Physica Scripta

**PAPER • OPEN ACCESS**

# Identifying molecules with high electrical strength

To cite this article: Chunlin Wang *et al* 2023 *Phys. Scr.* **98** 065401

View the article online for updates and enhancements.

You may also like

- Methane mitigation timelines to inform energy technology evaluation
Mandira Roy, Morgan R Edwards and Jessika E Trancik
- Stable climate metrics for emissions of short and long-lived species—combining steps and pulses
William J Collins, David J Frame, Jan S Fuglestvedt et al.
- GWP*is a model, not a metric
Malte Meinshausen and Zebedee Nicholls

This content was downloaded from IP address 193.60.240.99 on 12/06/2023 at 22:29

Physica Scripta

OPEN ACCESS

RECEIVED
11 January 2023

REVISED
22 March 2023

ACCEPTED FOR PUBLICATION
4 May 2023

PUBLISHED
16 May 2023

Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence.

Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

PAPER

# Identifying molecules with high electrical strength

**Chunlin Wang**[1,2], **Bridgette Cooper**[1] **and Jonathan Tennyson**[1]

[1] Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom
[2] Huaneng (Zhejiang) Energy Development Co., Ltd. Hangzhou Zhejiang 310014, People's Republic of China

**E-mail:** j.tennyson@ucl.ac.uk

**Keywords:** electrical strength, global warming potential, fluorocarbons, resonances

## Abstract

A search is conducted for possible gases with high electrical strength which could replace the widely used $SF_6$ which has high global warming potential (GWP). The possible electrical strength of a molecule is assessed on the basis of low-energy electron collisions with low-energy resonances or weakly bound states taken as a possible indicator of high electrical strength. At the same time the energy of the highest occupied molecular orbital (HOMO) is used to assess the molecules' GWP. A total of 62 small flourocarbon molecules are considered allowing the influence of different molecular structures (double bonded, triple bonded and cyclic) and the inclusion of different elements (hydrogen, nitrogen and oxygen) on the electrical strength to be assessed. Eight molecules show low-energy resonance and a further four have negative R-matrix poles implying that they support an anionic state. Our calculations suggest that molecules with double bonded structures, especially involving C = N, should have the best electrical strength, followed by cyclic and then triple bonded structures. Calculation on the $C_3F_{6-n}H_n$ ($n = 0, 6$) series suggest that introducing H atoms in selected positions can decrease GWP while retaining the electrical strength of pure fluorocarbon gases like $C_3F_6$.

## 1. Introduction

$SF_6$ is thought to be the gas with the highest global warming potential (GWP), 23 500 on a scale which puts $CO_2$ as 1 [1], and the atmospheric abundances of $SF_6$ doubled during 1995-2015 [2]. As a gas with high electrical strength, $SF_6$ is widely used in many electrical applications as a gaseous insulator. The desire to replace $SF_6$ with an alternative gas with lower GWP has attracted widespread attention in recent years [3–11].

Insulation performance is an important indicator of whether an $SF_6$ alternative gases could be used in power systems. For a molecule to be a suitable replacement for $SF_6$ it has to have the following three properties (a) it must show high electrical strength, (b) should have a low GWP and (c) it should be a gas a room temperature or temperatures envisaged for its use. Other considerations include the stability and toxicity of the gas, its flammability and its potential effect of stratospheric ozone. Research on the insulation performance of $SF_6$ alternative gases has started from a number of perspectives. For example, Devins [12] studied the electrical strength of halogen gases using breakdown experiments; Chachereau *et al* [13] investigated the insulation properties of pure $C_4F_7N$ and its mixtures using the pulsed Townsend method; Zhong *et al* [14] assessed four carbon-fluoride insulating gases by calculating the reduced critical electric field strength; Rabie *et al* [15] developed an electrical strength prediction function based on the regression analysis of the gas's electric strength and certain molecular properties; while Sun *et al* [16] constructed an electrical strength prediction model employing machine learning methods; while Hou *et al* [17] proposed a simple group-additivity method to predict the electrical strength of insulating gases. Progress in identifying replacement gases for $SF_6$ has been reviewed by Tian *et al* [18]. Despite these various efforts there is still no perfect gas to replace the use of $SF_6$ as a gaseous electrical insulator.

A gas breakdown or pulsed Townsend experiment can provide credible results, but such experiments require pure gases, equipment and long experimental periods, which are expensive. This makes experiment

© 2023 The Author(s). Published by IOP Publishing Ltd

more suitable for verifying theoretical results than conducting long searches. The reduced critical electric field strength can be calculated by solving Boltzmann's equation with a complete set of electron-molecule collision cross sections [19–21]. However, for molecules with incomplete collision cross-section sets (i.e. most molecules), the reduced critical electric field strength is hard to compute in this way. Regression analysis and machine learning methods rely on training samples. For structures which are not included in the samples, the reliability of the prediction results needs to be verified. Recently, we [22] analyzed the underlying physical reasons why gases such as $SF_6$ have good insulating properties by studying their electron collision behaviour. This analysis was extended to the species $CH_xF_yCl_z$ where $x + y + z = 4$; it was shown that there was an excellent correlation between species having a low-energy quasibound state (resonance) or a weakly bound anion state and possessing high electrical strength. Species which are known not to show high electrical strength did not have this property. This correlation can be expected as the ability of a molecule to attach electrons is thought to be the key to them showing high electrical strength [23]. In this context low-lying means that the resonance must be low enough to accessible by thermal electrons. It is this correlation between low-energy collision properties and electrical strength that we exploit here.

In this work we assess 62 fluorine and carbon containing molecules to consider whether they may have high electrical strength and (relatively) low GWP. This list of molecules is restricted to one with three or less carbons to ensure that they have suitably low boiling points. While we were able to find boiling points for most species we consider in the literature, GWPs for these species are generally unknown. We therefore follow the standard practice [24, 25] of using the position of the highest occupied molecular orbital (HOMO) as an indicator of the GWP. As well as assessing these molecules we also try to assess the influence of molecular structure and composition on the gas's electrical strength. This information should help the search for or design of new alternative gases. Our method is based on electron collision properties which should directly reflect the ability of the gas to absorb electrons. Here we use the R-matrix method [26] to perform *ab initio* scattering calculations which do not rely on experimental data. This means that molecules can easily be tested even if they are not (readily) available for experimental study. Our aim is to provide a reduced list of molecules which should show good electrical strength and can be studied further.

