

Electron collisions with CF_x radicals using the R-matrix method

Iryna Rozum

Thesis submitted for the Degree of Doctor of Philosophy



UNIVERSITY
COLLEGE LONDON

December 2003

Abstract

Radicals CF_x ($x=1-3$) are formed in the upper atmosphere by photolysis of fluorocarbons the bulk of which are generated in the plasma industry. Fluorocarbon plasmas are used in plasma etching technology and surface modification of materials. Many of the processes that occur in these plasmas are poorly characterized and understood, providing a significant roadblock for the construction of reliable models of the etching process. In order to construct/develop models of electron driven processes in such plasma reactors it is necessary to investigate electron interaction with the product radicals (CF_x). This has to be done theoretically since it is not currently possible to prepare such radicals with sufficient number densities for electron beam experiments to be performed.

The purpose of the work presented in this thesis is to develop a full description of the electron collision processes with the radicals CF_x at the energies below 10 eV. Particular emphasis is given to determining the formation of resonances in the energy region around 2 eV, as this is the typical energy in industrial etching plasmas.

The first *ab initio* calculations of total elastic and electron impact excitation cross sections have been performed for the CF, CF_2 and CF_3 radicals. The quality of the scattering model depends on a satisfactory representation of the target. Deriving the target parameters is, therefore, a necessary precursor to scattering calculations. The first data on vertical excitation energies for the CF_3 radical are calculated. The first potential energy curves for the CF_2 radical are also obtained. Electron scattering resonances are identified for CF and CF_2 . These are analysed and assigned. Scattering electron – CF_3 system has no low-lying resonances. Low energy electron molecule collisions are often accompanied by negative ionic states, which are important for etching plasmas, as they support possible dissociation processes.

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Acknowledgements

I would especially like to thank Professor Jonathan Tennyson and Professor Nigel Mason for their dedicated care, well humoured guidance and encouragement over the last three years.

I am grateful to Jimena Gorfinkiel, Natalia Vinci, Alex Faure, Jean-Paul Booth and K.L. Baluja for many useful discussions and comments during the same period. My gratitude to all the people in the department of Physics and Astronomy that, regardless of titles and positions, made my time here such a valuable and enjoyable experience.

Also I would like to thank the Graduate School at UCL for travel support to attend a number of summer schools and conferences and the British Government and EPSRC both for travel support and postgraduate awards.

My thankfulness to my family and friends, especially Michael Waite, for their loyalty and moral support.

Chapter 1

Introduction

'Low-temperature plasmas have a wide range of applications in industry but there is still a need to learn much more about their basic properties...'

Bill Graham, Physics World, March 2001.

1.1 Electron-driven processes and their importance

Electrons are found everywhere in the Universe. Electron – molecule collisions occur in many natural environments, such as planetary atmospheres, the interstellar medium and stellar plasmas. Such collision processes lead to both chemical and physical changes of matter in environments associated with radiation chemistry, stability of waste repositories, plasma-enhanced chemical vapour deposition (CVD), the lighting industry and plasma processing of materials for microelectronics.

In the upper atmosphere of the Earth and other planets, inelastic electron – molecule collisions lead to thermalization of photoelectrons produced by cosmic-ray or secondary-electron ionization of atmospheric molecules (Dalgarno 1968, Takayanagi & Itikawa 1970). The Northern Lights, which can be seen in the northern sky, occur as a result of ionization of atmospheric molecules by energetic electrons (figure 1.1). In the interstellar medium, rotational excitation of molecules in electron collisions is an important mechanism for electron cooling (Dalgarno



Figure 1.1: The Northern Lights phenomenon also known as Aurora Borealis (from Jan Curtis <http://www.geo.mtu.edu/weather/aurora/images/aurora/jan.curtis>).

& McCray 1972, Thaddeus 1972, Dickinson 1977). Electron – molecule collisions also play an important role in the physics of supernovae explosions (Yan & Dalgarno 1998). Electron collision processes such as dissociative attachment and associative detachment are believed to be responsible for the creation of the hydrogen molecule H_2 at early stages of the Universe after the Big Bang. The appearance of H_2 caused an efficient cooling effect of the hot material which eventually led to the creation of stars and galaxies (Houfek et al. 2002).

In industry CO_2 lasers require electron impact excitation of vibrational and rotational states of CO_2 and N_2 to lase (Demaria 1979), hence an accurate knowledge of the relevant cross sections is necessary for modelling and optimization of this laser system. In material science, electron scattering is used to probe the structure of materials such as molecular crystals (Dorset 1996). The molecules used to etch semiconductor materials do not react with silicon surfaces unless they are subjected to electronic collisions to produce highly reactive radicals and ions in the low-temperature plasmas used in plasma etching and in plasma enhanced chemical vapour deposition. Most recently, it has been shown that strand breaks in the DNA, caused by ionizing radiation, are due primarily to collisions with secondary electrons and their ionic and radical reaction products (Boudaïffa et al. 2000). The experiment of Boudaïffa et al. (2000) was performed with the room-temperature DNA solids, while in cellular DNA about 2/3 of strand breaks come from radicals in the surrounding water. During the collision electrons attach to the components of DNA molecules (or to the water around them) and initiate bond

dissociation (figure 1.2). Secondary electrons in radioactive / chemical waste drive much of the

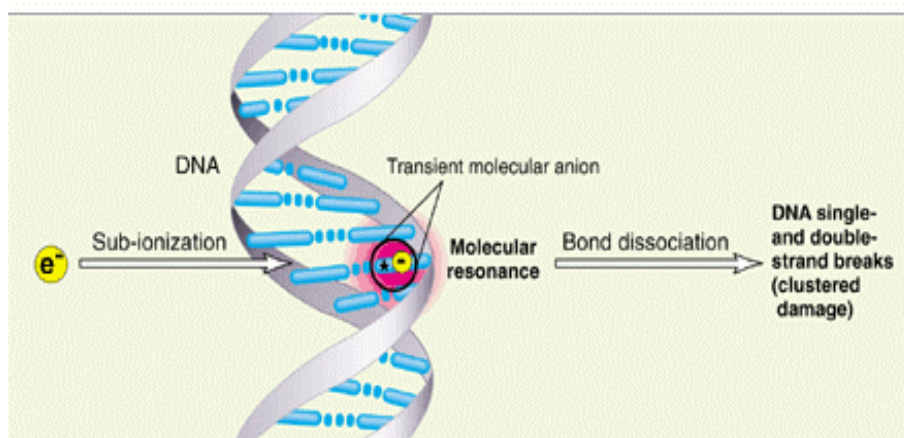


Figure 1.2: DNA single and double strand breaks caused by electrons with energies between 1 eV and 20 eV (Boudaïffa et al. 2000).

chemistry that determines how those materials age and change. Electron collisions also create the reactive molecular fragments in the plasma devices which are used to destroy undesirable compounds or remediate NO_x in combustion exhaust. Electron collisions are exceptionally effective in transferring energy to and from electronic degrees of freedom of the target, a feature that is utilized to increase the energy efficiency of the modern fluorescent lamps (figure 1.3).



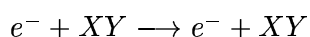
Figure 1.3: High-intensity plasma arc lamp (OSRAM-Sylvania).

These are only a few examples of the electron-driven processes. However, despite their importance, not all physics and chemistry underpinning such processes are well understood and

only a few of the required cross sections for the most important molecules are known. To understand any of the above mentioned chemical and physical changes the scientific community therefore requires an understanding of the fundamental electron molecule interaction processes that underlie them. The lack of experimental data represents a systematic impediment to theory, and the absence of theoretical data is a major obstacle for experimentalists (Gillenwater M et al. 2002).

Most of the fundamental processes driven by electronic collisions can be classified as follow (in approximate order of the threshold energy of an incident electron):

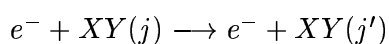
1. Elastic scattering



During elastic scattering, the fragments after the scattering are in the same rotational or vibrational state as before the scattering. Elastic scattering can lead to a change in the direction of scattering fragments and hence momentum transfer.

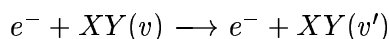
2. Inelastic scattering

rotational excitation



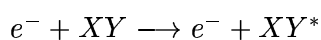
After scattering the target molecule is left in a rotationally excited state.

vibrational excitation



After scattering the target molecule is left in a vibrationally excited state. Generally, electron collisions are not as effective in vibrational energy transfer as they are in electronic energy transfer, except for the case of resonant vibrational excitation. The latter happens when an incident electron attaches temporarily to a molecule for a time comparable with a vibrational period. In molecular plasmas, vibrational excitation is an important energy loss mechanism for the plasma electrons at low energies (below 1 eV) and thus influences the energy distribution of the plasma electrons.

electronic excitation

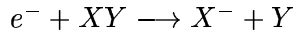


After scattering the target molecule is left in an electronically excited state. Electron impact

electronic excitation plays a vital role in molecular plasmas for several reasons: (1) it is the main route of electron impact dissociation, (2) while stable electronically excited states are very chemically active, part of the energy transmitted into excited states can be lost to the plasma by emission of photons that leads to electron cooling and is often the main diagnostic for studying plasma processes in situ.

3. Fragmentation

dissociative electron attachment (DEA)

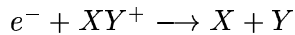


DEA by its nature is a resonant process and significant only over certain narrow energy ranges. DEA is subjected to the energy balance:

$$\Delta E = D_0(XY) - A(X) \quad (1.1)$$

where D_0 is the dissociation energy and A is the electronic affinity of X . This process can occurs even with virtually zero kinetic energy electrons since ΔE is often negative. The DEA reaction does not only break the molecular bonds (with often very large cross sections) but also produces free radicals and stable negative ion fragments to induce further 'chemistry'. DEA reactions are very sensitive to the energy and lifetime of the temporarily negative ionic intermediate state and the cross sections for this process may vary significantly even within a family of related molecules. DEA is probably the best categorized electron interaction with many of the molecular species relevant to plasma processing.

dissociative recombination

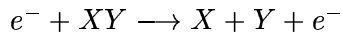


Here the electron recombines with a cation. In this case the energy balance is

$$\Delta E = D_0(XY^+) - I(X) \quad (1.2)$$

where I is the ionization potential of X , and ΔE is always negative.

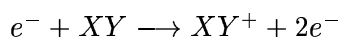
electron impact dissociation



This process occur at higher energies than *DA*. In practice it goes *via* electronic excitation to a dissociative excited state. The description of molecular fragmentation following electron

impact excitation is one of the most important processes to understand in modelling low-temperature plasma processing and electron-driven environmental chemistries. Indeed, all electronically excited states of technologically important molecules, such as CF_4 , are believed to be dissociative.

electron impact ionization



Electron impact ionization, especially ionization from excited states, is important in many applications, such as ionized metal plasma vapour deposition, where a substantial number of neutral molecules are in metastable states.

Which of the above processes occur depends on the energy of an incident electron. All the inelastic processes can occur in any combination. The fact that a molecule consists of at least two atoms and, therefore, has more degrees of freedom makes electron-molecule collisions much more complicated than electron-atom collisions. These additional degrees of freedom are vibration and rotation of the nuclei and dissociation into two or more fragments. In addition to the dissociation of a molecule into neutral ground-state fragments, dissociation can also be combined with any other inelastic process. This results in dissociative excitation, dissociative electron attachment and dissociative ionization which greatly increases the number of possible final states of electron-molecule collision processes.

The ability of a molecule to dissociate as a result of an electron collision creates a possibility for new species to be generated. These new species are often more reactive than the parent molecule, and chemically and physically very different from the parent molecule. For example, CF_3 produced from CF_4 in etching plasmas is very different from the parent molecule and O is very different from O_2 . The dissociation of polyatomic molecules is the key mechanism by which radicals and molecular fragments are produced in many environments ranging from planetary atmospheres to etching plasmas used in the microelectronics industry. Only the rudiments of these dissociative collisions are understood.

Low energy electron-molecule collision cross sections (total, elastic, momentum transfer, rotational and vibrational excitation) from threshold up to a few electron volts play a crucial role in determining electron transport properties and electron energy distribution, and have significant importance for modelling low temperature plasmas.

1.2 Applications to technological plasmas

Low-temperature plasmas play a key role in semiconductor, materials and lighting industries and are used to process everything from computer chips to aircraft components. For example, the car and aircraft industries use 'plasma hardened' metallic components to improve their wear and corrosion resistance, large screen televisions in which each pixel is a small plasma and spectacle lenses with scratch-resistant and anti-reflecting coatings are now available in the high street. The latest designs for plasma-powered lamps in the lighting industry are much more energy efficient than the usual incandescent lamps, leading to significant cost savings as more than one billion fluorescent lamps are made and used every year.

The importance of technological plasmas is proved by the fact that about one-third of the processes needed to make a modern microchip involve a plasma-based process. Thus, worldwide revenue growth in the semiconductor industry increased from 50 billion USD to 140 billion USD for the period from 1990 to 1995 (*Semiconductor International* 1996). The forecast is that the growth will continue (Graves & Kushner 1996). Also, it was estimated that about 60% of the 2 billion USD, required to set up a plant for the next generation of microchips, will be spend on the purchase and installation of plasma-processing equipment (Graham 2001, *The National Technology Roadmap for Semiconductors* 1994). Plasma etching technology has therefore become one of immense commercial importance.

Despite its high cost and technical importance, plasma equipment is still largely designed empirically, with little help from computer simulations. The high cost of developing new plasma equipment and optimization of plasma reactor operation has motivated development of a large modelling and simulation infrastructure (Makabe 2001, Kushner 1998) – the 'virtual factory' programme – allowing new reactors/plants to be developed computationally prior to the construction of commercial plants. The major roadblock to further development of this strategy is the lack of a database for many chemical and physical processes that occur in the plasma, in particular collision processes (Graves & Kushner 1996, Kushner 1998). In particular, Kushner (1998) stated that 'the application of this modelling infrastructure to industrially relevant problems has, to date, been limited by the availability of fundamental data (e.g., electron impact cross sections, reactive surface sticking coefficients) and validated reaction mechanisms...'.

Fluorocarbons are the most common feedstock gases used in etching plasmas. However, perfluorinated gases (PFCs) have been found to be detrimental to the environment and global climate, as most of the compounds are strong greenhouse gases and ozone depletors. PFCs are consumed only partially in the etching processes and the waste gases are emitted into the atmosphere. They have an extremely high global warming potential (up to 4 orders of magnitude higher than CO_2) and atmospheric lifetimes that are practically infinite on the time scale of human life (see table 1.1). The global warming potential (GWP) depends upon infrared (IR) absorption and time horizon (hold up time) in the atmosphere. It is defined as the cumulative radiative forcing, or heating, integrated over a period of time from the emission of a unit mass of gas relative to some reference gas. Carbon dioxide (CO_2) was chosen as this reference gas. The Kyoto protocol on gas emissions requires the phasing out of the use of CF_4 , C_2F_6 , C_3F_8

Species	GWP ₁₀₀	GWP ₂₀	Lifetime
CO_2 ^a	1	1	50-200
CF_4 ^a	6500	4400	50000
C_2F_6 ^a	9200	6200	10000
c- C_4F_8 ^f	8700	–	3200
CF_3I	0.25 ^b	< 5 ^c	< 0.006 ^c
C_2F_4 ^d	0.07	0.021	0.005

Table 1.1: GWP, calculated over 100 and 20 years time horizon, and atmospheric lifetimes (in years) for the molecular species used in plasma etching of silicon surfaces.

^aFrom Gillenwater M et al. (2002).

^bFrom Sam Eden, private communications.

^cFrom Solomon et al. (1994).

^dFrom Acerboni et al. (2001).

^fFrom IPCC 1996 p.121.

and c- C_4F_8 as feedstock gases by 2010. Emission reduction strategies have to combine both optimization of plasma equipment efficiency and search for the new plasma compounds. CF_3I , C_2F_4 and i- C_4F_8 have been proposed as new plasma reactants (Samukawa et al. 1999). The first two are of particular interest from the point of view of controlling the composition of CF_2 and CF_3 radicals in the plasma (Mason et al. 2003). There appears to be only little information about how CF_x radicals interact with low energy electrons. Recent studies have shown that the concentration of these radicals has a significant effect on the behaviour of fluorocarbon

plasmas (Chabert et al. 2003) and that these radicals also occur in significant concentrations in other plasmas (Chabert et al. 2001). CF_3I and C_2F_4 have received a special attention as new feedstock gases also because they both have a low global warming potential and short lifetimes (table 1.1). CF_x radicals are highly reactive and experimental studies on highly reactive radicals are extremely difficult. *Ab initio* calculations can, therefore, play an important role in providing data upon which models can be based (Winstead & McKoy 2000).

1.2.1 Plasma reactors

The equipment for plasma processing typically uses partially ionized (fractional ionization less than 1%), low pressure (a few mTorr to 1 Torr) plasmas to provide activation energy to dissociate and ionize feedstock gases. The resulting radicals and ions interact with the semiconductor surface, either removing or adding material, to define the desired features or modify the surface. The densities of electrons or ions in such plasmas are 10^9 to 10^{11} cm^{-3} . Most of the plasma electrons have kinetic energies below 20 eV with a mean energy of a few electron volts (Tanaka & Inokuti 2000). The densities of neutral molecules (in the ground electronic state) are higher by orders of magnitude than the densities of electrons or ions. Therefore, such a plasma is characterized as 'weakly ionized'. The kinetic energies of ions are much lower than the kinetic energies of electrons, therefore, such plasmas are also described as 'low-temperature' and 'thermally non-equilibrium'.

Figure 1.4 shows schematically the basic structure of a capacitively coupled, parallel-plate plasma reactor with a high-frequency capacitor (Tanaka & Inokuti 2000, Graham 2001). A high frequency electric field is applied to a gas between the two electrodes. The applied voltage is sufficiently high, so that electrons are accelerated in the electric field and gain sufficient energy to cause excitation, dissociation and ionization of the molecules by electron collision processes. This leads to the establishment of a stable glow-discharge plasma. The central part of the glow has an electric potential which is always positive and is called the *bulk* plasma. The anode and cathode have lower potentials than the bulk plasma. As the plasma develops, the thermal motion of the ions and electrons will cause them to diffuse towards the electrodes and the walls of the vacuum chamber (Hippler 1999). The positive potential of the plasma means that there are more ions than electrons in the region near the electrodes and the other surfaces in

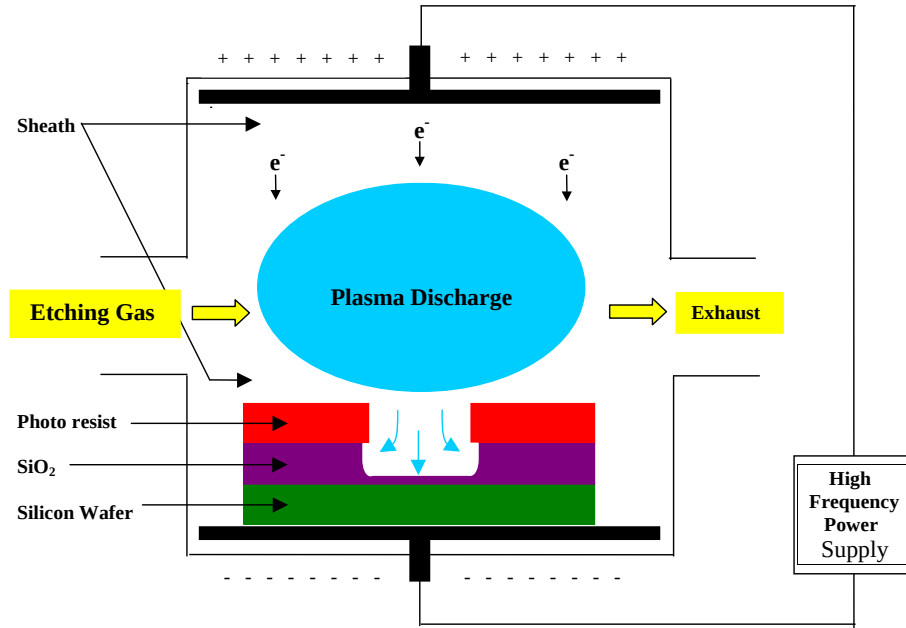


Figure 1.4: A schematic diagram of a capacitively coupled, parallel-plate plasma reactor.

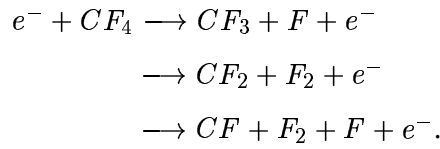
contact with the plasma. As a result, a negative potential is established in the regions near the electrodes which do not glow. This region is known as the *sheath* and typically extends less than a centimetre from the electrodes. The glow is most intense in a region of the bulk plasma close to the sheath that shows the presence of many electrons of high energies. Although there is no electric field in the plasma, there is an electric field in the sheath, which reflects most of the electrons back into plasma.

The use of the RF voltage reduces the voltage needed to establish the plasma. Most commercial reactors operate at a frequency of 13.56 MHz, as it was allocated to the plasma processing industry by the international broadcasting committees.

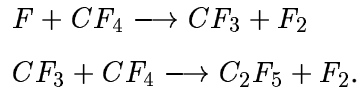
1.2.2 Plasma chemistry

There are three key features of the plasma that are important for applications: (1) the production of light; (2) the production of chemically active species from inert species; and (3) the deposition of sufficient energy onto surfaces by ion bombardment to drive chemical reactions without excessive heating or damage.

Figure 1.5 shows schematically what happens during etching of a silicon wafer using CF_4 feedstock gas (Graham 2001). The etching of 'patterns' in an SiO_2 layer to expose parts of the silicon layer underneath is one of the most important processes in the whole microelectronics industry. The SiO_2 -coated silicon wafer is placed on the electrode in a plasma reactor into which CF_4 gas is injected. The SiO_2 layer is covered by a resist layer which is made of a material that does not react with the chemicals produced in the plasma. The resist exposes parts of the surface that are needed to be etched and covers the other parts. The CF_4 molecules dissociate as a result of collisions with the electrons (Winters & Inokuti 1982) and produce CF_3 , CF_2 and CF and other radicals which are chemically reactive:



Radicals, electrons and ions react mostly with the ground state molecules (CF_4) and less frequently among themselves. Secondary reactions lead to F and F_2 , and polymers C_xF_y are formed (Tanaka & Inokuti 2000):



The fluorine atoms and CF_x radicals diffuse to the surface and stick to it. The fluorine atoms combine with the silicon atoms to form volatile compounds that evaporate from the surface and are pumped away.

The carbon radicals form a polymer that would prevent etching if it remained on the surface. However, the polymer reacts with the SiO_2 under ion bombardment and produces carbon dioxide. This carbon dioxide escapes from the surface allowing the fluorine atoms to etch the surface. When the required SiO_2 areas have been etched away to reveal the silicon underneath, polymer (SiF_x) starts to build up at the bottom of the trench as there are no longer any oxygen atoms present. This polymer layer prevents the plasma from damaging the underlying silicon layer.

It is very important to control the fluorine – carbon ratio and the ion energy in the plasma. Thus, the ion energy should be high enough to effectively remove surface products, but not too high as to damage layers or structure underlying the surface.

Electron collisions initiate almost all of the relevant chemistry associated with the tech-

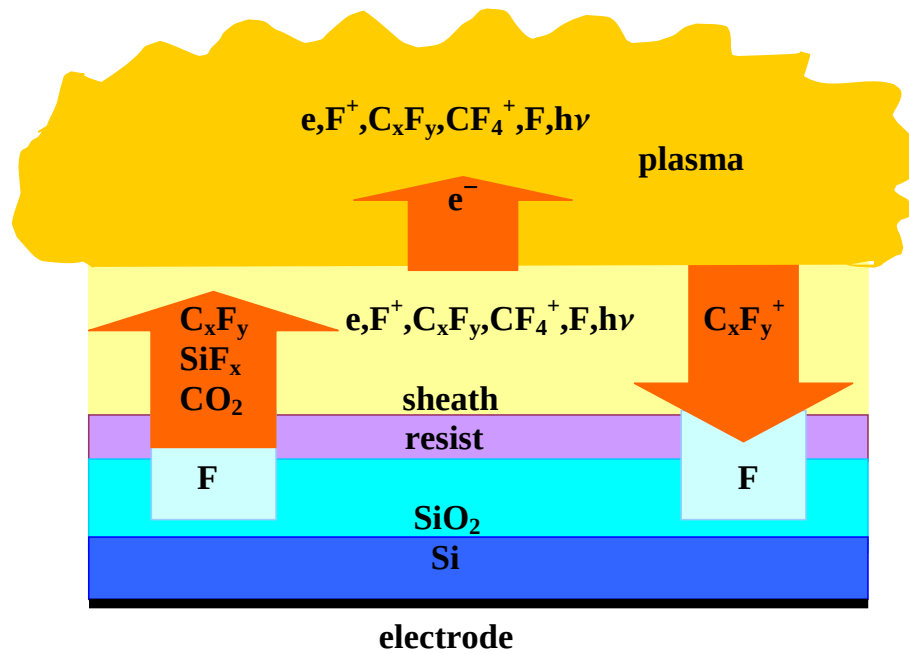


Figure 1.5: A schematic diagram of plasma etching of a SiO_2 layer on a silicon surface. The regions to be etched are shown by the resist. Electrons in the plasma collide with the CF_4 molecules producing a range of collision products. The CF_x and F interact with the surface, creating other products, such as SiF_x and CO_2 , that are pumped away. The overall aim is to remove the SiO_2 layer without damaging the silicon layer underneath (Graham 2001).

nology of plasma etching (Lieberman & Lichtenberg 1994, Bruno et al. 1995, Tanaka & Inokuti 1999). Electron collision processes involving all possible reactants, products, and intermediates must therefore be investigated. Dissociation, ionisation and attachment cross sections are of particular importance since they determine the ionisation balance within the plasma and thus influence plasma properties such as the electron energy distribution. Experiments to monitor the production pathways of ionic fragments from polyatomic molecules are well established and may be readily performed once apparatus is characterised on simple diatomics but, in contrast, there have been only a few experiments developed to determine the yield of neutral fragments and it is currently not possible to study experimentally electron interactions with many neutral radical species, for example CF, CF₂ and CF₃ produced in the fragmentation of CF₄ and other fluorocarbons. Hence, in order to provide the plasma modelling community with data on the interaction of electrons with the most prominent radical species in fluorocarbon plasmas, a research programme to study electron scattering from the CF_x radicals (x = 1-3) has been undertaken and these results are reported in this thesis. First however it is necessary to comment upon the complexity of electron molecule interactions.

1.3 The electron – molecule scattering problem

There are only three outcomes of electron – atom collisions: i) elastic scattering, when the electron scatters off the atom leaving the atom in its original electronic state; ii) the electron excites the atomic electrons leaving the atom in an excited state; iii) the incident electron has enough energy to remove an electron from the atom, leaving it positively ionized. The incident electron can also be captured by the atom to form a negative ion. The latter process is not possible without a third body or by radiative capture.

As was mentioned in the beginning of this chapter, the electron – molecule collisions are far more complicated. First, the molecule has rotational and vibrational degrees of freedom which can be excited with little energy. Second, the interaction between an incident electron and molecule is multicentred which leads to a coupling between states. Third, the molecule can break up in a variety of different paths through dissociation, dissociative attachment and dissociative ionization (figure 1.6).

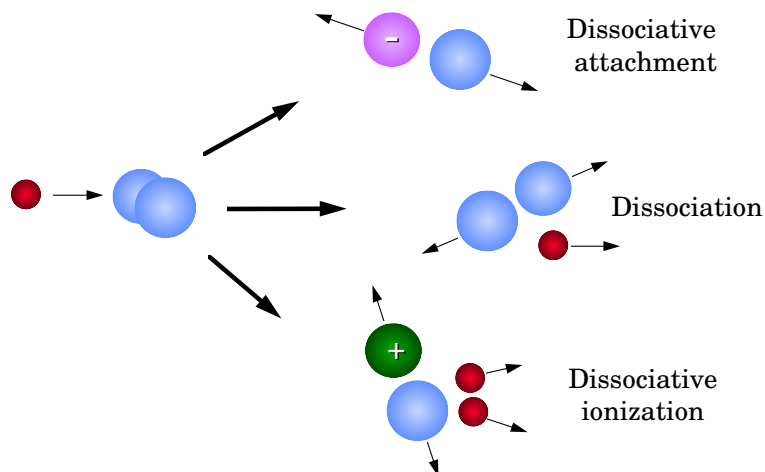


Figure 1.6: Schematic representation of different possibilities for the break up of a molecule due to electron impact.

Classical mechanics can describe only the most basic elastic scattering process and the system must be treated quantum mechanically. This requires the solution of the Schrödinger equation, but, because of the size of the system involved, it is not possible to solve the equation exactly (even the smallest electron-molecule system, $H_2 + e^-$, is already large enough to require an approximate approach). Different methods of electron – molecule scattering are characterized by the different approximations used in order to solve the problem as accurately as possible. Some of these methods are described in chapter 3.

The physics of low-energy electron molecule scattering and the different methods which can be implemented for its solution have been excellently reviewed by Morrison (1993). Details of modern computational methods used to treat the problem can be found in Huo & Gianturco (1995).

Any electron-molecule system can be described by the Schrödinger equation:

$$(\mathcal{H} - E)\Psi = 0 \quad (1.3)$$

where $\mathcal{H}$ is the Hamiltonian for the electron-molecule system that can be written in the molecular frame as:

$$\mathcal{H} = H_N(\mathbf{x}) + \hat{T}_e(\gamma) + \hat{V}_{int}(\mathbf{x}, \gamma), \quad (1.4)$$

where $\mathbf{x} = (\mathbf{r}, \mathbf{R})$ includes both the electronic and nuclear coordinates of the molecule, and γ is the coordinate of the incident electron. $H_N(\mathbf{x})$ is the Hamiltonian of the target-molecule and includes all the kinetic and potential terms of the target electrons and the nuclei. $\hat{T}_e(\gamma)$ is the kinetic energy operator of the incident electron and $\hat{V}_{int}(\mathbf{x}, \gamma)$ is the interaction energy between the scattering electron and the molecule. Explicit spins have not been included for simplicity.

