Journal of Physics B: Atomic, Molecular and Optical Physics

PAPER • OPEN ACCESS

Why SF_6 eats electrons: identifying high electrical strength molecules from their electron collision properties

To cite this article: Chunlin Wang *et al* 2021 *J. Phys. B: At. Mol. Opt. Phys.* **54** 025202

OPEN ACCESS
IOP Publishing
Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **54** (2021) 025202 (8pp)
https://doi.org/10.1088/1361-6455/abd0a2

Why SF_6 eats electrons: identifying high electrical strength molecules from their electron collision properties

Chunlin Wang[1,2], **Bridgette Cooper**[2], **Yi Wu**[1], **Hao Sun**[1,*] and **Jonathan Tennyson**[2,*]

[1] State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an Shaanxi 710049, People's Republic of China
[2] Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

E-mail: sunhao1031@xjtu.edu.cn and j.tennyson@ucl.ac.uk

Received 2 September 2020, revised 24 November 2020
Accepted for publication 3 December 2020
Published 22 January 2021

Abstract

The electrical strength of a molecule is a measure of its ability to act as an insulator and to absorb electrons. SF_6 is a high electric strength gas. This work tries to explain why molecules like SF_6 have a high electrical strength from the perspective of electron molecule scattering. The presence of a very low energy ($<<1$ eV) totally symmetric state in form of a very low-lying resonance, virtual state or very weakly bound state appears to be crucial. R-matrix calculations performed at the static exchange plus polarisation (SEP) level are performed for a number of molecules that show a range of electrical strengths. SEP calculations suggest that SF_6 has a strong low energy ^2A_g resonance feature which becomes a weakly bound state as more virtual orbitals are included in the calculation. High electrical strength molecules such as CCl_4, CCl_3F and CCl_2F_2 also have a totally-symmetric low-energy resonance, while the low electrical strength molecules such as CH_4, CH_3F... CF_4 and $CClF_3$, do not show any resonance behaviour in the low energy region. It is suggested that this low energy feature can be used as an indicator when searching for new molecules with high electrical strength facilitating searches for new gases which could provide an alternative to SF_6.

Keywords: R-matrix, electrical strength, resonances, virtual state

(Some figures may appear in colour only in the online journal)

1. Introduction

The electrical strength provides a measure of the ability of a gas to act as an electrical insulator. High electrical strength gases play a key role in electrical engineering as insulating gases. SF_6 is the standard insulating gas but for several decades scientists have searched for gases with the potential for better electrical strength than SF_6 (Devins 1980, Brand 1982). Recently, there is an added urgency to these searches due to the need for an environmentally-friendly alternative to SF_6 for use in circuit breakers; this issue has received much attention (Loucas *et al* 1997, Christophorou et al 1997, Preve *et al* 2016, Seeger *et al* 2017, Rabie and Franck 2018). Potential alternative gases such as CF_3I (de Urquijo 2007, Cressault *et al* 2011), C_4F_7N (Kieffel and Biquez 2015, Chachereau *et al* 2018, Li and Zhao 2018, Wu *et al* 2018), $C_5F_{10}O$ (Simka and Rangan 2015, Wu *et al* 2017, Yokomizu *et al* 2020), HFO1234 ($C_3F_4H_2$, Koch and Franck 2015, Preve *et al* 2017), and R134 ($C_2F_4H_2$, Ullah *et al* 2018) have been considered.

Among these species, C_4F_7N is the most popular one and has indeed been used in practical applications

---

[*] Authors to whom any correspondence should be addressed.

Table 1. Electrical strength relative to SF_6, E_r, and polarizabilities, α_0 in Å^3, of 10 molecules. The electrical strength data from Brand (1982); calculated values are from this work,using HF/cc-pVDZ.

Molecules	E_r	α_0 (Expt.)	α_0 (Calc.)	Molecules	E_r	α_0 (Expt.)	α_0 (Calc.)
CCl_4	2.36	10.00[a]	6.99	CH_4	0.43	2.45[a]	1.85
CCl_3F	1.72	8.25[b]	5.54	CF_4	0.41	2.82[a]	1.75
CCl_2F_2	1.01	6.37[a]	4.13	CH_2F_2	0.30	2.76[b]	1.71
SF_6	1.00	4.49[b]	2.86	CHF_3	0.27	2.80[b]	1.71
$CClF_3$	0.58	4.65[b]	2.80	CH_3F	—	2.54[a]	1.76

[a] Polarizabilities are from Olney *et al* (1997),

[b] Gussoni *et al* (1998).

(Ficheux *et al* 2019). However, there are still issues with properties such as boiling point, self-recovery, and toxicity (Li *et al* 2019) which should all ideally be improved. This means that there is still a requirement to identify good insulating gases with low GWP (global warming potential). For this purpose, methods of numerically predicting the gas electrical strength have been developed (Rabie *et al* 2013, Wu *et al* 2017, Yu *et al* 2017, Rabie and Franck 2018). Thus far these methods have largely focussed on target properties such as polarisability and electronegativity but have not considered electron-collision behaviour. Although these regression predictions can give satisfactory assessment results, they do not explain why such gases have a high or low electrical strength.