In selecting gases for study, we first considered carbon halogen compounds, because these types of gases have long been considered as possible insulating gases [9]. At the same time, popular $SF_6$ alternative gases, such as $CF_3I$ [4], c-$C_4F_8$ [27], HFO1234 ($C_3F_4H_2$) [28], R134 ($C_2F_4H_2$) [29], $C_4F_7N$ [5] and $C_5F_{10}O$ [30], belong to this class of gas or are modified halocarbons. Therefore, a systematic search examining the relationship between the molecular structure and electrical strength of this type of gas is valuable. Since chlorine and bromine are ozone destructive, and iodine is relatively heavy, fluorine-containing gases are the main focus of this work. The influence of different structures such as double bonded, triple bonded and cyclic structures, as well as the influence of including elements such as hydrogen, nitrogen and oxygen on the insulation properties of fluorocarbon gases are considered. The influence of different composition and structures are tested first following our electron collision procedure [22]; this allows us to identify gases with potential good insulation characteristics. We then take $C_3F_6$ as an example to study the influence of the number and position of hydrogen atoms on the insulation properties; we note that HFO1234 is part of this series. The introduction of H atoms tends to reduce atmospheric lifetimes of fluorocarbon gases, thereby reducing GWP.

Section 2 describes the electron calculation method we use. In section 3.1, we give the chosen molecules and calculation results. In section 3.2, we analyze the influence of introducing hydrogen atoms on the electrical strength and HOMO energy of $C_3F_6$. Finally, in section 4 we give our conclusions for high electrical strength molecules and structures.

## 2. Method

The physical mechanism for electron trapping is believed to be a key reason for gases like $SF_6$ having good insulation performance [23, 31]. Christophorou [32] called these electronegative gases because they have large electron attachment cross sections at low energy but these attachment cross sections are hard to obtain from either measurements or calculations. However, it is well known that resonances are a prerequisite for electron attachment or dissociative attachment [33]. Indeed resonance parameters can be used as a basis to estimate dissociative attachment rates [34]. Based on this, we studied the relationship between low-energy resonances and gas insulation properties [22] and found that for high electrical strength molecules like $SF_6$ there will be a strong low-energy ($<<1$ eV) resonance or a (weakly) bound anionic state which manifests itself as a negative R-matrix pole in the scattering calculation [35]. These low-energy resonances provide a signal for the formation of compound anionic states in the form of a (weakly) bound state. This suggest that gas insulation properties can be predicted on the basis of the presence (or not) of a low-energy resonance [22].

**Table 1.** Fluorocarbon compounds considered.

| Chemical formula | SMILES [41] | | |
|---|---|---|---|
| CFN | FC#N. | | |
| $CF_2O$ | FC(F) = O. | | |
| $CF_3N$ | FC(F) = NF. | | |
| $CF_4$ | FC(F)(F)F. | | |
| $CF_4O$ | FC(O(F))(F)F. | | |
| $CF_5N$ | FC(N(F)(F))(F)F. | | |
| $C_2F_2$ | FC#CF. | | |
| $C_2F_4$ | FC(F) = C(F)F. | | |
| $C_2F_6$ | FC(C(F)(F)F)(F)F. | | |
| $C_2F_2O$ | FC#COF, | FC(F) = C = O. | |
| $C_2F_3N$ | FC#CN(F)F, | FC(C#N)(F)F, | FC(F) = C = NF, |
| | C1(= C(N1F)F)F, | C1(= NC1(F)F)F. | |
| $C_2F_4O$ | C(= O)(C(F)(F)F)F, | C1(C(O1)(F)F)(F)F, | FC(F) = C(F)OF. |
| $C_2F_5N$ | FC(F) = NC(F)(F)F, | FC(F) = C(F)N(F)F, | FC(F)(F)C(= NF)F, |
| | C1(N(C1(F)F)F)(F)F. | | |
| $C_2F_6$ | C(C(F)(F)F)(F)F. | | |
| $C_2F_6O$ | FC(F)(F)OC(F)(F)F, | C(C(F)(F)F)(OF)(F)F. | |
| $C_2F_7N$ | FC(F)(F)N(F)C(F)(F)F, | (C(F)(F)F)(N(F)F)(F)F. | |
| $C_3F_4$ | C(= C(F)F) = C(F)F, | C(#CF)C(F)(F)F. | |
| $C_3F_6$ | C(= C(F)F)(C(F)(F)F)F, | C1(C(C1(F)F)(F)F)(F)F. | |
| $C_3F_8$ | C(C(F)(F)F)(C(F)(F)F)(F)F. | | |

The electron collision resonance information used in this work is calculated using the R-matrix method [26] at the static exchange plus polarisation (SEP) level which was recommended by our previous study [22]. All collision calculations use QEC (Quantemol electron collisions) [36], which is an expert system which can be used to solve electron collision problems and provides collision cross sections and resonance parameters. Target wave functions used by QEC are produced by Molpro [37] and in the static exchange plus polarisation (SEP) model are based on the Hartree–Fock method. The electron collision calculation uses R-matrix theory as implemented in the UKRmol+ code [38]. QEC obtains resonance positions and widths using code RESON [39] to automatically detect and fit them to a Breit-Wigner form.

All the calculations in this work use an R-matrix sphere of radius 10 $a_0$, a partial wave expansion up to $\ell = 4$ (g-wave) and a cc-pVDZ basis set as recommended by our previous study [22]. Our SEP calculations retained all virtual orbitals up to a maximum of 40 to provide the polarisation potential, see our previous study for further details.

