Electron collisions with the CF$_3$ radical using the $R$-matrix method

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Abstract. Fluorocarbons are the main species used in etching plasmas and their properties are driven by CF$_x$ ($x = 1–3$) radicals. Previous calculations on CF and CF$_2$ show low-lying resonances which may lead to dissociative electron attachment under standard plasma conditions. Here the $R$-matrix method is used to treat electron collisions with the polyatomic radical CF$_3$ at its equilibrium geometry using a coupled states expansion. These calculations concentrate on obtaining low-energy, sub-10 eV, elastic and excitation cross-sections. A CF$_3^-$ bound state of $^1A_1$ symmetry is detected but no low-lying resonances. These findings suggest that CF$_3$ is unlikely to undergo dissociative electron attachment; the possible consequences of this for etching plasmas are discussed.

Contents

1 Introduction 2
2 Theoretical approach 3
3 Target model 4
  3.1 MOLPRO calculations ........................................... 4
  3.2 $R$-matrix calculations .......................................... 6
  3.3 Scattering model ............................................... 7
4 Cross-sections and bound states 9
5 Conclusions 10
Acknowledgments 11
References 11
1. Introduction

The plasma-processing technology used in the processing of materials for microelectronics has underpinned one of the most vibrant and commercially successful industries of the late 20th century. Current research effort is being directed towards (i) developing new techniques for in situ plasma diagnosis [1] and (ii) employing large-scale computer modelling to simulate conditions within such plasmas [2]. The immediate aim of such studies is to elucidate the plasma characteristics through an understanding of the fundamental atomic, molecular (and optical) physics and thus place this technology on a firm theoretical basis, rather than on the empiricism and intuition which have been relied upon so far. The ultimate goal is to advance our understanding of plasma characteristics to such a level that it will be possible to custom-design, through computer models (entitled the ‘virtual factory’), plasma reactors for any specified commercial requirement.

Fluorocarbons are the most common feedstock gases used in etching plasmas. However, all these species have high global warming potentials (GWP) as they absorb strongly in the infrared and have very long residence times in the Earth’s atmosphere. CF₄, for example, remains for up to 50,000 years. Hence, under the terms of the Kyoto Protocol on gas emissions, CF₄, C₂F₆, C₃F₈ and c-C₄F₈ should be phased out by 2010. The need to replace these gases, added to the continued drive for smaller scale devices, has led to alternative fluorocarbon gases, such as l-C₄F₈, CF₃I and C₂F₄, being actively considered. The latter two are of particular interest from the point of view of controlling the composition of radicals in the plasma since they interact with electrons to yield CF₃ and CF₂ respectively. Recent studies have shown that the concentration of CF₄ radicals has a significant effect on the behaviour of fluorocarbon plasmas [3] and that these radicals also occur in significant concentrations in other plasmas [4]. It is therefore important to model accurately the role of CF₄ radicals in such plasmas—hence the need for accurate electron scattering cross-sections from such species. However, at present, there are little or no data on electron interactions with such species.

One reason for the dearth of data is the extreme difficulty in performing experimental studies with transient radicals species, hence it is necessary to consider theoretical treatments. In two recent studies [5, 6], we presented calculated cross-sections for electron collisions with the CF and CF₂ radicals. For both of these species, our calculations identified low-lying resonances, i.e. temporarily bound anion states, which may lead directly to dissociation. This process, known as dissociative electron attachment, can yield F⁻ ions in both cases, behaviour which could have significant consequences for the charge distribution and electron energy distribution in a fluorocarbon plasma. In this paper, we report new results on CF₃ for which there are even fewer data available than there were on the CF and CF₂ radicals.

CF₃ radicals play an important role in the plasma processing of Si and SiO₂ in the microelectronics industry [7–10]. The CF₃ free radical is also an important species in atmospheric chemistry because of its role in the oxidative degradation of both perfluorocarbons and hydrofluorocarbons [11].