It has been found that SF_6 has large electron scattering cross section and especially attachment cross section at low (thermal) energies which appears to be the key reason for its good insulation properties (Ferch *et al* 1982, Gerchikov and Gribakin 2008). However, it is not easy to find SF_6 alternative species with large low-energy attachment cross sections by searching through available experimental measurements or theoretical calculations. For high electrical strength one would expect a large low-energy total scattering cross section; however, for polar molecules such cross sections are all very large (Zhang *et al* 2009), but, as we show below, this property is not a reliable predictor of high electrical strength. Instead, we focus on another important scattering process which reflects the interaction between the electron and the molecule. The formation of compound anionic states in the form of (weakly) bound states, virtual states or resonances attracts. Electron attachment or dissociative attachment occurs via appropriate resonances (Fabrikant *et al* 2017). Here we study the relationship between resonances and molecular electrical strength with the hope that this property can be used as indicator of SF_6 alternative gases. For this we studied ten sample molecules which are listed in table 1. The polarizabilities of these molecules are also listed in table 1; these are used predictors used by Rabie *et al* (2013) and Yu *et al* (2017). However, this property cannot be related either to the discharge process directly or used to predict the insulation strength of individual gases. Taking $CClF_3$ as an example, its polarizability is similar to SF_6, but the electrical strength is much lower than SF_6. Therefore polarisabilities will not be a focus of this work.

The following section gives a short description of quantemol electron collision (QEC) package used for this work and our methodology. Section 3.1 gives the elastic cross sections of the sample molecules. Section 3.2 presents the resonances and discusses the relationship between resonances and electrical strength. Section 4 gives our conclusions.

2. Method

Our calculations used the R-matrix method which is designed for the study of low-energy electron collisions (Tennyson 2010). Specifically we used the QEC expert system (Cooper *et al* 2019) which uses Molpro (Werner *et al* 2012) to generate target wavefunctions and the UKRmol+ code (Mašín *et al* 2020) to perform the electron scattering studies giving electron scattering cross sections and resonance parameters. Importantly for this work QEC obtains resonance positions and widths using an automated fit of the eigenphase sum to a Breit–Wigner form (Tennyson and Noble 1984). As the representation of a resonance is systematically improved it will become lower in energy and, under certain circumstances, may become a (zero energy) virtual state or even a weakly bound state. It is possible to perform negative energy scattering calculations to identify such bound states (Sarpal *et al* 1991, Little and Tennyson 2013); here a simpler approach was taken: we monitored the position of the lowest R-matrix pole. If for a particular calculation the lowest pole has negative energy, i.e. lies below the energy of the target state, then it is assumed to represent a bound state and if it lies above the target state energy then no bound state is assumed to exist for that calculation. As will be seen, our computed eigenphases are consistent with this assumption.

QEC supports three generic scattering models: SE (static exchange), SEP (static exchange plus polarization) and CC (close-coupling). The SE model is the most basic one which uses a frozen Hartree–Fock (HF) representation of the target. The SE model only considers the electrostatic interactions with the target, and exchange effects between the scattering electron and those in the target. The SE model can identify shape resonances, which can be thought of as the electron occupying an empty (virtual) orbital of the target; however, the SE model give resonances which normally lie too high in energy.

The SEP model improves on the SE model by introducing target polarization effects by allowing the promotion of an electron from an occupied target orbital to a virtual orbital. This allows for the representation of short-range polarisation

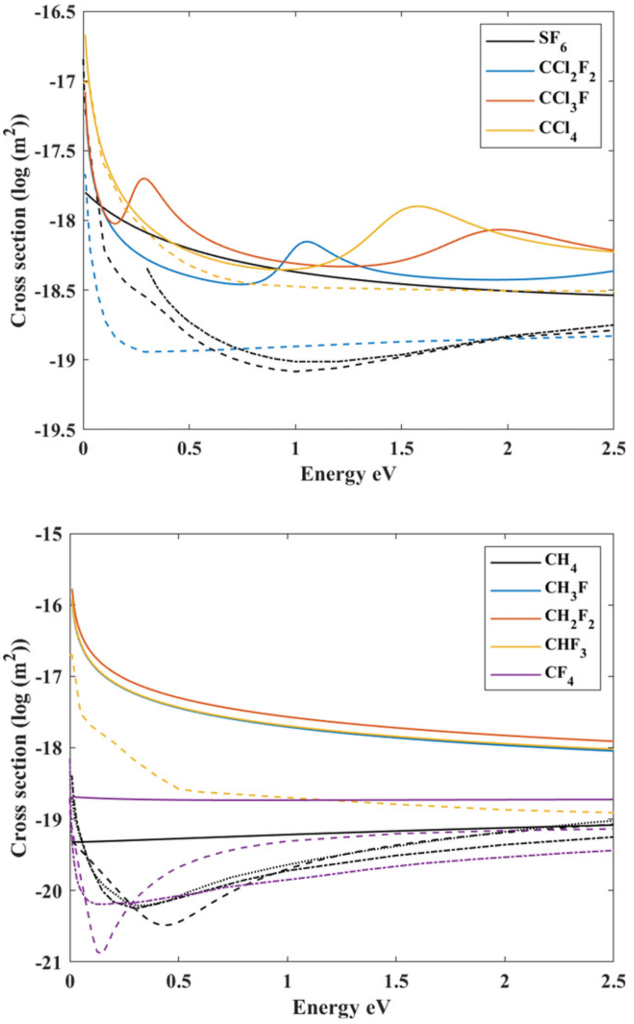

Figure 1. Elastic cross sections. Solid lines: QEC calculations, this work; broken lines, previous studies. Upper figure: dash black lines: SF_6 derived from swarm data by Biagi (2014); Dash dot black lines: SF_6 experimental data by Christophorou and Olthoff (2000); Dash blue lines: CCl_2F_2 experimental data by Hayashi (1987); Dash yellow lines: CCl_4 experimental data by Hayashi (1987). Lower figure: dash black lines, CH_4 theoretical data by Varambhia *et al* (2008); dash dot black lines: CH_4 experimental data by Morgan (1992); dot black lines: CH_4 experimental data by Hayashi (1987);dash yellow lines: CHF_3 experimental data by Bordage and Segur (2001); dash purple lines: CF_4 experimental data by Bordage *et al* (1996); dash dot purple lines: CF_4 experimental data by Hayashi (1987).

effects which are important in lowering the energy of the resonance. Unlike the SE model, experience shows that it is necessary to include many virtual orbitals (VOs) to converge an SEP calculation (Fujimoto *et al* 2012). SEP calculations greatly improve the accuracy by which low-energy resonance positions and widths can be predicted but are capable of placing these resonances too low in energy due to the imbalance caused by the extensive correlation of the scattering electron for an uncorrelated (HF) target wavefunction. The SEP model is capable of representing both shape and Feshbach resonances.