The solution for a neutral molecular target, assuming no ionization nor dissociation, can be written in the asymptotic form as

$$\Psi(\mathbf{x}, \gamma) \sim \exp(ik_0 \cdot \gamma) \psi_0(\mathbf{x}) + \frac{1}{\gamma} \sum_n \exp(ik_n \cdot \gamma) f_{n0}(\mathbf{k}_n, \mathbf{k}_0) \psi_n(\mathbf{x}), \quad (1.5)$$

where ψ_n is the wavefunction of the n_{th} unperturbed target state, $\mathbf{k}_0$ and $\mathbf{k}_n$ are the initial and energetically allowed final momenta of the scattered electron and f_{n0} is the scattering amplitude. The first term represents an initial plane wave incident on the ground state and the second term consists of a superposition of outgoing waves associated with each of the energy accessible target states.

The interaction energy $V_{int}(\mathbf{x}, \gamma)$ in equation 1.4 can be further split into two parts:

$$\hat{V}_{int} = \hat{V}_{nuc-elec} + \hat{V}_{elec-elec} \quad (1.6)$$

where $\hat{V}_{nuc-elec}$ is the attractive potential between the nuclei and the scattering electron, and $\hat{V}_{elec-elec}$ is the repulsion between the target electrons and the scattering electron. The potential $\hat{V}_{nuc-elec}$ introduces a coupling between the nuclear and electronic motions which makes the resulting equations extremely difficult to solve. It is therefore usual to invoke the Born-Oppenheimer approximation (Born & Oppenheimer 1927, Morrison et al. 1977) which assumes that the electrons travel very fast and can react instantaneously to the motion of the nuclei. This makes the wavefunction separable into a nuclear part and an electronic part, which can be solved separately.

A common practice is to invoke the fixed-nuclei approximation where the nuclei are considered to remain stationary, simplifying the Hamiltonian even further. It is also possible to approximate nuclear motion *post facto* (Morrison 1993) performing a series of fixed-nuclei calculations as a function of bond length.

Electrons are indistinguishable, therefore the Pauli exclusion principle requires that the total wavefunction be antisymmetric with respect to exchange of electrons. This requirement can be imagined as an ‘exchange force’ which prevents the electrons sharing the same space. Exchange is actually responsible for spin-changing transitions. In some methods it is modelled explicitly as an exchange potential $\hat{V}_{exch}$ (Morrison 1993). This effect results in a coupling between states, and hence introduces a coupling between equations which complicates their solution for certain methods. Close-coupling methods treat exchange implicitly by forcing each of the components of the (N+1) wavefunction to be antisymmetric.

Because the scattering electron has a charge, polarization and correlation effects arise from the distortion of the molecular charge cloud due to the electric field of the incident electron. Quantum mechanically, polarization and correlation effects arise through virtual excitation into energetically inaccessible excited electronic states. In some methods, such as those which use a single centred expansion (Gianturco et al. 1995), polarization and correlation are treated explicitly by the use of a model potential. In close-coupling methods these effects are treated implicitly by including couplings between the states in the close-coupling expansion and by including square-integrable (L^2) configurations in the (N+1) wavefunction.

The scattering problem can be treated at different levels, depending on what effects are included in the calculation. The different levels used by electronically elastic calculations are as follows:

- Static

At this level, the scattering electron is deemed to be a separate entity from the target molecule. The exchange is neglected and it is assumed that the target itself remains undistorted by the approaching electron, i.e. the polarization is also neglected. Treating the problem at this level has the advantage that the equations are easily solved. It has the disadvantage that the answers may be wrong quantitatively and, more often than not, even qualitatively, particularly at low collision energies.

- Static exchange (SE)

In this approximation, exchange is included either implicitly or explicitly. However, the target molecule is not allowed to be perturbed, assuming once again that the polarization

is zero. The polarization is a necessary requirement for Feshbach resonances.

- Static exchange plus polarization (SEP)

In this case, along with exchange, the target is allowed to be perturbed through the inclusion of polarization and correlation effects.

For electronically inelastic calculations, close-coupling methods (of which the R-matrix method is one) are used. These involve the expansion of the (N+1) wave function over configurations made of target eigenfunctions multiplied by one-particle scattering functions (1.7)

$$\psi_k^{N+1} = \mathcal{A} \sum_I \psi_I^N(\mathbf{X}_1, \dots, \mathbf{X}_N) \sum_j \bar{\xi}_j(\mathbf{X}_{N+1}) a_{Ijk} + \sum_m \chi_m(\mathbf{X}_1, \dots, \mathbf{X}_N, \mathbf{X}_{N+1}) b_{mk}, \quad (1.7)$$

The first summation accounts for couplings between target and incident electrons. The second term is known as L^2 functions, where all electrons are placed in target molecular orbitals (see chapter 2). Such calculations will include exchange and polarization since, as mentioned previously, exchange is included implicitly by forcing the configurations to be antisymmetric. Correlation can be included through the addition of L^2 terms as mentioned above.

1.4 Objectives

In an attempt to obtain a complete picture of low energy electron collisions with the molecular radicals CF, CF₂ and CF₃ the objectives of this work are as follows:

- To create target models for the CF, CF₂ and CF₃ radicals which give satisfactory target parameters (eg. vertical excitation energies and ground state dipole moments).
- To run R-matrix calculations to obtain integral elastic and excitation cross sections for the CF_x radicals.
- To detect and fit energetically low-lying electron scattering resonances.
- To calculate integral elastic and excitation cross sections as a function of internuclear separation in order to study the dissociative behaviour of detected resonances.

1.5 Layout of the thesis

Chapter 2 describes some approximation methods used to solve the electron – molecule scattering problem outlined in this introduction. Terminology used throughout the thesis is also explained.

In chapter 3 the adiabatic molecular R-matrix theory for polyatomic and diatomic molecules is introduced. The computer codes used to implement this theory are also described.

Chapter 4 describes the utilization of the codes for the electron – CF radical scattering. The calculations are considerably complicated by the fact that the second excited state of CF is Rydberg-like for $R_0 < 2.6a_0$. These calculations concentrate on obtaining low energy (less than 10 eV) elastic and excitation cross sections of the five lowest lying electronically excited states of the symmetries $^4\Sigma^-$, $^2\Sigma^+$, $^2\Delta$, $^2\Sigma^-$ and $^4\Pi$, with vertical excitation energies in the range of 2.86 - 10 eV, over the range of bond lengths.

In chapter 5 the R-matrix method is used to treat electron collisions with the molecular radical CF_2 as a function of internuclear geometry. These calculations concentrate on obtaining low energy (less than 10 eV) elastic and excitation cross sections of the five lowest lying electronically excited states of the CF_2 molecule. These states have symmetry $^3B_1$, $^1B_1$, $^3A_2$, $^1A_2$ and $^3B_2$ and vertical excitation energies in the range of 2.44 - 10 eV.

Chapter 6 portrays the applications of the R-matrix method to the electron scattering off the CF_3 radical at its equilibrium geometry. These calculations concentrate on obtaining low energy (sub 10 eV) elastic and excitation cross sections. The main difficulty in this calculations is the absence of target parameters for the CF_3 , eg. vertical excitation energies. Therefore, the present scattering study had to be prefaced by a series of electronic structure calculations aimed at characterising the low lying electronic states of CF_3 .

In the conclusion (chapter 7), the results are summarised and suggestions for improvements to the calculations are given. Applications of the results to plasma studies and possible future directions for the work are also discussed.

Chapter 2

Theoretical background

In this chapter some approximations used to solve the electron – molecule scattering problem, outlined in the introduction, and their validity are described. Terminology used throughout the thesis is also briefly explained.

2.1 The Born-Oppenheimer approximation

Since electrons are much lighter than nuclei, they move much faster. Because of this difference in masses, electrons can respond almost instantaneously to the displacement of the nuclei. Hence, to a good approximations, one can consider that the electrons in a molecule move in the field of the fixed nuclei. Therefore, it is possible to solve the Schrödinger equation for the electrons in the static electric potential created by the fixed nuclei, instead of trying to solve the problem for all the particles simultaneously. These calculations can then be repeated for different arrangements of nuclei to obtain molecular potential energy curves for diatomics and, in general, potential energy surfaces for polyatomic species. The Born-Oppenheimer approximation is very reliable for ground electronic states, but it is less reliable for excited states (Atkins & Friedman 1997).

Let $\mathbf{r}$ and $\mathbf{r}'$ represent the coordinates of the scattered electron in the LAB and BODY frame respectively, and $\mathbf{r}_m$ and $\mathbf{R}_m$ be the electronic and nuclear coordinates of the molecule (Lane 1980) (figure 2.1). The LAB frame has a space-fixed z axis, often chosen along the

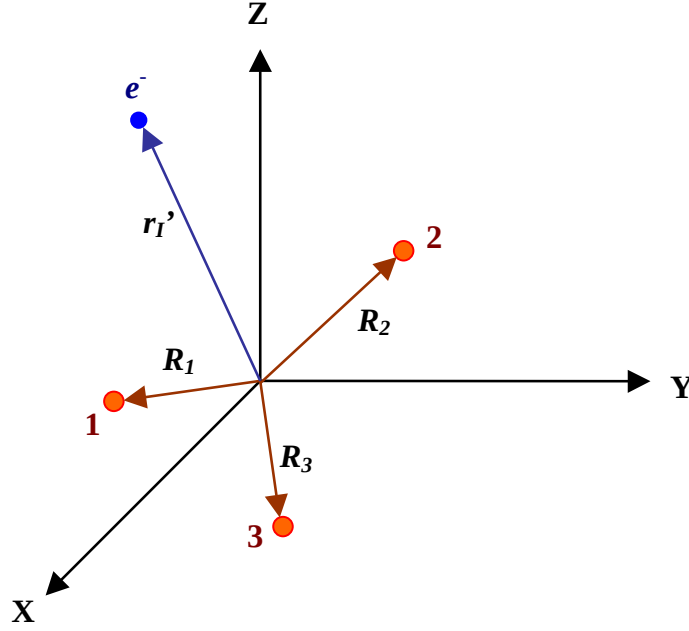


Figure 2.1: Nuclear and electronic coordinates in the LAB frame.

initial momentum k_o , and the BODY frame is directed along a symmetry axis of the molecule. Using the coordinate system thus defined the molecular Hamiltonian in equation (1.4) can be written as

$$H_N(\mathbf{r}, \mathbf{R}') = H_N^{(e)}(\mathbf{r}, \mathbf{R}') + H_N^{(n)}(\mathbf{R}') \quad (2.1)$$

where $H_N^{(e)}$ is the electronic contribution

$$H_N^{(e)}(\mathbf{r}, \mathbf{R}') = -\frac{1}{2} \sum_{j=1}^{N_e} \nabla_j^2 - \sum_{\alpha=1}^{N_n} \sum_{j=1}^{N_e} \frac{Z_\alpha}{|\mathbf{r}_j - \mathbf{R}'_\alpha|} + \sum_{i=1}^{N_e} \sum_{j>i}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2.2)$$

and $H_N^{(n)}$ is the nuclear contribution

$$H_N^{(n)}(\mathbf{R}') = -\frac{1}{2} \sum_{\alpha=1}^{N_n} \frac{1}{M_\alpha} \nabla_\alpha^2 + \sum_{\alpha=1}^{N_n} \sum_{\beta>\alpha}^{N_n} \frac{Z_\alpha Z_\beta}{|\mathbf{R}'_\alpha - \mathbf{R}'_\beta|} \quad (2.3)$$

In the above equations, α and β are nuclei indexes, N_e and N_n are numbers of electrons and nuclei respectively, and Z_α and M_α are nuclei charges and masses respectively. The scattering electron – molecule interaction potential energy can be expressed as

$$\hat{V}_{em}(\mathbf{r}, \mathbf{r}_m, \mathbf{R}') = - \sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}'_\alpha|} + \sum_{j=1}^{N_e} \frac{1}{|\mathbf{r} - \mathbf{r}_j|} \quad (2.4)$$

The Born-Oppenheimer approximation allows a separation of nuclear and electronic terms so that it is possible to solve the electronic problem with the nuclei fixed and obtain electronic

wavefunctions and energies that depend on the nuclear coordinates parametrically (Flygare 1978). Then it is assumed that the nuclei move in response to the adiabatic potential energy corresponding to the stationary electronic state. The wavefunction can be written as a product of an electronic Ψ_ε^{FN} function, which depends parametrically on the R_m , and a nuclear function $\chi(\mathbf{R}')$

$$\Psi_\varepsilon(\mathbf{r}', \mathbf{r}'_m, \mathbf{R}') = \Psi_\varepsilon^{FN}(\mathbf{r}', \mathbf{r}'_m; \mathbf{R}')\chi(\mathbf{R}') \quad (2.5)$$

In the case of highly excited vibrational states (large nuclear velocities), high lying Rydberg electronic states (small electronic speeds), or when electronic energy curves cross or come close to each other, the Born-Oppenheimer approximation can be broken. The perturbation theory may then be used in order to correct for the 'breakdown' (Herzberg 1950, Flygare 1978).

In the electron-molecule scattering problem one is dealing with continuum or scattering states for which the total energy is positive with respect to the ground state of the molecule. The approximate form of the equation (2.5) is valid in two cases:

1. When the electronic wavefunction Ψ_ε^{FN} is highly confined in the vicinity of the molecule, the nuclei respond adiabatically to the potential energy of the negative molecular ion and rotational – vibrational states, described by resonant functions χ , are established. This adiabatic limit corresponds to resonant scattering.
2. When the incident electron energies are high, so that the velocities of the incident and outgoing electrons are much higher than those of the nuclei, the nuclear wavefunction χ is simply the unperturbed nuclear wavefunction for the molecule. This impulsive limit is appropriate for nonresonant scattering (Chang & Temkin 1969, Chang 1970, Temkin & Faisal 1971).

When neither of the above limits apply, it is essential to use some more appropriate approximation, such as a full coupled-state approach which treats the nuclei and electrons on a more equal basis. In this approach, the system wavefunction is expanded in terms of unperturbed target wavefunctions.

2.2 The Hartree-Fock self consistent field method

The simplest wavefunction, which can be used to describe an n -electron system, can be expressed as the Slater determinant, where electron-electron interactions are neglected:

$$\Psi^o(\mathbf{x}, \mathbf{R}) = (n!)^{-1/2} \det|\Phi_a(1)\Phi_b(2)\dots\Phi_z(n)| \quad (2.6)$$

where Φ_u with $u = a, b, \dots, z$ are orthonormal spinorbitals; $\mathbf{x}$ and $\mathbf{R}$ are the electronic and nuclear coordinates of the molecule respectively. Electron-electron repulsions are important for any accurate treatment of the problem. The Hartree-Fock (HF) approach considers the wavefunction (2.6) with averaged electron-electron repulsions. It is assumed that each electron is moving in the field of the nuclei and the averaged field of remaining $(n - 1)$ electrons. The best wavefunctions are found by minimizing the Rayleigh ratio (Atkins & Friedman 1997):

$$\varepsilon = \frac{\int \Psi^*(\mathbf{x}, \mathbf{R}) H \Psi(\mathbf{x}, \mathbf{R}) d\mathbf{x}}{\int \Psi^*(\mathbf{x}, \mathbf{R}) \Psi(\mathbf{x}, \mathbf{R}) d\mathbf{x}} \quad (2.7)$$

subject to the condition that the spinorbitals are orthonormal. The lowest value of ε is the electronic energy for the selected nuclear configuration. This procedure leads to the Hartree-Fock equations for the individual spinorbitals:

$$f_1 \Phi_a(1) = \varepsilon_a \Phi_a(1) \quad (2.8)$$

where $\Phi_a(1)$ is the spinorbital of the electron 1, ε_a is the orbital energy of the spinorbital and f_1 is the Fock operator:

$$f_1 = h_1 + \sum_u (J_u(1) - K_u(1)) \quad (2.9)$$

The sum in the above equation represents the averaged potential energy of electron 1 due to the presence of the remaining $(n - 1)$ electrons. In (2.9) h_1 is the core hamiltonian for the electron 1, $u = a, b, \dots, z$, and $J_u(1)$ and $K_u(1)$ are Coulomb and exchange operators respectively, which are defined as (in atomic units):

$$J_u(1)\Phi_a(1) = \left[\int \Phi_u^*(2) \frac{e^2}{r_{12}} \Phi_u(2) d\mathbf{x}_2 \right] \Phi_a(1) \quad (2.10)$$

$$K_u(1)\Phi_a(1) = \left[\int \Phi_u^*(2) \frac{e^2}{r_{12}} \Phi_a(2) d\mathbf{x}_2 \right] \Phi_u(1) \quad (2.11)$$

The Coulomb operator takes into account the coulombic repulsion between electrons, and the exchange operator takes into account the effect of the Pauli principle.

The essence of the Hartree-Fock approximation is to replace a complicated many-electron problem by an one-electron problem in which electron-electron repulsion is treated in an averaged way. Commonly, the HF equations are solved iteratively until the solutions are self-consistent, therefore the name self-consistent field (SCF) is used for this approach. In SCF procedure a trial set of spinorbitals is used to construct the Fock operator, then a set of HF equations is solved to obtain a new set of improved spinorbitals which are used to construct an improved Fock operator and so on. This procedure is repeated until convergence is reached.

SCF calculations produce SCF molecular orbitals which often do not give good representation of excited states, and especially degenerate states. One reason for this may be that excited states are inaccurately described by a single determinant and require a better description in terms of configuration interaction (CI). Configuration interaction, which is the mixing of configurations of the same overall symmetry, lowers the energy of states and leads to an improved description of the ground state and also excited states. SCF, CI and other types of molecular orbitals will be discussed in chapter 3.

2.3 Fixed-nuclei formulation for scattering

Assume that the nuclei are held fixed. Then, only the electronic Hamiltonian for the electron – molecule system has to be taken into account (Lane 1980)

$$H_{N+1}^{(e)} = -\frac{1}{2}\nabla_{\mathbf{r}'}^2 + H_N^{(e)} + \hat{V}_{em} \quad (2.12)$$

where $\nabla_{\mathbf{r}'}^2$ is the Laplacian in BODY frame coordinates $\mathbf{r}'$. The target Hamiltonian $H_N^{(e)}$ and the interaction potential V_{em} are given by (2.2) and (2.4) respectively. The 'target molecule + incident electron' system can be characterized by the $(N + 1)$ -electron Schrödinger equation

$$(H_{N+1}^{(e)} - \varepsilon)\Psi_{\varepsilon}^{FN}(\mathbf{r}', \mathbf{r}'_m; \mathbf{R}') = 0 \quad (2.13)$$

where $(\mathbf{r}', \mathbf{r}'_m) = (\mathbf{r}', \mathbf{r}'_1, \mathbf{r}'_2, \dots, \mathbf{r}'_{N_e})$ denotes all $N_e + 1$ electron coordinates. The equation (2.13) contains only the electronic Hamiltonian, but not the nuclear Hamiltonian. The fixed-nuclei approximation is valid when the collision time τ_c is much shorter than the nuclear rotation τ_R ($\geq 10^{-12} s$), or nuclear vibration τ_v ($\sim 10^{-14} s$) periods. This corresponds to a 'fast collision'.

The fixed-nuclei approximation is not valid when the scattering is dominated by strong long-range interactions as in the case of electron scattering by polar molecules. This approach also breaks down if the collision energy is close to a narrow, long-lived resonance, where the time of the collision is long.

The fixed-nuclei approach can be combined with other methods in order to obtain reliable scattering cross sections (Lane 1980). Thus, in the frame-transformation procedure (Fano 1970, Chang & Fano 1972) the fixed-nuclei approximation is used only in the region close to the nuclei using the BODY frame of the molecule. Then, at some boundary, the solutions are transformed to the LAB frame and the nuclear Hamiltonian is introduced, and the resulting equations are solved in the asymptotic region. The boundary is chosen so that the nuclear Hamiltonian can be ignored in the inner region, where exchange and electron-electron correlations are strong, and complicated short range exchange interactions can be ignored in the outer region. The frame-transformation approach also lies behind the R-matrix method used in the present work and described in the next chapter.

2.4 Adiabatic nuclei approximation

In some situations the inner region used in the frame-transformation approach can be extended up to infinity and the whole problem can be solved to a good approximation in the BODY frame without the nuclear Hamiltonian. The frame transformation is performed at the end of the calculations. This method is equivalent to the adiabatic approximation applied to the nuclear motion (Chang & Temkin 1969, Hara 1969, Temkin 1976). It is generally valid under the following conditions: (i) the incident electron energy is well above threshold; (ii) the scattering is nonresonant; (iii) the scattering is not dominated by strong long-range interactions.

The Born-Oppenheimer approximation is valid and the total wavefunction (2.5) can be rewritten for diatomics as

$$\Psi_{\varepsilon\alpha_o\nu_o}(\mathbf{r}', \mathbf{r}'_m, \mathbf{R}') \cong \Psi_{\varepsilon\alpha_o}^{FN}(\mathbf{r}', \mathbf{r}'_m; \mathbf{R}') \chi_{\alpha_o\nu_o}(\mathbf{R}') \quad (2.14)$$

where $\chi_{\alpha_o\nu_o}$ is the unperturbed initial nuclear-state wavefunction of the target, and ν_o represents vibrational and rotational quantum numbers for this state. The adiabatic nuclei approxi-

mate scattering amplitude for the transition $\alpha_o \nu_o \rightarrow \alpha \nu$ is

$$f_{\alpha\nu, \alpha_o \nu_o}(\mathbf{k}_\alpha, \mathbf{k}_o) = \langle \chi_{\alpha\nu}(\mathbf{R}') | f_{\alpha, \alpha_o}^{FN}(\mathbf{k}_\alpha, \mathbf{k}_o; \mathbf{R}') | \chi_{\alpha_o \nu_o}(\mathbf{R}') \rangle \quad (2.15)$$

where $f_{\alpha, \alpha_o}^{FN}$ is the fixed-nuclei (FN) scattering amplitude corresponding to an electronic transition $\alpha_o \rightarrow \alpha$. The $\mathbf{k}_\alpha$ and $\mathbf{k}_o$ are the momenta in the LAB-frame. The validity of the adiabatic nuclei approximation is based on the assumption that the fixed nuclei approximation is valid even in the asymptotic region $r \rightarrow \infty$.

Adiabatic molecular R-matrix theory and implementation

In the first part of this chapter, the theory behind the molecular R-matrix method is introduced. Particular emphasis is given to molecular orbitals. In the second part, the UK molecular R-matrix group computer codes, both polyatomic and diatomic, developed to utilise the method, are described. Some other methods used to treat low-energy electron-molecule collisions and their advantages and disadvantages are briefly discussed in the final part of this chapter.

3.1 General considerations

The R-matrix method first was introduced by Wigner (1946) and by Wigner & Eisenbud (1947) in the mid 1940s to describe nuclear reactions, dominated by compound state formation. In the original paper the 'R' in R-matrix stood for resonance, but this usage has now largely been lost. In the early 1970s this method was further developed to describe a broad range of atomic processes including electron-atom scattering (Burke et al. 1971, Burke & Robb 1975, Burke 1976). And also, within this period Schneider (1975) and Schneider & Hay (1976) extended the method to treat electron molecule collisions. They first showed how the scattered electron can be represented by analytic basis orbitals. In 1977 their ideas were developed further by

Burke and co-workers to describe electron scattering by diatomic molecules (Burke et al. 1977). Later the R-matrix method was further developed to treat electron collisions with polyatomic molecules (Morgan et al. 1997).

Adiabatic R-matrix theory is based on the splitting of coordinate space into two regions by a spherical boundary at $r = a$ centred on the centre of mass of the molecule: the inner region and the outer region (figure 3.1). The boundary is placed so that the inner region contains all the electronic charge cloud of the target molecule. In the internal region ($r < a$) the scattering electron lies within the molecular charge cloud and it is necessary to accurately account for all short-range interactions, such as exchange and correlation. The target molecule plus scattering electron are similar to a bound state, and quantum chemistry methods can be used to find the wavefunctions. In the outer region ($r > a$) the particles are still interacting but the forces are direct and multi-polar in character, the exchange and correlation are negligible, the scattering electron moves in the long-range multipole potential of the target and the single-centre expansion of the total wavefunction can be used. Thus it is possible to reduce the scattering problem in the external region to the solution of a set of coupled, ordinary differential equations which are much easier to handle than when the particles are close together and the interactions are non-local.

In the inner region, energy independent eigenfunctions and eigenvalues are found for the $(N + 1)$ -electron system using a close coupling expansion, where N is the number of target electrons and '1' represents the incident electron. The final inner region wavefunction is a linear combination of these with the coefficients found by matching with the computed outer region functions at the boundary using the R-matrix. This is a sum over quantities related to the overlap integrals of the internal and external wavefunctions evaluated at the surface of the sphere and the eigenenergies of the internal states (Burke et al. 1977).

In the outer region, the R-matrix on the boundary is propagated outward (Morgan 1984a, Baluja et al. 1982) until the inner region solutions can be matched with asymptotic solutions. Finally the coupled single-centre equations describing the scattering in the outer region are integrated to define the K-matrix, then physical observables, such as cross sections, can be derived from the T-matrix, which is found from the K-matrix.

The R-matrix approach to electron – atom and electron – molecule scattering is well doc-

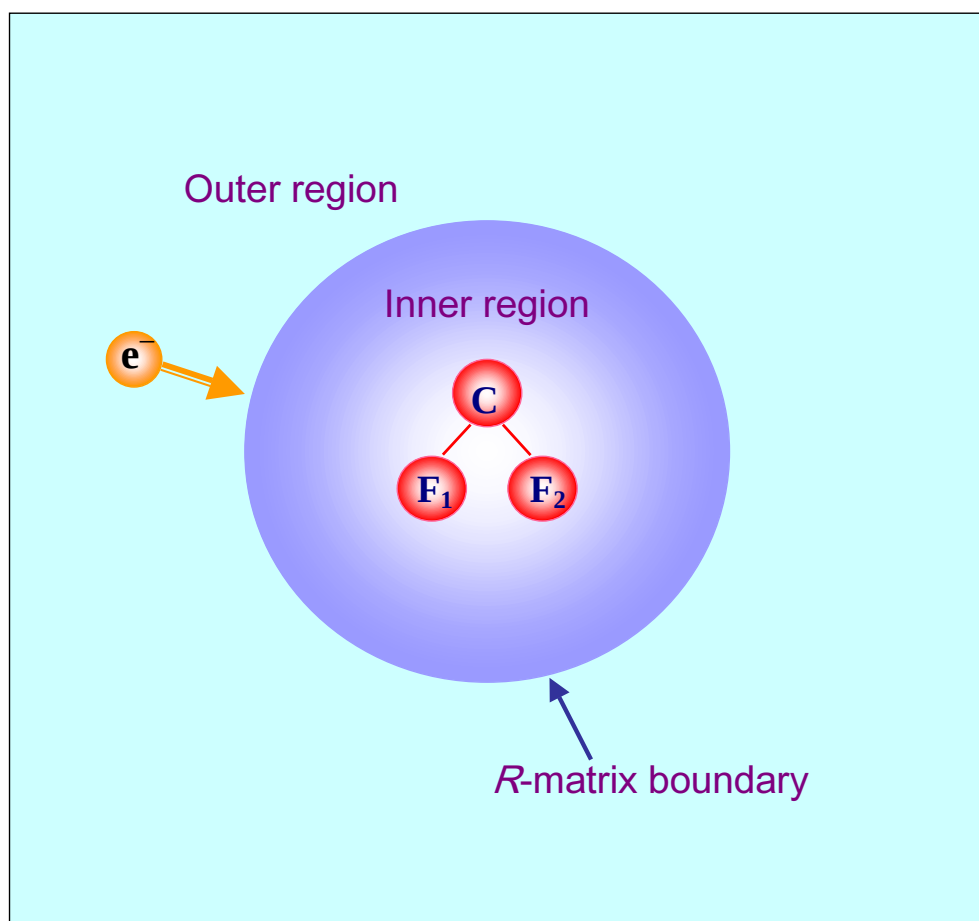


Figure 3.1: Division of configuration space in the fixed nuclei *R*-matrix theory.

umented by Burke & Berrington (1993). The general application of the R-matrix method to polyatomic molecules employing the UK R-matrix code has been described in the literature (Morgan et al. 1998, Tennyson & Morgan 1999).

3.2 The inner region

3.2.1 Target molecular orbitals and wavefunctions

The target molecular orbitals are constructed from atomic orbitals which can be expressed using basis functions centred on the nuclei. These orbitals represent the molecular charge distribution and must be negligibly small on the R-matrix surface. Two types of target basis functions have been tested: Slater-type orbitals (STOs) and Gaussian-type orbitals (GTOs). STOs are based on solutions of the hydrogenic atom problem and give a correct representation of the cusp of the wavefunction on the nucleus and the exponential fall-off of the wavefunction at long range. GTOs have the computational advantage that integrals involving them are over all space and can be evaluated analytically in closed form. In general, the R-matrix packages use STOs for diatomic molecules and GTOs for polyatomic molecules.

Normalized Slater type atomic orbitals are of the form (Slater 1960)

$$\rho_{ik}(n, l, m, \zeta_i) = \sqrt{\frac{(2\zeta_i)^{2n+1}}{(2n)!}} r_k^{n-1} e^{-\zeta_i r_k} Y_{lm}(\theta, \phi) \quad (3.1)$$

where i is the orbital index, k is the nuclear centre index, n , l and m have their usual hydrogenic meanings, ζ_i , the orbital exponent, can be varied to provide optimum representation, and the Y_{lm} are complex spherical harmonic functions.

Gaussian type orbitals, which are the familiar Gaussian functions, have the form (see for example Atkins & Friedman (1997))

$$g_{ik}(\alpha_i, n, l, m) = N r_k^{n-1} e^{-\alpha_i r_k^2} Y_{lm}(\theta, \phi) \quad (3.2)$$

where N is the normalization constant and α is the orbital exponent; all the other indexes have the same meaning as in the case of STOs.

The target molecular orbitals (MOs), γ_i , are linear combinations of the atomic orbitals (LCAO),

$$\gamma_i = \sum_l D_{li} \rho_l \quad (3.3)$$

with the coefficients D_{li} generally found through a self-consistent field (SCF) or Hartree-Fock calculation (see, for example, Bransden & Joachain (1983)). As discussed below, orbitals can be obtained using other techniques, such as MCSCF or NO procedures.

The electrons are placed in certain combinations of the target molecular orbitals (equation (3.3)) multiplied by spin functions to produce configuration state functions (CSFs) ϕ_i^N of different total symmetries. A configuration interaction (CI) target molecular wavefunction ψ_I^N is expressed as a linear combination of CSFs with the wavefunction's symmetry in a CI expansion

$$\psi_I^N = \sum_i c_{iI} \phi_i^N. \quad (3.4)$$

The coefficients c_{iI} are found by diagonalizing the N -electron target Hamiltonian matrix given by

$$\langle \phi_i^N | H_N | \phi_{i'}^N \rangle, \quad (3.5)$$

using the configuration state functions as a basis. It is important to note that a scattering calculation requires that the same orbital set must be used for all target states.

