choose four compounds for further investigation. R-1234yf (2,3,3,3-tetrafluoropropene) is replacing R-134a in automotive air conditioning; it has zero ODP and very low GWP. It is slightly flammable (ASHRAE classification 2L). A similar, even less flammable (but also less widely available) compound is R-1234ze(E) (*trans*-1,3,3,3-tetrafluoropropene). R-218 (octafluoropropane) is non-flammable, but has a high GWP. R-131I (CF<sub>3</sub>I, trifluoroiodomethane) is nonflammable; while iodine catalyzes the destruction of stratospheric ozone, UV radiation in the atmosphere causes CF<sub>3</sub>I to decompose quickly (before reaching the stratosphere) so that its ODP and GWP are small [18,19]. We also list R-12 and R-134a for comparison purposes. In Table 1, it is evident that the alternatives have sufficient volatility for this application, with the possible exceptions of R-1234ze(E) and R-131I, both of which will liquefy at a somewhat lower pressure than R-12.

**Table 1**  
Vapor pressure at 20 °C calculated from reference EOS.

Compound	Vapor pressure (MPa)	EOS reference
R-12	0.566	Marx et al. [11]
R-134a	0.572	Tillner-Roth and Baehr [13]
R-1234yf	0.592	Richter et al. [14]
R-1234ze(E)	0.427	Thol and Lemmon [15]
R-218	0.756	Lemmon and Span [16]
R-131I	0.427	Lemmon and Span [17]

After this work was submitted, Saviano et al. [20] published a review (based on a CERN report [21]) of properties of ecologically friendly gases for potential use in particle detectors. While Refs. [20] and [21] contain much useful information, refractivity was not among the properties examined.

## 3. Estimation of electronic polarizability

The polarizability is known from experiment for some but (to our knowledge) not all of the compounds in Table 1. We therefore examine methods for estimating polarizability, applying them to the compounds whose polarizability is known as a check on their reliability. We use experimental values for R-12, R-134a, R-218, and R-131I recommended by Hohm [7]; in Table 2 we give these along with references to the original measurements [22–25].

The electronic polarizability of a molecule can be estimated as a sum of contributions from its constituent atoms, or from groups of atoms or from individual bonds. These polarizability contributions are regressed to a large set of data for compounds with known polarizability, and the results are used to provide estimates for other molecules. Many such group-contribution methods have been proposed; we apply two relatively simple ones here. Le and Weers [26] developed group contributions based on data for 160 fluorine-containing compounds. Wang et al. [27] examined several methods based only on atomic composition and the hybridization state of carbon atoms; we use their “model 2E” which gave the best results in their study. Both methods are, according to their authors, able to reproduce experimental polarizabilities within roughly 5%. In Table 2, we present the results of these methods for the molecules identified in Section 2. The two group-contribution methods differ significantly for R-218 and for R-131I, but are consistent within less than 6% for the other compounds. The agreement with existing experimental values is within 10% in all cases.

It is also possible to calculate the electronic polarizability of small molecules from quantum mechanics (DFT in this work) applied to the molecular wavefunction. In principle, high accuracy can be achieved; in practice, error is introduced by the approximations necessary to perform the calculations in a reasonable amount of computer time. We calculated isotropic polarizabilities with the B3LYP density functional [28,29], using basis sets of triple-zeta quality (aug-cc-pVTZ-PP [30] for I; aug-cc-pVTZ [31,32] for other elements). A recent study [33] showed that this approach agrees with experimental polarizabilities within a standard deviation of approximately  $0.3 \times 10^{-24} \text{ cm}^3$ , which is less than 5% of the polarizability of the molecules considered here. The DFT calculations were performed with Gaussian 09 [34,35]. The polarizabilities calculated in this manner are given in Table 2. The agreement with group-contribution estimates is good, and agreement with experiment for the previously measured R-12, R-134a, R-218, and R-131I is within 6%.