The CC method employs a multi-state expansion to represent the target wavefunction, while SE and SEP are based on ground HF target wavefunctions. Generally, the CC method can be accurate but, for example, full representation of polarisation effects at low energy require very extensive and expensive calculations (Gorfinkiel and Tennyson 2004, Brigg *et al* 2014). Unlike the SE and SEP methods, the CC method also gives electronic excitation cross sections. However, electronic excitation processes usually only happens at energies of a few eV or above which is not the energy region of importance for quasi-thermal electrons. So for characterising SF_6 alternative gases, and given that a large number of gases maybe be possible candidates, the cheap and fast SEP model is used in this work.

Unless otherwise stated, all calculations presented below used 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 to represent the target.

3. Calculations

Devins (1980) and Brand (1982) report the electrical strength relative to SF_6, E_r, for over 40 molecules. Among these molecules, besides SF_6, most of the high electrical strength molecules are carbon based halogen compounds. The influence of halogen atoms and carbon chain length are studied by Devins (1980), who gives interesting examples of high E_r species. Since chlorine containing molecules are known to destroy ozone in the upper atmosphere current gases deemed to be environmentally friendly are largely chlorine free. However, CCl_4 was an early insulating gas with a high electrical strength; it can therefore be used as a prototype when trying to understand the properties of gases with $E_\mathrm{r} > 1$. Recently, promising new gases are generally carbon–fluorine based molecules (such as HFO1234, C_4F_7N and $C_5F_{10}O$), so fluorocarbon molecules are also interesting species. However, these molecules have more than 3 carbon atoms and over 10 heavy atoms, which makes them computationally expensive for an initial study. By considering existing experimental results, recent research interests, the cost of calculation and that we are interested in the relationship between the electrical strength and electron–molecule scattering characteristics, we chose the following sample molecules: SF_6, CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, CF_4, CHF_3, CH_2F_2, CH_3F and CH_4. The electrical strength relative to SF_6 and polarisabilities of these molecules are listed in table 1.

3.1. Elastic cross sections

Elastic cross sections of the sample molecules are calculated using the SEP model, and compared with the previous experimental and theoretical results, as shown in figure 1. A Born correction was added for the polar molecules CCl_2F_2, CCl_3F, CH_3F, CH_2F_2 and CHF_3 to allow for partial waves with $\ell > 4$ which are important for systems with a long-range dipole (Norcross and Padial 1982, Kaur *et al* 2008).

To show the results clearly, the sample molecules are divided into two groups; the molecules with electrical strength comparable and higher than SF_6 are shown in the upper panel of figure 1, and the ones with lower E_r are in the lower panel of figure 1. In upper figure of figure 1, the elastic cross sections

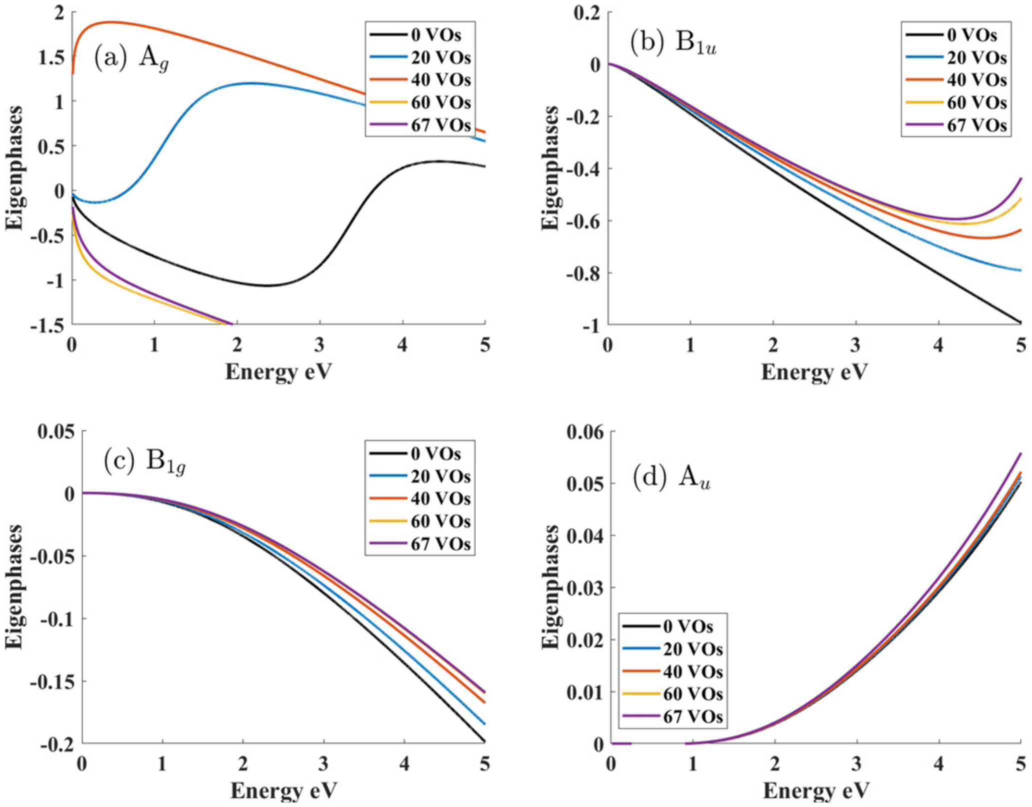

Figure 2. Eigenphase sums for SF_6 as a function of the number of virtual orbitals considered in the calculations.