The quality of the scattering model depends on a satisfactory representation of the target. Getting the target parameters (eg. vertical excitation energies and the ground state dipole moment) right is, therefore, a necessary precursor to scattering calculations. This raises the question what does one do if SCF orbitals do not give satisfactory target parameters, particularly for electronically excited states. Good target properties can still be achieved in two ways: by using the pseudo-natural orbitals (NOs) or taking molecular orbitals from somewhere else, for example, from the quantum chemistry program MOLPRO (H.J. Werner and P.J. Knowles, <http://www.molpro.net>).

MOLPRO generates complete active-space self-consistent field (CASSCF) and multireference configuration interaction (MRCI) molecular orbitals. The CASSCF method is a type of multiconfiguration self-consistent field (MCSCF) methods. In the MCSCF method expansion coefficients D_{li} in (3.3) and c_{iI} in the configuration expansion of the total wavefunction (3.4) are optimized together. This optimization of both expansion coefficients makes calculation

computationally more demanding, but accurate results can be achieved using a relatively small number of configuration state functions. In the CASSCF method the orbitals are divided into three groups

1. inactive orbitals, which are lowest in energy and doubly occupied in all determinants;
2. virtual orbitals, which are very higher in energy and not occupied;
3. active orbitals, which are energetically intermediate between the inactive and virtual orbitals; these orbitals form the complete active space (CAS).

The CSFs included in the CASSCF calculations are configurations that arise from all possible ways of distributing the movable electrons over the active space. As the number of active orbitals increases, the number of CSFs rises very fast. The choice of active orbitals is, therefore, crucial.

In the MRCI method, a set of reference configurations is created. These reference configurations are used to form excited CSFs for use in CI calculations. For each of the reference configurations, one or two electrons are moved from occupied orbitals to unoccupied orbitals to create more CSFs for inclusion in the CI expansion. CI is then performed with the optimization of all the expansion coefficients. Reference configurations themselves often are singly and doubly excited configurations with respect to the ground state. The final MRCI wavefunction, therefore, includes triply and quadruply excited configurations. Normally, MRCI calculations give good energies with a relatively small number of configurations.

Similar to the CASSCF method, the target molecular orbital space in the R-matrix approach is divided into core (inactive), valence (active) and virtual orbitals. If the target molecule has very many valence electrons, some of the active orbitals may have to be frozen in order to decrease the number of configurations in the expansion of the target wavefunction (3.4) and, therefore, the size of the Hamiltonian matrix, to avoid computational problems. But, the size of expansion determines the quality of the target wavefunction and target parameters. An option here is to take the molecular orbitals, giving good target properties, from MOLPRO calculations. Thus, the ground state of the CF_3 radical is characterised by the electronic configuration with 8 core and 25 valence electrons in CAS $(1a' \dots 3a' 1a'')^8 (4a' \dots 13a' 2a'' \dots 7a')^{25}$. CAS CI calculations generate about 247 000 CSFs for the ground state of the CF_3 . This can not be handled within the R-matrix codes. Therefore, some of the active orbitals have to be frozen. The target properties, obtained using such restricted model, can be poor. In this case, molecular

orbitals, which give good target parameters, were obtained from MOLPRO calculations.

In theory, as more orbitals are used, more CSFs are included in the expansion of the target wavefunction (3.4) and the lower the state energies are. In practice, the number of configurations is restricted by computational limitations. Target properties can be improved by using so called natural orbitals (NOs), obtained as eigenfunctions of the 1-electron density matrix. A density matrix can be interpreted as the total electron density in some overlap region and represents the best wavefunction for the molecule under consideration. Let us consider the 1-electron density matrix, expanded in spin-orbitals $\psi_k(x_1)$ and written in general form (Löwdin 1955, McWeeny 1989)

$$D(x_1; x'_1) = \sum_{k,p} d_{kp} \psi_k(x_1) \psi_p^*(x'_1) \quad (3.6)$$

where ψ_k are spin orbitals of some complete orthonormal set and d_{kp} are numerical expansion coefficients. The matrix D is hermitian, therefore, it is possible to transform it to a diagonal form using a unitary transformation $\mathbf{U}^\dagger \mathbf{D} \mathbf{U} = \mathbf{n}$, where $\mathbf{U}$ is a unitary matrix and $\mathbf{n}$ is a diagonal matrix. Further, we can write $\mathbf{D} = \mathbf{U} \mathbf{n} \mathbf{U}^\dagger$. Introducing a new set of spin-orbitals $\bar{\psi} = \psi U$, the density matrix can be rewritten as

$$D(x_1; x'_1) = \sum_k n_k \bar{\psi}_k(x_1) \bar{\psi}_k^*(x'_1) \quad (3.7)$$

The orthonormal spin-orbitals defined by the above equation are called the natural spin-orbitals or simply natural orbitals (NOs). n_k , which are the eigenvalues of the density matrix D , represent the average number of electrons in each NO and are called the occupation numbers. Any natural orbital, whose population is small, is less important for a CI expansion. Therefore, a truncated expansion can approach a complete expansion as rapidly as possible (Coleman 1963). The NOs used in the R-matrix approach are pseudo-natural orbitals (they are called NOs for simplicity), as they are obtained using approximate wavefunctions and represent the best guess to the real NOs. In the R-matrix approach, the NOs are generated using a procedure similar to that for the generation of target molecular orbitals, but using all single and double excitations into orbital space spanned by all the target basis functions. Then the NOs with the largest occupation numbers are selected (these normally are the lowest energetically lying orbitals) and used as starting molecular orbitals in target calculations. The number of selected NOs is the same as the number of molecular orbitals in CAS, as this provides a necessary balance between

target and continuum molecular orbitals. It is also possible to state average the NOs belonging to several electronic states through the averaging of the density matrices. State-averaged NOs give molecular orbitals that are reliable for several different target states. The use of NOs allows to obtain good target properties using a relatively small CAS.

In multistate scattering studies it is necessary to use a CI representation of the target states in the valence orbital space, to get good target properties (Ermler et al. 1982). In valence configuration interaction (VCI) calculations the molecular Hamiltonian for each symmetry is diagonalized in CAS of all possible valence electronic states. For example, the CAS space for the ground state of the CF₂ molecule in the valence CI representation using the 6-311G* Gaussian basis set is defined by the electronic configuration $(1a_1 2a_1 1b_2)^6 (3a_1 \dots 7a_1 1b_1 2b_1 2b_2 \dots 5b_2 1a_2)^{18}$. The lowest three orbitals are frozen and the remaining 18 electrons are distributed in all possible ways over the remaining 12 valence molecular orbitals. This gives rise to 4 067 electronic states of X¹A₁ symmetry, 5 827 of ³B₁, 3 858 of ¹B₁, etc. Also, the use of 6-311G* Gaussian basis set gives 22 basis functions for *a*₁ symmetry, 9 for *b*₁, 17 for *b*₂ and 6 for *a*₂. The orbital space, used to generate the NOs, consists of 22*a*₁, 9*b*₁, 17*b*₂ and 6*a*₂ orbitals, when CAS for the same target consists of 7*a*₁, 2*b*₁, 5*b*₂ and 1*a*₂ orbitals.

3.2.2 Continuum molecular orbitals

The target molecular orbitals are supplemented with a set of continuum orbitals, centred on the centre of gravity of the molecule. These orbitals are of longer range than the orbitals centred on the nuclei, as they represent the scattering electron and do not vanish on the R-matrix boundary. The continuum functions have the form

$$\eta_{il_i}(\mathbf{r}_G) = \frac{1}{r_G} u_{il}(r_G) Y_{l_i m_i}(\hat{\mathbf{r}}_G) \quad (3.8)$$

where the Y_{lm} are complex spherical harmonics, the u_{il} are effective atomic orbitals and $\hat{\mathbf{r}}_G$ are the coordinates of the centre of gravity of the target molecule.

In diatomic R-matrix calculations u_{il} found by solving the model, single channel scattering problem (Gillan et al. 1995)

$$\left[\frac{\partial^2}{\partial r^2} - \frac{l(l+1)}{r^2} + 2V_0(r) + k_i^2 \right] u_{il}(r) = 0 \quad (3.9)$$

with the boundary conditions

$$u_{il}(0) = 0 \quad (3.10)$$

and

$$\frac{1}{u_{il}} \frac{du_{il}}{dr} \Big|_{r=a} = b. \quad (3.11)$$

where k_i^2 are the eigenenergies in Rydbergs, V_0 is an arbitrary spherical potential and b is an arbitrary constant, both taken to be zero in this work. The continuum basis functions are numerical. Any finite expansion over these functions will exhibit the Gibbs phenomenon near the R-matrix boundary (Gillan et al. 1995). The Gibbs phenomenon is a peculiarity of the sum of a finite number of terms of a Fourier series at a simple discontinuity (Arfken 1985, Jeffreys & Jeffreys 1988). Increasing the number of terms does not remove this peculiarity, but shifts it nearer to the discontinuity. In 1967 Buttle proposed a correction to the diagonal elements of the R-matrix in order to compensate for the finite expansion length (Buttle 1967). It is discussed in section 3.2.4.

The continuum and target molecular orbitals are orthogonalized using the Schmidt orthogonalization process (Tennyson et al. 1987). The final continuum orbitals are, therefore, of the form

$$\xi_j(\mathbf{r}_G) = \sum_i \frac{1}{r_G} u_{ij}(r_G) Y_{l_i m_i}(\hat{\mathbf{r}}_G) + \sum_i \rho_i^A B_{ij} + \sum_i \rho_i^B C_{ij} \quad (3.12)$$

where i is the orbital index, A and B are the two nuclear centres. In some cases, when there is a need to use diffuse target basis functions or in electron-ion scattering, when numerical basis functions are compact and look like target basis functions, linear dependence can arise, then the continuum functions may be orthogonalized to several of the target molecular orbitals using Lagrange orthogonalization (Tennyson et al. 1987).

The continuum basis functions, used in polyatomic R-matrix calculations, are the Gaussian functions and do not require fixed boundary conditions and the Buttle correction. Initially, Gaussian type continuum basis functions were generated by fitting GTO basis sets to Bessel functions withing the finite region of the R-matrix sphere (Nestmann & Peyerimhoff 1990). Later Faure et al. (2002) provided a program which constructs adequate GTO continuum basis sets for representing both Bessel and Coulomb functions using the procedure described by Nestmann & Peyerimhoff (1990). As the integrals involving continuum basis functions are evaluated in the whole configuration space, the contribution from the region outside the R-

matrix sphere is subtracted from the integrals over infinite range (Tennyson & Morgan 1999). First, target and continuum molecular orbitals are orthogonalized using the Schmidt orthogonalization procedure. Then the symmetric or Löwdin orthogonalization is used to orthogonalize continuum molecular orbitals among themselves and remove linearly dependent functions (Morgan et al. 1997, Nestmann et al. 1994).

3.2.3 (N+1) inner region wavefunction

According to basic quantum mechanics, when the system has energy E then it has a wavefunction Ψ , given by

$$(H_{N+1} - E)\Psi_E = 0 \quad (3.13)$$

where H_{N+1} is the non-relativistic Schrödinger Hamiltonian for the $(N + 1)$ -electron system. The inner region target plus scattering electron eigenfunction for a state of some specific spatial symmetry can be expanded as

$$\psi_k^{N+1} = \mathcal{A} \sum_I \psi_I^N(\mathbf{X}_1, \dots, \mathbf{X}_N) \sum_j \bar{\xi}_j(\mathbf{X}_{N+1}) a_{Ijk} + \sum_m \chi_m(\mathbf{X}_1, \dots, \mathbf{X}_N, \mathbf{X}_{N+1}) b_{mk}, \quad (3.14)$$

where $\mathcal{A}$ is the anti-symmetrization operator, $\mathbf{X}_n = (\mathbf{r}_n, \sigma_n)$ with $\mathbf{r}_n$ are the spatial coordinate and σ_n spin state of the n^{th} electron, $\bar{\xi}_j$ is a continuum molecular orbital spin-coupled with the scattering electron and a_{Ijk} and b_{mk} are variational coefficients.

The first term summation runs over target states which themselves are usually CI expansions (3.4). It accounts for one electron in a continuum state with the remaining electrons in a target state, known as a ‘target+continuum’ configuration.

The second term summation runs over configurations χ_m in which all the electrons are placed in target molecular orbitals and are known as L^2 functions. Since the molecular orbitals are orthogonal, the L^2 functions are needed to ensure that important regions of configuration space are not omitted. These configurations also account for correlation effects involving virtual excitation to higher electronic states not included in the first expansion.

The variational coefficients a_{Ijk} and b_{mk} are found through diagonalization of the Born-Oppenheimer Hamiltonian matrix for the relevant system. Initially, matrix elements of this

Hamiltonian are constructed in terms of the individual configurations making up the target states of interest. Then these matrix elements transformed to ones written in terms of the CI target wavefunctions given by (3.14). As the number of target states is usually less than the number of terms in the CI target expansion, the transformed Hamiltonian matrix is, therefore, significantly reduced. This procedure is known as CI contraction (Tennyson 1996).

As was mentioned before, the target molecular functions are considered zero at the R-matrix boundary. Therefore, the logarithmic boundary condition on the continuum functions (equation 3.11) in the diatomic R-matrix approach also holds for the $(N + 1)$ -electron total wavefunction

$$\frac{1}{\psi^{N+1}} \frac{d\psi^{N+1}}{dr} \bigg|_{r=a} = b \quad (3.15)$$

The use of the logarithmic boundary condition cancels out surface terms, arising from the scattering electron kinetic energy operator and makes the Hamiltonian hermitian inside the R-matrix sphere.

In polyatomic R-matrix calculations the continuum orbitals are not restricted to special boundary conditions at $r = a$. The surface or Bloch operator (Bloch 1957) (discussed in more details in the next section 3.2.4) is added to the Hamiltonian to make it hermitian inside the R-matrix sphere. The Bloch operator is of the form

$$L_{N+1} = \frac{1}{2} \sum_{i=1}^{N+1} \sum_j |\psi_j^N Y_{l_j m_{l_j}}(\hat{r}_i) > \delta(r_i - a) \left(\frac{d}{dr_i} - \frac{b-1}{r_i} \right) < \psi_j^N Y_{l_j m_{l_j}}(\hat{r}_i)| \quad (3.16)$$

where a is the radius of the R-matrix sphere.

Finally, by diagonalizing the modified inner region Hamiltonian

$$< \Omega_p^{N+1} | H_{N+1} + L_{N+1} | \Omega_{p'}^{N+1} > \quad (3.17)$$

where the Ω_p^{N+1} are the basis configurations, the inner region $(N+1)$ -electron eigenfunctions ψ_k^{N+1} can be found.

3.2.4 Generation of the R-matrix

The R-matrix on the boundary can now be determined from the solutions of the Hamiltonian matrix. The R-matrix contains a complete description of the collision problem in the inner

region and provides the boundary conditions necessary to match the inner and outer regions wavefunctions, and solve the problem in the outer region.

Let us begin by considering the Schrödinger equation for the system

$$H_{N+1}|\Psi\rangle = E|\Psi\rangle, \quad (3.18)$$

where Ψ is the total $(N + 1)$ -electron wavefunction and E is the total energy of the system. In the polyatomic R-matrix approach the R-matrix on the boundary can be found using the technique based on the Bloch operator (Shimamura 1977). By adding and subtracting the Bloch operator (3.16) and rearranging the Schrödinger equation becomes

$$(H_{N+1} + L_{N+1} - E)|\Psi\rangle = L_{N+1}|\Psi\rangle \quad (3.19)$$

The Bloch operator projects the total wavefunction onto all of the possible products of the R-matrix surface. This projection is itself a wavefunction in the relative coordinate of the scattered fragments. From a mathematical point of view the addition of the L operator to the Hamiltonian makes the sum of $H_{N+1} + L_{N+1}$ a hermitian operator (Bloch 1957). A formal solution of the equation (3.19) can be written as

$$|\Psi\rangle = (H_{N+1} + L_{N+1} - E)^{-1} L_{N+1}|\Psi\rangle. \quad (3.20)$$

We need to note that the inner region ψ_k^{N+1} are eigenfunctions of the $(H_{N+1} + L_{N+1})$ Hamiltonian with eigenvalues e_k , the inverse operator can be rewritten as an expansion over these functions to obtain

$$|\Psi\rangle = \sum_k \frac{|\psi_k^{N+1}\rangle \langle \psi_k^{N+1}| L_{N+1} |\Psi\rangle}{(e_k - E)} \quad (3.21)$$

with

$$\langle \psi_k^{N+1} | L_{N+1} | \Psi \rangle = \frac{1}{2} \sum_j F_j(r) \left(\frac{dF_j}{dr} - bF_j(r) \right)_{r=a} \quad (3.22)$$

where $F_j(r)$ are the reduced radial functions evaluated on the R-matrix sphere and defined as

$$F_i(r) = \langle \psi_{I_i}^N Y_{l_i m_{l_i}} | \Psi \rangle \quad (3.23)$$

To determine the scattering wavefunction completely it is necessary to specify $F_j(r)$ and their derivatives on the R-matrix sphere. By substituting in the Bloch operator (3.16), the radial wavefunctions can be written as (Gillan et al. 1995)

$$F_i(r) = \sum_j R_{ij}(E) \left(a \frac{dF_j}{dr} - bF_j \right)_{r=a} \quad (3.24)$$

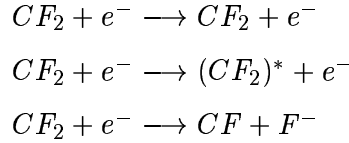
where $R_{ij}(E)$ is the R-matrix defined as

$$R_{ij}(E) = \frac{1}{2a} \sum_k \frac{f_{ik}(a)f_{jk}(a)}{e_k - E} \quad (3.25)$$

The summation in (3.25) is over the surface amplitudes f_{ik} and therefore, over the eigenfunctions ψ_k^{N+1} . The surface amplitudes f_{ik} are defined by the following equation

$$f_{ik} = \langle \psi_{I_i}^N Y_{l_i m_{l_i}} | \psi_k^{N+1} \rangle \quad (3.26)$$

where $\langle \psi_{I_i}^N Y_{l_i m_{l_i}} |$ are channel functions. A channel, in a general sense, refers to each possible grouping of the various particles involved in the scattering event and is defined by a particular set of labels l and m_l . For example, let assume that the possible results of electron scattering by the CF_2 radical are



where a superscript * refers to a vibrationally or rotationally excited state of the CF_2 molecule. Each grouping on the right side of the arrow represents a different channel. In practice, degeneracy of the molecular partial wave expansion means that each grouping on the right side of the arrow has several channels. Which processes are actually possible depends on the scattering energy.

In the diatomic R-matrix calculations the boundary conditions on the continuum orbitals make the Hamiltonian operator symmetric inside the R-matrix sphere. The R-matrix on the boundary is obtained from the solutions of the Hamiltonian matrix and in principle, has the form (3.25). The expansion in the equation (3.25) must be truncated at some point to include only a finite number of terms N_{il} for each value of l . This gives a truncation error which is increased by the boundary conditions (3.10) and (3.11). A ‘Buttle correction’ (Buttle 1967, Shimamura 1978) is added to the diagonal terms of the R-matrix in order to compensate for the truncation error. The Buttle correction takes the form

$$B_{ll}(E) = \frac{1}{2a} \sum_{i=N_{li}+1}^{\infty} \frac{[u_{li}(a)]^2}{\frac{1}{2}k_{li}^2 - E} \quad (3.27)$$

where $k_{li}^2 = 2e_{ki}$, u_{li} and e_{ki} are the eigenvector and eigenvalues respectively of equation (3.9), not explicitly included in the continuum basis set. The Buttle correction is evaluated as part of the continuum numerical function generation.

The R-matrix (3.25) is propagated (Morgan 1984b) to an appropriate radius, where the interaction between the target molecule and incident electron is assumed to be zero. Then, solutions to the scattering problem are obtained by using the Gailitis expansion technique (Noble & Nesbet 1984).

3.3 Inner region program modules

The UK Molecular R-matrix scattering package has been developed over many years by a variety of people. R-matrix calculations can be broken down into a number of basic computational steps. These are the generation of integrals, the generation of a set of molecular orbitals, the construction and diagonalization of the inner region Hamiltonian matrix, calculation of the target parameters and solution of the outer-region scattering program. In this section the inner region diatomic and polyatomic program modules are described. The modules CONGEN, SCATCI, DENPROP and PSN are the same for both codes. In case of calculations with the natural orbitals the NOs can be generated by using the same program modules as for the N target calculations with the added PSN module in the end. Then the N target calculations are repeated with the generated NOs, used as an input for the modules MOS (diatomics) or SWED-MOS (polyatomics). It is important to remember that the modules SCF (diatomics) or SWSCF and SWFJK (polyatomics) are not used in the latter calculations. If molecular orbitals are generated externally (using MOLPRO, for example), the orbital generators SCF and SWSCF are not used at all.

3.3.1 Diatomic codes

The inner region diatomic code was originally based on the quantum chemistry package ALCHEMY (McLean 1971), developed by IBM in the 1970s, with many modifications to make it suitable for the scattering problem (Noble 1982). This code is built assuming the use of STOs and is intrinsically limited to treating collisions with linear molecules. The flow diagram for the inner region N -electron target calculation is shown in figure 3.2 and for the $(N + 1)$ -electron calculation in figure 3.3.

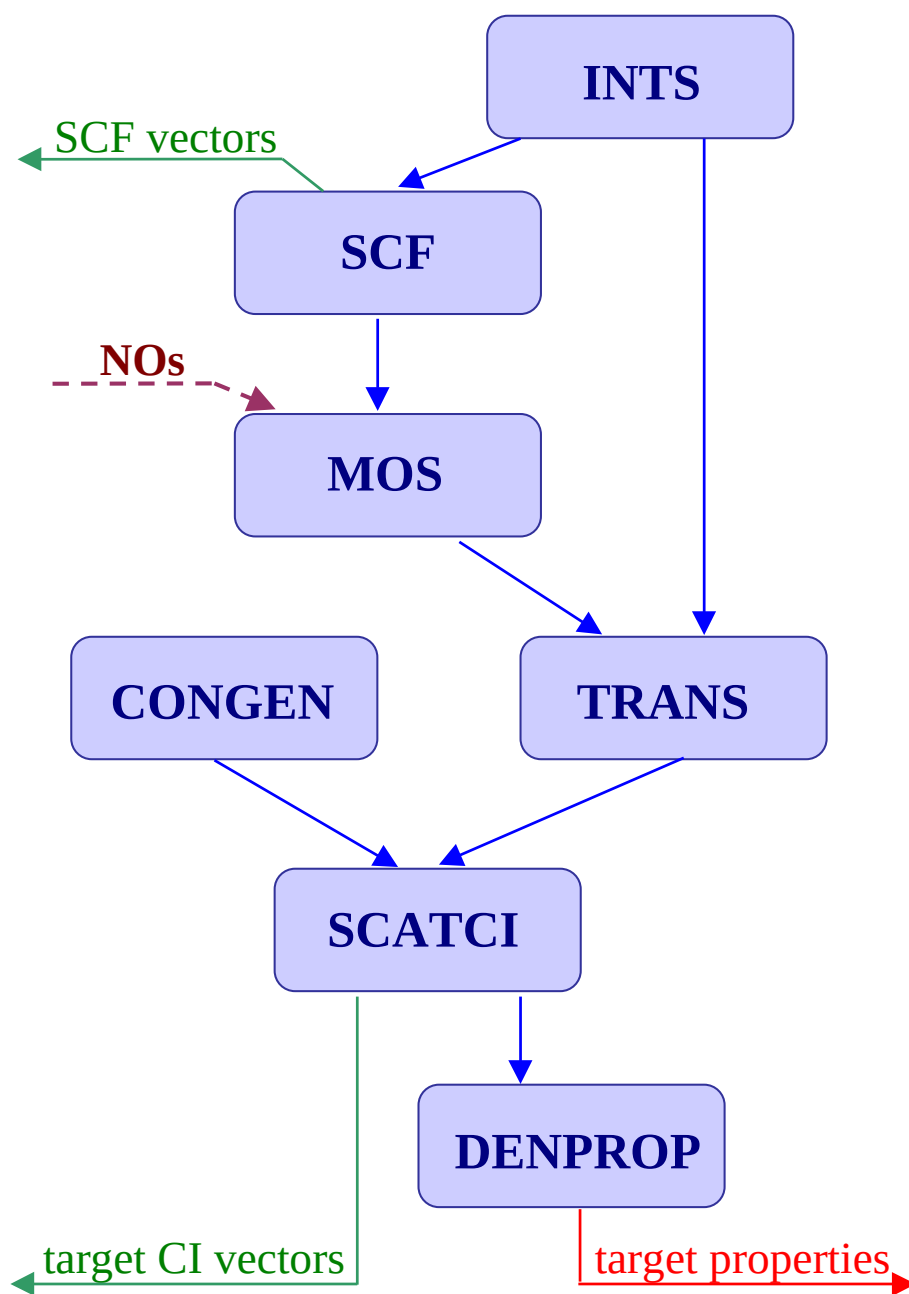


Figure 3.2: Flow diagram for the inner region diatomic target state calculations. Red arrows indicate an input required by the outer region codes. If NOs are used (dashed line) then the module SCF is omitted.

INTS evaluates 1 and 2-electron atomic integrals and, optionally, property integrals. This program was developed from **ALCHEMY** by Noble (1982), who modified it in order to restrict optionally the range of integration to a finite sphere. The radial integrals are evaluated by numerical quadrature. Two electron integrals which have more than one electron in a continuum orbital are discarded. INTS provides the necessary integrals to be used by the SCF module in setting up the target. It is later used to provide the integrals for the (N+1) calculation.

SCF performs a self consistent field (Hartree-Fock) calculation to produce target orbitals γ_i (equation 3.3), from linear combinations of atomic orbitals.

NUMBAS generates numerical continuum orbitals of the form of equation (3.8) with fixed logarithmic boundary conditions at the R-matrix boundary (3.10) and (3.11). The model potential V_0 can be set to zero for neutral targets and to a simple point charge for ionic targets. The Buttle correction (equation 3.27) is also calculated by this module and are stored for later use.

MOS takes as its input the target orbitals from SCF or elsewhere to output orthogonal molecular orbitals used in the target CI calculation. Externally generated molecular orbitals can be input via parameter VCIN. In the scattering calculations MOS orthogonalizes target orbitals and continuum orbitals, generated by NUMBAS, to produce orthogonal molecular orbitals. It uses Schmidt and Lagrange orthogonalization scheme (Tennyson et al. 1987). The Lagrange orthogonalization procedure is used to eliminate linear dependence between target and continuum molecular orbitals. Each time a Lagrange orthogonalization is performed, the linear combinations of continuum orbitals most linearly dependent on a target orbital are removed. MOS also computes the amplitudes of the continuum orbitals on the R-matrix boundary.

TRANS carries out the four-index transformation of atomic integrals. TRANS first orders the atomic integrals produced by INTS and then multiplies them by combinations of molecular orbital coefficients to transform them into molecular integrals which are required for the construction of the Hamiltonian.

CONGEN generates configuration state functions (CSFs) with appropriate spin and symmetry couplings. The code can generate configurations in the abelian group D_{2h} and its subgroup and non-abelian groups $D_{\infty h}$ and $C_{\infty v}$. The molecular orbitals to be included are hand

picked by the user. The module also computes a phase factor for each target orbital, to keep the phases between the target and $(N + 1)$ -electron system consistent (Tennyson 1996). CONGEN has been adapted for scattering calculations to allow explicit coupling of the continuum electron to individual target states (Noble 1982).

SCATCI constructs and diagonalizes the Hamiltonian matrix for both N and $(N + 1)$ -electron calculations, to find the eigenvalues and eigenvectors. For large calculations this part of the codes is the slowest, as the Hamiltonian can become very large. It takes configurations generated by CONGEN and molecular integrals supplied by TRANS to build up the Hamiltonian matrix. A special algorithm, called contraction and described in section 3.2.3, is used to reduce the size of the $(N + 1)$ -electron Hamiltonian matrix. SCATCI first performs the contraction, then multiplies $\bar{\xi}_j$ by ψ_I^N in (3.14). The use of the contraction speeds up the Hamiltonian construction phase, but the problem with diagonalizing very large Hamiltonian matrices still exists.

SCATCI also generates CI target wavefunctions. For N -electron calculations, when only one or two eigenvalues and eigenvectors are required from a large matrix, the iterative Davidson diagonalization procedure is implemented *via* subroutine DVDSON, written by Stathopoulos & Fisher (1982). For $(N + 1)$ -electron calculations all eigenvalues and eigenvectors are needed and in-core Givens-Householder diagonalization is used. Initially, Givens-Householder diagonalization was implemented *via* NAG subroutine *f02faf*. Later this subroutine was replaced with LAPACK routine *dsyev*. Substitution of NAG library routines with LAPACK, LINPACK and BLAS made the Hamiltonian construction and diagonalization phase faster.

DENPROP calculates properties such as permanent dipoles, transition moments and polarizabilities from input target wavefunctions generated by SCATCI and the property integrals produced by INTS. The target properties are then used in the outer region calculation.

PSN generates pseudo-natural orbitals by diagonalizing the density matrices provided by DENPROP. It has an option to average the density matrices (J.D. Gorfinkiel, private communications) giving different weights to target states to generate state-averaged NOs. The weights for each state are specified by using the parameter WGT.