Knowledge of the cross-sections of molecular species is important for plasma diagnosis techniques, plasma modelling [12] and to study the dynamics of discharges [13]. The absolute partial electron-impact ionization cross-section for the CF₃ was measured in [14]. Diniz et al [15] calculated the elastic differential cross-sections for electron collision with the CF₃ in the energy range below 30 eV using the Schwinger multichannel method at the static-exchange level. They found a similarity between the elastic differential cross-section for CF₃ and CF₃H.
The agreement between these two differential cross-sections increases with the energy of the incident electron. No experimental or theoretical data on low-energy collisional integral cross-sections for the CF$_3$ radical have been reported. In this work, we present the results of $R$-matrix calculations on the low-energy collision of electrons with CF$_3$. In contrast to our studies on CF and CF$_2$, we find no evidence for low-lying resonances in CF$_3$ which suggests that this radical is unlikely to undergo dissociative electron attachment with quasi-thermal electrons.

2. Theoretical approach

The $R$-matrix method is based on the splitting of co-ordinate space into two regions, an inner and an outer region, separated by a spherical boundary of radius $r = a$ centred on the centre of mass of the molecule [16, 17]. The boundary is placed so that the inner region contains all the electronic charge cloud of the target molecule. The interaction between the electron and the target molecule has different features in the inner and outer regions. Inside the $R$-matrix sphere, the scattering electron lies within the molecular-charge cloud, and exchange interactions and electron–electron correlation must be explicitly taken into account. Quantum chemistry methods can be adopted to find the wavefunction in this region. In the outer region, exchange and correlation are assumed to be negligible and only long-range multipolar interactions between the scattering electron and the target are included. Thus it is possible to reduce the scattering problem in the external region to the solution of a set of coupled, ordinary differential equations.

In the inner region, the total wavefunction describing scattering of an electron by an $N$-electron molecule can be expanded as [16]

$$\Psi_k^{N+1} = A \sum_{I} \psi_I^{N}(x_1, \ldots, x_N) \sum_{j} \xi_j(x_{N+1}) a_{Ijk} + \sum_{m} \chi_m(x_1, \ldots, x_N, x_{N+1}) b_{mk},$$

(1)

where $A$ is the anti-symmetrization operator, $x_n$ is the spatial and spin co-ordinate of the $n$th electron, $\psi_I^{N}$ is a target molecular wavefunction, $\xi_j$ is a continuum orbital spin-coupled with the scattering electron and $a_{Ijk}$ and $b_{mk}$ are variational coefficients determined by our program. The first summation runs over all configuration interaction (CI) target states and gives terms known as ‘target + continuum’ configurations. The second summation runs over configurations $\chi_m$, where all electrons are placed in target molecular orbitals. These configurations are generally described as square integrable.

A CI target molecular wavefunction $\psi_I^{N}$ is expressed as a linear combination of configuration state functions (CSF) $\phi_i^{N}$ with the wavefunction’s symmetry

$$\psi_I^{N} = \sum_i c_{iI} \phi_i^{N},$$

(2)

where coefficients $c_{iI}$ are found by diagonalizing the $N$-electron target Hamiltonian matrix within this CSF expansion. The quality of the scattering calculation is strongly dependent on obtaining a good representation of the target wavefunctions and the associated target properties. A particular problem which faces scattering studies is the need to represent all...
target states using a single set of orbitals. This places particular emphasis on the choice of a suitable orbital set.

The self-consistent field (SCF) solution to the Hartree–Fock approximation yields orbitals which often give a satisfactory representation of the ground state but are less appropriate for excited states. In practice, for CF$_3$, the SCF approximation significantly overestimates the permanent dipole moment of CF$_3$, a property which is of great importance for low-energy scattering. There are a number of ways of improving the orbital representation for a multistate problem. We explore two of these, multi-channel (MC) SCF and natural orbitals (NOs). The MC-SCF method obtains orbitals optimized simultaneously for a number of electronic states. Conversely, NOs are obtained by diagonalizing the density matrix, ideally of the exact wavefunction, but in practice of a large CI calculation. Use of such orbitals is discussed below.