Table 2. SF_6 resonance position (width) and energy of the lowest R-matrix pole, P_1, relative to the target energy as a function of number of virtual orbitals (VOs) for a calculation using a cc-pVDZ basis set.

SF_6	0 VOs	20 VOs	40 VOs	60 VOs	67 VOs
Resonance (eV)	3.36(1.06)	1.12(1.01)	—	—	—
P_1 (eV)	0.62	0.39	0.01	−0.17	−0.31

for SF_6 calculated using QEC are compared with those of Biagi (2014) (taken from LXCat, Pitchford *et al* 2017), and Christophorou and Olthoff (2000). CCl_2F_2 and CCl_4 are compared with results of Hayashi (1987). Although the results of SF_6 and CCl_2F_2 in this work are higher than the previous results at energies above 0.1 eV, it can be still found that the cross sections of these high electrical strength molecules have high values (above 10^{-18} m^2) as the electron energy tends to 0 eV.

The lower panel of figure 1 compares the results for methane with those of Varambhia *et al* (2008), Morgan (1992) and Hayashi (1987). For CH_4, the SEP results, which used all 29 VOs available, do not agree well with the previous works which show a Ramsauer–Townsend minimum at about 0.4 eV; but this work does not. This issue is discussed extensively by Brigg *et al* (2014). However, the values of the cross section near zero energy are still in agreement at about 10^{-19} m^2 which is similar to those for to CF_4. Varambhia *et al* (2008) present a detailed comparison between CC and SE calculations for methane; these shows that both method give the same result at low energy which is important for discussions given below.

Comparing the upper and lower figures, it is found that high electrical strength molecules have high cross section values (10^{-18}–10^{-17} m^2) at about 0 eV while low electrical strength molecules like CH_4 and CF_4 have low cross sections (around 10^{-19} m^2). But as shown in the lower panel and by Zhang *et al* (2009), polar molecules like CHF_3 which do not have good strength, also have high cross sections at low energy. So the value of the elastic cross section is not suitable for directly estimating molecular electrical strength.

3.2. Eigenphases

Eigenphases give information on resonances in the electron molecule scattering process; here the eigenphases we present for SF_6 and the other molecules are calculated using the SEP model with a varying number of VOs. As mentioned above, an anion state is essential for the attachment processes which are thought to play a key role in the gas breakdown process. In the first part of this section, SF_6 eigenphases and resonance parameters are computed with different numbers of VOs to provide a reference standard for high electrical strength molecules. In the second part, eigenphases and resonances of the other

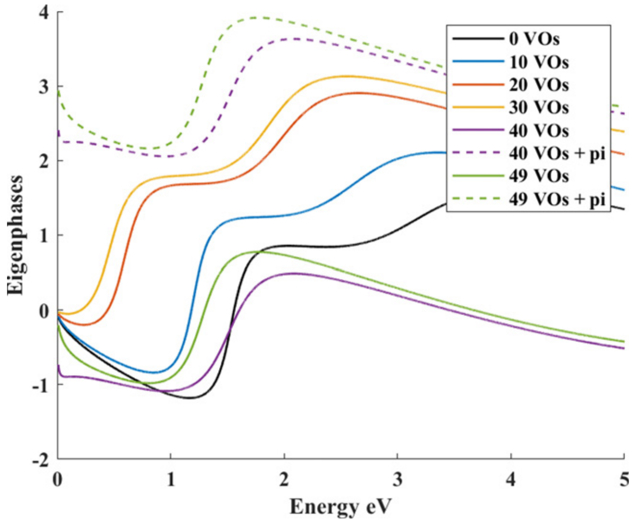

Figure 3. A_1 symmetry eigenphase sums for CCl_4.

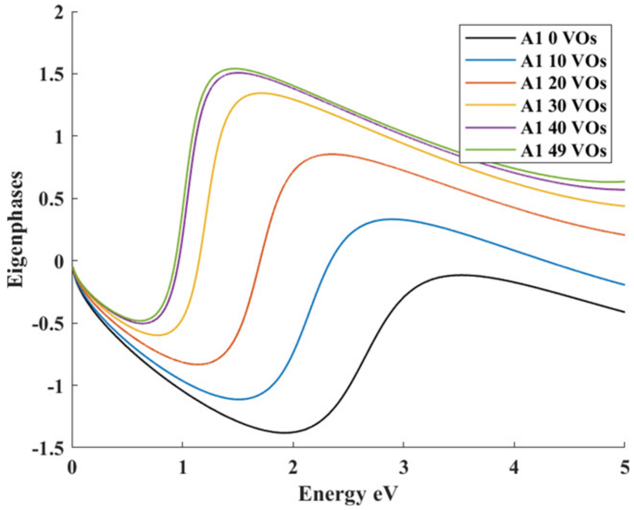

Figure 4. A_1 symmetry eigenphase sums for CCl_2F_2.

molecules are considered. When considering the eigenphases two things should be noted. Our calculations are variational so as the number of VOs included in the calculation increases, the eigenphase sum should increase monotonically and the position of any resonance should move to lower energy. Our computed eigenphases all show this behaviour with the caveat that they are arbitrary modulo π and QEC generally gives them in the range $-\pi$ to π which means that sometimes the eigenphase appears to decrease significantly. Similarly the resonances also visibly move to lower energy as the calculations improve but some disappear as they become bound states. We again emphasize that the SEP model can lead to over-correlation of the scattered electron meaning, for example, that resonances are too low in energy or become artificial bound states because the scattering calculation is more complete than the HF calculation used to characterise the target ground state.