## 4. Experimental refractivity measurements

Refractivities ( $n - 1$ ) were measured with the apparatus described in Ref. [36]. The refractometer consists of a gas triple-cell integrated into a monolithic heterodyne interferometer; we call the device a monolithic interferometer for refractometry (MIRE). A simplified schematic of the apparatus is shown in Fig. 1. It features a quad-pass triple-cell, where both measurement and reference arms of the interferometer pass twice through the center cell filled with gas at the same pressure and temperature. The MIRE also features closely spaced co-propagating beams, which pass through optical paths at almost the same temperature, minimizing temporal drifts in the interferometer phase difference that can otherwise preclude high-accuracy measurement.

To measure gas refractivity, we begin by measuring the interferometer phase when all three cells are pumped to high vacuum (below 1 mPa); then we fill the center cell with the gas of interest and

**Table 2**  
Electronic polarizability (in  $10^{-24} \text{ cm}^3$ ) for compounds considered in this work.

Compound	Group contribution [26]	Group contribution [27]	DFT	Experiment	Experimental reference
R-12	6.48	6.66	6.71	6.35	Bulanin & Kislyakov [22]
R-134a	4.96	4.74	4.61	4.55	Meyer & Morrison [23]
R-1234yf	6.52	6.49	6.24	6.199	This work
R-1234ze(E)	6.85	6.49	6.24	6.199	This work
R-218	6.32	7.08	6.85	6.52	Bulanin et al. [24]
R-1311	7.04	8.25	7.72	7.48	Swift et al. [25]

remeasure the phase. The total change in phase is some integer increment  $N$  plus a fraction  $\Delta\phi$  of a fringe. The gas refractivity is calculated as

$$n-1 = \frac{(2\pi N + \Delta\phi) \cdot \lambda}{8\pi L} - \frac{2d_w p}{L}, \quad (2)$$

where  $\lambda = 632.9908 \text{ nm}$  is the vacuum-wavelength of the laser,  $L \approx 254 \text{ mm}$  is the length of the triple-cell at the point the laser beams pass through, and  $d_w$  accounts for changes in thickness and refractive index of the cell window, proportional to applied pressure  $p$ . These three terms were determined before refractivity measurements by other means: the vacuum-wavelength was calibrated relative to an iodine-stabilized laser; the triple-cell length was measured with a coordinate-measuring machine; window distortion was determined by making refractivity measurements in triple-cells of different length, but almost identical material properties, end geometries, and beam locations on the windows (achieving cancellation of systematic error) [36]. It is worth noting that the change in fringe number  $N$  in Eq. (2) cannot be predicted from the pressure change at a given temperature when the relationship between pressure and refractivity is unknown. Therefore, we electronically count  $N$  while the center cell is slowly filled from vacuum to final pressure ( $N \approx 1600$  for a change from vacuum to 100 kPa at 293 K).

We measured  $(n-1)$  at temperatures near  $20^\circ\text{C}$ , at pressures from approximately 31–113 kPa. The experimental data are reported in Table 3 for R-1234yf and in Table 4 for R-1234ze(E).

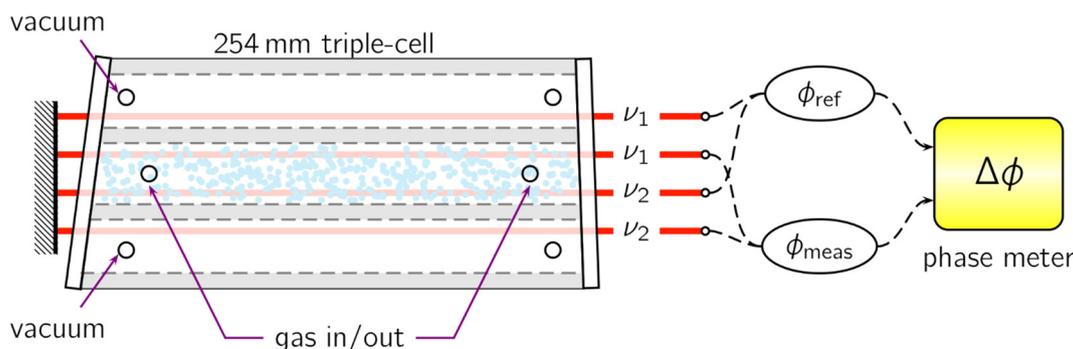
Uncertainty in these measurements is dominated by sample purity; the samples and their impurity analysis were described in Ref. [14] for R-1234yf and in Ref. [37] for R-1234ze(E). We estimate that roughly 0.04% mole fraction impurities contribute a  $200 \times 10^{-6} \cdot (n-1)$  uncertainty to the refractivity measurement. By comparison, uncertainties in pressure and temperature measurements contribute  $14.6 \times 10^{-6} \cdot (n-1)$  uncertainty at 100 kPa, while errors in MIRE only contribute  $0.2 \times 10^{-6} \cdot (n-1)$  uncertainty. However, an additional uncertainty arises due to absorption of the gas into elastomer o-rings: our apparatus has two 6.35 mm diameter silicone, and one 40 mm diameter viton, o-rings exposed to a gas volume of  $150 \text{ cm}^3$ . It is known that elastomers increase in weight when exposed to these refrigerants [38]. When we fill our cell with gas, we observe a decrease in pressure