The general application of the $R$-matrix method to polyatomic molecules employing the UK polyatomic $R$-matrix code has been described in the literature [17, 18].

3. Target model

The ground-state structure of the CF$_3$ has been characterized by experimental and $ab$ $initio$ methods [19–23]. The CF$_3$ radical has a pyramidal structure and belongs to C$_{3v}$ point group. Its ground $^2$A$_1$ state has the following electronic configuration: 1e$^4$1a$^2_1$2a$^2_3$3a$^2_2$2e$^4$4a$^2_3$3e$^4$5a$^2_4$4e$^4$5a$^2_6$6a$^1_1$. The equilibrium geometry of the CF$_3$ was derived from infrared laser spectroscopy experiments [24]. According to these studies, the C–F bond length is 2.53$\pm$0.01 Å and FCF angle is 110.7$^\circ$ at equilibrium. All calculations reported below use this geometry. The ground-state dipole moment of the CF$_3$, determined by the method of molecular beam focusing in an inhomogeneous electric field, is 0.43 ± 0.07 D [25].

Surprisingly, we could find no data on excitation energies for the CF$_3$ in the published literature. This means that the present scattering study had to be prefaced by a series of electronic structure calculations aimed at characterizing the low-lying electronic states of CF$_3$. To determine reliable target parameters, such as vertical excitation energies, we performed a series of electronic structure calculations using quantum chemistry package MOLPRO [26].

As both the UK polyatomic $R$-matrix codes and MOLPRO only work with symmetries lower than D$_{2h}$, all calculations were performed in C$_s$ point group. In C$_s$ symmetry, the ground-state electronic configuration is (1a$'$...10a$'$)$^2$ (1a$''$...6a$''$)$^2$ 11a$'$. Note that degenerate e symmetry states and orbitals are split between a$'$ and a$''$ symmetries in C$_s$. Not all the calculations described below maintained the true degeneracy between these orbital pairs.

3.1. MOLPRO calculations

$Ab$ $initio$ complete active-space self-consistent field (CASSCF) and multireference configuration interaction (MRCI) calculations have been carried out on the low-lying electronic states of the CF$_3$ at its equilibrium geometry. CASSCF is a form of MCSCF whereas the MRCI method, which is the most powerful tool for calculating accurate molecular properties, augments an MCSCF calculation with a large CI calculation. The main bottleneck of the MRCI method is the fact that the size of the CI expansion rapidly increases with the number of reference configurations.

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Table 1. The ground $X^2A'$ state total energy (in Hartree) and vertical excitation energies (in eV) for the CF$_3$ target states. All calculations are for the equilibrium geometry using the CASSCF method and different basis sets. Also given is the ground-state dipole moment (in D).

| State   | 6-311G*  | 6-31G*  | Sadlej pVTZ | aug-cc-pVDZ | aug-cc-pVTZ |
|---------|----------|---------|-------------|-------------|-------------|
| $X^2A'$ | $-336.30399$ | $-336.2117$ | $-336.2909$ | $-336.1979$ | $-336.3487$ |
| $A^2A''$ | $8.20$ | $8.40$ | $8.35$ | $7.78$ | $8.17$ |
| $2^2A'$ | $8.78$ | $9.00$ | $7.80$ | $8.99$ | $8.77$ |
| $2^2A''$ | $8.78$ | $9.00$ | $8.93$ | $-$ | $8.77$ |
| $3^2A'$ | $9.69$ | $-$ | $-$ | $-$ | $-$ |
| $3^2A''$ | $9.69$ | $-$ | $-$ | $-$ | $-$ |
| $\mu(X^2A')$ | $0.55$ | $0.63$ | $0.69$ | $0.34$ | $0.64$ |

Preliminary results showed that only five excited states of symmetries $A^2A''$, $2^2A'$, $2^2A''$, $3^2A'$ and $3^2A''$ have vertical excitation energies below 10 eV. Therefore, only the above excited states are included in our test calculations. Higher states rapidly take on greater Rydberg character, which makes them difficult to treat within an $R$-matrix calculation (see [5]).