3.2.1. Eigenphases of SF_6. SF_6 has T_d symmetry but the highest point group used by Molpro and QEC is D_{2h}, so the eigenphases are divided into 8 representations: A_g, B_{3u}, B_{2u}, B_{1g}, B_{1u}, B_{2g}, B_{3g} and A_u. In D_{2h}, the cc-pVDZ basis gives 67 unoccupied orbitals, so the maximum number of VOs that can be included is 67. Figure 2 shows the eigenphases as a function of the number of VOs included in the calculation. As would be expected, the (B_{1u}, B_{2u}, B_{3u}) and (B_{1g}, B_{2g}, B_{3g}) eigenphases were found to be degenerate. The A_g, B_{1u}, and B_{1g} eigenphases all converge at 60 VOs, so that the results for 67 VOs and 60 VOs overlap; there are fewer orbital with A_u symmetry, meaning that the various A_u eigenphases curves substantially overlap with each other.

As shown in figure 2, only the A_g symmetry has a resonance below 5 eV which moves to lower energy as the number of VOs included increases. B_{1u}, B_{1g} and A_u symmetries show no low energy resonance.

The resonance details of A_g, as shown in figure 2(a), are listed in table 2. With no VOs, there is a sharp phase change at 3.3 eV which represents a resonance, see the black line in figure 2(a). As the number of VOs increases, the resonance position moves to energy lower, below 1 eV, and then it disappears. Inspection of the lowest R-matrix pole position shows that when the low energy resonance disappear, the pole moves to negative energy, consistent with the presence of a weakly bound state. The sharp change behaviour of the A_g eigenphases at zero energy as the number of VOs is increased is, according to Levenson's theorem, consistent with the formation of an extra bound state. Given the possibility that the SEP model can over stabilize a resonance it is difficult to say on the basis of these calculations whether SF_6 supports a very low-lying resonance, a very weakly bound state or even, possibly a virtual state; indeed it appears that the nature of this state of SF_6^- has yet to be firmly established. However, it is clear that there is a state of SF_6^- which very close to the energy of SF_6 itself. The state has ${}^2A_g$ symmetry; that is it is totally symmetric. Capture of thermal electrons by this state can provide a route to attachment via coupling to the vibrational motion as discussed by Gerchikov and Gribakin (2008), who assume that the feature is indeed a weakly bound state.

The key to the ability of SF_6 to 'eat' the free electrons thus appears to be the presence of this very low-lying, totally symmetric state of SF_6^- which leads to a large attachment cross section and a high electrical strength.

3.2.2. Eigenphases of sample molecules. The eigenphases of high electrical strength molecules are given in figures 3–5 and the low electrical strength molecules are listed in figure 6. For the systems studied here the very low energy resonances are only found in the totally symmetric representation (A' or A_1) symmetry of each molecule, therefore only eigenphases of these symmetries are shown below. However, calculations were performed for all symmetries but identified no other very low energy resonance features.

Figure 3 gives the eigenphases of CCl_4 as functions of the number of VOs, which varies from 0 to 49, the maximum number available. The dashed lines are eigenphases increased by π which ensures that the change in the eigenphases with number of VOs is monotonic. There is a resonance at 1.5 eV with no VOs, when the VOs increase to 30, the resonance position

Table 3. Resonance position (width) and energy of lowest R-matrix pole, P_1, as a function of the number of virtual orbitals (VOs) used in the calculation.

Molecule		0 VOs	20 VOs	40 VOs	49 VOs
CCl_4	Resonance (eV)	1.5(0.23)	0.59(0.28)	—	—
	P_1 (eV)	0.80	0.34	−0.05	−0.20
CCl_3F	Resonance(eV)	2.4(0.63)	1.00(0.25)	0.33(0.18)	0.26(0.17)
	P_1 (eV)	0.76	0.55	0.21	0.16
CCl_2F_2	Resonance(eV)	2.6(0.88)	1.7(0.48)	1.04(0.25)	1.02(0.25)
	P_1 (eV)	0.70	0.61	0.54	0.53

Table 4. Calculated resonance positions (positive numbers in eV) or lowest R-matrix pole position (negative numbers in eV) compared with previous experimental and theoretical determinations.

Molecule	This work	Calc	Expt
CCl_4	−0.20	−0.46[a]	0.0[b]
	1.27	0.7[a]	1.22 ±0.06[b]
CCl_3F	0.26	0.45[c]	0.0[b]
	1.89	1.8[c]	1.76 ±0.03[b]
CCl_2F_2	1.02	1.1[c]	1.02 ±0.02[b]
	2.7	2.7[c]	2.64 ±0.06[b]
$CClF_3$	2.2	2.1[c]	2.0 ±0.4[b]
	6.4	6.6[c]	5.94 ±0.07[b]
CF_4	7.1	8.58[d]	8.87 ±0.19[b]

[a] Moreira *et al* (2016).
[b] Jones (1985).
[c] Freitas *et al* (2016).
[d] Varella *et al* (2002).