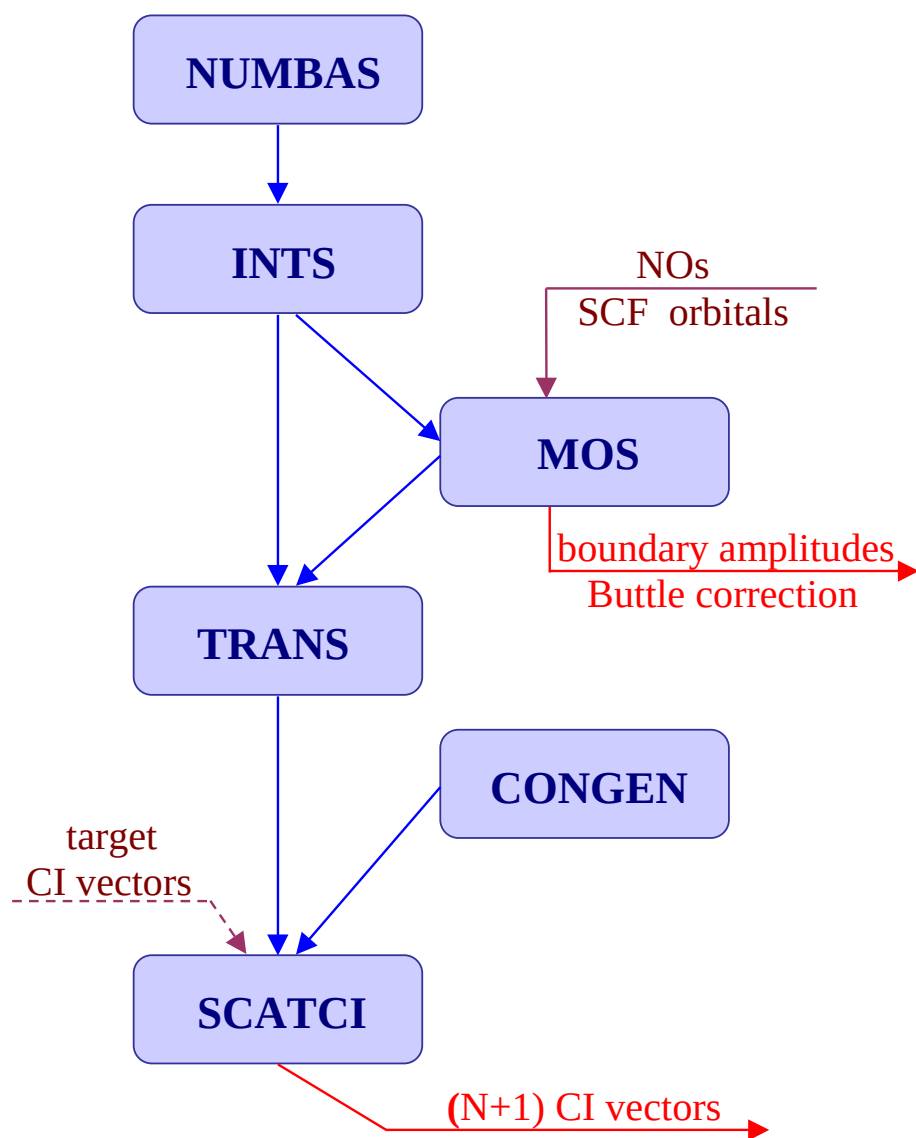


Figure 3.3: Flow diagram for the inner region scattering calculation involving a diatomic target. Red arrows indicate an input required by the outer region codes.

3.3.2 Polyatomic codes

The inner region polyatomic code is based on the quantum chemistry 'Molecule-Sweden' suite of codes developed by Almlöf & Taylor (1984). In the initial quantum chemistry code the range of integration is over an infinite region, while in the inner $(N + 1)$ R-matrix calculations the range of spatial integration must be restricted to the finite sphere. In order to achieve that with minimal computational efforts, the contribution from the region outside the sphere was subtracted from the integrals over an infinite range. This was implemented in the program GAUSTAIL by Morgan *et al* (Morgan *et al.* 1997, Morgan *et al.* 1998). Figures 3.4 and 3.5 represent the flow diagrams for the inner region N and $(N + 1)$ -electron calculations respectively.

SWMOL3 generates one and two electron atomic integrals. It has the same functionality as its diatomic equivalent INTS, only does not produce property integrals. This program was developed from a Cray version of the integral generator 'MOL3'.

GAUSTAIL evaluates the contribution to each integral from outside the R-matrix sphere, which has to be subtracted from the integrals over an infinite range. Also, this module modifies the Hamiltonian matrix, by adding matrix elements of a Bloch operator, to make it hermitian. These matrix elements are surface terms which are included in the 'tail' integrals.

SWORD first subtracts the 'tail' integrals from the atomic integrals output from SWMOL3 and then carries out reordering of the integrals.

SWFJK forms combinations of Coulomb and exchange integrals for the Fock Matrix to be used in an SCF calculation.

SWSCF performs a self consistent field (Hartree-Fock) calculation to produce target orbitals from linear combinations of atomic orbitals. SWSCF is virtually unaltered version of the equivalent module in the Molecule-Sweden package.

SWEDMOS produces orthogonal molecular orbitals. It has the same functionality as its diatomic equivalent MOS but uses a different orthogonalization strategy. First, it uses the Schmidt method to orthogonalize each of the continuum orbital to all the target orbitals, then it uses the symmetric method to orthogonalize the continuum orbitals among themselves and

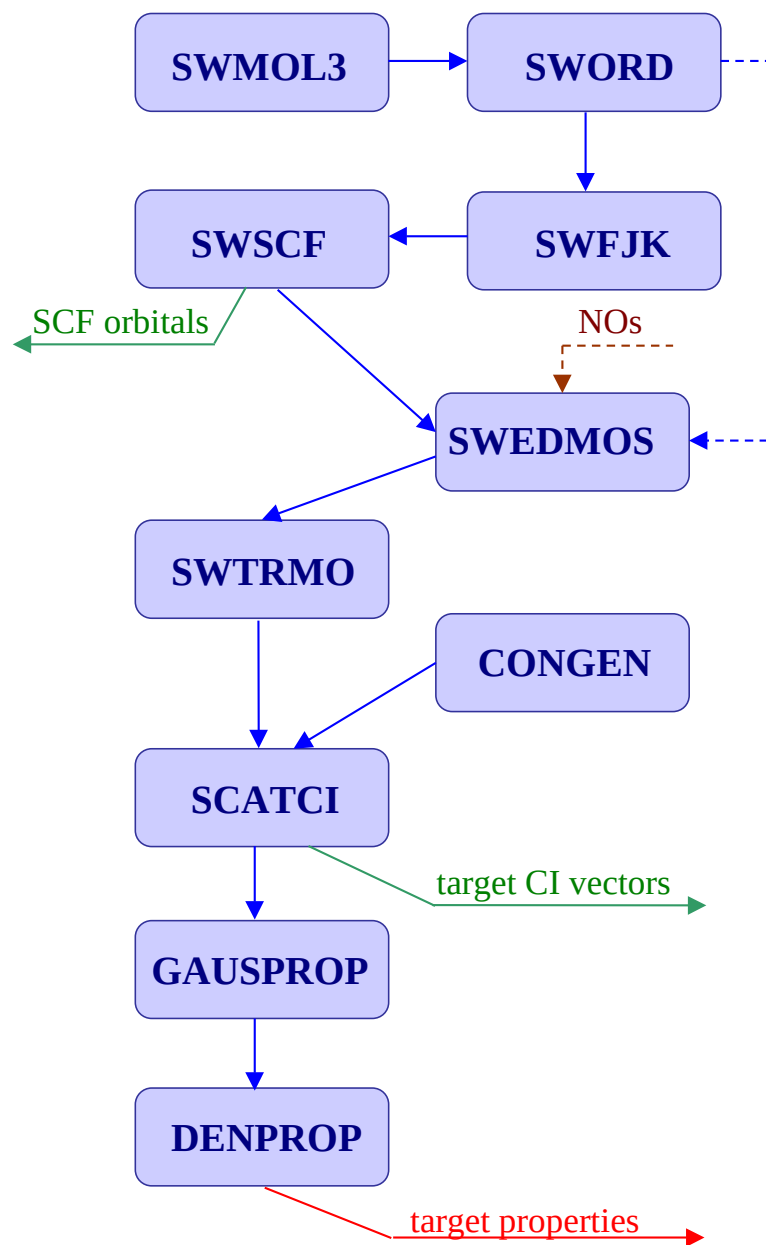


Figure 3.4: Flow diagram for the inner region polyatomic target state calculation. Red arrows indicate an input required by the outer region codes. If NOs are used (dashed line) then the modules SWFJK and SWSCF are omitted.

remove those orbitals which correspond to very small eigenvalues of the overlap matrices. Externally generated molecular orbitals can be input via parameter *VMORB*.

SWTRMO performs the four-index transformation of ordered integrals produced by **SWMOL3**.

GAUSPROP evaluates the property integrals required by **DENPROP** since **SWMOL3** does not provides them. This code is based on **GAUSTAIL**.

The meaning of the modules **CONGEN**, **SCATCI**, **DENPROP** and **PSN** is the same as in the diatomic codes.

3.4 The outer region

In the outer region the exchange and correlation are negligible and the physical interactions dominate the scattering process. The scattering electron moves in the long-range multipole potential of the target and a single centre, no exchange, close coupling expansion of the scattering wavefunction can be used (Gillan et al. 1995)

$$\Psi = \sum_i \bar{\phi}_i(\mathbf{x}_1 \dots \mathbf{x}_N, \sigma_{N+1}) r_{N+1}^{-1} F_i(r_{N+1}) Y_{l_i m_{l_i}}(\hat{\mathbf{r}}_{N+1}), \quad (3.28)$$

where $\mathbf{x}_j = (\hat{\mathbf{r}}_j, \sigma_j)$, the position and spin of the j th target electron, the functions $\bar{\phi}_i$ are formed by coupling the scattering electron spin σ_{N+1} with the target state ϕ_i , and the F_i are reduced radial wavefunctions. Substituting the equation for the Ψ into the Schrödinger equation and projecting onto the channel functions $[\bar{\psi}_i Y_{l_i m_{l_i}}]$, a set of coupled, homogeneous differential equations for the reduced radial wavefunctions F_i can be written as

$$\left(\frac{\partial^2}{\partial r^2} - \frac{l_i(l_i + 1)}{r^2} + k_i^2 \right) F_i(r) = 2 \sum_j V_{ij}(r) F_j(r), \quad (3.29)$$

where V_{ij} is the potential matrix in the outer region which describes the coupling between the channels i and j , the quantity k_i^2 is

$$k_i^2 = 2(E - \epsilon_i), \quad (3.30)$$

with ϵ_i the eigenenergy of the target state ϕ_i and E the total energy of the system.

The equation (3.29) can be solved by propagating the R-matrix from the boundary to sufficiently large distances where the interaction between the scattering electron and target molecule

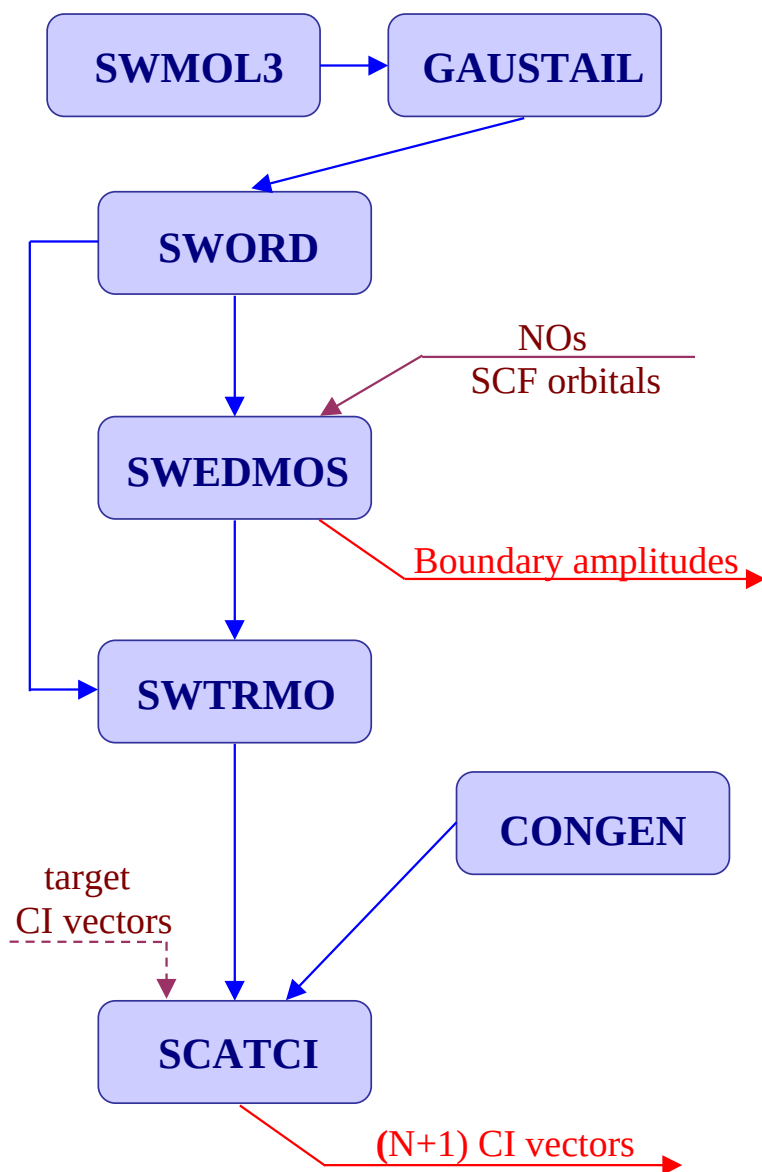


Figure 3.5: Flow diagram for the inner region scattering calculation involving a polyatomic target. Red arrows indicate an input required by the outer region codes.

may be assumed to be zero (Baluja et al. 1982, Morgan 1984a). Gailitis (1976) asymptotic expansion techniques are then used to solve for the outer region functions (Noble & Nesbet 1984). In the limit $r \rightarrow \infty$, the equations (3.29) have different, linearly independent, standing wave asymptotic solutions j for each energetically open channel i

$$F_{ij} \sim \frac{1}{\sqrt{k_i}} \left(\sin(k_i r - \frac{1}{2}l_i\pi)\delta_{ij} + \cos(k_i r - \frac{1}{2}l_i\pi)K_{ij} \right) \quad (3.31)$$

and $F_{ij} \sim 0$ for closed channels. The coefficients K_{ij} define the real, symmetric K-matrix, which contain all the scattering information. In the closed channels, the radial function decays exponentially

$$F_{ij} \sim e^{-|k|_i r} \quad (3.32)$$

indicating that there is no flux lost at infinity.

The solution of the external region equations produces initially a K-matrix at each energy. The eigenphase sum, δ , which can be used for the detection and parametrization of resonances, can be found directly from the diagonalized K-matrix K_{ii}^D :

$$\delta = \sum_i \arctan(K_{ii}^D), \quad (3.33)$$

where the sum is over the open channels. Resonances will be discussed in the next subsection.

The scattering matrix $\mathbf{S}$ is a transformation of the K-matrix,

$$\mathbf{S} = (\mathbf{1} + i\mathbf{K})(\mathbf{1} - i\mathbf{K})^{-1}. \quad (3.34)$$

The T-matrix which is formed trivially from the S matrix, $\mathbf{T} = \mathbf{S} - \mathbf{1}$, can be used to derive physical observables such as integral and differential cross sections. So, the integral cross section for excitation from state i to i' is (Burke 1982):

$$\sigma(i \rightarrow i') = \frac{\pi}{k_i^2} \sum_S \frac{(2S+1)}{2(2S_i+1)} \sum_{\Gamma ll'} |T_{ii'l'}^{\Gamma S}|^2, \quad (3.35)$$

where S_i is the spin angular momentum of the i_{th} target state, S is the total spin angular momentum, Γ runs over symmetry, l and l' are orbital angular momentum quantum numbers corresponding to i and i' states. In the case of electron-linear molecules scattering $\Gamma = \Lambda$ is the total electronic angular momentum projected onto the molecular axis.

When the interaction potential includes long range multipole potentials, such as dipole potential, the number of partial waves required to converge the cross section can be very large. On the other hand, the partial waves above a certain minimum angular momentum L_m are only weakly scattered. The partial wave expansion of the scattering amplitude is truncated at some value L_m . Therefore, the integral cross section (3.35) includes contributions from a finite number of angular momenta L . The remaining terms can be obtained from a weak-scattering theory, such as the first Born approximation (FBA) (Chu & Dalgarno 1974, Gibson et al. 1987). The FBA cross section can be obtained in closed form (Watson & McKoy 1979, Fliflet & McKoy 1980), without resorting to a partial wave expansion, and contains contributions from all angular momenta. The final integral cross section can be written as

$$\sigma^B(i \rightarrow i') = \sigma^R(i \rightarrow i') + \Delta\sigma \quad (3.36)$$

where $\sigma^R(i \rightarrow i')$ is the approximate cross section obtained using the R-matrix approach and represented by (3.35), $\Delta\sigma$ is the Born correction, described by the formula

$$\Delta\sigma = \sigma^{FBA} - \sigma_{L_m}^{FBA} \quad (3.37)$$

where σ^{FBA} is the plane wave Born approximation cross section and $\sigma_{L_m}^{FBA}$ is the cross section obtained from a finite expansion of the first Born cross section containing the same number of partial waves as $\sigma^R(i \rightarrow i')$.

A nuclear motion is not taken into account in this work. If the nuclear motion is taken into account, one has to account for couplings between rotational and vibrational channels. In this case the differential cross section has to be calculated using a more sophisticated multipole-extracted adiabatic-nuclei (MEAN) approximation of Norcross & Padiyal (1982). The essential idea of this approach is that the differential cross section for some rovibrational transition can be separated into two terms and treated independently (Norcross & Padiyal 1982).

The program for calculation of the Born correction using (3.37) was written by K. L. Baluja (private communications). Later this program was implemented into the outer region R-matrix codes with many changes. It should be noted that the scheme of using the FBA to include contributions to the cross section from high angular momenta has been used in many applications, including electron collisions with water molecule (Tennyson & Morgan 1999), ClO molecule (Baluja et al. 2000), methylidyne (CH) radical (Baluja & Msezane 2001), Cl₂O (Baluja et al. 2001a).

3.4.1 Resonances

In general the eigenphase sum, and therefore the cross section, vary slowly as a function of the incident energy. However, in certain cases it may happen that the eigenphase sum increases rapidly in a certain energy interval of width Γ about a given energy value E^r (superscript 'r' stands for a resonance), causing a dramatic change in the corresponding partial cross section in that energy range (figure 3.6). This behaviour is called a resonance. A resonance can be described as a long lived metastable state of the target molecule where the scattering electron is temporarily captured. The lifetime τ of this metastable state is much longer than a typical collision time. Any resonance is characterized by its position E_i^r and width Γ_i^r which can be found by fitting the eigenphase sum (3.33) to a Breit-Wigner profile (see, for example, Atkins & Friedman (1997))

$$\eta(E) = \sum_i \tan^{-1} \left[\frac{\Gamma_i^r}{E - E_i^r} \right] + \sum_j a_j(E)^j \quad (3.38)$$

where $a_j(E)$ is the background eigenphase and $\eta(E)$ is the eigenphase sum.

In the R-matrix calculations resonances are detected and fitted automatically using *RESON* (Tennyson & Noble 1984). In fact, resonances can often appear on top of a threshold which can have the effect of distorting the resonance or of cutting off some part of the resonance. This makes the resonance difficult to fit.

The lifetime τ can be related to the resonance width Γ by using the Heisenberg uncertainty relation for time and energy $\Delta t \Delta E \geq \hbar/2$. Thus, with $\Delta t \simeq \tau$ and $\Delta E \simeq \Gamma$, the lifetime is

$$\tau \simeq \frac{\hbar}{\Gamma} \quad (3.39)$$

Normally the eigenphase sum undergoes an increase by π in a resonance region, as shown in figure 3.6 A. This behaviour is consistent with Levinson's theorem (Levinson 1949). The theorem states that

$$\eta_l(0) = N_l \pi \quad (3.40)$$

where $\eta_l(0)$ is the scattering phase shift at threshold (zero momentum) and N_l is the number of bound states with angular momentum $l\hbar$. For half-bound states or zero-energy resonances ($l = 0$) the Levinson's theorem has to be modified (Newton 1960, Swan 1954)

$$\eta_0(0) = (N_0 + \frac{1}{2})\pi \quad (3.41)$$

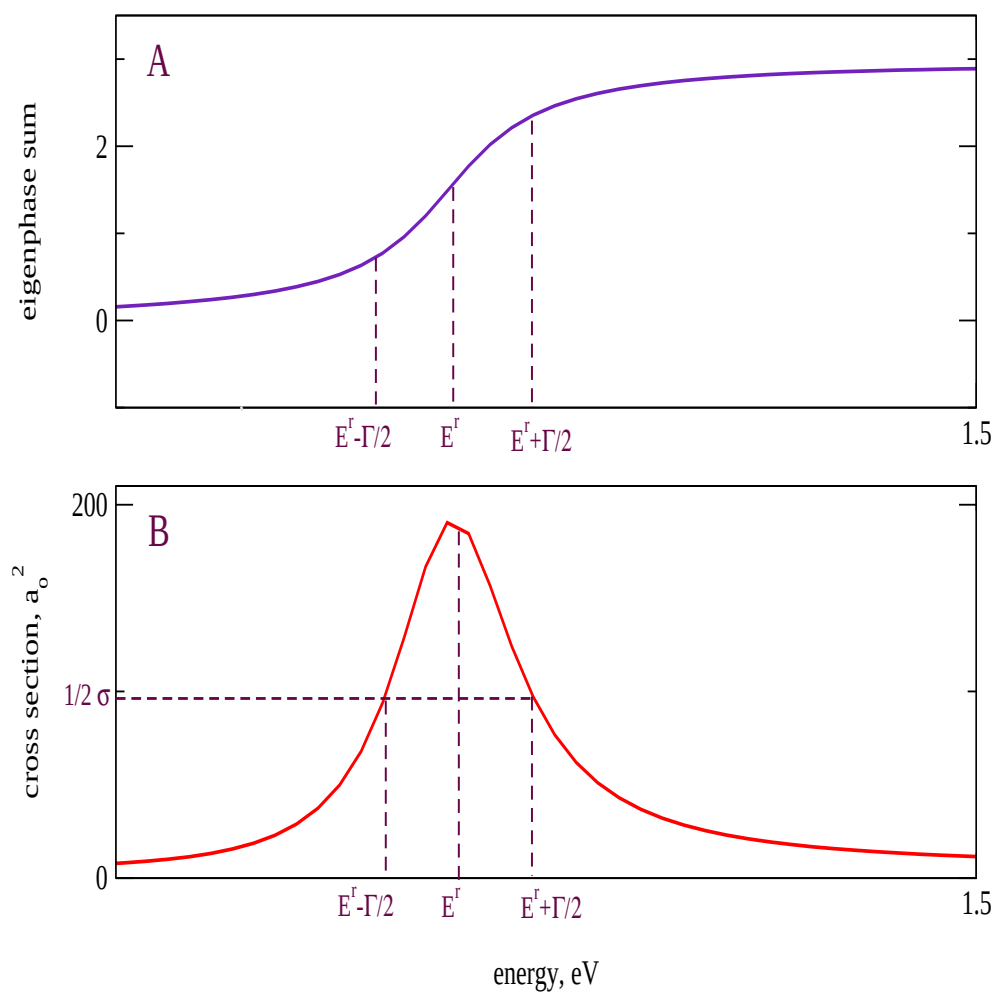


Figure 3.6: Graph A presents the eigenphase sum for the $^2B_1$ symmetry for the ($CF_2 + e^-$) system plotted at equilibrium geometry of the CF_2 . Graph B presents the corresponding contribution of the $^2B_1$ symmetry to the total elastic cross section. Both graphs present the $^2B_1$ resonance. The energy scale is expanded to show only a range of energies about E^r .

Levinson's theorem is fairly general and has many potential applications in various fields of physics (Jauch 1957, Newton 1960, Polyatzki 1993). This theorem could not be applied to the present research as in the R-matrix calculations the eigenphase sum η is normally obtained modulo π .

Consider scattering by spherical potential and call f_l the contribution of the l_{th} partial wave to the scattering amplitude. Also assume that the contribution of the other partial waves to the scattering amplitude can be completely neglected, then the full scattering amplitude in the vicinity of $E = E_r$ can be written as (Bransden & Joachain 1983)

$$f \simeq \frac{2l+1}{k} \frac{\Gamma/2}{E_r - E - i\Gamma/2} P_l(\cos \theta) \quad (3.42)$$

and the corresponding differential cross section is

$$\frac{d\sigma}{d\Omega} \simeq \frac{(2l+1)^2}{k^2} \frac{\Gamma/4}{(E_r - E)^2 + \Gamma^2/4} P_l^2(\cos \theta) \quad (3.43)$$

where $P_l(\cos \theta)$ is a Legendre polynomial and k is the wave number of the incident particle. This situation corresponds to a 'pure resonance' (Bransden & Joachain 1983). For any scattering angle θ the 'pure resonance' differential cross section (3.43) exhibits a sharp peak of width Γ about the resonance energy $E = E_r$. Integrating (3.43) over the scattering angle, the 'pure resonance' total cross section is

$$\sigma_{tot} \simeq \sigma_l = \frac{4\pi(2l+1)}{k^2} \frac{\Gamma/4}{(E_r - E)^2 + \Gamma^2/4} \quad (3.44)$$

This total cross section is called the Breit-Wigner formula. It is worth stressing that a 'pure resonance' is an idealisation. In real situation it is necessary to take into account the contribution of the other (non-resonant) partial waves to the scattering amplitude and the complex structure of the particles involved into the collision. This is the background of equation (3.38).

Resonances can be classified as shape, core-excited or nuclear-excited resonances. The first two types of resonances occur for atoms and molecules. Nuclear excited resonances occur exclusively for molecules.

Shape resonances are characterized as a one-electron phenomenon and occur when the scattering electron is trapped by the effective potential, created by a target, before tunnelling out (figure 3.7 A). This potential is a combination of the attractive polarization potential and centrifugal repulsive potential ($l(l+1)/r^2$). Shape resonances are normally associated with

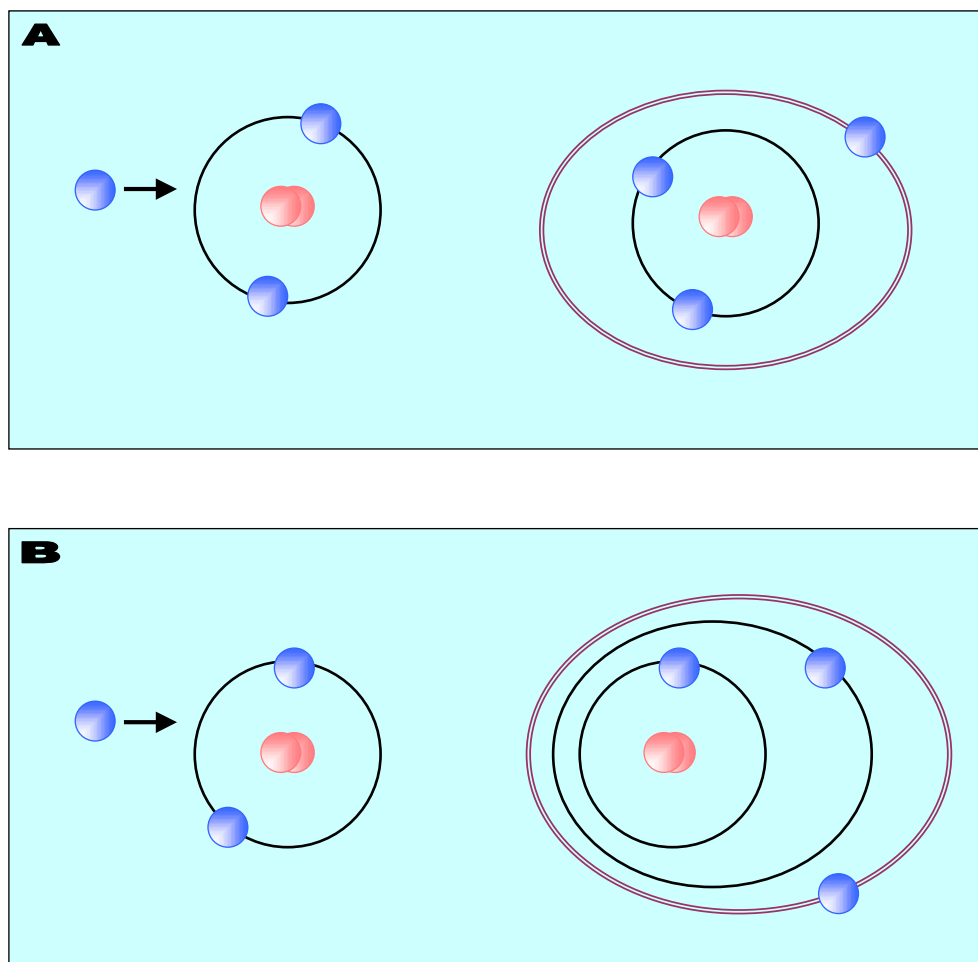


Figure 3.7: Diagrammatic representation of shape and core-excited resonances. Top diagram presents a shape resonance. Bottom diagram presents a core-excited resonance.

the ground state of the target and appear a few eV above the ground state threshold. They are normally broad and have short lifetimes (and hence no vibrational structure) as they can decay easily back into the ground state. This type of resonance does not occur for s-waves, $l = 0$. Low lying shape resonances can form a bound state when the molecule is pulled apart providing a route for dissociative attachment.

Core-excited resonances occur when the scattering electron excites the target molecule to an electronically excited state and becomes trapped or forms a bound state. These resonances are associated with excited states where one electron is in an orbital of the field produced by the excited target state (figure 3.7 B). There are two types of core-excited resonance: Feshbach and core-excited shape resonances.

Feshbach resonances (or closed-channel) (Feshbach 1958, Feshbach 1962) are associated with parent single excited states that have a positive electron affinity. The resonance lies below its parent and the resonance energy curve follows to the parent potential energy curve. The resonance is thus prevented from decaying into its parent by energy restrictions and must decay into lower target states. These resonances are normally long lived and narrow, and are possible for all partial waves. Feshbach resonances can not be modelled with a frozen target.

Core-excited shape resonances are associated with a single excited state which has parent negative electron affinity. The resonance lies above its parent. These resonances have some similarities with the ground state shape resonances as they can decay into all lower target states but normally decay preferentially into their parent excited state.

In the case of scattering by positively charged molecular ions, Feshbach resonances are to be expected because positively charged molecular ions have a positive electron affinity. For a neutral molecular target, any Rydberg excited states are also likely to have a positive electron affinity (Weiss & Krauss 1970) and Feshbach resonances would be also expected. Valence target states may have either positive or negative electron affinity and can result in either type of core-excited resonance. The difference between the two types of core-excited resonance is over simplified and for a molecule it is possible for a resonance to move between the two types as the nuclear separation changes.