The CASSCF calculations consisted of eight core electrons frozen in $1a'$, $2a'$, $3a'$ and $1a''$ molecular orbitals and 25 valence electrons moving freely among remaining $4a'$, ..., $13a'$, $2a''$, ..., $7a''$ molecular orbitals in a complete active-space representation. Initial molecular orbitals were taken from SCF calculations for the CF$_3$ ground state. Test calculations were performed using several basis sets (6-31G*, 6-311G*, Sadlej pVTZ, aug-cc-pVDZ and aug-cc-pVTZ) (http://www.cse.clrc.ac.uk/qcg/basis). The ground-state energy, vertical excitation energies and the ground-state dipole moment, calculated using CASSCF method and different basis sets, are shown in table 1.

In C$_3v$ point group E states of the CF$_3$ are degenerate. This means that the $2^2A'$ and $2^2A''$, and $3^2A'$ and $3^2A''$ states in C$_3$ are degenerate (table 1). We could not determine the vertical excitation energies for the $3^2A'$ and $3^2A''$ states for selected basis sets due to poor convergence. The increase of primary configuration space did not cure this problem. The 6-311G* basis set, which we have also used in our calculations on CF$_2$ [5], does not give any convergence problems and also provides satisfactory target parameters. We used this basis set in all further calculations. The magnitude of the 6-311G* CASSCF ground-state dipole moment, presented in table 1, is slightly higher than the experimental value $0.43 \pm 0.07$ D [25].

Internally contracted MRCI calculations were performed on the ground-state and low-lying excited states of the CF$_3$ radical. Reference orbitals were taken from CASSCF calculations for three states of $A'$ and $A''$ symmetries, with eight core electrons frozen in $1a'$, $2a'$, $3a''$ and $1a''$ molecular orbitals and 25 valence electrons moving freely among the remaining $4a'$, ..., $13a'$, $2a''$, ..., $7a''$ molecular orbitals in a complete active-space representation. MRCI calculations using these numbers of core and valence electrons generated too many configurations to be computationally practicable. Therefore, in our MRCI calculations, 16 electrons were frozen and 17 electrons were redistributed among 12 molecular orbitals. The ground-state energy, vertical excitation energies and the ground-state dipole...
moment for the electronic states of CF3 calculated using the MRCI approach and different basis sets are presented in table 2. It should be noted that the use of CASSCF reference orbitals in our MRCI calculations give correct degeneracy of the CF3 target states.

The magnitude of the MRCI ground-state dipole moment of the CF3 obtained using the 6-311G* basis set is 0.20 D, which is much lower than the experimental value of Butkovskaya et al [25], 0.43 ± 0.07 D.

3.2. R-matrix calculations

Our inner-region R-matrix target calculations have been carried out on the six electronic states of CF3: X 2A′, A 2A″, 2 2A′, 2 2A″, 3 2A′ and 3 2A″ in C3v symmetry. We used equilibrium geometry and the 6-311G* Gaussian basis set (11s5p1d/4s3p1d). In order to get a satisfactory representation of the CF3 target, we used natural orbitals (NOs) generated during MOLPRO CASSCF calculations. Analysis of the CASSCF natural orbital energies shows that orbital pairs (5a′, 2a″), (3a″, 8a′), (4a″, 9a), (6a″, 10a′) and (7a″, 13a′) are degenerate and therefore have e symmetry in C3v.

Test calculations were performed using four different complete active space valence CI models:

1. (1a′ . . . 3a′1a″)8 (4a′ . . . 13a′2a″ . . . 7a″)25
2. (1a′ . . . 5a′1a″2a″)14 (6a′ . . . 13a′3a″ . . . 7a″)19
3. (1a′ . . . 6a′1a″2a″)16 (7a′ . . . 13a′3a″ . . . 7a″)17
4. (1a′ . . . 8a′1a″ . . . 3a″)22 (9a′ . . . 13a′4a″ . . . 7a″)11

Model 1 generates about 247 700 configuration state functions per state. Target calculations using this model are computationally possible but the (N + 1)-electron scattering calculations using this model are not feasible. Clearly, our calculations need to be restricted.