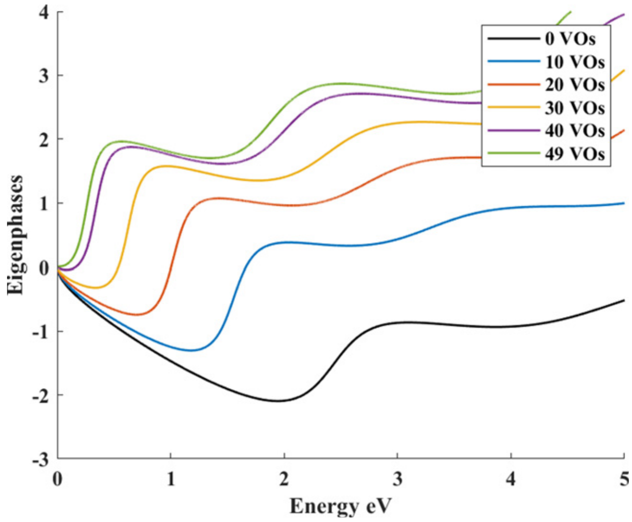

Figure 5. A' symmetry eigenphase sums for CCl_3F.

decreases to 0.5 eV, which is a low energy resonance. With further increases in the VOs, the low energy resonance disappears, see the purple and green lines in figure 3. Correspondingly, when the resonance disappears, the lowest R-matrix pole becomes lower than the target energy, which is same behaviour as SF_6; details are given in table 3. The bound state in electron-CCl_4 scattering, indicates that CCl_4 should display high electrical strength which is in line with the experimental results in table 1. Table 4 compares our cc-pVDZ results for CCl_4 and CF_4 with the previous experimental and theoretical data.

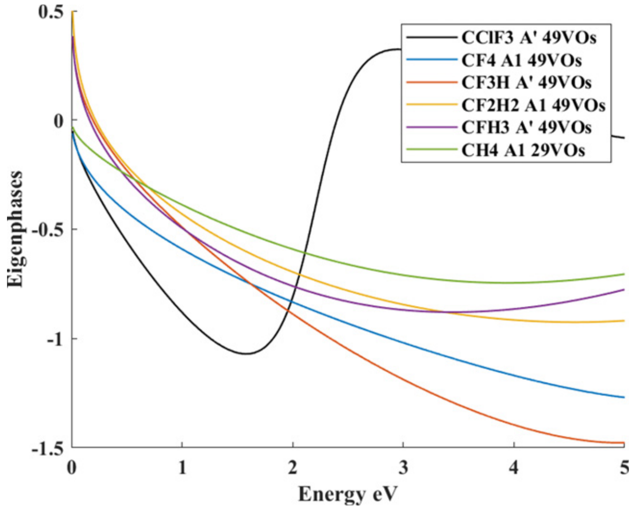

Figure 6. A_1 symmetry eigenphase sums of low E_r molecules: $CClF_3$, CF_4, CF_3H, CF_3H_2, CFH_3 and CH_4.

Generally speaking, they are in good agreement. It is worth noting that our aug-cc-pVDZ CCl_3F calculation gives a negative R-matrix pole which is in line with the experimental result (Jones 1985).

Figure 5 gives the eigenphases of CCl_3F, which is also a high electrical strength molecule. As we can seen in figure 5 and table 3, there is no bound state for this molecule with a cc-pVDZ calculation, but a low energy resonance appears when the number of VOs is increased to 30. This seems to be a counter example of the relationship between bound state and electrical strength. However, as shown in SF_6 and CCl_4, for the SEP model a bound state appears only when a large number of VOs are included in the calculation. To demonstrate this a CCl_3F calculation was performed using an aug-cc-pVDZ basis which gives with 80 VOs. Using all these VOs gave an R-matrix pole at −0.09 eV. This result is in line with those obtained for SF_6 and CCl_4.

A similar situation occurs for CCl_2F_2. But in the recalculation using aug-cc-pVDZ with 80 VOs, there is a low energy resonance at 0.64 eV, but no bound state. Due to calculation costs, no further calculations with larger basis set and more VOs were performed. But the low energy resonance shown in the results obtained with 80 VOs and the trend of resonance moving shown in results of 0–40 VOs listed in table 3 agree with the behaviour found for SF_6.

Figure 6 gives the eigenphases of the low electrical strength molecules with their maximum number of VOs under cc-pVDZ. No low energy resonances or bound states are found by our calculations. Our results for CF_4 and CH_3F are in good agreement with those of Varella *et al* (2002) who also do not find any low energy resonances for these molecules. For CH_4, our SEP results are in agreement with the high accuracy CC calculation of Varambhia *et al* (2008) and Brigg *et al* (2014) who found no low energy resonances. Only $CClF_3$ shows a resonance and this at the higher energy of 2.2 eV. To check the rule found in the high strength molecules, $CClF_3$ was also recalculated under aug-cc-pVDZ with 80 VOs. However, even with 80 VOs, the resonance only moves to 1.7 eV. This group of results illustrate that there is no low energy resonance or bound state in the scattering calculation for the low electrical strength molecules.

4. Conclusion

In this work, a group of molecules were selected as samples from previous research on gas insulators to study the gas's electrical strength from the perspective of electron molecule scattering. Elastic cross sections and eigenphases are computed for SF_6 and our sample molecules using the SEP model with different numbers of VOs included in the calculation.

From the electron-SF_6 scattering calculation, we identify the collision behaviour which allows SF_6 to absorb electrons and display high electrical strength. Our calculations find a resonance at 1.12 eV with 20 VOs included in the SEP model. With more ($\geqslant$40) VOs taken into consideration, the low energy resonance disappears and the lowest R-matrix pole moves to negative energy, consistent with the presence of a weakly bound state. The presence of this very low energy resonance/virtual state/very weakly bound state is what drives attachment in SF_6 with thermal electrons (Gerchikov and Gribakin 2008) which allows SF_6 to mop up these electrons. This result suggests that molecules which show similar behaviour at low in energy in the electron scattering process will also have high electrical strengths.