Nuclear-excited resonances occur at low energy, when the $(N + 1)$ -electron system has a weakly bound state. By 'nuclear excitation' here one means vibrational excitation or nuclear

motion rather than excitation of a nucleus. These resonances are normally very narrow and low in energy. They always occur when a target is an ion and can only be studied by going beyond the Born-Oppenheimer approximation.

3.5 Reflection Approximation and DEA

Some low-lying resonances can lead to the breakdown of the target molecule through dissociative electron attachment (DEA). The resonance that may provide a route for DEA must become a bound state and be created with a sufficient energy to dissociate (see the energy balance equation (1.1)). Furthermore, the resonance must have a long enough lifetime to reach dissociation before autoionising. The fate of such low-energy resonances can be estimated using the Reflection Approximation.

Consider figure 3.8 . Potential energy curves for the neutral molecule and the negative ion

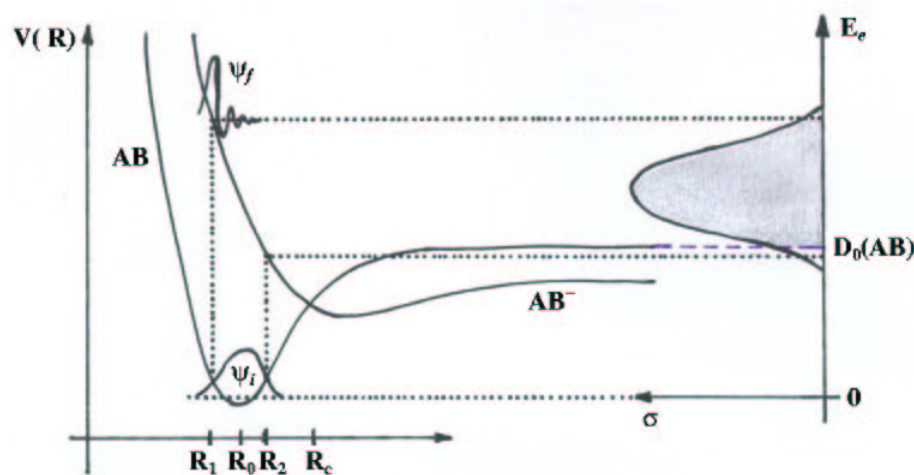


Figure 3.8: Schematic representation of the Reflection Approximation. Vertical axis: potential of the bonding in the molecule $V(R)$; horizontal axis: internuclear distance R .

are given by the curves AB and AB^- respectively. R_0 represents the mean nuclear separation in the ground state. The wavefunction Ψ_i , corresponding to the nuclear distance R_0 , has considerable density between R_1 and R_2 . Let's consider that the electron approaches the molecule

and becomes attached to it forming a temporary negative ion (TNI) $(AB^-)^*$ in an unchanged geometric shape. This process corresponds to a vertical transition from AB to AB^- and the electronic energy must match the vertical energy gap between the states. The TNI $(AB^-)^*$ is very unstable, therefore its energy is not well defined. In the region $R > R_c$ the TNI becomes a stable anion with the well-defined potential energy curve, as there are no transitions from the TNI to the neutral molecule.

The technique of the Reflection Approximation lies in the projection of the crossing points of the vibration wavefunction Ψ_i ($v = 0$) from the ground state potential energy curve of the molecule AB onto the potential energy curve of the negative ion AB^- . Then the projected points are again projected onto the vertical axis E_e . This gives the cross section as a function of energy, $\sigma(E_e)$, accessible in electron attachment experiments. Formally, the cross section emerges from a reflection of the probability density $|\Psi_i|^2$ of the initial state of the target molecule at the potential curve of the temporary negative ion AB^- . This construction is therefore known as the Reflection Approximation.

Further, one can plot the dissociation energy $D_0(AB)$ on the energy axis. If the potential energy curve of the anion AB^- in its asymptotic limit corresponds to the dissociation energy, then the molecule can dissociate through DEA. If the dissociation energy is near the energy where the cross section $\sigma(E_e)$ has a maximum, then the probability for the molecule to undergo DEA is large. The shaded area in figure 3.8 represents the part of the resonance (temporarily negative ionic state AB^-) that will undergo DEA, the remaining part will form a stable negative ion AB^- . This description of the reflection approximation does not allow for the finite resonance width and is therefore not precise.

3.6 Outer region program modules

The outer region codes for the scattering of electron by diatomics and polyatomics molecules differ only in the interface programs INTERF and SWINTERF. The codes have been developed by Morgan unless otherwise stated.

A flow diagram for standard outer region calculations is shown in figure 3.9. The outer region suite of codes also contains some other programs which are not used in our calculations.

They will be described in the end of this section.

INTERF and **SWINTERF** provides the interface between the inner and outer regions. As an input this module uses data from the inner region: boundary amplitudes (MOS/SWEDMOS), eigenvalues and eigenvector of the $(N + 1)$ -electron Hamiltonian (SCATCI), target data (DENPROP) and possibly Buttle correction. It outputs two files required for further outer region calculations. First contains target properties, channel data and the overall symmetry of the system. Second contains data for the construction of the R-matrix and the coefficients of a multipole expansion of the long range scattering potentials.

RSOLVE takes the output data from INTERF/SWINTERF and constructs the R-matrix, solves the outer region scattering equations (3.29) and constructs K-matrices for the specified energies. It uses subroutine RPROP (Baluja et al. 1982, Morgan 1984a) to propagate the original R-matrix out to an asymptotic region. Then the K-matrices are calculated using subroutine CFASYM (Noble & Nesbet 1984).

EIGENP diagonalizes the K-matrices, generated by RSOLVE, to obtain eigenphase sums using (3.33).

RESON searches the eigenphase for resonances (Tennyson & Noble 1984). It reads energy points and corresponding eigenphases, then it constructs numerically the second derivative $d^2 E/d\eta^2$ and searches it for changes from positive to negative sign. This information is used to construct a grid of points on which to calculate eigenphases. Then it fits the eigenphase sums to Breit-Wigner profile.

TMATRIX calculates the T-matrix from the K-matrix. For adiabatic vibrational calculations, it has the option to average a set of T-matrices at different bond lengths over vibrational functions which are input separately, although this has not been used in the present work. The T-matrices can then be used by IXSECS and DCS (Malegat 1990) which calculate integral and differential cross sections respectively.

BOUND solves the scattering problem with bound state boundary conditions to obtain true bound state energies and wavefunctions of the $(N + 1)$ system. The algorithm used by BOUND (Sarpal et al. 1991, Branchett & Tennyson 1992) was originally developed for atomic problems (Seaton 1985).

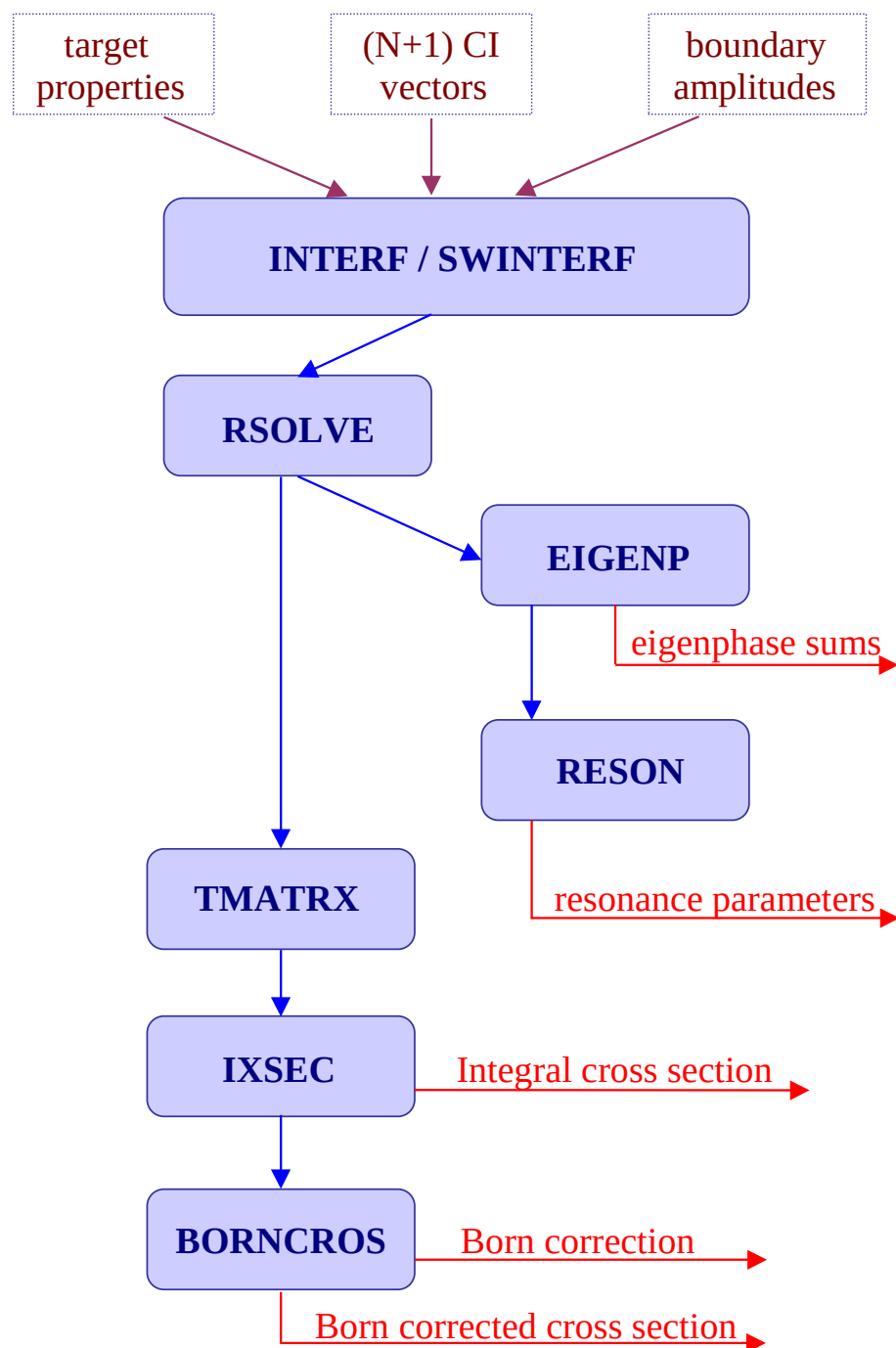


Figure 3.9: Flow diagram for the outer region scattering calculation. The interfaces modules INTERF and SWINTERF are used for scattering by diatomics and polyatomics targets respectively. In case of electron scattering by diatomics, INTERF also requires the Buttle correction.

IXSECS calculates the integral cross sections using the T-matrices produced by the module **TMATRIX**.

BORNCROS calculates the Born corrections and adds them to the total integral cross section. It also has an option to sum the integral cross sections of different total symmetries calculated by **IXSECS** to produce the total integral cross section.

Other modules, such as **MQDT**, which calculates multichannel quantum defects, and **RATES**, which gives the integration of collision strengths over a Maxwellian temperature distribution, are also available.

3.7 Practical use of the R-matrix codes

The UK R-matrix codes are well documented and can be found on the web site

<http://www.tampa.phys.ucl.ac.uk/rmat>.

Initially, the R-matrix calculations, described in this work, were performed on a 2-processor *alpha* computer called 'Scatter' and various LINUX desktop machines. When more computer resources became available, I transferred the molecular R-matrix codes to the 32-processor (4Gb each processor) *Sun v880 computer cluster 'Ra'*, where all further calculations were carried out. This allowed us to perform much larger calculations and to run them in parallel.

The R-matrix codes were written by many physicists in FORTRAN. In order to make our codes more portable between different platforms, the NAG routine libraries in the N and $(N + 1)$ -electron codes and the interface modules **INTERF**/**SWINTERF** were replaced with freely available LAPACK, BLAS and LINPACK libraries which can all be found on www.netlib.org. This substitution has also made R-matrix codes faster. The correspondence between the libraries is shown in table 3.1. LAPACK and LINPACK routines require the BLAS library. NAG library routines in all the other codes, not presented in table 3.1, were replaced with BLAS routines.

In order to adapt the R-matrix codes for the scattering calculations on CF_x , I changed some modules. Thus, an option to store more than one set of NOs was implemented in module **PSN**. Parameter *buf* in **MOS**, specifying the size of the array for the molecular orbitals, was increased to 5000. These changes were important for the electron scattering calculations on CF. **SWEDMOS** was updated in order to let the user input externally generated molecular orbitals.

Program	NAG	LAPACK	LINPACK
SCATCI, SWEDMOS, PSN	f02faf	dsyev	
	f03aaf		dgedi
MOS	f04arf	dgesv	
	f03aaf		dgedi

Table 3.1: Substitution of NAG routines with LAPACK and LINPACK.

This can now be done *via* parameter *VMORB*. An option to smooth the eigenphase sums, was implemented in the module EIGENP. The modules SWINTERF/INTERF were changed in order to adapt them to Sun computer clusters. I also wrote the module BORNCROS, which sums the cross sections of different total symmetries, calculates the Born correction (Chu & Dalgarno 1974, Gibson et al. 1987) and adds it to the summed cross section. The part of this module, which calculates the Born correction, is based on the original program written by K. L. Baluja (private communications). An option to switch between the Born corrections for the elastic and excitation cross sections was implemented into BORNCROS.

As our Sun computer cluster does not have NAG routine libraries, all the inner region calculations and interface modules are run on 'Ra'. Then the files, holding the R-matrix data and channel data, are transferred to 'Scatter' or a LINUX desktop, where further outer region calculations are carried out. It is important to note that the channel and R-matrix data must be formatted. Care needs to be exercised when compiling the R-matrix codes on SUN computer clusters, as some modules are sensitive to optimization flags. Thus, all the modules described in this work were compiled on 'Ra' using a combination of two optimization flags *-fast* and *-xtarget=ultra3cu* for maximum performance. CONGEN, SWSCF and SWFJK were compiled using only one flag *-xtarget=ultra3cu*. For a description of individual flags see Fortran User's Guide in Sun Product Documentation (<http://docs.sun.com>)

3.8 Other methods used in scattering calculations

The R-matrix approach is a variational method, based on the variational principle for the eigenphase sums: calculations with high lying eigenphases give better results. The Buttle correction, used in the diatomic R-matrix calculations, is a perturbative correction, that makes this

approach almost variational. One of the advantages of the R-matrix method is that it can perform repeated calculations as a function of scattering energy almost for free. This means that calculations for many scattering energies with the same symmetry do not take extra time.

Low-energy electron-molecule collisions can be treated using different methods. In this section I discuss briefly the advantages and disadvantages of Kohn variational principle and Schwinger multichannel methods. These methods are based on variational principles - stationary principles for the scattering amplitude or some related quantity (Winstead & McKoy 2000). Although variational methods are the most computationally demanding, they are also the most accurate, as they make fewer approximations than some other methods (Huo & Gianturco 1995).

The variational procedure of Kohn (1948) is based on the variational expression involving the Hamiltonian operator H and an operator describing the scattering: T operator or the related reactance K or scattering S operator. The Kohn expression is designed so that the part of this expression that depends on H (a matrix element between two approximate wavefunctions) approaches zero quadratically as those wavefunctions approach the exact scattering wavefunctions, while the remaining part approaches the exact T-matrix (or S- or K-matrix) element. As in other variational methods, the trial wavefunction is taken as a linear expansion

$$\Psi = \sum_i x_i f_i, \quad (3.45)$$

where f_i are known functions and x_i are the variational parameters. Mathematical techniques are then applied to locate the stationary points. The approximate wavefunction must behave appropriately at large distances from the molecule - as an electronic wavefunction for the target molecule times the wavefunction of an incident electron with the proper kinetic energy and direction of propagation. To satisfy this boundary condition, new basis functions must be introduced. Procedures for evaluating the Hamiltonian matrix elements, involving these new basis functions, must be developed (McCurdy & Rescigno 1989, Rescigno, McCurdy & Orel 1995, Winstead & McKoy 2000). The most severe difficulties in evaluating these matrix elements are the treatment of exchange integrals, which give rise to six-dimensional integrals. The principal advantage of the Kohn method lies in avoiding the computation of Green's function matrix elements and in the fact that it involves only matrix elements of the Hamiltonian and the electron-molecule interaction.

The Kohn method has been successfully applied to a number of small molecules (Resigno, Lengsfeld & McCurdy 1995) and to linear molecules. Studies of polyatomics, such as NF_3 (Resigno, McCurdy & Orel 1995) and CF_4 (Isaacs et al. 1998), using the Kohn method have also been reported.

Similar to Kohn and R-matrix methods, the Schwinger multichannel (SMC) method (Schwinger 1947, Takatsuka & McKoy 1981, Takatsuka & McKoy 1984) employs a variational technique to obtain an approximation to the scattering amplitude. As opposed to the Kohn principle, the SMC principle involves complicated matrix elements of the Green's function for the electron-molecule system and matrix elements of the electron-molecule interaction itself. Evaluation of the Green's function matrix elements is the most difficult and time consuming task, and therefore, the major obstacle to the application of Schwinger-type methods (Winstead & McKoy 2000).

The main advantage of the Schwinger variational expression is that all matrix elements (and Green's function) involve the electron-molecule interaction, which vanish at large distances. Therefore, short-range basis functions that vanish asymptotically can be used. In contrast to the Kohn and R-matrix methods, the trial wavefunctions do not need to satisfy any specific boundary conditions, as they are incorporated through the Green's functions. Also, the wavefunction always appears together with the potential and a trial basis needs only to cover the region of space where V does not vanish. Overall, the SMC method is one rank higher than the Kohn method and gives a better convergence (Takatsuka et al. 1981, Taylor 1983, Huo & Gianturco 1995).

The SMC method has been successfully applied to the treatment of many molecules that are important for plasma etching. Thus, Bettega (2000) studied low-energy electron scattering by boron trihalides (BCl_3 , BBr_3 and BI_3), that have been widely used in processes of dry etching of thin films and semiconductors. Bettega et al. (2001) also studied pentafluoroethane (C_2HF_5), that was considered among other hydrofluorocarbons as precursor gas in the plasma deposition of polymeric fluorocarbon layers, used as low-dielectric-constant insulators (Agraharam et al. 1999). The elastic differential cross section for the CF_3 radical, that has the greatest concentration and importance among CF_x in CF_4 plasma, was obtained by Diniz et al. (1999). Varella et al. (2002) investigated low-energy electron scattering by fluoromethanes (CH_3F , CH_2F_2 , CHF_3 and CF_4), important in the modelling of low-temperature

plasma, and derived differential cross sections. All these calculations are limited, as they were performed at Hartree-Fock self-consistent field level.

Most of the radicals, present in low-temperature plasma, are highly reactive. As a result, experimental measurements of the cross sections are a very difficult task (Tarnovsky & Becker 1993, Yamada & Hirota 1983). Consequently, *ab initio* methods, described in this section, play a significant role in providing the necessary data for plasma modelling.

Chapter 4

Electron collisions with the CF radicals

In this chapter, the R-matrix methods is used to treat electron collisions with the diatomic radical CF as a function of internuclear separation, R . These calculations concentrate on obtaining low energy (less than 10 eV) elastic and excitation cross sections for the ground $X^2\Pi$ state and five lowest lying electronically excited states $a^4\Sigma^-$, $A^2\Sigma^+$, $B^2\Delta$, $C^2\Sigma^-$ and $b^4\Pi$, with vertical excitation energies in the range of 2.86 - 10 eV. Special measures are used to treat the $A^2\Sigma^+$ state, which is Rydberg-like for $R < 2.6a_0$.

4.1 Introduction

The CF radical was first observed spectroscopically by Andrews & Barrow (1950) and has since been the subject of considerable experimental and theoretical interest because this molecule and its ions are present in fluorocarbon plasmas used to etch or modify silicon semiconductor devices (Faber & Malley 1992).

The equilibrium geometry of CF was derived from analysis of its emission spectrum (Porter et al. 1965, Carroll & Grennan 1970). According to these studies the CF has a bond length $2.44 a_0$ at equilibrium. *Ab initio* calculations on the geometry of CF, performed at multireference configuration interaction (MRCI) level (Hess & Buenker 1986, Rendell et al. 1989), are in good agreement with the experimental values and among themselves.

Several studies of the low-lying states of CF have been reported in the literature (Dunning et al. 1979, Hall & Richards 1972, Grieman et al. 1983, Petsalakis 1999). The earliest theoretical investigation of the low-lying electronic states of the CF was performed by Hall & Richards (1972), who also studied the $A\ ^2\Sigma^+$ state predissociation. It has been shown that $A\ ^2\Sigma^+$ is a Rydberg state in which the unpaired π electron has been promoted to the lowest unoccupied σ orbital (Carrington & Howard 1970). The lowest excited $a\ ^4\Sigma^-$ was predicted by White et al. (1979). Grieman et al. (1983) located experimentally the $a\ ^4\Sigma^-$ state of CF and investigated its role in the predissociation of the $A\ ^2\Sigma^+$ state. Rendell et al. (1989) showed that both the $A\ ^2\Sigma^+$ and $B\ ^2\Delta$ are metastable species dissociating to $C(^3P) + F(^2P)$. Valence and Rydberg states of CF were studied in detail by Dunning et al. (1979) at the HF level and by Petsalakis (1999) using the MRCI method with the aid of quantum defect theory. These studies yielded information on several valence and Rydberg states of the CF radical and their potential energy curves. These potential energy curves show crossings at large internuclear distances (R) between valence states with different dissociation limits and at short R crossings with Rydberg states. So far, no data on the $b\ ^4\Pi$ state of the CF have been reported.

The ground state dipole moment of the CF radical estimated from Stark effect by Saito et al. (1983) is 0.645 ± 0.014 Debye (1Debye = 0.3937 a.u.). This result agrees with the value 0.65 ± 0.05 Debye obtained by Carrington & Howard (1970) and by Byfleet et al. (1971).

The total electron impact ionization cross section for the CF radical was measured by Tarnovsky & Becker (1993) and Tarnovsky et al. (1993) in the energy range from 10 to 200 eV. *Ab initio* calculations which derive the electron impact ionization cross section for CF were performed by Bobeldijk et al. (1994) and Deutsch et al. (2000) using the semiclassical Deutsch-Märk formalism. These calculations showed some disagreement between the measured and calculated cross sections, as the calculated cross sections are significantly higher than the experimental ones.

In 2002 Lee et al. (2002) studied electron-free-radical scattering in the energy range (1-500) eV using a complex optical potential to represent the electron-molecule interaction dynamics and Schwinger variational iterative method combined with the distorted-wave approximation to solve the scattering equations. Lee et al. (2002) calculated elastic differential, integral (ICS), and momentum-transfer (MTCS) cross sections as well as grand total (elastic and inelastic) and absorption cross section and compared their results with experimental and theoretical

data for electron collisions with NO (which is an isoelectronic molecule of CF). Their ICS and MTCS show a shape resonance at around 15 eV. They found a very good agreement between the ICS and the MTCS for electron scattering by CF and NO for incident energies above 20 eV. No experimental or theoretical data on low-energy collisional integral cross sections for the CF radical have been reported.

4.2 Target representation

CF is an open shell, diatomic molecule with 15 electrons. The ground state of the CF is a $X^2\Pi$ state with the electronic configuration $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 2\pi^1$.

The target calculations were carried out on the six low lying states of CF which are $X^2\Pi$, $a^4\Sigma^-$, $A^2\Sigma^+$, $B^2\Delta$, $C^2\Sigma^-$ and $b^4\Pi$, using an equilibrium value for a C-F bond length $R_e = 2.44 a_0$. The basis set of Slater type functions consisted of 24σ and 14π functions equally distributed on the two nuclei (table 4.1). In order to describe the Rydberg state $A^2\Sigma^+$, the

Carbon ^a				Fluorine ^b			
orbital	ζ	orbital	ζ	orbital	ζ	orbital	ζ
1s	9.25	2p π	6.53	1s	7.94374	2p π	1.35836
1s	5.54	2p π	2.61	1s	14.10946	2p π	2.32912
2s	5.31	2p π	1.44	2s	1.93465	2p π	4.26145
2s	2.04	2p π	0.96	2s	3.25633	2p π	9.29742
2s	1.31	3d π	2.35	3s	9.92540	3d π	1.83539
2p σ	6.53	3d π	1.24	2p σ	1.40701	3d π	3.36796
2p σ	2.61	4f π	2.35	2p σ	2.37325	4f π	2.79365
2p σ	1.44			2p σ	4.27843		
2p σ	0.96			2p σ	8.97251		
3d σ	2.35			3d σ	1.83539		
3d σ	1.24			3d σ	3.36796		
4f σ	2.35			4f σ	2.70010		

Table 4.1: Original Slater type basis set for the CF radical.

^aFrom Cooper & Kirby (1987).

^bFrom McLean & Yoshimine (1967)

basis set was supplemented with up to two σ and two π functions with diffuse exponents on each atom, which are called 'Rydberg basis functions' below. Although, the excited states $2-4^2\Sigma^+$, $2^2\Delta$, $3^2\Delta$ and $2-5^2\Pi$ have vertical excitation energies below 10 eV (Petsalakis 1999), these states are not included in present calculations because they are Rydberg-like and require a large number of diffuse orbitals. It is numerically and computationally impractical to include large numbers of diffuse orbitals (ie. those with very small exponents) as they will require a very large R-matrix sphere. Neglecting Rydberg states can result in unphysical pseudo-resonances at collision energies above about 5 eV; the exact energy is geometry-dependent.

basis	orbitals on Carbon		orbitals on Fluorine	
	3s	3p σ	3s	3p σ
A ^a	0.5856, 0.30	0.4855, 0.24	1.77, 0.73	1.48, 0.54
B	0.5856, 0.40	0.4855, 0.30	1.77, 0.73	1.48, 0.54
C	0.5856, 0.44	0.4855, 0.38	1.77, 0.73	1.48, 0.54
D	0.5856	0.4855	1.77	1.48

Table 4.2: Exponents for the Rydberg basis functions 3s and 3p σ on C and F atoms.

^aFrom Cooper & Kirby (1987).

The target calculations consisted of two parts. Valence state-averaged natural orbitals (NOs), obtained from 'all singles and doubles' configuration interaction (CI) calculations for all six target states, were used for treating the valence target states. Valence NOs were obtained from single and double excitation CI calculations using orbital space spanned by valence basis functions (table 4.1). The number of configurations, used to build valence NOs, is 103 124 for the X $^2\Pi$ state, 46 124 for the quartet symmetry and around 65 000 for each other state of doublet symmetry. The Rydberg Slater type basis functions were not included on this stage of the calculations.

For a description of the Rydberg state A $^2\Sigma^+$ it was necessary to include Rydberg molecular orbitals in the wavefunctions. Rydberg molecular orbitals were obtained from Rydberg natural orbitals for Σ symmetry, following the prescription of Cooper & Kirby (1987). They were constructed from single-excitation configuration interaction (CI) calculations with 31 088 configurations, with all possible arrangements of ten valence electrons and one electron excited

into a separate Rydberg orbital space ($7\sigma - 14\sigma$ $3\pi - 6\pi$). In final target calculations the molecular orbitals were partitioned into three spaces: core orbitals ($1\sigma 2\sigma$), valence orbitals ($3\sigma \dots 6\sigma$ $1\pi 2\pi$) and Rydberg orbitals (7σ 3π). The valence, state-averaged NOs were used to calculate core and valence molecular orbitals. Rydberg NOs were first orthogonalized to the other target orbitals and then used for calculation of Rydberg molecular orbitals. The final complete active space configuration interaction (CASCI) model, therefore, consisted of two types of configurations:

$$(1\sigma 2\sigma)^4 (3\sigma \dots 6\sigma \ 1\pi 2\pi)^{11}$$

and

$$(1\sigma 2\sigma)^4 (3\sigma \dots 6\sigma \ 1\pi 2\pi)^{10} (7\sigma 3\pi)^1.$$

Considerable care must be taken when choosing the Rydberg orbital space. Too many diffuse orbitals can lead to problems with linear dependence in the N-electron target calculations which are even more severe in the (N+1) scattering calculations.

Several basis sets with different exponents for the Rydberg basis functions $3s$ and $3p\sigma$ on C atom were tested in the course of this work (table 4.2). Basis B did not give good vertical excitation energies. Target properties obtained using basis functions A and C are in a good agreement with the experimental and theoretical data at equilibrium geometry. At non-equilibrium geometries basis C gives severe linear dependence for $R < 2.0 a_0$ and basis A gives a strong orbital crossing at $R = 2.7 a_0$, which could not be removed. Finally, the basis D with only four added Rydberg basis functions was chosen, as this model gives the most stable results at different R matrix radii and satisfactory excitation energies. Table 4.3 compares the vertical excitation energies for the states considered in present calculations on CF with data available in the literature. The CASCI model, described above, gives the ground state dipole moment of 0.64 Debye. This value is in very good agreement with the experimental value of Saito et al. (1983) 0.645 ± 0.014 Debye.