## 3. Calculations

In this section, small molecules containing double, triple bonds and cyclic structures composed of carbon, nitrogen, oxygen and fluorine are selected, see table 1 and their low-energy collision behaviour studied. In the second part of this section, the influence of hydrogen atoms on the insulating properties of fluorocarbon gases is studied. According to the experimental results of Devins [12], fluorocarbon gases have higher electrical strength than hydrocarbon gases. However, including hydrogen can reduce the use of fluorine, which generally leads to a higher-lying HOMO, thereby reducing the atmospheric life time of the gas [24] and consequently reducing the GWP [40]. $C_3F_6$, which supports a low-energy resonance, is chosen to study the influence on the molecular insulation properties of different numbers and positions of H atoms in the $C_3F_{6-n}H_n$ ($n = 0, 6$) series.

### 3.1. Influence of molecular structure on electrical strength

In this section we study the relationship between molecular structure and electrical strength and identify some potential high electrical strength structures. Structural considerations include molecules with double bonds, triple bonds and cyclic structures. Since N and O atoms can also be included in these structures, the role of these atoms are also considered. To reduce the number of calculations, P and S atoms are not considered in this work, and the number of C atoms in given molecule is capped at three which both controls the total number of atoms and helps to ensure that the species considered are gases at room temperature. Table 1 lists the initial molecules we consider; the molecules are arranged in ascending order of the number of carbons and total number of atoms. Relevant structures can be found from the Simplified Molecular Input Line Entry Specification (SMILES)

**Table 2.** Molecules with a Low-energy Resonance: data only shown for the lowest resonance detected. Resonance parameters are in eV, electrical strengths ($E_r$), where known, are given relative to $SF_6$.

| ID | Formula | SMILES [41] | Resonance position (width) | $E_r$ | BP (K) |
|---|---|---|---|---|---|
| 1 | $CF_3N$ | FC(F) = NF | 1.1(0.7) | — | — |
| 2 | $C_2F_3N$ | FC(C#N)(F)F | 1.2(0.12) | 1.58[a] | 209[b] |
| 3 | c-$C_2F_3N$ | C1(= NC1(F)F)F | 0.7(0.03) | — | 222.75 ± 35[b] |
| 4 | $C_2F_5N$ | FC(F) = NC(F)(F)F | 0.3(0.02) | — | 217.55 ± 35[b] |
| 5 | $C_2F_5N$ | FC(F) = C(F)N(F)F | 0.8(0.03) | — | — |
| 6 | $C_2F_5N$ | FC(F)(F)C(= N/F)/F | 0.1(0.02) | — | 269.35 ± 35[b] |
| 7 | $C_3F_4$ | C(= C(F)F) = C(F)F | 0.6(0.04) | — | 237.05 ± 35[b] |
| 8 | $C_3F_6$ | C(= C(F)F)(C(F)(F)F)F | 0.7(0.16) | 0.97[c] | 243.8[a] |

[a] Devins [12].
[b] Chemspider[42].
[c] Brand[43].

**Table 3.** Molecules with Negative R-matrix Pole.

| ID | Formula | SMILES [41] | Pole energy (eV) | BP(K) |
|---|---|---|---|---|
| 1 | $C_2F_3N$ | FC(F) = C = NF | −3.8926 | 259.85 ± 35[a] |
| 2 | $C_2F_3N$ | C1(= C(N1F)F)F | −2.7314 | 230.85 ± 35[a] |
| 3 | $C_2F_4O$) | FC(F) = C(F)OF | −0.9657 | — |
| 4 | c-$C_2F_5N$ | C1(N(C1(F)F)F)(F)F | −0.2463 | — |

[a] Chemspider[42].

[41] given in table 1, in which = means double bound, # means triple bound, C1 means cyclic and H atoms are not specified.

To test the influence of double bonds, $CF_2O$, $CF_3N$, $C_2F_4$,$C_2F_2O$(FC(F) = C = O), $C_2F_3N$(FC(F) = C = NF), $C_2F_4O$(C(= O)(C(F)(F)F)F and FC(F) = C(F)OF), $C_2F_5N$ (FC(F) = NC(F)(F)F and FC(F) = C(F)N(F)F), $C_3F_4$(C(= C(F)F) = C(F)F) and $C_3F_6$ (C(= C(F)F)(C(F)(F)F)F) are considered. CFN, $C_2F_2$, $C_2F_2O$(FC#COF), $C_2F_3N$ (FC#CN(F)F and FC(C#N)(F)F) and $C_3F_4$(C(#CF)C(F)(F)F) are used to study triple bonds. For cyclic structures, $C_2F_3N$(C1(= C(N1F)F)F and C1(= NC1(F)F)F), $C_2F_4O$(C1(C(O1)(F)F)(F)F), $C_2F_5N$(C1(N(C1(F)F)F)(F)F) and $C_3F_6$ (C1(C(C1(F)F)(F)F)(F)F) are considered.

Our electron collision calculations and analysis of eigenphase sums found that 8 of the molecules shown in table 1 have low-energy resonance; these are listed in table 2. A further 4 molecules appear to support bound anion states; these are in table 3. The corresponding molecular structures are shown in figures 1 and 2, respectively.

Table 2 shows the details of low-energy resonance position and width, relative electrical strength ($E_r$) and boiling point (BP) of our 8 candidate molecules. The experimental $E_r$ of $C_2F_3N$ (table 2 ID 2) and $C_3F_6$ (table 2 ID 8) are close to that of $SF_6$ which is in line with our predictions on the basis of our resonance parameters.

Table 3 gives the details of the four molecules with negative R-matrix poles. Theoretically these 4 molecules could have higher electrical strengths but modelling suggest that for this to be so the anion state must be very weakly bound [23]. As we found no experimental electrical strengths for these 4 molecules, only the R-matrix pole positions and boiling points are listed. However, our predicted anion binding energies may be too large for the anion states to play an important role in electron capture.