From the sample molecules it is found that:

(a) High E_r molecules have high elastic cross section at about 0 eV (10^{-18}–10^{-17} m^2). However, a high elastic cross section alone is not sufficient to give an enhanced electrical strength directly, because some low E_r molecules like CHF_3 also have a high cross section at 0 eV since they are polar molecules.

(b) For high E_r molecules, the low energy anion state is not found in all calculations due to the limitation of the SEP model. However, when enough VOs are taken into account, the low energy resonance always appears in high E_r molecules. When further VOs (up to the maximum number available for the given basis set) are considered, the resonance moves to lower energy, until it disappears; disappearance of the resonance is accompanied by the appearance of a negative R-matrix pole and a discontinuous change in the behaviour of the eigenphase at zero energy. Low E_r molecules do not show these features.

From our calculation on SF_6 and the sample molecules, we deduce that the presence of very low energy anion state is the crucial to having a high electrical strength. Thus relatively cheap SEP level calculations can be used to identify candidate molecules which could show useful insulation properties.

Finally it is interesting to note that the anion states we consider are all totally symmetric and therefore s-wave dominated. Static exchange calculations (as given by our SEP calculations with no VOs) all display these features as clearly defined resonances at a few eV. Conventional wisdom suggests that the only resonances found at SE level are shape resonances where the electron is temporarily trapped behind a centrifugal barrier. Such a barrier does not occur for s wave scattering. Calculations by Halmova and Tennyson (2008) identified s-wave shape resonances trapped by a polarisation potential. It would appear that the current low energy features are a mixture of a standard shape resonance, which is present albeit at too high an energy, when polarisation effects are omitted from a calculation, but move to about zero energy as the polarisation effects are fully included.

Acknowledgments

Chunlin Wang acknowledges financial support from the China Scholarship Council. This work was supported by STFC Grant ST/R005133/1 and the National Natural Science Foundation of China under Grant No. 52077170.

ORCID iDs

Chunlin Wang https://orcid.org/0000-0001-5828-0031
Hao Sun https://orcid.org/0000-0002-1673-6712
Jonathan Tennyson https://orcid.org/0000-0002-4994-5238

References

Biagi S F 2014 Fortran program MAGBOLTZ version 10.6

Bordage M C and Segur P 2001 Swarm determination of electron CHF_3 collision cross sections *ICPIG XXV* (Nagoya (Japan)) vol 3

Bordage M C, Ségur P and Chouki A 1996 Determination of a set of electron impact cross sections in tetrafluoromethane consistent with experimental determination of swarm parameters *J. Appl. Phys.* **80** 1325–36

Brand K P 1982 Dielectric strength, boiling point and toxicity of gases—different aspects of the same basic molecular properties *IEEE Trans. Electr. Insul.* **EI-17** 451–6

Brigg W J, Tennyson J and Plummer M 2014 R-Matrix calculations of low-energy electron collisions with methane *J. Phys. B: At. Mol. Opt. Phys.* **47** 185203

Chachereau A, Hösl A and Franck C M 2018 Electrical insulation properties of the perfluoronitrile C_4F_7N *J. Phys. D: Appl. Phys.* **51** 495201

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 SF_6* (Washington, USA: National Instutute of Standards and Technology (NIST), US Department of Commerce)

Christophorou L G and Olthoff J K 2000 Electron interactions with SF_6 *J. Phys. Chem. Ref. Data* **29** 267–330

Cooper B *et al* 2019 Quantemol electron collisions (QEC): an enhanced expert system for performing electron molecule collision calculations using the R-matrix method *Atoms* **7** 97

Cressault Y, Connord V, Hingana H, Teulet P and Gleizes A 2011 Transport properties of CF$_3$I thermal plasmas mixed with CO$_2$, air or N$_2$ as an alternative to SF$_6$ plasmas in high-voltage circuit breakers *J. Phys. D: Appl. Phys.* **44** 495202

Devins J 1980 Replacement gases for SF$_6$ *IEEE Trans. Electr. Insul.* **EI-15** 81–6

Fabrikant I I, Eden S, Mason N J and Fedor J 2017 Recent progress in dissociative electron attachment *Adv. At. Mol. Opt. Phys.* **66** 545–657

Ferch J, Raith W and Schroder K 1982 Total cross section measurement for e-SF$_6$ scattering down to 0.036 eV *J. Phys. B: At. Mol. Phys.* **15** L175–8

Ficheux A, Luescher R, Laruelle E and Maksoud L 2019 SF$_6$ alternative—what to learn from the high voltage experience *25th Int. Conf. Electricity Distribution SF6 Alternative* pp 3–6

Freitas T C, Lopes A R, Azeredo A D, Bettega M H F and A D 2016 Halogenation effects on electron collisions with CF$_3$Cl, CF$_2$Cl$_2$, and CFCl$_3$ *J. Chem. Phys.* **144** 164302

Fujimoto M M, Brigg W J and Tennyson J 2012 R-matrix calculations of differential and integral cross sections for low-energy electron collisions with ethanol *Eur. Phys. J.* D **66** 204

Gerchikov L G and Gribakin G F 2008 Electron attachment to SF$_6$ and lifetimes of SF$_6$—negative ions *Phys. Rev.* A **77** 1–15

Gorfinkiel J D and Tennyson J 2004 Electron-H + 3 collisions at intermediate energies H$_3^+$ collisions at intermediate energies *J. Phys. B: At. Mol. Opt. Phys.* **37** L343–50