The target model, described above for the equilibrium geometry, was also used for the calculation of target properties at non-equilibrium geometries. Electronic state energies for the CF radical as a function of changing a C-F bond are plotted in figure 4.1. The profiles of the energy curves for the states $X \ ^2\Pi$, $A \ ^2\Sigma^+$, $B \ ^2\Delta$ and $C \ ^2\Sigma^-$ are in agreement with results of Petsalakis (1999), who studied all the doublet electronic states of the CF using MRCI calculations. The $a \ ^4\Sigma^-$ state energy curve is generally comparable with the potential energy

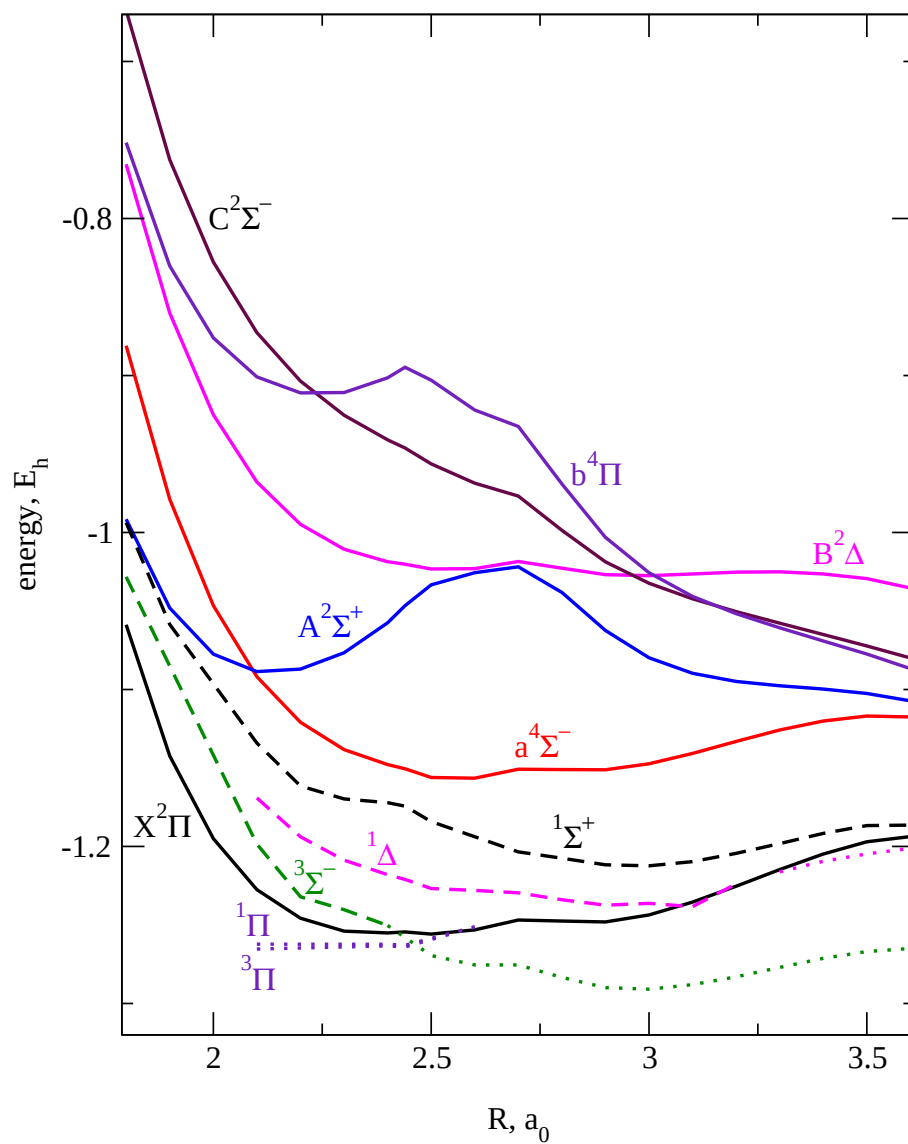


Figure 4.1: Electronic state energies of CF as a function of changing C-F bond length (R), solid lines. The dashed lines represent the $CF + e^-$ system resonance energy curves; the dotted lines below the ground state curve represent the CF^- bound state curves. -136.00 should be added to the energy entries.

State	Dominant configuration	This work			Theory	Observed
		N	Δ	E	Δ	Δ
X $^2\Pi$	$1\sigma^2 \dots 5\sigma^2 1\pi^2 2\pi$	1786	0	-137.2544	0	0
a $^4\Sigma^-$	$5\sigma^{-1} 2\pi$	797	2.83		$2.9^a / 2.66^b$	-
A $^2\Sigma^+$	$2\pi^{-1} 6\sigma$	1072	5.65		5.65^c	5.293^d
B $^2\Delta$	$5\sigma^{-1} 2\pi$	1100	6.37		6.36^c	6.125^d
C $^2\Sigma^-$	$2\pi^{-1} 6\sigma$	1016	8.39		7.96^c	-
b $^4\Pi$	$5\sigma^{-1} 6\sigma$	1269	9.79		-	-

Table 4.3: Excitation energies Δ (in eV) for the CF target states generated at equilibrium geometry. Also given are the dominant configuration of each state and the number of configurations N in the calculations. The absolute energy E (in Hartree) of the ground state is also given. Calculated vertical excitation energies are given in column Theory; experimental adiabatic excitation energies are given in column Observed.

^aFrom Hall & Richards (1972).

^bFrom Dunning et al. (1979).

^cFrom Petsalakis (1999).

^dFrom Huber & Herzberg (1979).

curve for the same state derived from *ab initio* calculations by Luque et al. (2003). There are no data on the absolute and excitation energies for the b $^4\Pi$ state of the CF available in the literature.

At bond lengths below $2.6 a_0$ the potential energy curve of the excited Rydberg A $^2\Sigma^+$ state follows the ground state potential energy curve of the CF⁺ cation and has a Rydberg-like shape (Petsalakis 1999). However, the character of this state changes from Rydberg to valence at a C-F bond length $2.6 a_0$. This can be explained by considering the second Rydberg-like $2^2\Sigma^+$ state, not included in present calculations. The first $^2\Sigma^+$ state is characterised by a single configuration, with an open shell in the 6σ orbital, which has Rydberg *s* character at bond lengths below $2.6 a_0$. At larger bond lengths 6σ passes the Rydberg *s* character to the next σ orbital, which has Rydberg *p* character at shorter bonds, and takes the valence character. Therefore, the shape of the Rydberg A $^2\Sigma^+$ state energy curve results from an avoided crossing with the second Rydberg $^2\Sigma^+$ state (Petsalakis 1999). The B $^2\Delta$ potential energy curve has a weak maximum at a bond length around $3.5 a_0$. This is a result of an avoided crossing with the second repulsive $^2\Delta$ state (Petsalakis 1999). It should be noted that b $^4\Pi$ potential energy curve also have a double well structure. From the analysis of the CF potential energy curves, the b $^4\Pi$ state shows a behaviour similar to that of the Rydberg A $^2\Sigma^+$ state and may also be

Rydberg-like. The shape of the $b\ ^4\Pi$ potential energy curve at $R \sim 2.5\ a_0$ probably results from an avoided crossing.

The potential energy curves presented in figure 4.1 show a weak structure at a bond length $2.7\ a_0$ for most of the states of CF. This structure is caused by a crossing of 6σ and 7σ orbitals in the orbital set, which could not be removed.

4.3 Scattering model

The final calculations used the six states given in table 4.1. Since CF is an open shell radical with the ground state $X\ ^2\Pi$, two spin-specific scattering schemes, the singlet and triplet couplings, between the scattering electron and the isolated 2π electron of the target are considered in this study.

Test calculations for several R-matrix radii ($a = 10\ a_0$, $12\ a_0$ and $13\ a_0$) were performed to test the stability of the model and assign resonances. The R-matrix radius $10\ a_0$ is too small for scattering calculations on CF. This caused weak linear dependence in the $(N+1)$ calculations in almost all of the states of CF, that was partially cured by removing one π orbital using Lagrange orthogonalization (Tennyson et al. 1987). With $10\ a_0$ all results showed significant unphysical structure which was attributed to the target wavefunctions leaking outside the R-matrix sphere. Tests, using $a = 12\ a_0$ and $a = 13\ a_0$, showed that the structure largely disappeared. All calculations show strong dependence of the excitation cross section $X\ ^2\Pi \rightarrow A\ ^2\Sigma^+$ on the R-matrix radius (figure 4.2). All other cross sections are much less dependent upon the R-matrix radius. The final calculations used the R-matrix radius of $13\ a_0$ and propagation to a radius of $80.1\ a_0$, as this model does not give any linear dependence.

In all calculations, the continuum basis functions were represented by numerical orbitals of up to $l \leq 6$ partial waves, centred on the centre of gravity of the molecule. At $a = 13\ a_0$ continuum orbitals consisted of 82σ , 69π and 56δ orbitals that were orthogonalised to the target orbitals using only Schmidt orthogonalisation (Tennyson et al. 1987). The $(N+1)$ electron calculations must use a model which balances that of the CF target. The L^2 configurations χ_m in (3.14) are constructed from the target orbitals and contain the incident and target electrons placed in the target molecular orbitals. In this work the square integrable term consists of two

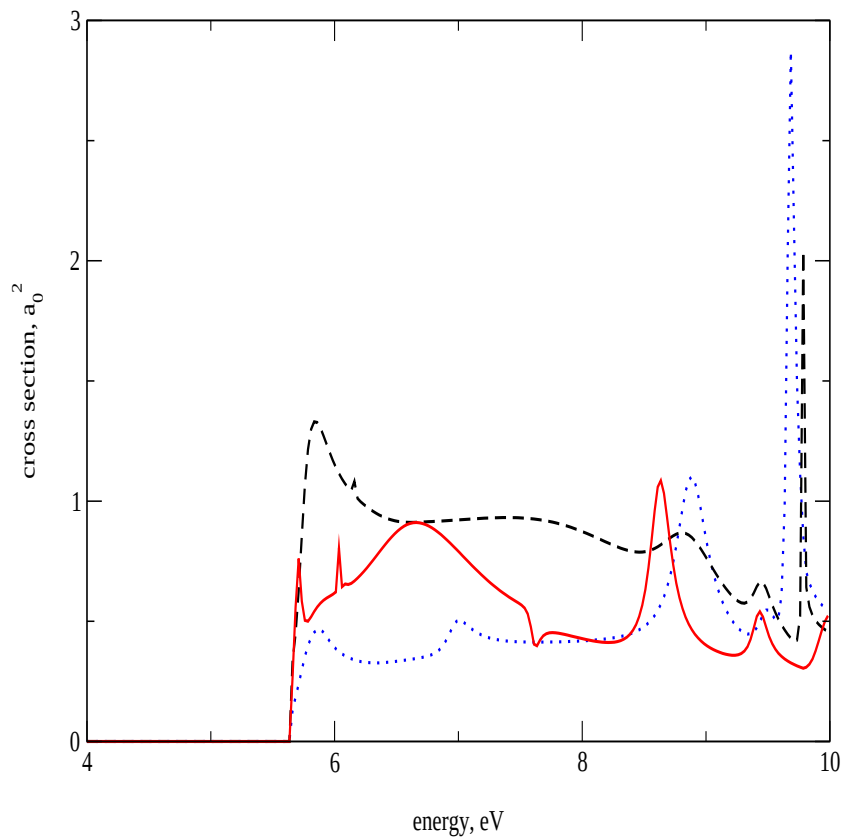


Figure 4.2: Total cross sections for electron impact excitation of the second excited Rydberg $^2\Sigma^+$ state plotted at different R-matrix radii. Dotted line presents the cross section calculated using the R-matrix radius $a = 10a_0$; dashed line presents the cross section at $a = 12a_0$; solid line presents the cross section at $a = 13a_0$.

types of configurations that allow for the relaxation of the orthogonality between the target and continuum molecular orbitals:

$$(1\sigma 2\sigma)^4 (3\sigma \dots 6\sigma \ 1\pi 2\pi)^{12}$$

and

$$(1\sigma 2\sigma)^4 (3\sigma \dots 6\sigma \ 1\pi 2\pi)^{11} (7\sigma 3\pi)^1.$$

CF is a polar molecule and, as was discussed in section 3.4, the elastic scattering cross section of a static molecule with a permanent dipole moment is divergent. A very large number of partial waves and rotational effects must be included in order to obtain convergent results. States with $l > 6$ omitted from present calculations were added using a Born correction (Chu & Dalgarno 1974). A Born correction depends on target properties and a number of partial waves included in the expansion of the scattering amplitude but does not depend on the radius of the R-matrix sphere. Tests showed that the maximum effect from using a Born correction was for the excitation to A $^2\Sigma^+$ and B $^2\Delta$ states at short bond lengths.

The range of scattering energies was restricted to energies below 10 eV, as this is the typical energies of electrons in etching plasmas. Resonance positions and widths were found by fitting the eigenphase sum to a Breit-Wigner profile, using *RESON* program (Tennyson & Noble 1984). Particular emphasis was given to resonances in the energy range below 5 eV. Such low-lying resonances can become bound and then dissociate. This can affect surface chemistry. Calculations, in which a C-F bond was stretched from $R = 1.8 a_0$ to $3.6 a_0$ in steps of $0.1 a_0$, were performed in order to study the dissociative behaviour of resonances.

4.4 Results

4.4.1 Elastic scattering

Elastic cross sections for the electron scattering off the CF radical were calculated at different geometries. Previous R-matrix calculations show disagreement between Born-corrected cross sections and experimental values at energies below 100 meV, as the calculated cross sections do not reproduce a sharp minimum observed in the experiments (see for example Baluja et al. (2001b)). According to Field et al. (2000), this structure is due to interference effects between

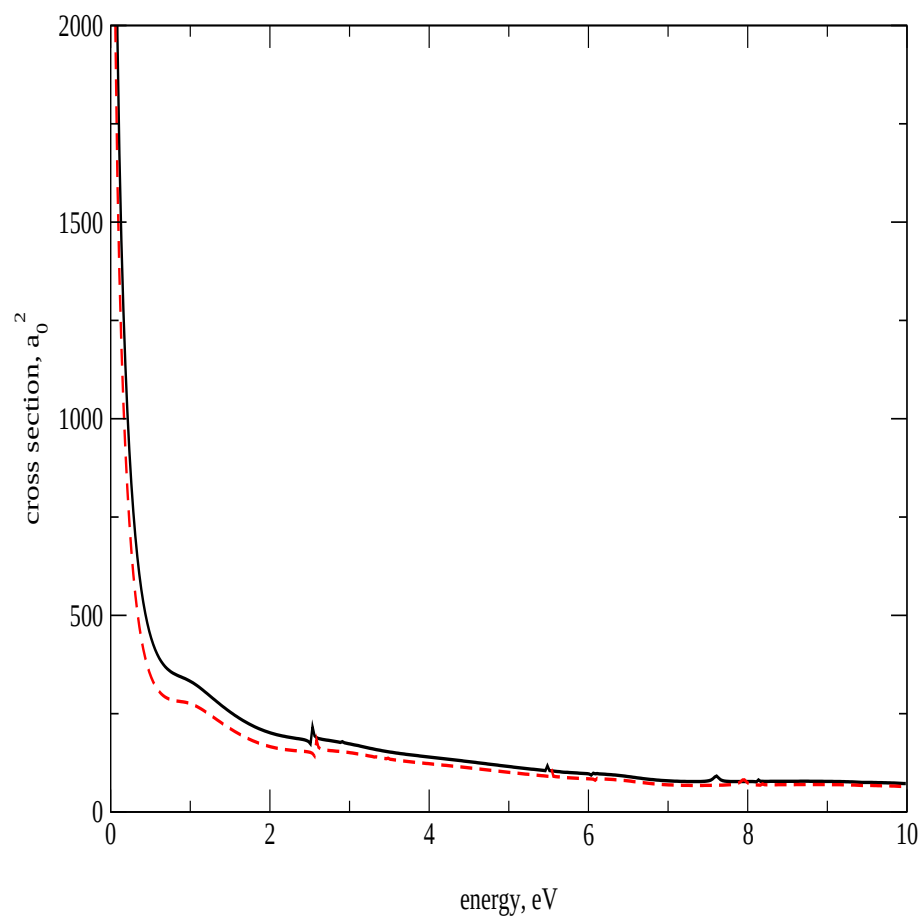


Figure 4.3: Total elastic cross section for the CF radical at equilibrium geometry. Dashed line represents the cross section without a Born correction. Solid line represents the cross section with added Born correction.

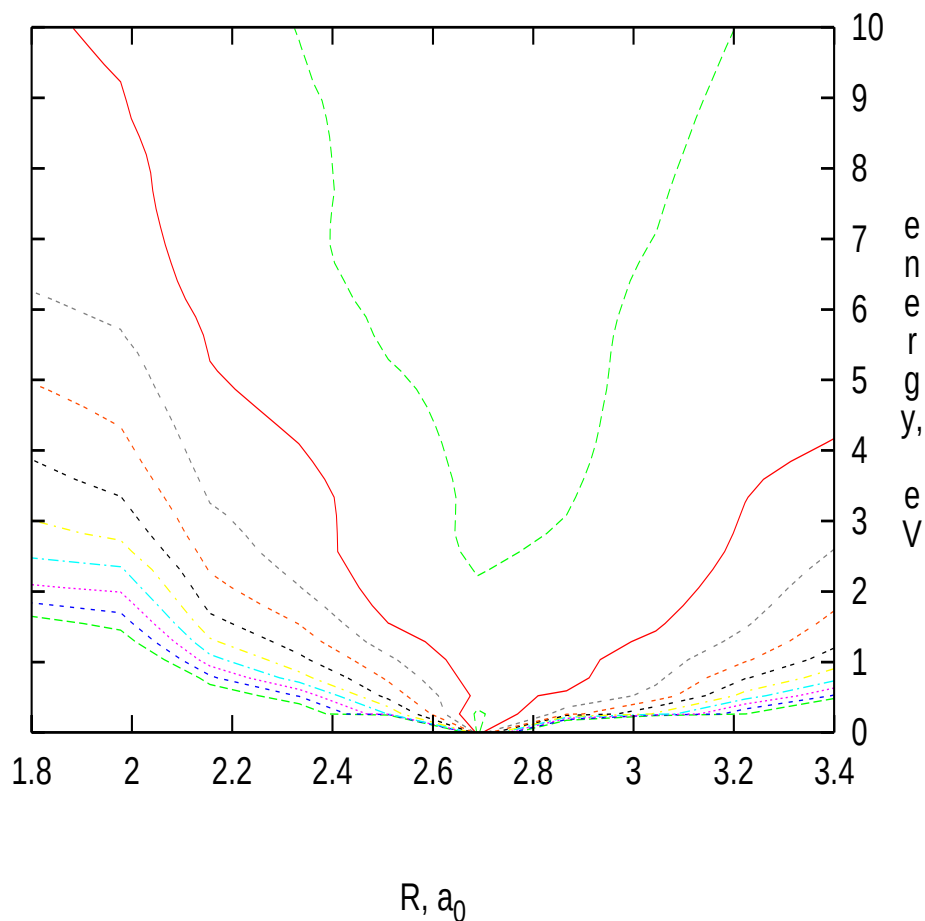


Figure 4.4: Contour plot of the total elastic cross sections for molecule CF plotted at different C-F bond lengths, R . Contours range from $90 a_0^2$ (top contour) to $900 a_0^2$ (bottom line) in steps of $90 a_0^2$.

rotational (and other) channels. The model used in present calculations does not include rotational coupling and, therefore, will not be reliable at these ultra low energies.

The resulting elastic cross sections for CF summed over all singlet and triplet symmetries for the 6-state model are shown in figure 4.3. It can be seen that the Born correction for the elastic cross section at the equilibrium geometry of CF is small. Figure 4.4 gives the contour plot of the Born corrected elastic cross sections at different bond lengths.

The main feature in the elastic cross section is the presence of three prominent resonances of symmetries $^1\Delta$, $^1\Sigma^+$ and $^3\Sigma^-$ (figure 4.5). At equilibrium geometry the $^1\Delta$ resonance has a position and width of 0.91 eV and 0.75 eV respectively. The corresponding parameters for

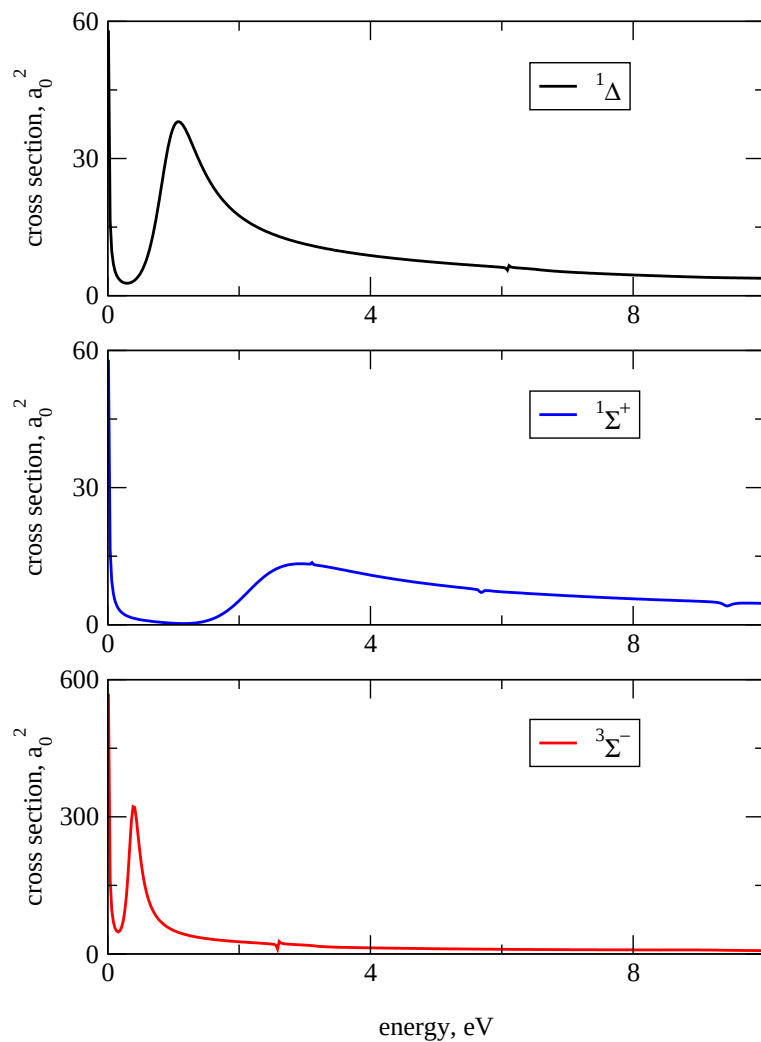


Figure 4.5: The top and middle graphs present $^1\Delta$ and $^1\Sigma^+$ contributions to the total elastic cross section respectively, plotted at the equilibrium geometry of CF. The bottom graph presents $^3\Sigma^-$ contribution to the total elastic cross section plotted at the CF bond length $2.3 a_0$. All the graphs illustrate shape resonances.

the $^1\Sigma^+$ resonance are 2.19 and 1.73 eV. The position of the $^3\Sigma^-$ resonance at equilibrium geometry could not be determined as it is very close to zero energy and the resonance is about to become bound. It will be discussed in the next subsection. The energies of these resonances as a function of a bond length are plotted in figure 4.1 and their widths in figure 4.6. As

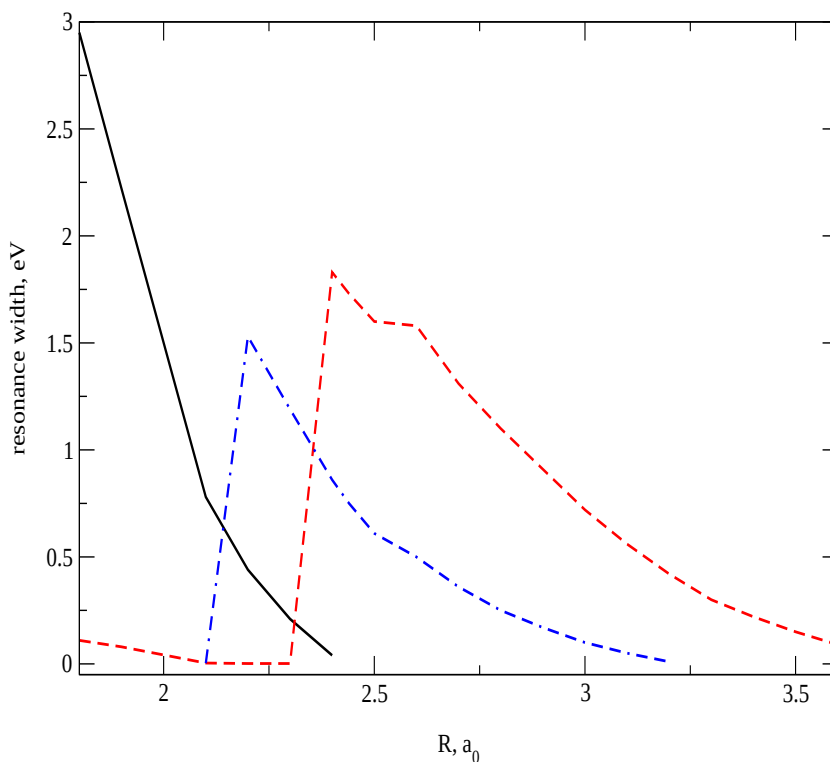


Figure 4.6: Resonance width as a function of C-F bond length. Solid line represents a width of the shape resonance of $^3\Sigma^-$ symmetry. Dashed and dot-dashed lines represent a width of the shape resonances of $^1\Sigma^+$ and $^1\Delta$ symmetries respectively.

can be seen from the figure 4.6, the $^3\Sigma^-$ resonance narrows rapidly with increasing R . The structure in the resonance widths of $^1\Sigma^+$ and $^1\Delta$ symmetries below $2.4 a_0$ may be caused by crossings of the potential energy curves (figure 4.1). The $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ resonances are shape resonances with the same dominant configuration $2\pi^2$.

Figure 4.4 shows the magnitude of the total elastic cross section as a function of the CF bond length. It decreases as R increases from 1.8 to $2.7 a_0$ and has a minimum about

$R = 2.7 a_0$, where the ground state dipole moment changes sign. With a further increase of the CF bond from 2.8 to 3.4 a_0 the magnitude of the total elastic cross section increases.

4.4.2 Bound states

The energies of the bound states were calculated from the scattering wavefunctions using program *BOUND* (Sarpal et al. 1991). Present calculations show a presence of two weakly bound states of symmetries $^1\Pi$ and $^3\Pi$ for $R < 2.6a_0$ with binding energy of 0.23 and 0.26 eV respectively at equilibrium. These bound states are very diffuse and have only 0.2 and 1% of their wavefunctions respectively in the R-matrix box at equilibrium, that makes it difficult to determine their energies accurately. These states are largely dipole bound and are, therefore, sensitive to the value of the target dipole moment. At $R = 2.6 a_0$ the ground state dipole moment of CF is near zero and the $^1\Pi$ and $^3\Pi$ bound states become unbound and create two resonances with positions 0.054 eV for $^1\Pi$ and 0.050 eV for $^3\Pi$ symmetries. These are shape resonances with the same configuration $2\pi 7\sigma$. These resonances could not be detected for $R > 2.7a_0$. The $^1\Pi$ and $^3\Pi$ bound states may become unbound in the whole range of R if rotational motion is taken into account.

As can be seen from the figure 4.1, with increasing C-F bond length the $^3\Sigma^-$ and $^1\Delta$ resonance energy curves approach the ground state energy curve. At $R = 2.5a_0$, $^3\Sigma^-$ resonance becomes bound. This bound state has 99% of the wavefunction inside the R-matrix sphere. For $R > 3.3a_0$ the resonance $^1\Delta$ also becomes bound. The energies of these bound states are plotted in figure 4.1. The resonance parameters suggest that the $^1\Sigma^+$ resonance will also become bound, but only at bond lengths larger than those considered here.

Not all low energy resonances lead to dissociative electron attachment (DEA). In order to determine a fate of the resonance it is necessarily to consider the energy balance equation for the DEA process, as the incident electron may not have enough energy to dissociate a molecule. Thus, the energy balance equation for the DEA process involving the $^1\Sigma^+$ resonance of CF is

$$\Delta E = D_0(CF) - A(F) \quad (4.1)$$

where $D_0(CF)$ is the dissociation threshold for CF and $A(F)$ is the electronic affinity of F. The formula (4.1) gives the energy $\Delta E = 2.10 \text{ eV}$. The energy of an incident electron,

forming the $^1\Sigma^+$ resonance, is 2.19 eV at equilibrium which may be enough to dissociate CF. The use of the reflection approximation (see section 3.5) implies that about 20% of the $^1\Sigma^+$ resonance asymptotically may dissociate to $C(^1D) + F(^1S)$, as the electronic affinity of F is higher than the affinity of C. The remaining 80% forms a negative ion $(CF^-)^*$. From the same approximation the $^3\Sigma^-$ and $^1\Delta$ resonances form vibrationally excited negative ions $(CF^-)^*$ which do not dissociate.

4.4.3 Inelastic scattering

Figure 4.7 presents the electron-impact excitation cross section from the ground $X\ ^2\Pi$ state to the first excited metastable $^4\Sigma^-$ state. This spin-changing transition is dipole forbidden. The resonance features in the energy region 7 - 9 eV are unphysical due to neglect some of the Rydberg excited states with the excitation energies in this region.

Transitions from the ground $X\ ^2\Pi$ state to the second, third and fourth excited states are dipole allowed. The cross sections for the transition into the Rydberg $A\ ^2\Sigma^+$ state is shown in figures 4.8 and 4.9. The cross section is rich in resonance features in the energy region above 5 eV, most of which are, probably, pseudo-resonances. The double minimum nature of the $A\ ^2\Sigma^+$ state means, that, as R increases from $1.8\ a_0$ the threshold initially increases, then decreases from $R = 2.6\ a_0$. The structure of the cross section for excitation to the Rydberg-like $A\ ^2\Sigma^+$ state, at small R , differs significantly from that for excitation to the valence $A\ ^2\Sigma^+$ state, at larger R (figure 4.8). This is also shown by unusual shape of the contours in figure 4.9, which show a minimum in the cross section at around $R = 2.6\ a_0$. Inclusion of vibrational effects would give somewhat unusual dependence on vibrational quantum numbers for this cross section.

Figure 4.10 presents the Born corrected cross section for the transition into the third excited state $B\ ^2\Delta$. The Born correction is significant at incident electron energies above 8 eV and increases with the increasing R . There are no resonance features apparent in this excitation cross section.

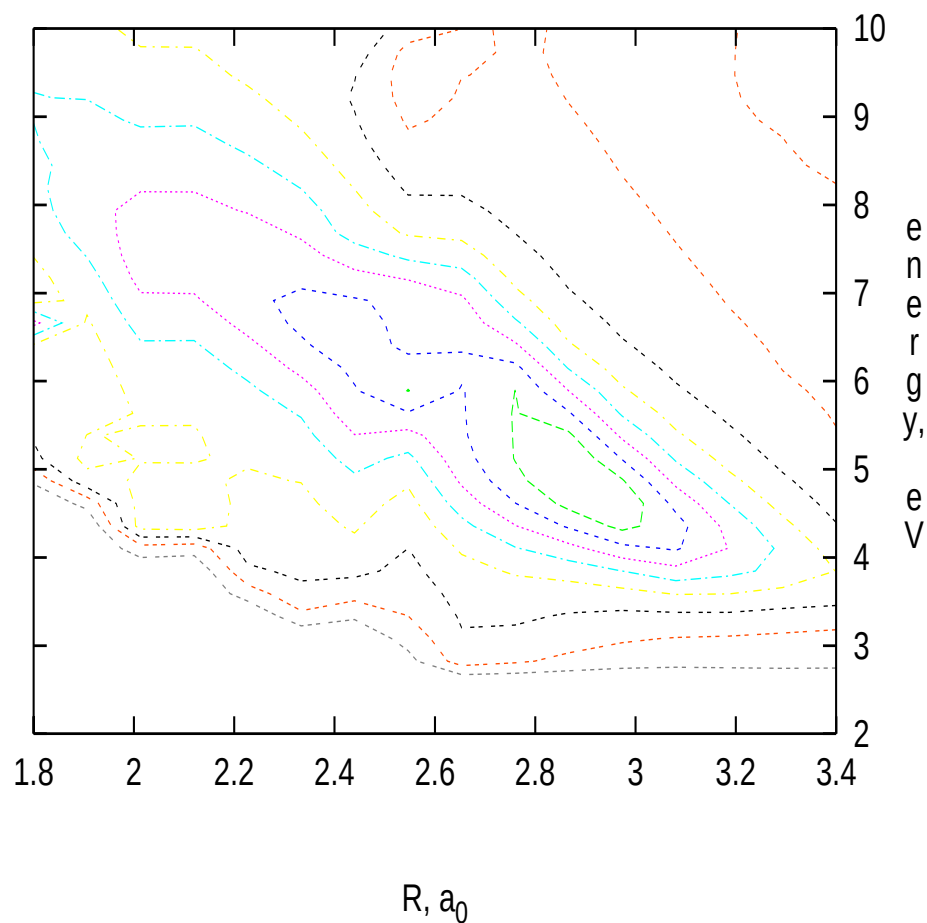


Figure 4.7: Contour plot of total cross sections for electron impact excitation of the lowest excited $4\Sigma^-$ state of CF plotted as a function of bond length, R . Contours range from $0.4 a_0^2$ (bottom line) to $3.2 a_0^2$ (innermost closed contour) in steps of $0.4 a_0^2$.