**Table 3**  
Measured refractivity for R-1234yf at  $\lambda = 632.9908 \text{ nm}$ .

Pressure (kPa)	Temperature (K)	$10^6(n-1)$
37.6502	293.156	365.756
40.3159	293.156	391.918
45.6089	293.156	443.971
50.7584	293.156	494.741
55.8743	293.156	545.324
60.4444	293.157	590.608
66.7925	293.156	653.685
70.2356	293.157	687.954
77.0123	293.158	755.645
81.4092	293.157	799.653
86.0775	293.157	846.508
87.2459	293.157	858.233
95.0413	293.157	936.753
95.1996	293.157	938.339
99.4731	293.159	981.524
102.8133	293.159	1015.294
105.8875	293.157	1046.477
105.9283	293.158	1046.899
110.1592	293.158	1089.822
112.7656	293.158	1116.368

of about  $5.6 \times 10^{-4} p/h$ , but the concurrent decrease in refractivity is about  $45 \times 10^{-6} \cdot (n-1)$  larger than would be expected from Eq. (1). We therefore extrapolate back to the time immediately after a gas fill, but this extrapolation adds a  $9 \times 10^{-6} \cdot (n-1)$  uncertainty to our measured refractivity. These stated uncertainties are relative standard uncertainties ( $k = 1$ ).

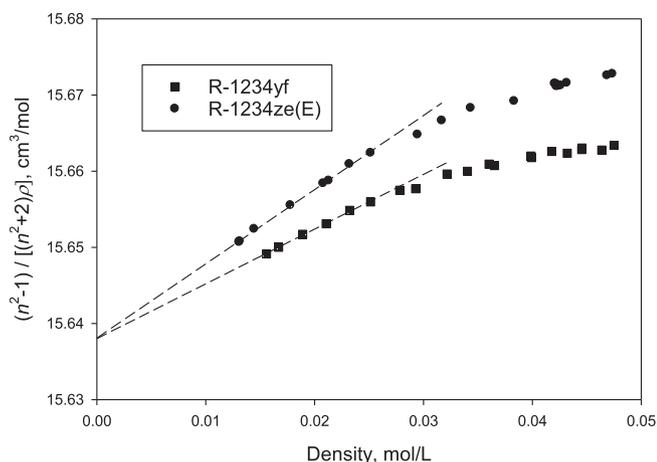
Our uncertainty in pressure measurement comes from using MIRE as a primary pressure standard with helium gas [39] to calibrate a pressure transducer. The calibrated transducer was subsequently used to gauge pressure within an uncertainty of  $u(p) = [(0.6 \text{ Pa})^2 \pm (12.5 \times 10^{-6} p^2)]^{1/2}$  when MIRE was used to measure the refractivity of other gases; the 0.6 Pa offset in the calibration is chiefly due to instability in the interferometer phase, which dominates uncertainty in MIRE when measuring helium refractivity at low pressure. This calibration procedure allowed us to accurately measure refractivity as a function of pressure. The molecular polarizability is determined from a plot on coordinates suggested by Eq. (1). In the low-