We find that 7 of the 8 molecules in Tables 2 and 3 of the 4 molecules in table 3 have double bond structures, and, in particular, C = N appears 7 times whiles no molecules with C = O appear in the list. This suggests that molecule with a C = N bond have more favourable electrical strengths, C = C containing molecules also show some enhancement. For perfluoro-olefins, only $C_3F_6$ (table 2 ID 8) shows a low-energy resonance. As c-$C_4F_8$[27] is also know to have a high $E_r$, we suggest that to obtain high electrical strength, the carbon chain length of perfluoro-olefins needs to be three or more.

Among the triply-bonded molecules considered, only $C_2F_3N$ (table 2 ID 2) exhibits a low-energy resonance, which is consistent with its high $E_r$ property. Other triple bond molecules do not show low-energy resonance or negative pole. We suggest that in terms of electrical strength, C#N is better than C#C, and a double bonded structure is better than a triple bonded structure. For molecules with cyclic structure, only $C_2F_3N$ (table 2 ID 3

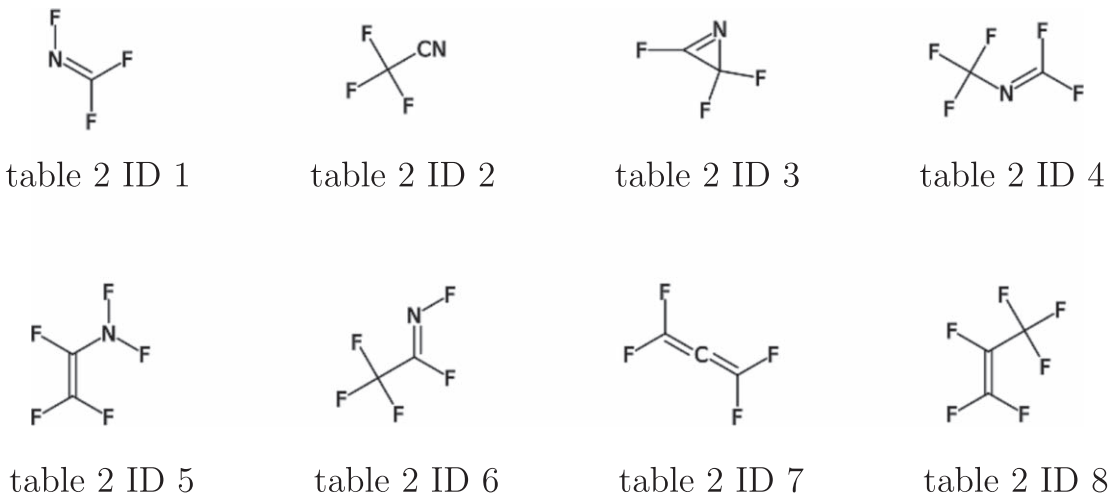


**Figure 1.** Molecular structures of molecules with low energy resonance in Table 2.

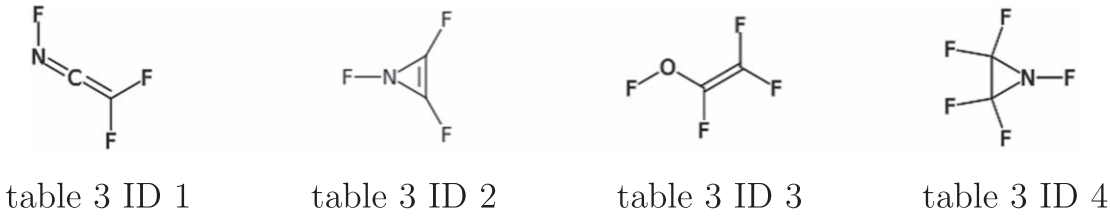


**Figure 2.** Molecular structures of molecules with negative R-matrix pole in table 3.

**Table 4.** $C_3F_6O$ Series.

| ID | SMILES | Lowest resonance(eV) | R-matrix pole(eV) |
|---|---|---|---|
| 1 | C(=C(F)F)(OC(F)(F)F)F | 2(0.02) | 0.56 |
| 2 | C(=C(F)F)(C(F)(F)F)OF | 0(0) | −0.51 |
| 3 | C(=C(F)F)(C(F)(F)OF)F | 0(0) | −0.58 |
| 4 | C(=C(\OF)/F)(\C(F)(F)F)/F | 0(0) | −1.45 |

and table 3 ID 2) and $C_2F_5N$ (table 3 ID 4) show good insulation potential. However, $C_2F_3N$ (table 2 ID 3) has a C = N double bond. By comparing $C_3F_6$(C1(C(C1(F)F)(F)F)(F)F) and $C_3F_6$(C(= C(F)F)(C(F)(F)F)F), it would appear that a double bonded structure is more important than a cyclic structure.

Our calculations suggest that molecules with two double bonds, like $C_3F_4$ (table 2 ID 7) and $C_2F_3N$ (table 3 ID 1) have good insulation potential. From calculations on $CF_4O$, $CF_5N$, $C_2F_6O$ and $C_2F_7N$ molecules, we believe that introducing N or O atoms without special structures does not improve the electrical strength of fluorocarbon molecules. Conversely, all the molecules we consider which contain a C = N appear in either table 2 or table 3; we therefore suggest that N has a greater improving effect on $E_r$ than other subsitutions we tested. In particular, with the exception of $C_2F_4O$ (table 3 ID 4) which appears to be an interesting special case, including O does not seem to give an improved $E_r$.

As shown in table 3 ID 3, the $C_2F_4O^-$ appears to have a bound state. By comparing with its isomers, and other oxygen-containing molecules, we wanted to test whether the simultaneous appearance of C = C and -OF might result in good electron attachment properties. To test this supposition, we selected the four $C_3F_6O$ isomers listed in table 4 and shown in figure 3. It was found that only one of these molecules, ID 1 in table 4 which has a C = C bond but not -OF, does not show either a low-energy resonance or a negative R-matrix pole. The other three molecules all have C = C double bonds and an -OF group, and all appear to support a bound anion state. The insulating properties of molecules like $C_2F_4O$, or possibly $C_2F_{4-n}H_nO$, deserve further experimental study.

