Why SF₆ eats electrons: identifying high electrical strength molecules from their electron collision properties

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Why SF$_6$ eats electrons: identifying high electrical strength molecules from their electron collision properties

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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 ($\ll 1$ 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$_3$F and CCl$_2$F$_2$ also have a totally-symmetric low-energy resonance, while the low electrical strength molecules such as CH$_4$, C$_2$H$_3$F, … 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$_3$I (de Urquijo 2007, Cressault et al 2011), C$_4$F$_7$N (Kieffel and Biquez 2015, Chachereau et al 2018, Li and Zhao 2018, Wu et al 2018), C$_2$F$_4$O (Simka and Rangan 2015, Wu et al 2017, Yokomizu et al 2020), HFO1234 (C$_4$F$_6$H$_2$, Koch and Franck 2015, Preve et al 2017), and R134 (C$_2$F$_4$H$_2$, Ullah et al 2018) have been considered.

Among these species, C$_4$F$_7$N is the most popular one and has indeed been used in practical applications
(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 SF₆ 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 SF₆ 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 (Fabrikanet 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 SF₆ 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 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 CCIF₃ as an example, its polarizability is similar to SF₆, but the electrical strength is much lower than SF₆. Therefore polarisabilities will not be a focus of this work.

The following section gives a short description of quante-mol 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.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$E_i$</th>
<th>$\alpha_0$ (Expt.)</th>
<th>$\alpha_0$ (Calc.)</th>
<th>Molecules</th>
<th>$E_i$</th>
<th>$\alpha_0$ (Expt.)</th>
<th>$\alpha_0$ (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>2.36</td>
<td>10.00</td>
<td>6.99</td>
<td>CH₄</td>
<td>0.43</td>
<td>2.45</td>
<td>1.85</td>
</tr>
<tr>
<td>CCl₃F</td>
<td>1.72</td>
<td>8.25</td>
<td>5.54</td>
<td>CF₄</td>
<td>0.41</td>
<td>2.82</td>
<td>1.75</td>
</tr>
<tr>
<td>CCl₂F₂</td>
<td>1.01</td>
<td>6.37</td>
<td>4.13</td>
<td>CH₃F₂</td>
<td>0.30</td>
<td>2.76</td>
<td>1.71</td>
</tr>
<tr>
<td>SF₆</td>
<td>1.00</td>
<td>4.49</td>
<td>2.86</td>
<td>CHF₃</td>
<td>0.27</td>
<td>2.80</td>
<td>1.71</td>
</tr>
<tr>
<td>CCIF₃</td>
<td>0.58</td>
<td>4.65</td>
<td>2.80</td>
<td>CH₃F</td>
<td>—</td>
<td>2.54</td>
<td>1.76</td>
</tr>
</tbody>
</table>

$^a$Polarizabilities are from Olney et al. (1997), $^b$Gussoni et al. (1998).

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\(_2\)F\(_2\) 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); 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).

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 \(E_r > 1\). Recently, promising new gases are generally carbon–fluorine based molecules (such as HFO1234, C\(_4\)F\(_7\)Na and C\(_5\)F\(_{10}\)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\(_3\)F, CCl\(_2\)F\(_2\), CCl\(_2\)F\(_3\), CF\(_3\), CH\(_2\)F\(_2\), CH\(_3\)F 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\(_2\)F\(_2\), CCl\(_3\)F, CH\(_2\)F\(_2\) 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 can be accurate but, for example, full representation of polarization effects at low energy require very extensive and expensive calculations (Gorfinkel and Tennyson 2004, Briggs 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.
Figure 2. Eigenphase sums for SF6 as a function of the number of virtual orbitals considered in the calculations.

Table 2. SF6 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.