Gussoni M, Rui M and Zerbi G 1998 Electronic and relaxation contribution to linear molecular polarizability. An analysis of the experimental values *J. Mol. Struct.* **447** 163–215

Halmova G and Tennyson J 2008 Resonances in electron impact electron detachment of C$_2$– *Phys. Rev. Lett.* **100** 213202

Hayashi M 1987 Electron collision cross-sections for molecules determined from beam and swarm data *Swarm Studies and Inelastic Electron–Molecule Collisions* (Berlin: Springer) pp 167–87

Jones R K 1985 Absolute total cross sections for the scattering of low energy electrons by CCl$_4$, CCl$_3$F, CCl$_2$F$_2$, CClF$_3$, and CF$_4$ *J. Chem. Phys.* **84** 813

Kaur S, Baluja K L and Tennyson J 2008 Electron-impact study of NeF using the R-matrix method *Phys. Rev.* A **77** 032718

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* pp 1–5

Koch M and Franck C M 2015 High voltage insulation properties of HFO$_{1234}$ze *IEEE Trans. Dielect. Electr. Insul.* **22** 3260–8

Li X, Zhao H and Murphy A B 2018 SF$_6$–alternative gases for application in gas-insulated switchgear *J. Phys. D: Appl. Phys.* **51** 153001

Li Y, Zhang X, Zhang J, Xiao S, Xie B, Chen D, Gao Y and Tang J 2019 Assessment on the toxicity and application risk of C$_4$F$_7$N: a new SF$_6$ alternative gas *J. Hazard. Mater.* **368** 653–60

Little D A and Tennyson J 2013 An *ab initio* study of singlet and triplet Rydberg states of N$_2$ *J. Phys. B: At. Mol. Opt. Phys.* **46** 145102

Mašín Z, Benda J, Gorfinkiel J D, Harvey A G and Tennyson J 2020 UKRmol+: a suite for modelling of electronic processes in molecules interacting with electrons, positrons and photons using the R-matrix method *Comput. Phys. Commun.* **249** 107092

Moreira G M, Barbosa A S, Pastega D F and Bettega M H F 2016 Low-energy electron scattering by carbon tetrachloride *J. Phys. B: At. Mol. Opt. Phys.* **49** 035202

Morgan W L 1992 A critical evaluation of low-energy electron impact cross sections for plasma processing modeling. II: Cl$_4$, SiH$_4$, and CH$_4$ *Plasma Chem. Plasma Process.* **12** 477–93

Norcross D W and Padial N T 1982 The multipole-extracted adiabatic-nuclei approximation for electron–molecule collisions *Phys. Rev.* A **25** 226–38

Olney T N, Cann N M, Cooper G and Brion C E 1997 Absolute scale determination for photoabsorption spectra and the calculation of molecular properties using dipole sum-rules *Chem. Phys.* **223** 59–98

Preve C, Maladen R and Piccoz D 2016 Method for validation of new eco-friendly insulating gases for medium voltage equipment *2016 IEEE Int. Conf. Dielectrics, ICD 2016* 1 pp 235–40

Preve C, Piccoz D and Maladen R 2017 Application of HFO$_{1234}$ZEE in MV switchgear AS SF$_6$ alternative gas *CIRED Open Access Proc. J.* **2017** 42–5

Pitchford L C *et al* 2017 LXC at: an open-access, web-based platform for data needed for modeling low temperature plasmas *Plasma Process. Polym.* **14** 1600098

Rabie M, Dahl D A, Donald S M A, Reiher M and Franck C M 2013 Predictors for gases of high electrical strength *IEEE Trans. Dielect. Electr. Insul.* **20** 856–63

Rabie M and Franck C M 2018 Assessment of eco-friendly gases for electrical insulation to replace the most potent industrial greenhouse gas SF$_6$ *Environ. Sci. Technol.* **52** 369–80

Sarpal B K, Branchett S E, Tennyson J and Morgan L A 1991 Bound states using the R-matrix method: Rydberg states of HeH *J. Phys. B: At. Mol. Opt. Phys.* **24** 3685–99

Seeger M *et al* 2017 Recent trends in development of high voltage circuit breakers with SF$_6$ alternative gases *Plasma Phys. Techn.* **4** 8–12

Simka P and Ranjan N 2015 Dielectric strength of C$_5$ perfluoroketone *Proc. 19th Int. Symp. High Voltage Engineering* p 5

Tennyson J and Noble C J 1984 RESON-A program for the detection and fitting of Breit–Wigner resonances *Comput. Phys. Commun.* **33** 421–4

Tennyson J 2010 Electron-molecule collision calculations using the R-matrix method *Phys. Rep.* **491** 29–76

Ullah R, Ullah Z, Haider A, Amin S and Khan F 2018 Dielectric properties of tetrafluoroethane (R134) gas and its mixtures with N$_2$ and air as a sustainable alternative to SF$_6$ in high voltage applications *Electr. Power Syst. Res.* **163** 532–7

Varambhia H N, Munro J J and Tennyson J 2008 R-matrix calculations of low-energy electron alkane collisions *Int. J. Mass Spectrom.* **271** 1–7

Varella M T do N, Winstead C, McKoy V, Kitajima M and Tanaka H 2002 Low-energy electron scattering by CH$_3$F, CH$_2$F$_2$, CHF$_3$, and CF$_4$ *Phys. Rev.* A **65** 022702

Werner H-J, Knowles P J, Knizia G, Manby F R and Schütz M 2012 Molpro: a general-purpose quantum chemistry program package *WIREs Comput. Mol. Sci.* **2** 242–53