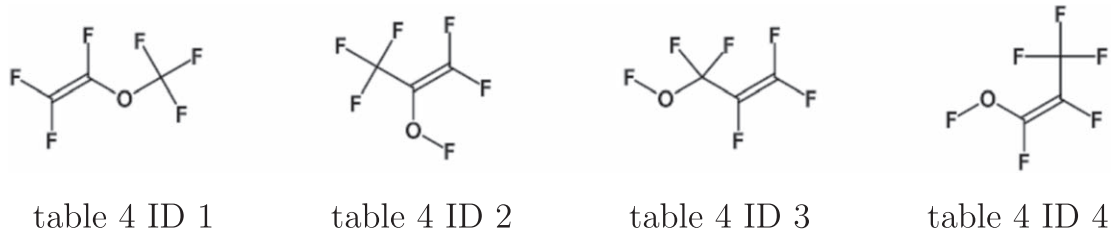


**Figure 3.** Molecular structures of $C_3F_6O$ isomers listed in table 4.

**Table 5.** Properties of the $C_3F_{6-n}H_n$ series. Parameters are given for the lowest resonance in the form resonance symmetry position(width) in eV.

| ID | SMILES | Resonance parameters | BP(K)[a] | HOMO(Hartree) |
|---|---|---|---|---|
| **$C_3F_6$** | | | | |
| 1 | C(=C(F)F)(C(F)(F)F)F | $A_2$ 0.7(0.2) | 209 | −0.42 |
| **$C_3HF_5$** | | | | |
| 2 | C(=C(F)F)C(F)(F)F | $A_2$ 0.5(0.04) | 252 | −0.43 |
| 3 | C(=C(/C(F)(F)F)\F)\F(Z) | $A_1$ 0.6(0.03) | 255 | −0.42 |
| 4 | C(=C(\C(F)(F)F)/F)\F(E) | $A_1$ 0.5(0.05) | 262-264 | -0.42 |
| 5 | C(C(=C(F)F)F)(F)F | $A_1$ 1.2(0.2) | 274-275 | −0.41 |
| **$C_3H_2F_4$** | | | | |
| 6 | C = C(C(F)(F)F)F | $A_2$ 0.5(0.1) | 245 | −0.41 |
| 7 | C(=C(F)F)C(F)F | $A_1$ 1.2(0.2) | 313-315 | −0.41 |
| 8 | C(C(=C(F)F)F)F | $A_2$ 2.0(0.1) | 281 ± 8 | −0.39 |
| 9 | C(=C/F)\C(F)(F)F[b] | $A_2$ 0.55(0.02) | 257 | −0.42 |
| 10 | C(=C\F)\C(F)(F)F | $A_1$ 0.52(0.07) | 294 | −0.42 |
| 11 | F\C = C(\F)C(F)F | $A_1$ 1.1(0.2) | 289 ± 0 | −0.40 |
| 12 | F\C = C(/F)C(F)F | $A_1$ 1.2(0.2) | 289 ± 0 | −0.41 |
| **$C_3H_3F_3$** | | | | |
| 13 | C=CC(F)(F)F | $A_2$ 0.7(0.07) | 255-257 | −0.41 |
| 14 | C(=C/F)\C(F)F | $A_1$ 1.2(0.2) | 277 ± 8 | −0.40 |
| 15 | CC(=C(F)F)F | $A_2$ 2.4(0.1) | 264 ± 8 | −0.37 |
| 16 | C = C(C(F)F)F | $A_1$ 1.1(0.3) | 263 ± 8 | −0.40 |
| 17 | C(=C\F)\C(F)F | $A_1$ 1.2(0.2) | 277 ± 8 | −0.40 |
| 18 | C(/C(=C\F)/F)F(E) | $A_2$ 1.9(0.3) | 304 ± 8 | −0.38 |
| 19 | C(C=C(F)F)F | $A_2$ 2.0(0.1) | 266 ± 8 | −0.38 |
| 20 | C(/C(=C/F)/F)F(Z) | $A_2$ 2.1(0.4) | 304 ± 8 | −0.38 |
| **$C_3H_4F_2$** | | | | |
| 21 | CC=C(F)F | $A_1$ 1.0(0.4) | 241 ± 8 | −0.37 |
| 22 | C = C(F)CF | $A_2$ 1.9(0.5) | — | −0.37 |
| 23 | C=CC(F)F | $A_2$ 1.1(0.2) | — | −0.40 |
| **$C_3H_5F$** | | | | |
| 24 | C=CCF | $A_2$ 1.9(0.4) | 263 | −0.37 |
| 25 | CC(=C)F | $A_2$ 2.2(0.6) | 249 | −0.36 |
| **$C_3H_6$** | | | | |
| 26 | C=CC | $A_2$ 2.2(0.5) | 226 | −0.35 |

[a] Boiling point data from Chemspider [42]; [b] HFO1234.

### 3.2. Influence of hydrogen on $E_r$ and the HOMO energy

Replacing F atoms with H atoms in fluorocarbon gases usually will weaken their insulating performance [12]. However, the partially hydrogenated HFO1234 ($C_3F_4H_2$) shows good insulation properties [28], which aroused our interest. In this section, the $C_3F_{6-n}H_n$ series is tested by replacing the F atoms with H atoms in $C_3F_6$ (table 2 ID 8) to study the influence on electrical strength and HOMO binding energy. $C_3F_6$ (table 2 ID 8) has a low energy resonance at 0.7 eV, which meets the criterion of potential good insulation performance. Reducing the F atom content is conducive to environmental protection as it leads to higher-lying HOMOs which implies