<table>
<thead>
<tr>
<th>SF6</th>
<th>0 VOs</th>
<th>20 VOs</th>
<th>40 VOs</th>
<th>60 VOs</th>
<th>67 VOs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resonance (eV)</td>
<td>3.36(1.06)</td>
<td>1.12(1.01)</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$P_1$ (eV)</td>
<td>0.62</td>
<td>0.39</td>
<td>0.01</td>
<td>-0.17</td>
<td>-0.31</td>
</tr>
</tbody>
</table>

for SF6 calculated using QEC are compared with those of Biagi (2014) (taken from LXCat, Pitchford et al 2017), and Christophorou and Olthoff (2000). CCl2F2 and CCl4 are compared with results of Hayashi (1987). Although the results of SF6 and CCl2F2 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 CH4, 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 CF4. 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 CH4 and CF4 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 CHF3 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 SF6 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, SF6 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
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 $\pi$ and QEC generally gives them in the range $-\pi$ to $\pi$ 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 $^7A_g$ 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 $\pi$ 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.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>0 VOs</th>
<th>20 VOs</th>
<th>40 VOs</th>
<th>49 VOs</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>1.5(0.23)</td>
<td>0.59(0.28)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>$P_1$ (eV)</td>
<td>0.80</td>
<td>0.34</td>
<td>−0.05</td>
</tr>
<tr>
<td>CCl$_3$F</td>
<td>2.4(0.63)</td>
<td>1.00(0.25)</td>
<td>0.33(0.18)</td>
<td>0.26(0.17)</td>
</tr>
<tr>
<td></td>
<td>$P_1$ (eV)</td>
<td>0.76</td>
<td>0.55</td>
<td>0.21</td>
</tr>
<tr>
<td>CCl$_2$F$_2$</td>
<td>2.6(0.88)</td>
<td>1.7(0.48)</td>
<td>1.04(0.25)</td>
<td>1.02(0.25)</td>
</tr>
<tr>
<td></td>
<td>$P_1$ (eV)</td>
<td>0.70</td>
<td>0.61</td>
<td>0.54</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>This work</th>
<th>Calc</th>
<th>Expt</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>$-0.20$</td>
<td>$-0.46^a$</td>
<td>$0.0^b$</td>
</tr>
<tr>
<td></td>
<td>1.27</td>
<td>$0.7^a$</td>
<td>$1.22 \pm 0.06^b$</td>
</tr>
<tr>
<td>CCl$_3$F</td>
<td>0.26</td>
<td>$0.45^c$</td>
<td>$0.0^b$</td>
</tr>
<tr>
<td></td>
<td>1.89</td>
<td>$1.8^a$</td>
<td>$1.76 \pm 0.03^b$</td>
</tr>
<tr>
<td>CCl$_2$F$_2$</td>
<td>1.02</td>
<td>$1.1^c$</td>
<td>$1.02 \pm 0.02^b$</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>$2.7^c$</td>
<td>$2.64 \pm 0.06^b$</td>
</tr>
<tr>
<td>CCIF$_3$</td>
<td>2.2</td>
<td>$2.1^c$</td>
<td>$2.0 \pm 0.4^c$</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>$6.6^c$</td>
<td>$5.94 \pm 0.07^b$</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>7.1</td>
<td>$8.58^d$</td>
<td>$8.87 \pm 0.19^b$</td>
</tr>
</tbody>
</table>

$^a$Moreira et al (2016).
$^b$Jones (1985).
$^d$Varella et al (2002).

Generally speaking, they are in good agreement. It is worth noting that our aug-cc-pVDZ CCl$_3$F calculation gives a negative R-matrix pole which is in line with the experimental result (Jones 1985).

Figure 5 gives the eigenphases of CCl$_3$F, 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$_3$F 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$_2$F$_2$. 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. $A_1$ symmetry eigenphase sums of low $E_i$ molecules: CCIF$_3$, CF$_4$, CF$_3$H, CF$_3$H$_2$, CF$_2$H$_3$ and CH$_4$. 

Figure 5. $A^\prime$ symmetry eigenphase sums for CCl$_3$F.
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 CF₄ and CH₃F are in good agreement with those of Varella et al (2002) who also do not find any low energy resonances for these molecules. For CH₄, 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 CClF₃ shows a resonance and this at the higher energy of 2.2 eV. To check the rule found in the high strength molecules, CClF₃ 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 SF₆ and our sample molecules using the SEP model with different numbers of VOs included in the calculation.

From the electron-SF₆ scattering calculation, we identify the collision behaviour which allows SF₆ 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 (≥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 SF₆ with thermal electrons (Gerchikov and Gribakin 2008) which allows SF₆ 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 ($10^{-18}−10^{-17}$ m²). However, a high elastic cross section alone is not sufficient to give an enhanced electrical strength directly, because some low $E_r$ molecules like CHF₃ 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 SF₆ 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 resonance. 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.

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