**Fig. 1.** Simplified schematic of MIRE.

**Table 4**  
Measured refractivity for R-1234ze(E) at  $\lambda = 632.9908$  nm.

Pressure (kPa)	Temperature (K)	$10^6(n - 1)$
31.6586	293.157	307.307
31.8003	293.157	308.695
34.9653	293.157	339.722
42.9285	293.157	418.009
50.0961	293.158	488.771
51.2969	293.159	500.649
55.8042	293.158	545.339
60.4300	293.156	591.296
70.5924	293.158	692.630
75.8183	293.158	744.990
82.0430	293.159	807.530
91.3429	293.159	901.291
99.9910	293.161	988.986
100.3664	293.160	992.798
100.3666	293.161	992.777
100.7295	293.161	996.463
101.2697	293.158	1001.964
102.5648	293.161	1015.133
111.1069	293.159	1102.230
112.2327	293.159	1113.742



**Fig. 2.** The Lorentz-Lorenz quotient  $\frac{n^2 - 1}{(n^2 + 2)\rho}$  as a function of molar density. Dashed lines indicate extrapolation of Eq. (1) to zero density.

density limit, the quotient  $\frac{n^2 - 1}{(n^2 + 2)\rho}$  is  $A_R = \frac{4\pi}{3} N_A \alpha$ ; the  $B_R$  term gives a small variation of the quotient with density. Fig. 2 shows our data on these coordinates, with density computed from the reference EOS for each gas listed in Table 1.

Similar results are obtained for both gases. The curvature at higher density in Fig. 2 is surprising; terms of higher order than  $B_R$  should not be significant at pressures near 100 kPa. This may indicate inaccuracy in the nonideal gas behavior of the EOS used to calculate densities, or it might be an artefact of the absorption mentioned above. To extrapolate to zero density from the linear region, we fitted lines to points at densities below 0.026 mol/L. The resulting intercepts are nearly identical at  $15.638 \text{ cm}^3/\text{mol}$ , yielding  $\alpha = 6.199 \times 10^{-24} \text{ cm}^3$  for both R-1234yf and R-1234ze(E). While one might not expect such exact agreement, it is not surprising that structural isomers would have nearly identical polarizability, since the polarizability depends much more strongly on the atoms within a molecule than on the way in which the atoms are arranged. These experimental polarizabilities are within 1% of the values calculated by DFT. The largest components of the uncertainty are the extrapolation to zero density and the effect of impurities; we estimate a combined standard uncertainty in  $\alpha$  of  $0.002 \times 10^{-24} \text{ cm}^3$ .

## 5. Discussion and conclusions

Our measurements show that both R-1234yf and R-1234ze(E) have molecular electronic polarizabilities near that of R-12, making their refractivity sufficient for replacing R-12 as Cherenkov radiators. The polarizability of R-218 is slightly higher than that of R-12 [24], and that of R-131I is about 15% larger [25], so both of those gases should also be suitable.

If flammability were not a concern, R-1234yf might be preferred, since it is readily available, has a low GWP, and is more volatile than R-1234ze(E). If flammability is of concern but is not a disqualifying factor, R-1234ze(E) could be considered since its flammability is even less than the slightly flammable R-1234yf; a possible negative would be its lower volatility. If safety considerations allow no flammability at all, R-218 or R-131I would be good candidates. R-218 has sufficient refractivity and volatility. Its disadvantage is a high GWP, but this should not be a serious issue for a scientific application, particularly one in which the gas will not be released into the environment during normal operation. R-131I has the highest refractivity of all the gases considered here, potentially allowing a wider range of operation of detectors. Its disadvantage is a lower volatility than other candidates, and also potentially its stability. R-131I dissociates when exposed to UV radiation, with the absorption peak near 270 nm [18,19], near where Cherenkov detectors typically operate. It is not clear to the present authors to what degree this absorption and dissociation might compromise the operation of pressure threshold Cherenkov detectors. R-131I may also have toxicity issues related to cardiac sensitization [40].

If for some reason none of the gases identified here proves to be a suitable substitute for R-12, a logical next step would be to perform a more thorough search through the space of possible chemicals, as McLinden et al. [41] recently did for potential working fluids in refrigeration applications.

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