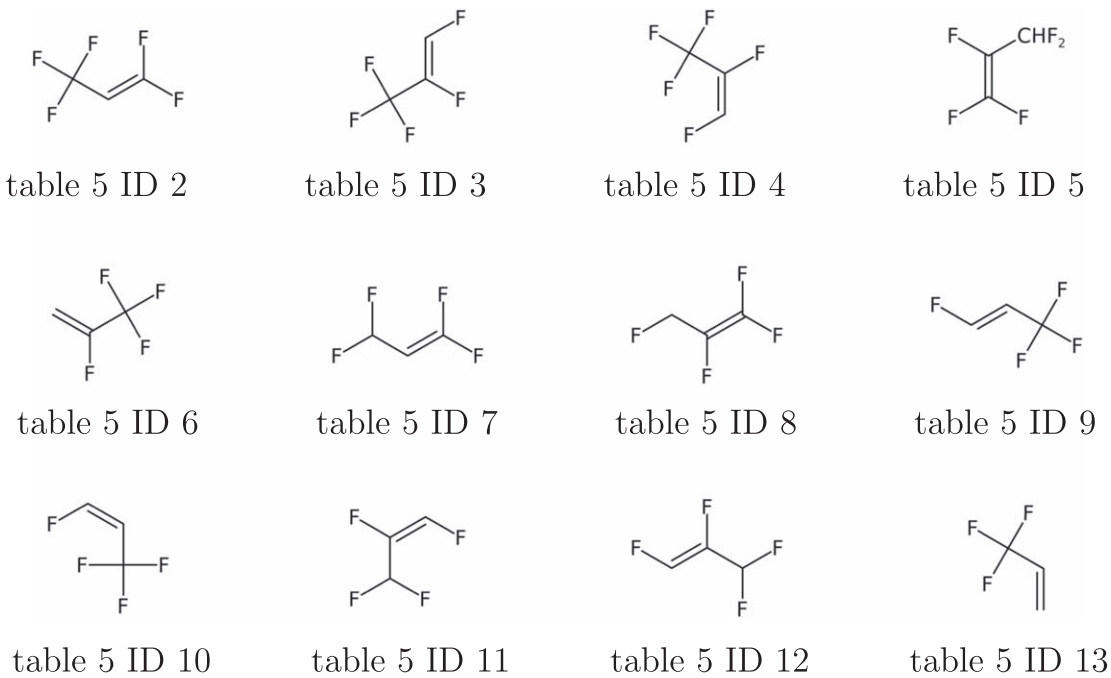


**Figure 4.** Molecular structures of the $C_3F_{6-n}H_n$ ($n = 0, 6$) molecules listed in table 5 part 1: ID 2-13.

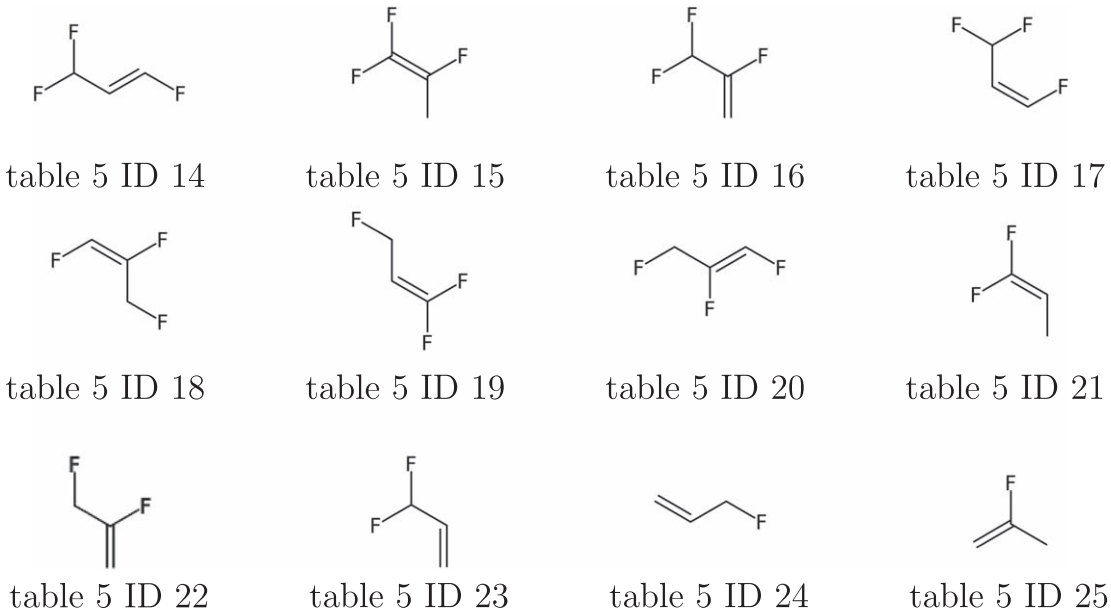


**Figure 5.** Molecular structures of the $C_3F_{6-n}H_n$ ($n = 0, 6$) molecules listed in table 5 part 2: ID 14-25.

shorter atmospheric lifetimes and lower GWPs. Our aim is to reduce the F content of while maintaining insulation properties.

Table 5 lists all $C_3F_{6-n}H_n$ molecules tested in this section, which includes a number of isomers. Also given is resonance information, boiling points and HOMO binding energies as well as the point group symmetry of the lowest resonance ($A_1$ or $A_2$). Molecules from table 5 ID 2-13 are depicted in figure 4 and ID 14-25 are depicted in figure 5.

When we replace one F atom with a H atom in $C_3F_6$, as shown as $C_3HF_5$ ID 2-5 in table 5, the first three molecules listed, table 5 ID 2-4, still exhibit a low-energy resonance. However, for isomer ID 5 the resonance position increases to 1.2 eV, which suggests that the insulation performance will be weakened. Comparing the structures of the four molecules shows that the H atoms in molecule table 5 ID 2-4 are located on the C = C, while the H atom of molecule table 5 ID 5 is in the form -$CF_2H$.