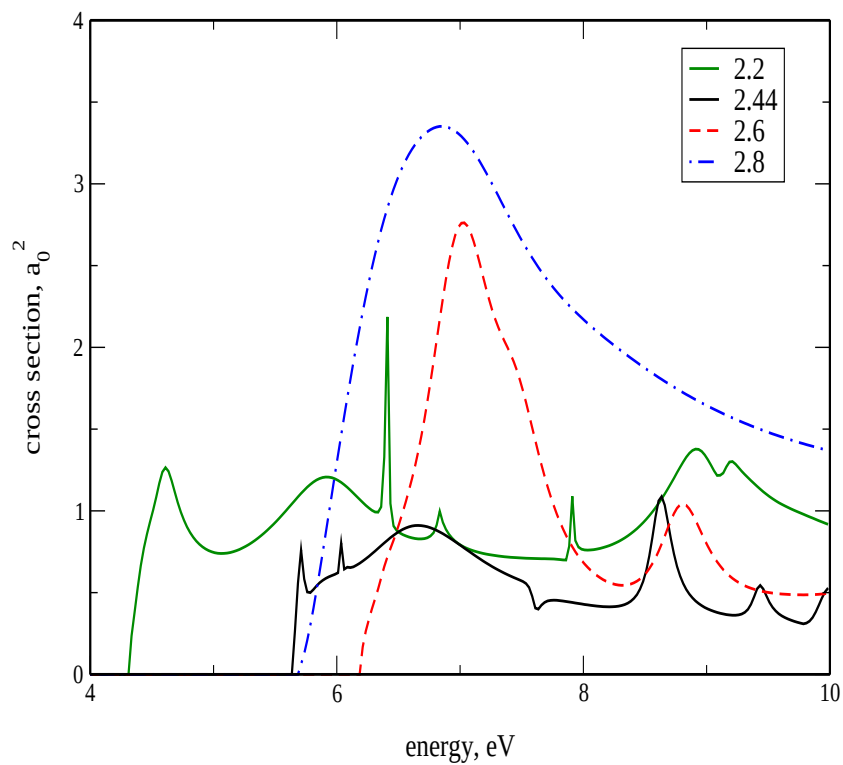


Figure 4.8: Total cross sections for the electron impact excitation of the $A^2\Sigma^+$ state of the CF radical plotted at $R = 2.2, 2.44, 2.6$ and $2.8 a_0$.

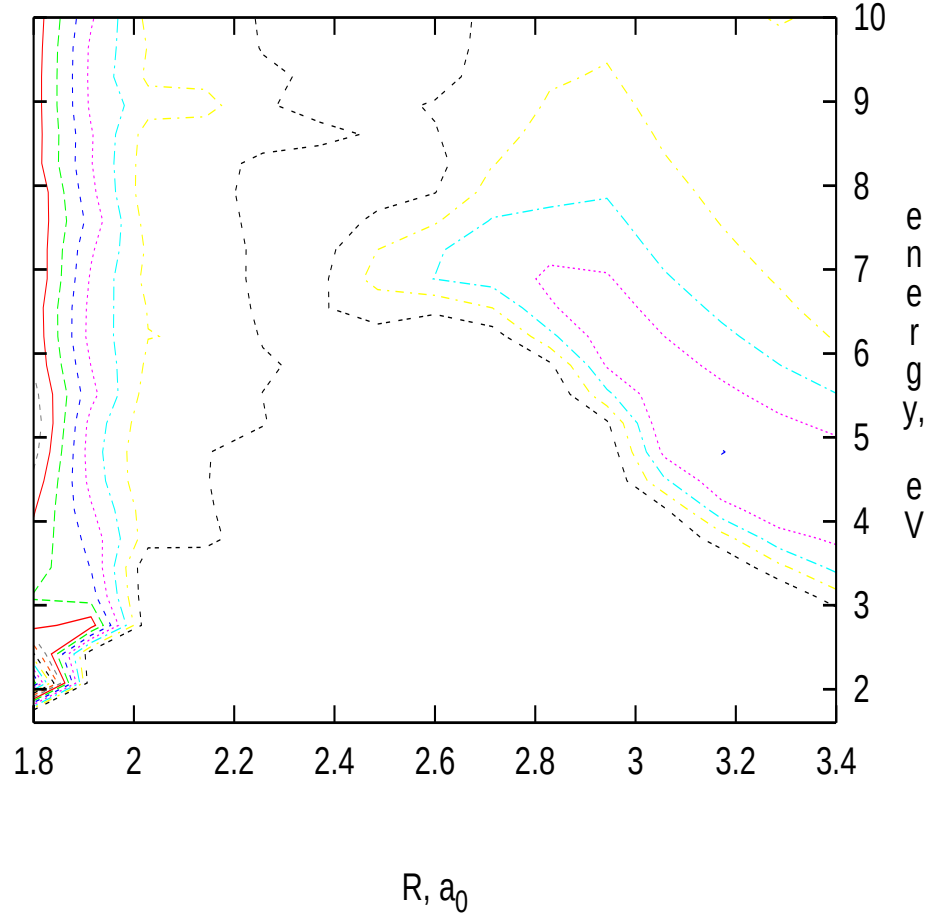


Figure 4.9: Contour plot of total cross sections, including Born correction, for the electron impact excitation of the second excited $^2\Sigma^+$ state, plotted as a function of C-F bond length R . The cross section for this process is small for intermediate bond length ($R \approx 2.5 a_0$). Contours start at $0.8 a_0^2$ from this region and increase in steps of $0.8 a_0^2$ to a maximum of $4.0 a_0^2$ (at $R = 3.2 a_0$ and $E = 4.8$ eV) at large R . At small R the cross section shows a strong peak at low energy rising to above $12 a_0^2$ (at $R = 1.8 a_0$ and $E = 2$ eV).

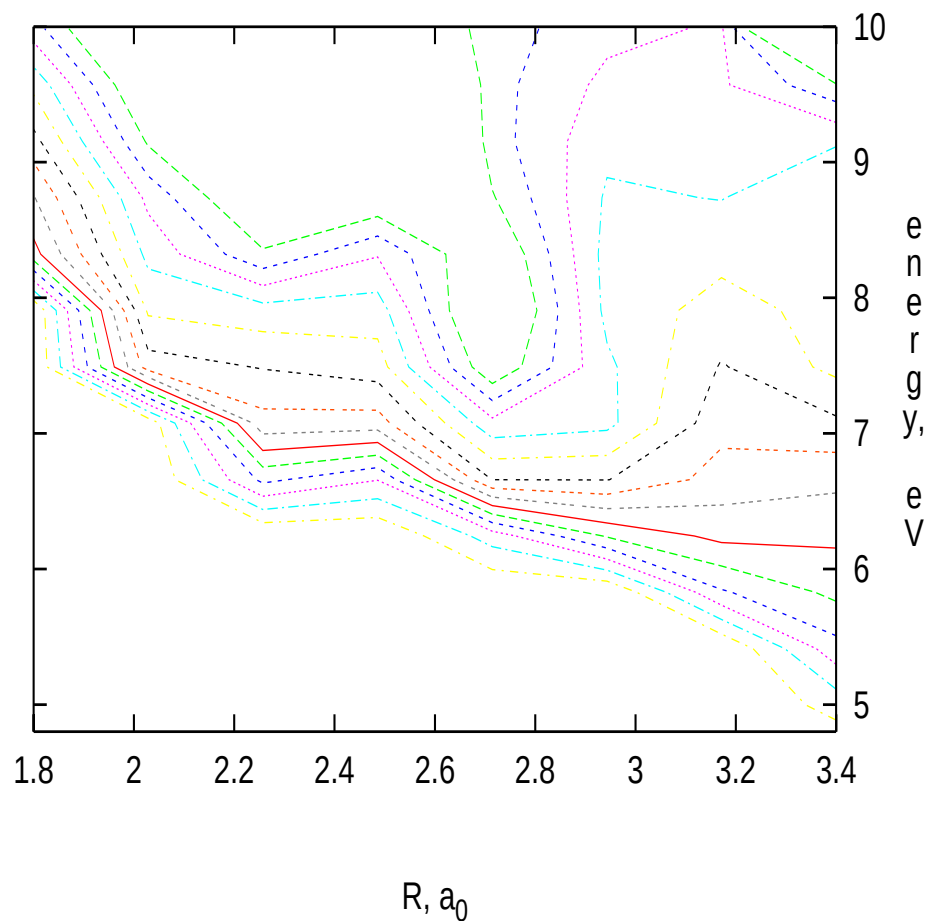


Figure 4.10: Contour plot of Born corrected total cross sections for electron impact excitation of the third excited $^2\Delta$ state plotted as a function of R . Contours range from $0.1 a_0^2$ (bottom line) to $1.4 a_0^2$ (top contour) in steps of $0.1 a_0^2$.

4.5 Summary

The first ever study of low-energy electron collisions with the CF radical was performed. The elastic cross section and the excitation cross sections for the five lowest lying electronically excited states of the CF were calculated with the UK polyatomic R-matrix code (Morgan et al. 1998), using a target model which gives good agreement with theoretical and experimental data for the vertical excitation energies and the ground state dipole moment. A new approach for treating molecules with Rydberg states within the R-matrix method was used in the course of this work. The profile of the A $^2\Sigma^+$ Rydberg state energy curve shows good agreement with the larger MRCI calculations of Petsalakis (1999). Although, target calculations, performed using a new approach discussed in section 4.2, gave good results, the Rydberg orbital space used to construct Rydberg NOs could probably be improved to give better target parameters over the whole range of R values.

Three shape resonances of symmetries $^1\Delta$, $^1\Sigma^+$ and $^3\Sigma^-$ were detected and fitted. These resonances are broad and short lived. Calculations, where a C-F bond was stretched from 1.8 to $3.6 a_0$, show that the resonances $^3\Sigma^-$ and $^1\Delta$ become bound at a bond length beyond 2.5 and $3.3 a_0$ respectively. Analysis of the $^1\Sigma^+$ resonance parameters suggests that this resonance will also become bound, but only at bond lengths larger than those considered here, and may provide a route for dissociative electron attachment (DEA) for the CF radical. From the reflection approximation the $^3\Sigma^-$ and $^1\Delta$ resonances form vibrationally excited negative ions $(CF^-)^*$, while approximately 20% of the $^1\Sigma^+$ resonance may dissociate to $C(^1D) + F^-(^1S)$. Therefore, a proportion of the product CF radicals in any plasma reactor may undergo DEA above the surface of the etching wafer. Such negative ions can produce a plasma sheaf above the surface which effects the surface chemistry.

Chapter 5

Electron collisions with the CF₂ radicals

In this chapter, the R-matrix method is used for the specific case of the electron - CF₂ collision calculations performed over a range of bond lengths. These calculations concentrate on obtaining low energy (less than 10 eV) elastic and excitation cross sections of the five lowest lying electronically excited states of the CF₂ molecule. These states have symmetries ³B₁, ¹B₁, ³A₂, ¹A₂ and ³B₂ and vertical excitation energies in the range of 2.44 - 10 eV.

5.1 Introduction

Difluoromethylene, CF₂, was first detected by its electronic emission spectrum arising from the $\tilde{A}^1B_1 - \tilde{X}^1A_1$ system by Venkateswarlu (1950). CF₂ radical plays a role in the upper atmosphere where it is created by the photodissociation of chlorofluoromethanes. In recent years, there has been an increasing interest in understanding the chemistry of CF₂, since it is an important intermediate in discharge environments containing CF₄, which is currently widely used as a source of F atoms and as a process gas in plasma etching applications.

The equilibrium geometry of the ground state of CF₂ was measured by absorption and microwave spectroscopy (Powel & Lide 1966, Kirchhoff et al. 1973, Charo & Lucia 1982, Mathews 1966, Mathews 1967). According to these studies the CF₂ molecule belongs to the C_{2v} symmetry group, the C-F bond length is 2.5 *a*₀ and the angle FCF is 104.8° at equilibrium.

In 1990, Francisco et al. (1990) calculated the geometry of the $^1A_1$ state at the MP2 level using the 6-31G* Gaussian basis set and obtained good agreement with experimental data. In 1991, Peterson et al. (1991) calculated the geometry and some spectroscopic properties of the X^1A_1 state at the CASSCF level with a 11s7p2d / 7s4p2d basis set, and their results were also in good agreement with the experimental data. Theoretical calculations on the geometry of CF₂ performed recently (Russo et al. 1992, Schwartz & Marshall 1999) are in good agreement with experimental results mentioned above. The equilibrium geometry of the excited $^1B_1$ state was also measured by absorption spectroscopy (Mathews 1966), and the bond length and angle are $2.53 a_0$ and 122.3° respectively. No experimental geometries have been reported for other electronic states of CF₂.

The molecular structure of CF₂ was first determined by Powel & Lide (1966), who measured its microwave spectrum. This early microwave study was extended by Kirchhoff et al. (1973) and by Charo & Lucia (1982) to much high level.

There have also been several *ab initio* calculations which derive the singlet-triplet energy splitting of the CF₂ (Carter & Goddard 1987, Carter & Goddard 1988a, Baird et al. 1989, Russo et al. 1992, Garcia et al. 1996, Cai 1993). These studies were carried out at different levels from Hartree-Fock to multireference configuration interaction (MRCI) method. In 1987 and 1988, Carter and Goddard (Carter & Goddard 1987, Carter & Goddard 1988a) calculated the excitation energy from the X^1A_1 to the first excited $^3B_1$ state and found that their results agree with previous experiments. Only Cai (1993) studied the seven low-lying electronic states of the CF₂ using MRCI calculations with a triple zeta plus double polarization (TZ + 2P) basis set and derived the adiabatic excitation energies. All these studies were performed at equilibrium geometry of CF₂. Theoretical calculations on the ground state potential energy surface of CF₂ were performed using small SCF calculations (Harrison 1971, Staemmler 1974, Rothenberg & Schaefer 1973, Bauschlicher et al. 1977, Clark et al. 1979) and CAS-SCF approach (Peterson et al. 1991).

The ionization cross section for the CF₂ radical was measured by Tarnovsky & Becker (1993) and by Tarnovsky et al. (1993) in the energy range (10-200) eV. Later Deutsch et al. (2000) calculated the electron impact ionization cross section for the CF₂ using semiclassical Deutsch-Märk formalism and found that their cross section lies significantly above the mea-

sured data. No experimental or theoretical data on low energy electron collisional cross sections for the CF₂ radical have been reported in the literature.

5.2 Target representation

CF₂ is a symmetrical, bent triatomic molecule with 24 electrons, belonging to C_{2v} point group.

The X¹A₁ ground state electronic configuration of the CF₂ can be written as

$$(1a_1 \dots 6a_1)^{12}(1b_1)^2(1b_2 \dots 4b_2)^8(1a_2)^2.$$

In complete-active space (CAS) 2s and 2p orbitals are open. The electronic configuration for the CF₂ molecule in CAS can be defined as $(1a_1 2a_1 1b_2)^6(3a_1 \dots 7a_1 1b_1 2b_1 2b_2 \dots 5b_2 1a_2)^{18}$.

Target calculations on CF₂ were carried out using the 6-311G* Gaussian basis set (11s5p1d / 4s3p1d) (<http://www.cse.clrc.ac.uk/qcg/basis>). A very large (diffuse) set can not be used in R-matrix calculations as it will extend outside the R-matrix sphere. Several test CASCI target calculations with smaller basis sets (DZP, 6-31G*, 6-311G, TZ) were performed. These basis sets gave a poor representation of the target properties (table 5.1), particularly the ground state dipole moment. The 6-311G* basis set was chosen as it gives the lowest state energies. This basis set was then used in all scattering calculations reported here. Target parameters,

Target parameters	Gaussian basis sets tested in present work					Previous results	
	TZ	6311G	DZP	6-31G*	6-311G*	CCCI ^a	B3LYP ^b
E(X ¹ A ₁)	-236.695	-236.688	-236.748	-236.362	-236.760	-236.801	-236.791
E(³ B ₁)	-236.586	-236.591	-236.631	-236.117	-236.646	-236.710	-236.707
Δ	2.96	2.65	3.18	6.66	3.10	2.49	2.27
μ(X ¹ A ₁)	0.08	0.01	0.23	0.89	0.28	0.44	-

Table 5.1: Preliminary target parameters for the CF₂ radical calculated using different basis sets. Total energies E (in Hartree), a singlet-triplet energy separation Δ(X¹A₁ - ³B₁) (in eV) and the ground state dipole moment μ (in Debye) generated using a CASCI model, described here, at equilibrium geometry. Also given are values calculated using correlation consistent CI (CCCI) computations and hybrid density functionals (B3LYP).

^aFrom Russo et al. (1992).

^bFrom Das & Whittenburg (1999).

calculated using the 6-311G* basis set and presented in table 5.1, are not satisfactory and need to be further optimized using pseudo-natural orbitals (NOs).

Theoretically, for good representation of target properties one must include a very large number of configurations, that is impossible in practice due to computational limitations, particularly for the (N+1)-electron calculations. Pseudo-natural orbitals were used in order to overcome this problem. First, Hartree-Fock self-consistent field (HF-SCF) calculations were performed using the basis set mentioned above, to get the molecular orbitals. Then, using these molecular orbitals, pseudo-natural orbitals were obtained from 'all singles and doubles' configuration interaction (CI) calculations for all six target states included in present calculations. The number of configurations used to generate the NOs were of the order of 23 000 and 31 000 for the singlet and triplet states respectively. A state-averaging of NOs was performed through weighted averaging of density matrices in order to get good representation of all target states. After several tests the best model, that provides the best threshold energies and the ground state dipole moment, was found. This model includes the NOs from the ground X^1A_1 state, the $^3B_1$, $^1B_1$ and $^3A_2$ excited states with weights 25, 65, 2 and 2 respectively. The final CASCI calculations were divided into 6 core electrons and 18 valence electrons. The core electrons were frozen in doubly occupied molecular orbitals $1a_1$, $2a_1$, $1b_2$. The complete active space consists of 18 electrons that were allowed to move freely between 15 molecular orbitals $3a_1$, $4a_1$, $5a_1$, $6a_1$, $7a_1$, $1b_1$, $2b_1$, $2b_2$, $3b_2$, $4b_2$, $5b_2$ and $1a_2$. Table 5.2 compares vertical excitation energies for the states considered in this calculation with data available in the literature. Calculated vertical excitation energies are normally higher than the adiabatic ones, which are normally derived from experiments. As can be seen, the agreement is good for the ground state and the two lowest excited states. CF_2 is rich in electrons and, in order to get good representation of all the states, one would need to use a basis set larger than the one used in the present calculations. The CASCI energy for the X^1A_1 ground state of the CF_2 at the equilibrium geometry, obtained during present calculations, is $-236.8145 E_h$ which is comparable with the value of Russo et al. (1992) $-236.8012 E_h$ and the value of Carter & Goddard (1988b) $-236.8013 E_h$ both obtained from correlation consistent CI (CCCI) computations.

As can be seen from table 5.2, the calculated singlet-triplet energy separation of 2.49 eV is in agreement with theoretical results (Cai 1993) and close to the experimental value 2.46 eV (Koda 1978, Koda 1982). The ground state dipole moment of 0.448 Debye, calculated using

State		Configuration	N	This work		Theory	Observed
C _{2v}	C _s			Δ	μ	Δ^a	Δ
X ¹ A ₁	X ¹ A'	(1a ₁ ² ...6a ₁ ²)1b ₁ ² (1b ₂ ² ...4b ₂ ²)1a ₂ ²	4067		0.448	0	0
³ B ₁	³ A''	1b ₁ ⁻¹ 7a ₁	5826	2.49	0.47	2.42	2.46 ^b
¹ B ₁	¹ A''	1b ₁ ⁻¹ 7a ₁	3858	5.42	0.38	4.64	4.62 ^c
³ A ₂	³ A''	1b ₁ ⁻¹ 5b ₂	5811	9.06	0.31	6.31	—
¹ A ₂	¹ A''	1b ₁ ⁻¹ 5b ₂	3843	9.11	0.31	6.52	7.84 ^d
³ B ₂	³ A'	4b ₂ ⁻¹ 7a ₁	5802	9.52	0.32	7.76	—

Table 5.2: Excitation energies (in eV) and dipole moments (in Debye) for the CF₂ target states generated using a CASCI model with state-averaged pseudo-natural orbitals at equilibrium geometry. Also given are the dominant configuration of each state and the number of configurations N in C_{2v} symmetry. Calculated vertical excitation energies are given in column Theory; experimental adiabatic excitation energies are given in column Observed.

^aFrom Cai (1993).

^bFrom Koda (1978, 1979, 1982).

^cFrom Mathews (1967).

^dFrom Carter & Goddard (1987).

the model presented here, is in good agreement with the experimental value of Kirchhoff et al. (1973) 0.469 ± 0.026 Debye and with 0.44 Debye calculated by Russo et al. (1992). The 6-311G* basis set thus gives a satisfactory compromise between singlet-triplet energy gap and dipole moment which both are in good agreement with experimental values.

At non-equilibrium geometries the CF₂ molecule belongs to the C_s point group. In C_s the CF₂ molecular states are labelled ¹A' ($\tilde{X}$), ³A'' , ¹A'' , ³A' respectively. The CF₂ electronic configuration in CAS can be written as (1a' 2a' 3a')⁶ (4a' ...12a' 1a'' ...3a'')¹⁸. The model used to calculate target properties of the CF₂ in this case is the same as the one described for equilibrium geometry. The electronic state energies as a function of changing one C-F bond are plotted in figure 5.1.

For clarity, the electronic states below are labelled by their C_{2v} designations (with C_s labels in parenthesis).

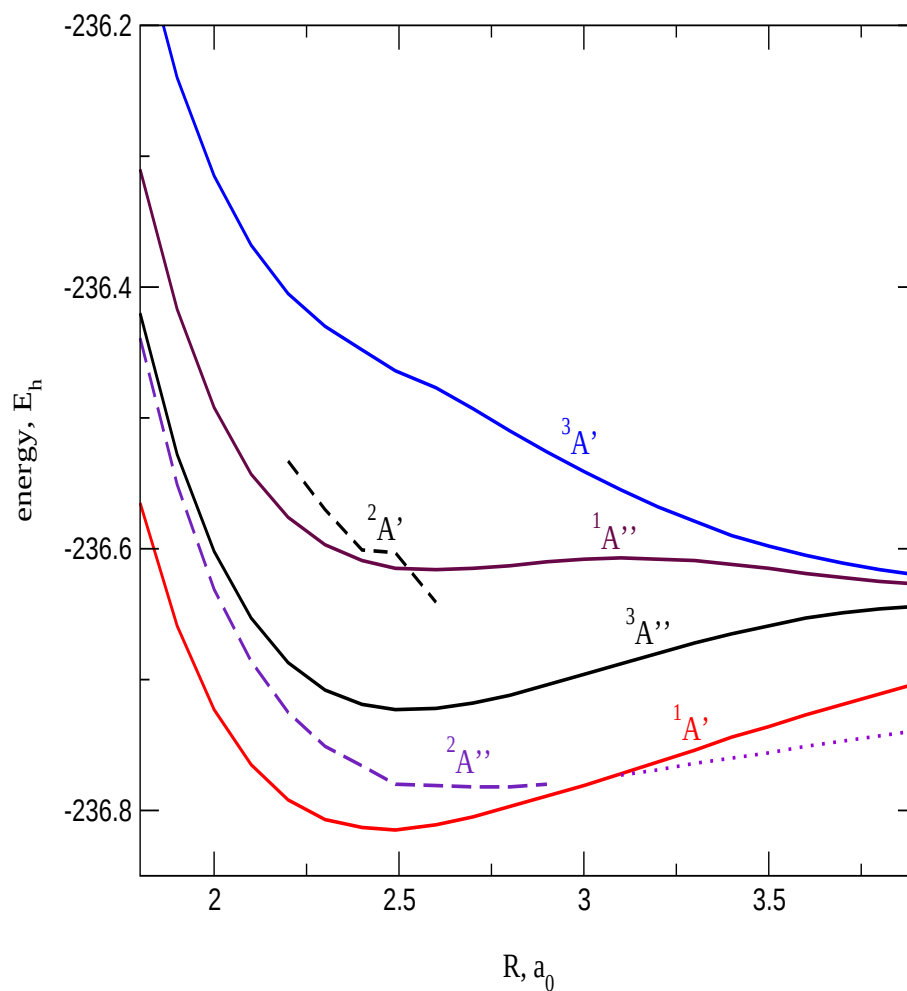


Figure 5.1: Electronic state energies of CF_2 as a function of changing one C-F bond, R , solid lines. The dashed lines represent the $\text{CF}_2 + e^-$ system resonance energy curves; the dotted line below ground state curve represents the CF_2^- bound state curve. Curves are labelled using C_s point group symmetries.

5.3 Scattering model

The R-matrix scattering calculations on CF₂ included the six states given in table 5.2. In all calculations the continuum orbitals describing the scattered electron were represented by Gaussians (GTO) centred on the centre of gravity of the CF₂. These continuum GTOs were then orthogonalized to the target molecular orbitals and among themselves. Test calculations were performed using several continuum basis sets: Nestmann & Peyerimhoff (1990) original continuum orbitals of up to f ($l \leq 3$) partial waves, continuum orbitals of Sarpal et al. (1996) with $l \leq 3$ and $l \leq 4$ partial waves, and orbitals of Faure et al. (2002) up to g ($l \leq 4$) partial waves. The final calculations used continuum orbitals of Faure et al. (2002) as these gave the highest and smoothest eigenphase sums (figure 5.2).

As was discussed in section 3.4, the elastic scattering cross section of a static molecules with a permanent dipole moment is formally divergent. It is well known that a large number of partial waves and rotational effects must be included in order to obtain convergent results. States with $l > 4$ omitted from scattering calculations were added using a Born correction (Chu & Dalgarno 1974). The calculated rotational constants for the CF₂ molecule in C_{2v} point group are 2.8295, 0.4028 and 0.3525 cm⁻¹. The dipole moment of CF₂ lies along the C_{2v} symmetry axis which was taken as the z axis. CF₂ molecule is an asymmetric top with the asymmetry parameter $k = (2B - A - C)/(A - C)$ value of -0.96, so, to a good approximation CF₂ can be treated as a symmetric top for the Born calculations.

The range of scattering energies was restricted to energies below 10 eV, as this is the range covered by the electronic states included in the calculations, reported here. Resonance positions and widths were found by fitting the eigenphase sum to a Breit-Wigner profile (Tennyson & Noble 1984). Calculations, in which one C-F bond was stretched from 1.8 a_0 to 3.7 a_0 with the other C-F distance and the angle CFC held at their equilibrium values, were performed in order to study the dissociative behaviour of the resonances.

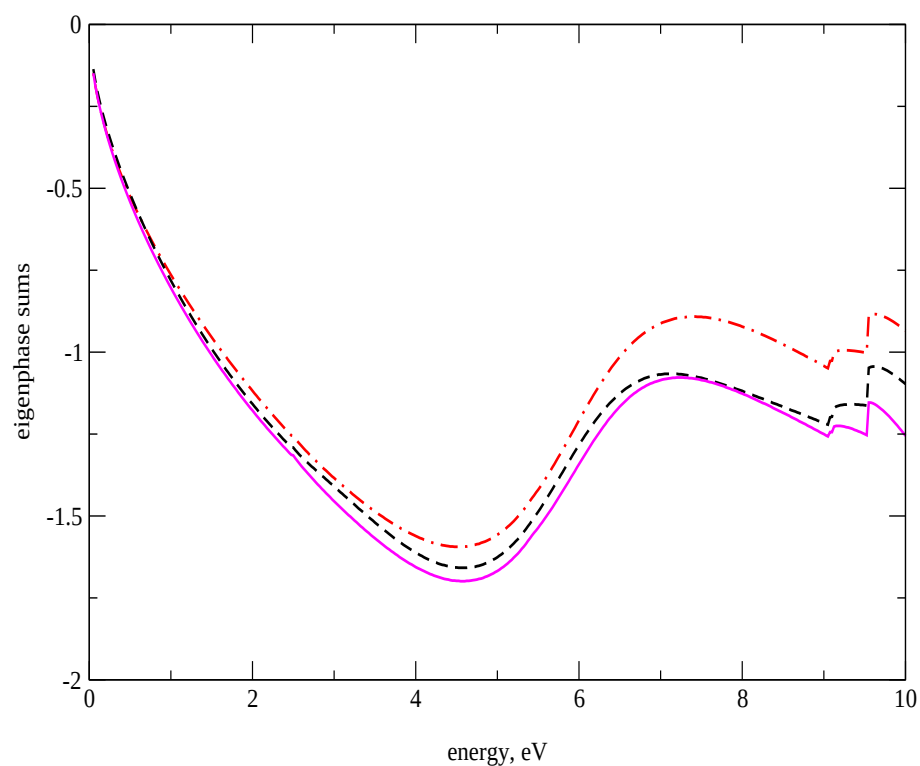


Figure 5.2: Eigenphase sums (in radian) for the $^2A_1$ symmetry of the $(\text{CF}_2 + e^-)$ system at equilibrium geometry as a function of energy. The dot-dashed line represents the eigenphase sums calculated using a continuum basis set of Faure *et al* (2002) with $l \leq 4$ partial waves; the dashed line represents the eigenphase sums calculated using a continuum basis set of Sarpal *et al* (1996) with $l \leq 4$ partial waves; solid line represents the eigenphase sums calculated using a continuum basis set of Sarpal with $l \leq 3$ partial waves.