The target properties generated using model 2, which gives about 50 000 CSFs per state, are poor, especially the ground-state dipole moment. Furthermore, (N + 1)-electron calculations using this model are probably computationally not possible with our present codes.

Table 2. The total ground X 2A′ state energy (in Hartree) and vertical excitation energies (in eV) for the CF3 target states calculated at equilibrium geometry using MRCI method and different basis sets. Also given is the ground-state dipole moment (in D)

| State  | 6-311G* | 6-31G* | aug-cc-pVDZ | aug-cc-pVTZ | Sadlej pVTZ |
|--------|---------|---------|-------------|-------------|-------------|
| X 2A′  | -336.65099 | -336.5045 | -336.5976 | -336.7724 | -336.6566 |
| A 2A″  | 8.04 | 8.18 | 8.89 | 7.91 | 7.93 |
| 2 2A′  | 8.86 | 9.01 | 7.94 | 8.75 | 8.79 |
| 2 2A″  | 8.86 | 9.01 | 9.43 | 8.75 | 8.79 |
| 3 2A′  | 9.94 | 10.33 | 10.52 | 10.07 | 10.09 |
| 3 2A″  | 9.94 | 10.33 | 9.86 | 10.07 | 10.09 |
| µ(X 2A′) | 0.20 | 0.33 | 0.40 | 0.29 | 0.28 |

Table 3. Column energy represents the total ground $X^2A_1$ state energy (in Hartree) and vertical excitation energies (in eV) for the CF$_3$ target states generated using state-averaged CASSCF natural orbitals at equilibrium geometry. Also given are the dominant configuration of each state in C$_{3v}$ and the number of configurations $N$ in the CI expansion.

| State   | Configuration | $N$  | Energy   |
|---------|---------------|------|----------|
| $C_x$   | $C_{3v}$      |      |          |
| $X^2A_1$ | $X^2A'$      | 28329 | =336.2903 |
| $A^2A_2$ | $A^2A''$     | 28299 | 7.91     |
| $B^2E$   | $2^2A'$      | 28329 | 8.66     |
|          | $2^2A''$     | 28299 | 8.66     |
| $2^2E$   | $3^2A'$      | 28329 | 9.72     |
|          | $3^2A''$     | 28299 | 9.72     |

Model 4 generates about 3000 CSFs per state. This model gives satisfactory vertical excitation energies, but the ground-state dipole moment value of 0.68 D is significantly higher than the experimental value.

Model 3 generates about 28,000 CSFs per state during the target calculations and gives us the best target excitation energies when compared to the described more comprehensive MRCI calculations. It gives the ground-state dipole moment of 0.56 D; this value is close to but a little higher than the experimental value $0.43 \pm 0.07$ D [25]. This model was used in all the scattering calculations reported here.

Care needs to be exercised when choosing a target model. Degeneracy can be easily broken by separating degenerate natural orbitals. A final set of NOs were obtained by state-averaging the six states in our calculations. In order to adjust target parameters, the CASSCF natural orbitals were state-averaged using $R$-matrix codes. In the averaging procedure, we included the ground $X^2A'$ state, $A^2A''$, $2^2A'$, $2^2A''$, $3^2A'$ and $3^2A''$ with weights 1, 2, 0, 0.8, 0 and 0.2, respectively. This procedure also helps to recover the correct degeneracy of the orbitals and states. We note that MOLPRO does not have the facility to produce symmetry state-averaged NOs. Table 3 presents target parameters for the CF$_3$ radical calculated using state-averaged natural orbitals. The ground-state dipole moment calculated using state-averaged NOs is 0.51 D, which is close to the experimental value $0.43 \pm 0.07$ D [25], and the vertical excitation energies are in line with those found using more sophisticated models and discussed above.