Table 5 ID 6-12 shows tests of $C_3H_2F_4$. For table 5 ID 6, 9 and 10, their H atoms are on the C = C, and each of them has low-energy resonance around 0.5 eV. For table 5 ID 7, 11, and 12, one H is on the C = C and the other is in -$CF_2H$; their resonances lie higher, at 1.1-1.2 eV, which is worse than $C_3F_6$. For table 5 ID 8, both the hydrogen atoms are in -$CFH_2$ and resonance is at 2 eV, which can no longer be considered a low-energy resonance. Consistent with the situation for $C_3HF_5$, when the hydrogen atoms appear on the C = C, the insulation performance appears to be maintained. It is worth noting that table 5 ID 9 is HFO1234 and it has a low-energy resonance at 0.55 eV which is in line with its observed good experimental insulation performance [28].

Then we test $C_3H_3F_3$, table 5 ID 13-20. Only table 5 ID 13 has a low-energy resonance similar to $C_3F_6$, and its three hydrogen atoms are all located on C = C.

Finally, from $C_3H_4F_2$ to $C_3H_6$, none of the molecule have a low-energy resonance similar to or lower than $C_3F_6$. For these species it is not possible to associate all the H atoms with a doubly-bonded carbon.

From the perspective of HOMOs, table 5 shows that increasing the number of hydrogen atoms in fluorocarbon gas can reduce the binding energy of the HOMO by small amounts. This is consistent with the expected result. It is found that molecules with low-energy resonance, such as table 5 ID 6, 9 and 10, have higher HOMO binding energies than other isomers that do not have a low-energy resonance. The results in table 5 suggest that the low-energy resonance and the HOMO energies are anti-correlated. We note that low-lying (shape) resonances are usually associated with the presence of a low-energy LUMO (lowest unoccupied molecular orbital); our observed anti-correlation would be explained if the HOMO–LUMO gap is approximately conserved in these systems. The relationship between insulation properties and atmospheric lifetime or GWP may be difficult and probably needs further study.

## 4. Conclusion

In this paper we report a search for possible gases which might replace the use of $SF_6$ as an gaseous insulator. Our methodology is based on trying to use an understanding of the basic physics of electron collision process that leads to good insulator properties. Our calculations are necessarily approximate and our aim is to provide a shortlist of gases which could benefit from further (experimental) investigation. We consider the influence of molecular composition and structure on the insulation performance of a gas by performing electron collision calculations of a series of fluorocarbon gases. For the electrical strength of fluorocarbon molecules with double bonded, triple bonded and cyclic structures, the following conclusions may be drawn:

1. In general, double bonded compounds show more promise as insulators than than cyclic structure and triply bonded molecules. Compounds with a C = N double bond shows the most promise, with C = C being also useful but a C = O bonded compounds do does not show any significant improvement effect for the molecules we considered.

2. Gases such as $C_3F_4$ and $C_2F_3N$ that contain two double bonds are predicted to have good electrical strengths.

3. For the small molecules tested which contain triple bonds, only the ones with a C#N triple bond show an improvement in potential electrical strength while those with a C#C triple bond show no significant improvement.

4. Molecules with both C = C and -OF, such as $C_2F_4O$, have negative R-matrix poles our calculations, which may indicate good insulator properties although in most cases our calculations suggest that these bound anionic states are likely to be too strongly bound to be useful in this regard.

5. A comparison of $C_2F_4$ and $C_3F_6$ suggests that for pure a fluorocarbon gases to give insulation performance comparable to $SF_6$ requires a the carbon chain with at least 3 carbons.

6. Based on the molecules considered in this work, adding N leads to a larger improvement than adding O.

Generally, the introduction of H atoms into fluorocarbon gases weakens the electrical strength; but HFO1234 ($C_3F_4H_2$) has good insulation properties. Conversely, the addition of H atoms reduce the GWP of a gas as well as reducing the release of F into the environment. We therefore, take $C_3F_6$ and analyse the influence of replacing F atoms with H atoms on both the molecular insulation and HOMO properties. We find:

1. When 3 or less H atoms are introduced whether the predicted insulating properties match those of $C_3F_6$ depends on the structure of the isomer.

2. When the H atoms are located on a C involved in a C = C double bond, the low-energy resonance is maintained, when H replaces F in -$CF_3$ functional group, the low-energy resonance disappears. We note that in HFO1234 both hydrogens are located on the C = C bond.

3. Generally as the number of H atoms in the molecule increases, the HOMO binding energy decreases, which implies a lower GWP.

4. Our work suggests that molecules which have a low-energy resonance have lower HOMOs than their isomers which do not show this resonance. This suggests that properties implying good electrical strength are anti-correlated with the requirements for a low GWP.

Based on the above calculations, we find 12 molecules which we predict should have good insulating potential and are therefore worthy of further study. Among them, structures like C = N, two double bond structures and C = C combined with OF show stable low-energy resonance or negative R-matrix poles, which deserve further study. Through the calculation of $C_3F_6$ - $C_3H_6$, a greenhouse improvement strategy for fluorocarbon gas is proposed: for gas molecules with double bonds, hydrogen atoms can be introduced at the double bonds to improve the greenhouse performance.

## Acknowledgments

Chunlin Wang acknowledges financial support from the China Scholarship Council; the work of Bridgette Cooper was supported by STFC grant ST/R005133/1.

## Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

## ORCID iDs

Jonathan Tennyson https://orcid.org/0000-0002-4994-5238

## References

[1] WMO 2018 *Scientific assessment of ozone depletion: 2018 - global ozone research and monitoring project eport*58World Meteorological Organization, Geneva, Switzerland https://wedocs.unep.org/20.500.11822/32140
[2] Hodnebrog A B, Fuglestvedt J S, Marston G, Myhre G, Nielsen C J, Sandstad M, Shine K P and Wallington T J 2020 *Rev. Geophys.* **58** e2019RG000691
[3] Christophorou L G, Olthoff J K and Green D S 1997 *Gases for electrical insulation and arc interruption: Possible present and future alternatives to pure SF6*1425National Institute of Standards and Technology, Gaithersburg, MD (https://doi.org/10.6028/NIST.tn.1425)
[4] Cressault Y, Connord V, Hingana H, Teulet P and Gleizes A 2011 *J. Phys.D: Appl. Phys. D* **44** 495202
[5] Kieffel Y, Biquez F, Ponchon P and Irwin T 2015 $SF_6$ alternative development for high voltage switchgears *2015 IEEE Power & Energy Society General Meeting (IEEE)* 1–5
[6] Kieffel Y and Biquez F 2015 $SF_6$ alternative development for high voltage switchgears *2015 IEEE Electrical Insulation Conference (Seattle, WA, 07-10 June 2015)* (Picastaway, NJ: IEEE) (https://doi.org/10.1109/ICACACT.2014.7223577)
[7] Wu Y, Wang C, Sun H, Rong M, Murphy A B, Li T, Zhong J, Chen Z, Yang F and Niu C 2017 *J. Phys. D: Appl. Phys.* **50** 385202
[8] Seeger M *et al* 2017 *Plasma Physics and Technology* **4** 8–12
[9] Rabie M and Franck C M 2018 *Environmental science & technology* **52** 369–80
[10] Li X, Zhao H and Murphy A B 2018 *J. Phys. D: Appl. Phys.* **51** 153001
[11] Dincer S, Tezcan S S, Duzkaya H and Dincer M S 2018 Insulation and Molecular Properties of Alternative Gases to $SF_6$ *II International Symposium on Multidisciplinary Studies and Innovative Technologies (ISMSIT)* 14–7
[12] Devins J C 1980 *IEEE Trans. Electr. Insul.* **15** 81–6
[13] Chachereau A, Hösl A and Franck C M 2018 *J. Phys. D: Appl. Phys.* **51** 495201
[14] Zhong L, Wang J, Wang X and Rong M 2018 *AIP Adv.* **8** 085122
[15] Rabie M and Franck C M 2013 Predicting the electric strength of proposed $SF_6$ replacement gases by means of density functional theory *XVIII International Symposium on High Voltage Engineering (Seoul, Korea)* pp. 25–30
[16] Sun H, Liang L, Wang C, Wu Y, Yang F and Rong M 2020 *IEEE Access* **8** 124204124204–16
[17] Hou H, Yu X and Wang B 2021 A simple group-additivity method to predict the dielectric strength of insulating gases for molecular design *2021 IEEE Electrical Insulation Conference (EIC) (Denver, CO, 07–28 June 2021)* (Picastaway, NJ: IEEE) (https://doi.org/10.1109/EIC49891.2021.9612297)
[18] Tian S, Zhang X, Cressault Y, Hu J, Wang B, Xiao S, Li Y and Kabbaj N 2020 *AIP Adv.* **10** 050702
[19] Kline L E, Davies D K, Chen C L and Chantry P J 1979 *J. Appl. Phys.* **50** 6789–96
[20] Yan J D, Fang M T C and Liu Q S 1997 *IEEE Trans. Dielectr. Electr. Insul.* **4** 114–9
[21] Hagelaar G J M and Pitchford L C 2005 *Plasma Sources Sci. Technol.* **14** 722–33
[22] Wang C, Cooper B, Wu Y, Sun H and Tennyson J 2020 Why SF6 eats electrons: identifying high electrical strength molecules from their electron collision properties *J. Phys. B: At. Mol. Opt. Phys.* **54** 025202
[23] Gerchikov L G and Gribakin G F 2008 *Phys. Rev.*A **77** 042724
[24] Suga A 1993 *Chem. Exp.* **8** 205–8
[25] Imasu R, Suga A and Matsuno T 1995 *J. Met. Soc. Japan* **73** 1123–36
[26] Tennyson J 2010 *Phys. Rep.* **491** 29–76
[27] Xiaoling Z, Juntao J, Bing L and Dengming X 2016 *Plasma Sci. Technol* **18** 292
[28] Koch M and Franck C M 2015 *IEEE Trans. Dielectr. Electr. Insul.* **22** 3260–8
[29] Ullah R, Ullah Z, Haider A, Amin S and Khan F 2018 *Electr. Power Syst. Res.* **163** 532–7

[30] Simka P and Ranjan N 2015 Dielectric strength of c5 perfluoroketone *Proceedings of the XIX International Symposium on High Voltage Engineering, Pilsen, Czech Republic* 23–8
[31] Ferch J, Raith W and Schroder K 1982 *J. Phys. B: At. Mol. Opt. Phys.* **15** L175
[32] Christophorou L G 1983 *Electronegative Gases* (Boston, MA: Springer US) pp 133–76
[33] Fabrikant I I, Eden S, Mason N J and Fedor J 2017 Recent progress in dissociative electron attachment: from diatomics to biomolecules *Advances in atomic, molecular, and optical physics* vol 66 (Amsterdam: Elsevier) pp 545–657
[34] Munro J J, Harrison S, Tennyson J and Fujimoto M M 2012 *J. Phys. Conf. Ser.* **388** 012013
[35] Sarpal B K, Branchett S E, Tennyson J and Morgan L A 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** 3685–99
[36] Cooper B *et al* 2019 *Atoms* **7** 97
[37] Werner H J, Knowles P J, Knizia G, Manby F R and Schütz M 2012 *Wiley Interdisciplinary Reviews: Computational Molecular Science* **2** 242–53
[38] Mašín Z, Benda J, Gorfinkiel J D, Harvey A G and Tennyson J 2020 *Comput. Phys. Commun.* **249** 107092
[39] Tennyson J and Noble C J 1984 *Comput. Phys. Commun.* **33** 421–4
[40] Hodnebrog Ø, Etminan M, Fuglestvedt J S, Marston G, Myhre G, Nielsen C J, Shine K P and Wallington T J 2013 *Rev. Geophys.* **51** 300–78
[41] Weininger D 1988 *J. Chem. Inf. Comput. Sci.* **28** 31–6
[42] Pence H E and Williams A 2010 Chemspider: an Online Chemical Information Resource http://chemspider.com/
[43] Brand K P 1982 *IEEE Trans. Electr. Insul.* **17** 451–6