3.3. Scattering model

Our scattering calculations were carried out on the six states of the CF$_3$, presented in table 3. In all calculations the continuum orbitals, describing the incident electron, were represented by the Gaussian type orbitals (GTOs) of Faure et al [27] of up to $g$ ($l \leq 4$) partial waves for both $a = 10a_0$ and $13a_0$. Our previous calculation on the CF$_2$ [5] showed that these continuum orbitals give better results than the orbitals of Nestmann and Peyerimhoff [28] or those of

New Journal of Physics 5 (2003) 155.1–155.12 (http://www.njp.org/)
Figure 1. Eigenphase sums (in rad) for the $^{1}A''$ (A), $^{1}A'$ (B), $^{3}A'$ (C) and $^{3}A''$ (D) states of the CF$_3$ plotted at $a = 10a_0$ (solid lines) and $a = 13a_0$ (dashed lines).

Sarpal et al [29]. In order to test stability of our model, scattering calculations were performed for two $R$-matrix radii $a = 10a_0$ and $13a_0$. The continuum GTOs were orthogonalized to the CASSCF state-averaged NOs and among themselves, and only those with an overlap smaller than $2 \times 10^{-8}$ for $a = 10a_0$ and $2 \times 10^{-9}$ for $a = 13a_0$ are retained.

For scattering energies below 8 eV both calculations give very similar results (see figure 1). Our final calculations used the $R$-matrix radius $a = 10a_0$ as this model gave us better (higher and smoother) eigenphases at higher energies. Note that for both singlet and triplet scattering, the eigenphases sums are very similar for both $A'$ and $A''$ symmetries. This suggests that the low-energy scattering is dominated by $^1E$ and $^3E$ symmetries.

The elastic scattering cross-section of static molecules with a permanent dipole moment is formally divergent. A large number of partial waves and rotation effects must be included in order to obtain convergent results. States with $l > 4$ omitted from our calculations were added using a Born correction [30]. CF$_3$ is a symmetric top molecule with the ground-state dipole moment lying along the $z$-axis. The rotational constants calculated using the experimental geometry are $B = 0.3525$ and $C = 0.18288$ cm$^{-1}$.

The range of scattering energies was restricted to energies below 10 eV, as this is the range covered by the electronic states included in our calculations. Resonance positions and widths are normally found by fitting the eigenphase sum to a Breit–Wigner profile [31].

The absence of experimental data on electron–CF$_3$ collisions makes it difficult to benchmark the present study. However, previous $R$-matrix calculations on low-energy electron collisions with the OCIO radical [32] gave generally excellent agreement with experimental measurements in the 0.1–10 eV energy range. At energies below 100 meV, however, the calculated cross-sections do not reproduce the sharp minimum observed in the experiments [33]. This structure is almost certainly due to rotational effects not included in the
Figure 2. Total elastic cross-section for molecule CF₃ at equilibrium geometry calculated using \( a = 10a₀ \). The dashed line represents the cross-section without Born correction. The solid line represents the cross-section with added Born correction.

Baluja et al calculations. Since we also neglect these effects, we can expect our cross-sections to be reliable only for energies above 100 meV.

4. Cross-sections and bound states

Elastic cross-sections were calculated at equilibrium geometry of the CF₃ using two values for the \( R \)-matrix radii. Figure 2 compares total elastic cross-sections with added Born correction and the same cross-section without Born correction calculated using \( a = 10a₀ \). Those obtained using \( a = 13a₀ \) are essentially identical. As can be seen, there are no resonances present in the elastic cross-section. This result is somewhat unusual and contrasts with CF and CF₂, both of which support rich low-energy resonant structures. In order to check if this is model-dependent, we also performed scattering calculations for target model 4 using \( a = 10a₀ \). The total elastic cross-section was found to be higher for model 4, due to the higher target dipole moment, but again the calculations showed no low-energy resonances. The absence of any low-lying resonances means that CF₃ will not undergo dissociative electron attachment.

Our scattering calculations do show the presence of a bound state of \( 1A₁ \) symmetry at the equilibrium geometry of CF₃. The vertical binding energy of this state, estimated from pure bound state calculations, is about 0.6 eV.

Figure 3 presents the electron-impact excitation cross-sections from the ground \( X^2A₁ \) state to the first, second and third excited states of the CF₃ in \( C_{3v} \) point group. The states \( 2^2A' \) and \( 2^2A'' \), and \( 3^2A' \) and \( 3^2A'' \) in \( C₃s \) symmetry are degenerate; therefore, the corresponding excitation cross-sections were summed. As can be seen, the excitation cross-sections are small, with the magnitude about 0.15\( a₀^2 \). These cross-sections show a number of resonance features.
above 9 eV which are probably due to Feshbach resonances associated with the electronically excited states.

5. Conclusions

We have performed the first study of low-energy electron collisions with the CF$_3$ molecular radical. The elastic cross-section and the excitation cross-sections for the five lowest lying electronically excited states of CF$_3$ were calculated with the UK polyatomic $R$-matrix code [17], using MOLPRO CASSCF NOs which give satisfactory target parameters. Our calculations show an absence of low-lying resonances.

In the present work, *ab initio* MRCI and CASSCF calculations are also presented on several electronic states of CF$_3$ in $C_s$ symmetry group. The first vertical excitation energies for CF$_3$ were calculated. The total ground-state energies, obtained using different basis sets, are in satisfactory agreement with available experimental and theoretical data.

The absence of any electron attachment to the CF$_3$ radical may have some major consequences for the plasma etching industry. Currently, it is expected that all fluorocarbon-containing plasma-etching gases lead to electronegative plasmas. In such electronegative plasmas, the role of product anions is key to understanding the dynamics and structure of...
the plasma-electrode/substrate boundary with the formation of a sheath above the etchant. Should there be a dearth of anions then such a sheath will be reduced (or absent), significantly changing the cation energies and transport properties to the surface [34, 35]. In addition, a common problem in fluorocarbon plasmas is the formation of polymers which periodically have to be removed from the reactor leading to a costly down-time in the processing plant. Polymerization reactions in radio frequency fluorocarbon plasmas of CF$_4$ and C$_2$F$_6$, and C$_4$F$_8$ have been attributed to the presence of anions formed by dissociative attachment [36] with anions acting as nuclei for polymerization. Hence, the adoption of a feed gas that is a precursor to CF$_3$ rather than the more electronegative CF and CF$_2$ could have significant consequences on the formation of polymers in the reactor as well as the ion-etching rate. It would therefore be interesting to contrast the characteristics of a reactor using a feedgas whose main product radical is CF$_3$ (e.g. CF$_3$I) with one having CF$_2$ (e.g. C$_2$F$_4$) both in the sheath dynamics and degree of resultant polymerization.

The calculations on electron collisions with CF$_3$ are probably the largest attempted with the UK $R$-matrix codes. When considering the size limits on such a calculation there are two distinct sizes that must be considered. The first is physical size of the system given either by the distance between its nuclei or, probably more importantly, the extent of its wavefunction. The $R$-matrix method requires that the target wavefunction is entirely contained within the $R$-matrix sphere. This clearly makes constraints on the physical size of the system, although systems larger than CF$_3$ could undoubtedly be treated.

The second size issue is the complexity of the wavefunctions involved. CF$_3$ is an electron rich system with 25 electrons in valence (i.e. $n = 2$) orbitals. As discussed above, calculations which explicitly consider configuration interaction and polarization issues for 25 active electrons are beyond the scope of our present codes. However, a new, partitioned $R$-matrix method for molecules has recently been proposed [37]. This method should significantly extend the complexity of the electronic problems that can be addressed within the UK $R$-matrix codes.

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