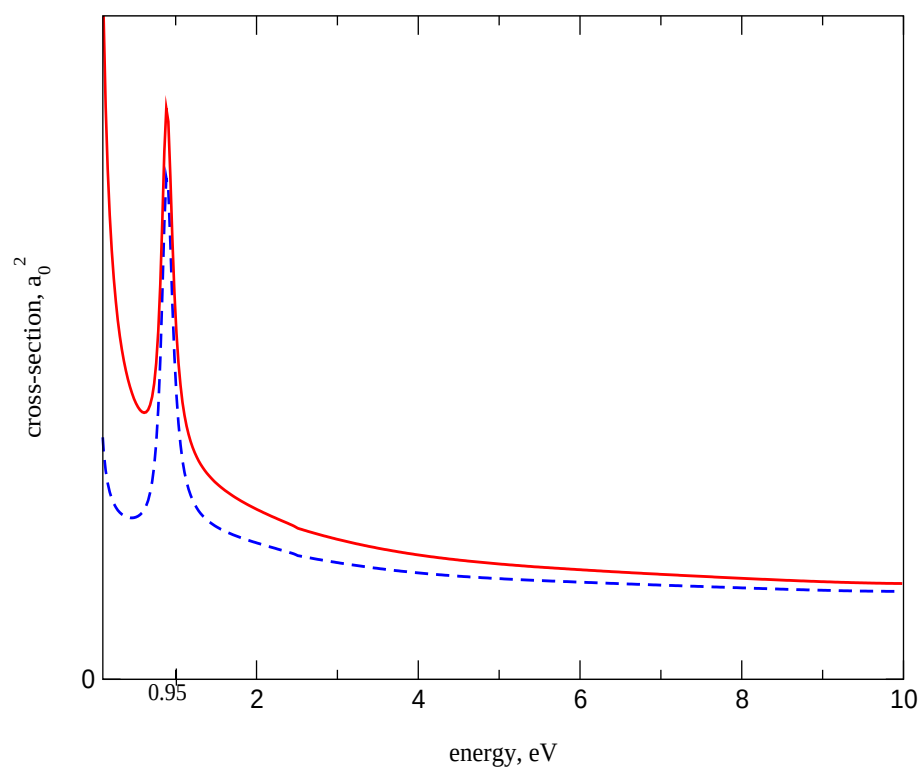


Figure 5.3: Total elastic cross section for molecule CF_2 at equilibrium geometry. Dashed line represents the cross section without Born correction. Solid line represents the cross section with added Born correction.

5.4 Cross sections and bound states

Elastic cross sections were calculated at different geometries. Previous R-matrix calculations on electron-OCIO performed by Baluja et al. (2001b) give generally excellent agreement with experimental measurements but show disagreement between Born-corrected cross sections and experimental values at energies below 100 meV. At very low energies, calculated cross sections do not reproduce the sharp minimum observed in the experiment. Field et al. (2000) suggest that this structure is due to interference effects between rotational (and other) channels. Neither Baluja *et al* nor present model includes rotational coupling.

The resulting elastic cross sections for CF₂ are shown in figure (5.3). The magnitude of the total elastic cross section at equilibrium geometry of the CF₂ is 2300 a_0^2 at the energy of scattering electron 100 meV. Figure 5.4 gives the elastic cross sections at different bond lengths. The Born correction has its minimum value near the equilibrium bond length, it increases with increase or decrease of the bond length in line with the ground state dipole moment.

The main feature in the elastic cross section is the presence of a shape resonance of $^2B_1(^2A'')$ symmetry. At equilibrium geometry this resonance has position and width of 0.95 eV and 0.18 eV respectively. Analysis of the inner region eigenvectors shows that it is a shape resonance with the extra electron in the $3b_1$ orbital. The resonance position and width as a function of bond length are plotted in figures (5.1) and (5.5) respectively.

CF₂ has an equilibrium dipole moment of 0.44 D, which may be enough to support a bound state. However, all the calculations show that CF₂ does not have any bound states at its equilibrium geometry. With increasing a C-F bond length the $^2B_1(^2A'')$ resonance energy curve approaches the ground state energy curve. As one C-F bond length is increased to 3.2 a_0 , this resonance becomes bound (see figure 5.1). At larger bond lengths the energy of the bound state was calculated from the scattering wavefunctions using program *BOUND* (Sarpal et al. 1991). Pure bound state calculations confirm a presence of this bound state. The reflection approximation (see section 3.5) suggests that approximately 5% of the $^2B_1(^2A'')$ resonance asymptotically may dissociate to CF($^2\Pi$) + F⁻(^1S) and 95% of the resonance forms a vibrationally excited negative ion (CF₂⁻)*.

Figures 5.6 and 5.7 present electron-impact electronic excitation cross section from the

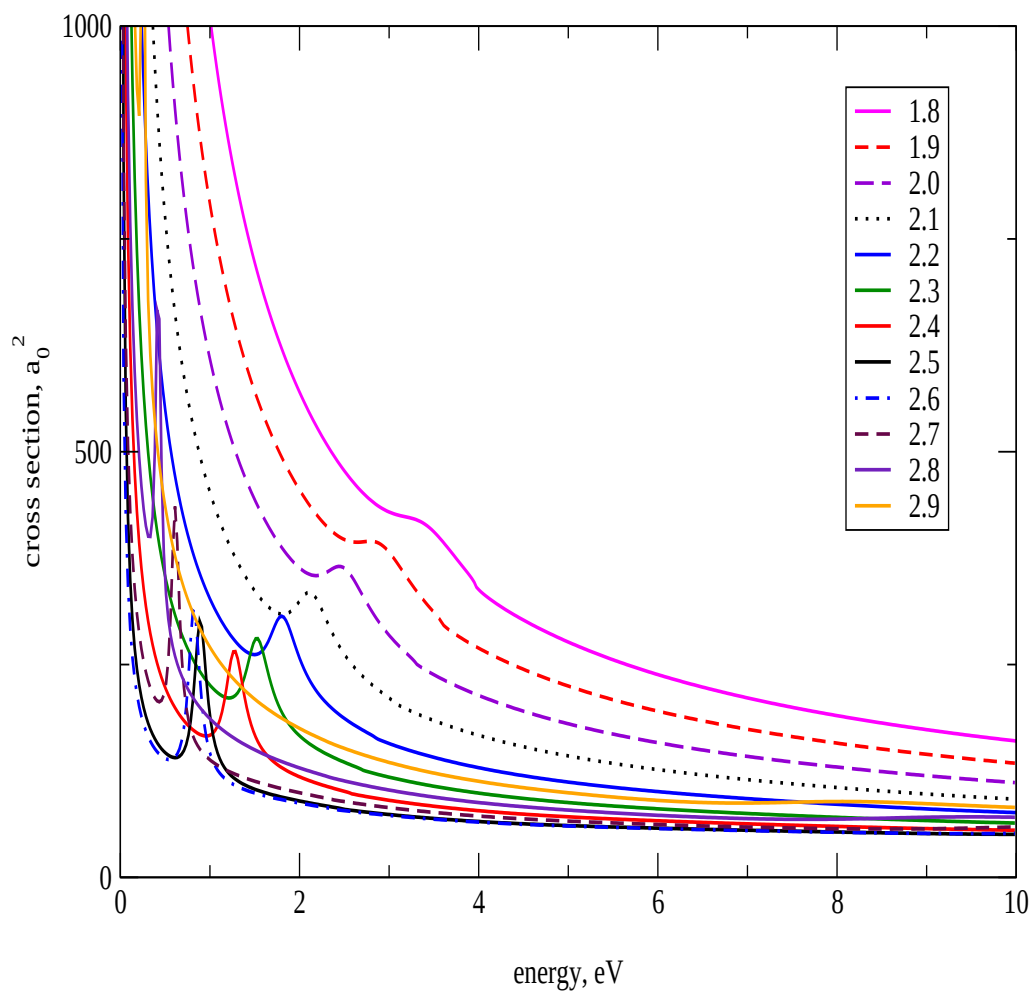


Figure 5.4: Total elastic cross sections for molecule CF_2 plotted at different C-F bond lengths, (from $1.8 a_0$ to $2.9 a_0$).

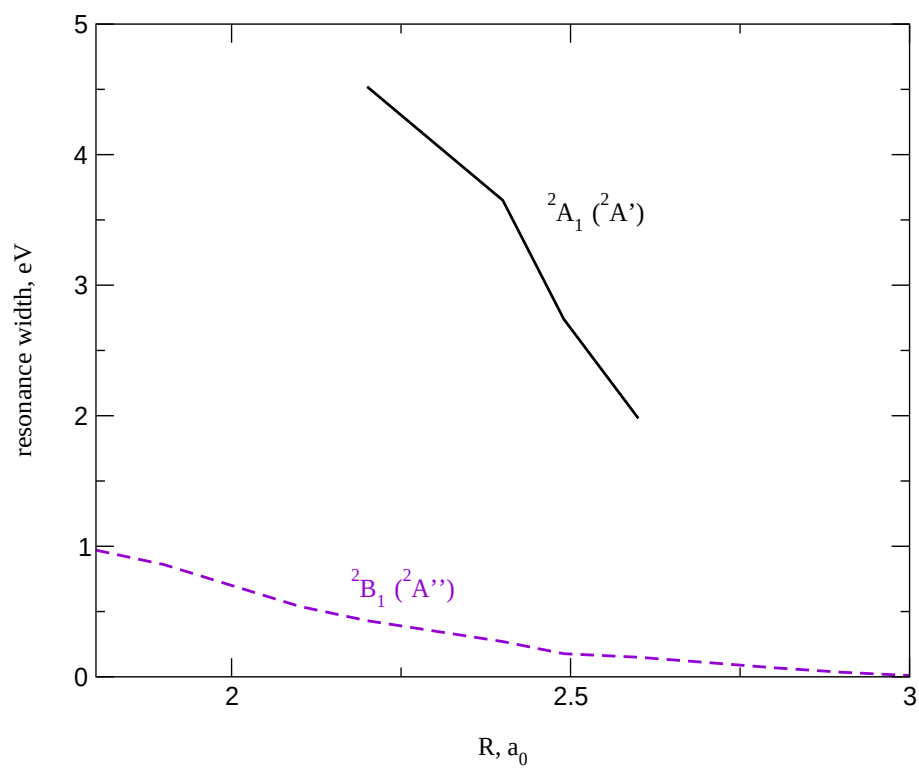


Figure 5.5: Resonance width as a function of a C-F bond length, R . Solid line represents a width of the $^2A_1 (^2A')$ shape resonance. Dashed line represents a width of the $^2B_1 (^2A'')$ shape resonance.

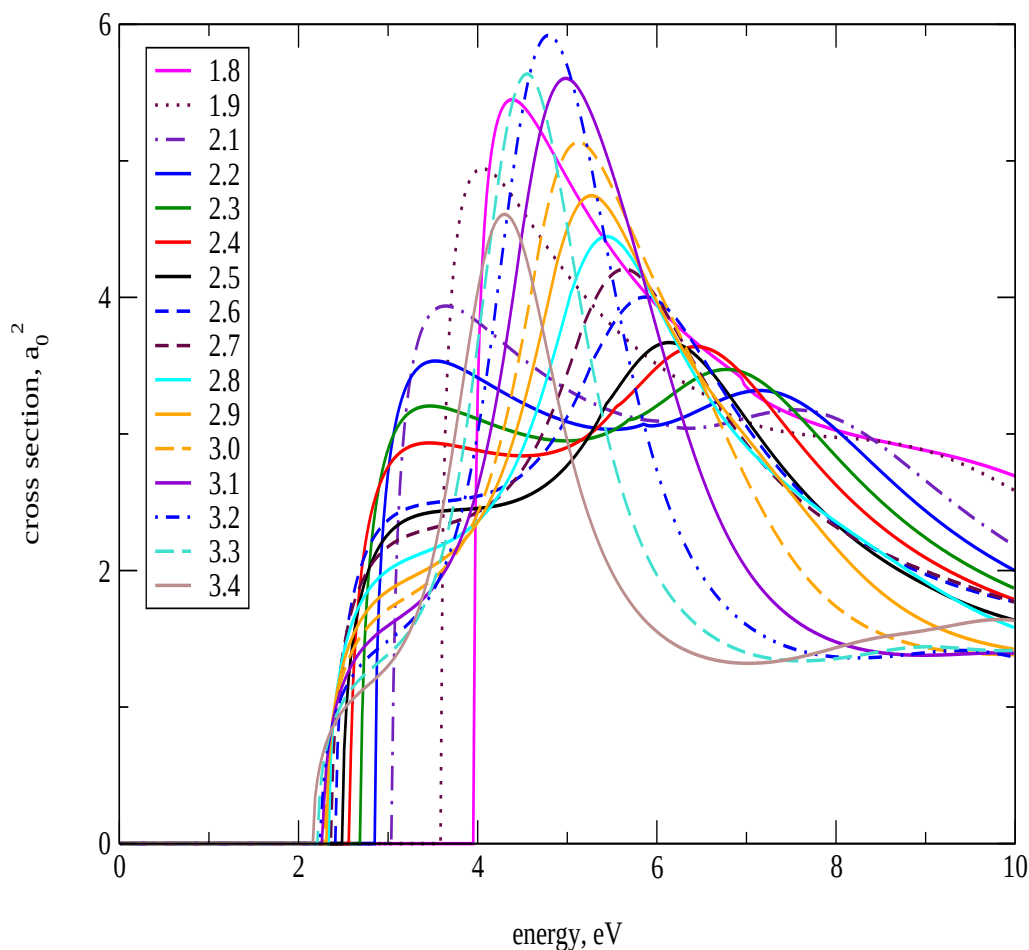


Figure 5.6: Total cross sections for electron impact excitation of the lowest excited $^3B_1$ ($^3A''$ in C_s) state plotted at different C-F bonds (from $1.8 a_0$ to $3.5 a_0$).

ground state $^1A_1$ to the first excited $^3B_1$ state. This spin-changing transition is dipole forbidden. This excitation process is dominated by the $^2A_1$ ($^2A'$) symmetry in which there is a prominent resonance with a position and width at equilibrium geometry of 5.61 eV and 2.87 eV respectively. This shape resonance binds the extra electron in the $7a_1$ orbital. It is a very broad and short lived resonance and could not be detected at a C-F bond length beyond $2.7 a_0$ (see figure 5.1).

Transitions from the ground state $^1A_1$ to the second excited state $^1B_1$ are allowed by dipole selection rules. The magnitude of the dipole moment for this transition is 1.5 Debye at equilib-

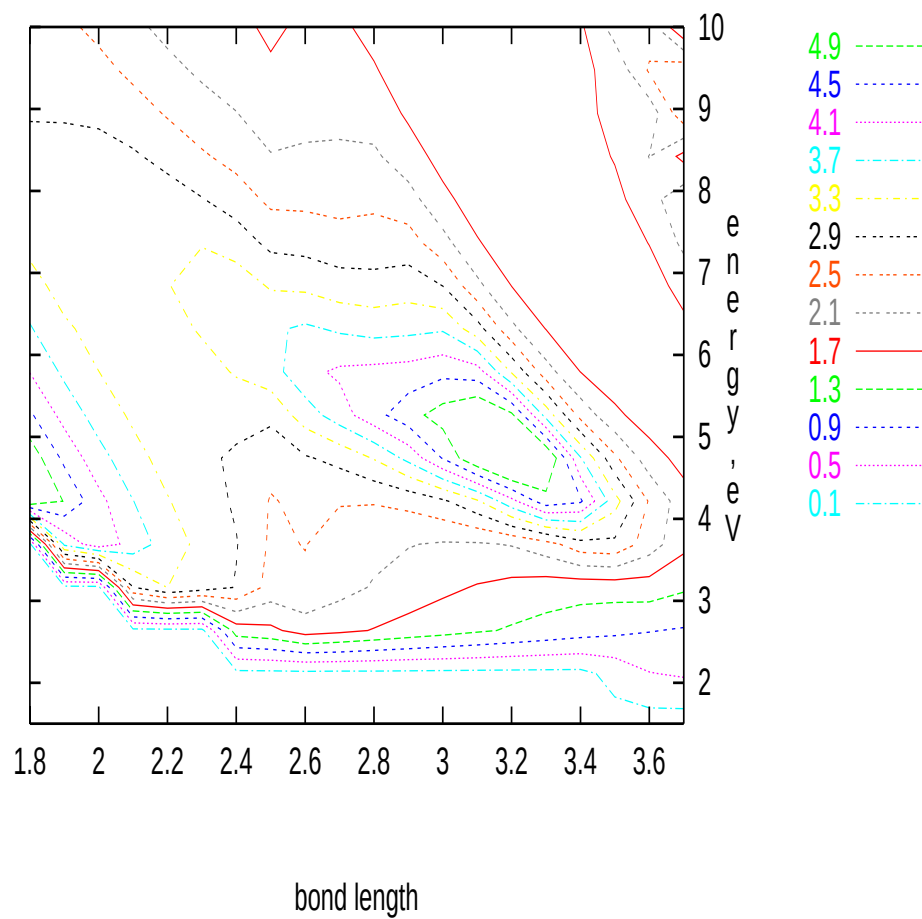


Figure 5.7: Contour plot of total cross sections for the excitation of the lowest excited $^3\text{B}_1$ ($^3\text{A}''$) state plotted at different C-F bonds (in a_0) from $1.8 a_0$ to $3.5 a_0$. Contours range from $0.1 a_0^2$ (bottom line) to $4.9 a_0^2$ (innermost closed contour) in steps of $0.4 a_0^2$.

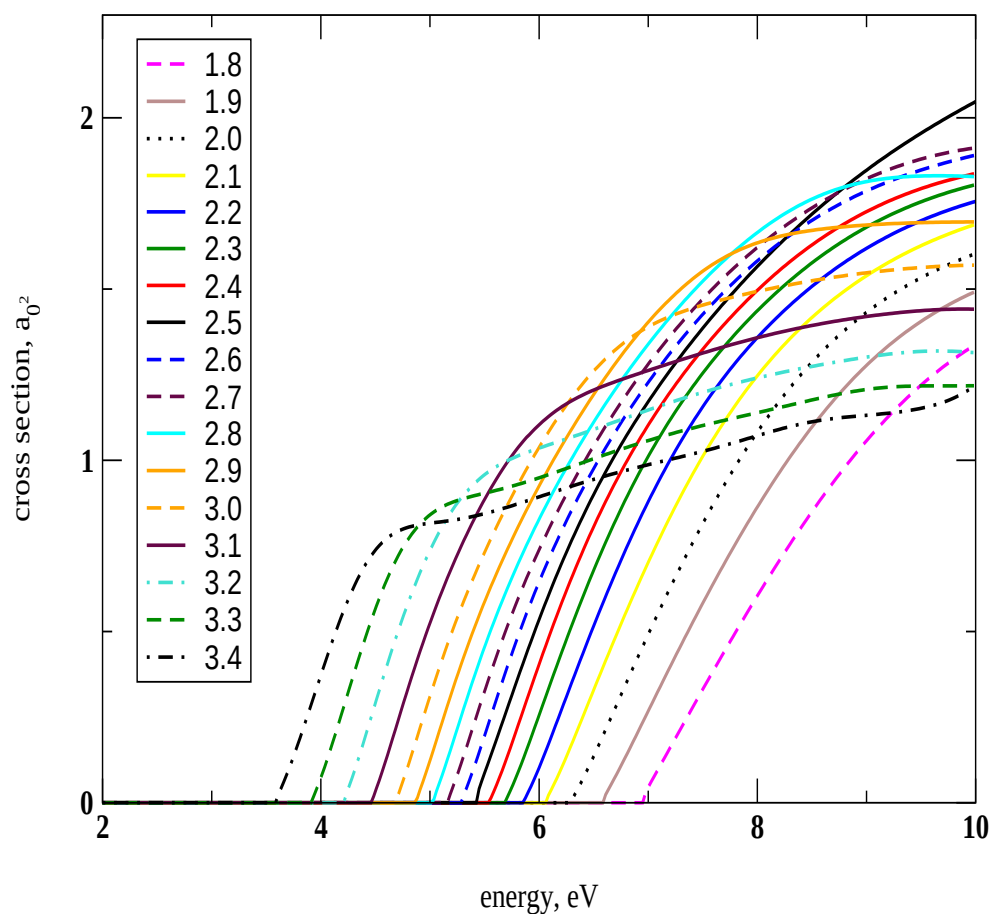


Figure 5.8: Total cross section for electron impact excitation of the second lowest excited $^1B_1$ ($^1A''$) state plotted at different C-F bond lengths (from $1.8 a_0$ to $3.4 a_0$).

rium geometry. The effect of high partial waves excluded from our calculations was added via a Born correction formula (Chu & Dalgarno 1974). Figure 5.8 displays the final cross sections for the excitation of $^1B_1$ state. The Born correction is very small but increases with increase in energy of an incident electron. There are no resonance features apparent in this excitation cross section.

5.5 Summary

The first ever study of low-energy electron collisions with the molecule CF₂ was performed using the R-matrix method. The elastic cross section and the excitation cross sections for the five lowest lying electronically excited states of the CF₂ were calculated with the UK polyatomic R-matrix code (Morgan et al. 1998), using a target representation which gives good agreement with experimental data for the energy separations and the ground state dipole moment. Two shape resonances of symmetries $^2A_1(^2A')$ and $^2B_1(^2A'')$ were detected and fitted.

Calculations, in which one C-F bond was stretched from $1.8 a_0$ to $3.7 a_0$ with the other C-F distance and the angle CFC held at their equilibrium values, show that $^2B_1(^2A'' \text{ in } C_s)$ resonance is bound at a bond length beyond $3.2 a_0$. From the reflection approximation about 5% of the $^2B_1$ resonance asymptotically may dissociate to CF($^2\Pi$) + F⁻(^1S), while the remaining 95% forms (CF₂⁻)*. Negative ions produced during DEA processes have a significant effect on the surface chemistry.

Chapter 6

Electron collisions with the CF_3 radicals

Previous calculations suggest that CF and CF_2 may undergo dissociative electron attachment under standard plasma conditions. In this chapter 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.

6.1 Introduction

CF_3 radicals play an important role in the plasma processing of Si and SiO_2 in the microelectronics industry (Donnelly & Flamm 1980, Coburn 1982, Winters & Coburn 1992, Takahashi et al. 1996). The CF_3 free radical is also an important species in atmospheric chemistry because of its role in the oxidative degradation of both perfluorocarbons and hydrofluorocarbons (Ravishankara et al. 1994). However there is even less data on CF_3 available than there was on the CF and CF_2 radicals. It is therefore appropriate to consider important processes involving the CF_3 radical.

The ground state structure of the CF_3 has been characterised by experimental and *ab initio* methods (Dixon 1985, Dixon et al. 1987, Pasto et al. 1987, Pouchan & Papailhou 1987, Curtiss & Pople 1987). The CF_3 radical has a pyramidal structure and belongs to C_{3v} point group. Its ground $^2\text{A}_1$ state has the following electronic configuration

$1e^4 1a_1^2 2a_1^2 3a_1^2 2e^4 4a_1^2 3e^4 5a_1^2 4e^4 5e^4 1a_2^2 6a_1^1$. The equilibrium geometry of the CF₃ was derived from infrared laser spectroscopy experiments (Jamada & Hirota 1983). According to these studies the C-F bond length is $2.53 a_0$ and FCF angle is 110.7° at equilibrium. *Ab initio* calculations on geometry of CF₃, performed using the density functional (DF) theory (Gutsev 1992), are in good agreement with the experimental values. All calculations reported in this chapter use this geometry.

The ground $^2A_1$ state of the CF₃ was studied by Dixon (1985), Pouchan & Papailhou (1987) and Miller et al. (1996). Their values for the ground state energy are in good agreement among themselves. Surprisingly, data on excitation energies for the CF₃ are not available in the published literature. The ground state dipole moment of the CF₃, determined by the method of molecular beam focusing in an inhomogeneous electric field, is 0.43 ± 0.07 Debye (Butkovskaya et al. 1979).

Knowledge of the cross sections of molecular species is important for plasma diagnosis techniques, plasma modelling (Graves & Kushner 1996) and to study the dynamics of discharges (Garscadden 1992). The absolute partial electron-impact ionization cross section for the CF₃ was measured by Tarnovsky & Becker (1993). Diniz et al. (1999) 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 incident electron. No experimental or theoretical data on low-energy collisional integral cross sections for the CF₃ radical have been reported.

There appears to be a lack of theoretical work on CF₃ radical, probably because of its size and the lack of experimental data. An absence of data on the vertical excitation energies of the CF₃ means that the present scattering study had to be prefaced by a series of electronic structure calculations aimed at characterising the low lying electronic states of CF₃. A series of electronic structure calculations were performed using the quantum chemistry package MOLPRO (Werner & Knowles 2002) in order to determine reliable target parameters, such as vertical excitation energies.

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 X^2A' state electronic configuration is $(1a'...10a')^{20} (1a''...6a'')^{12} 11a'$. 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.

6.2 Target representation

6.2.1 MOLPRO calculations

Ab initio complete active space self-consistent field (CASSCF) and multireference configuration interaction (MRCI) calculations were carried out on the low-lying electronic states of the CF_3 at its equilibrium geometry. As was mentioned in chapter 3, CASSCF is a form of MCSCF method 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.

Preliminary results showed that only five excited states of symmetries $1^2A''$, $2^2A'$, $2^2A''$, $3^2A'$ and $3^2A''$ have vertical excitation energies below 10 eV. Therefore, only the above excited states are included in present calculations. Higher states rapidly take on greater Rydberg character, which makes them difficult to treat within an R-matrix calculation (see chapter 4).

The CASSCF calculations consisted of 8 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 Hartree-Fock self consistent field calculations for the CF_3 ground state. Test calculations were performed using several basis sets, which are 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 6.1. 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_s are degenerate (table 6.1). The vertical excitation energies for the $3^2A'$ and $3^2A''$ states for se-

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

Table 6.1: 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 CASSCF method and different basis sets. Also given is the ground state dipole moment in Debye.

lected basis sets could not be determined due to poor convergence. The increase of primary configuration space did not cure this problem. The 6-311G* basis set, which was also used in the calculations on CF_2 (see chapter 5), does not give any convergence problems and also provides satisfactory target parameters. This basis set was used in all further calculations. The magnitude of the 6-311G* CASSCF ground state dipole moment, presented in table 6.1, is slightly high than the experimental value 0.43 ± 0.07 Debye (Butkovskaya et al. 1979).

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 the states shown in table 6.1, with 8 core electrons frozen in four molecular orbitals and 25 valence electrons moving freely among 16 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 the present 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 CF_3 calculated using the MRCI approach and different basis sets are presented in table 6.2. It should be noted that the use of CASSCF reference orbitals in our MRCI calculations give the correct degeneracy of the CF_3 target states.

The magnitude of the MRCI ground state dipole moment of the CF_3 obtained using the 6-311G* basis set is 0.20 Debye, which is much lower than the experimental value of Butkovskaya

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

Table 6.2: 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 Debye). The vertical excitation energies were generated using:

^a three reference states of each spacial symmetry;

^b two reference states of each spacial symmetry;

^c two reference states of the A' symmetry and one reference state of A'' symmetry.

et al. (1979) 0.43 ± 0.07 Debye.

6.2.2 R-matrix calculations

The R-matrix target calculations have been carried out on the six electronic states of CF₃ which are X ²A', A ²A'', 2 ²A', 2 ²A'', 3 ²A' and 3 ²A'' in C_s symmetry. The equilibrium geometry and the 6-311G* Gaussian basis set (11s5p1d / 4s3p1d) were used.

In order to get a satisfactory representation of the CF₃ target the natural orbitals (NOs) generated during MOLPRO CASSCF calculations were used. Analysis of the CASSCF natural orbital energies shows that orbitals pairs (5a', 2a''), (3a'', 8a'), (4a'', 9a'), (6a'', 10a') and (7a'', 13a') are degenerate and therefore have *e* symmetry in C_{3v} (table 6.3).

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 symmetry state. Target

Orbital	Energy
$1a'$	-26.402039
$1a''$	-26.402024
$2a'$	-26.394695
$3a'$	-11.357283
$4a'$	-1.645099
$5a'$	-1.606932
$2a''$	-1.606929
$6a'$	-0.865725
$7a'$	-1.061702
$3a''$	-0.935354
$8a'$	-0.935321
$4a''$	-0.713784
$9a'$	-0.713780
$6a''$	-0.687402
$10a'$	-0.687397
$5a''$	-0.656764
$11a'$	-0.278517
$12a'$	0.538381
$7a''$	0.606647
$13a'$	0.606570

Table 6.3: CASSCF natural orbital energies (in eV) for the CF_3 calculated at equilibrium geometry using the 6-311G* Gaussian basis set.

calculations using this model are computationally possible but the $(N + 1)$ -electron scattering calculations using this model are not feasible. Clearly, these calculations need to be restricted.

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

Model 4 generates about 3 000 CSFs per state. This model gives satisfactory vertical excitation energies, but the ground state dipole moment value of 0.68 Debye is significantly higher than the experimental value.

Model 3 generates about 28 000 CSFs per state during the target calculations and gives the best target excitation energies when compared to the more comprehensive MRCI calculations

described above. It gives the ground state dipole moment of 0.56 Debye; this value is close to but a little higher than the experimental value 0.43 ± 0.07 Debye (Butkovskaya et al. 1979). This model was used in the scattering calculations.

Care needs to be exercised when choosing a target model. Degeneracy can be easily broken by separating degenerate natural orbitals.

In order to adjust target parameters, the CASSCF natural orbitals were state averaged using R-matrix codes. The ground X^2A_1 state and the A^2A'' , $2^2A'$, $2^2A''$, $3^2A'$ and $3^2A''$ excited states with weights 1, 2, 0, 0.8, 0 and 0.2 respectively were included in the averaging procedure. This procedure also helps to recover the correct degeneracy of the orbitals and states. It should be noted that MOLPRO does not have the facility to produce symmetry state-averaged NOs. Under symmetry state-averaged NOs one means the NOs averaged among states of different spatial symmetries. Table 6.4 presents target parameters for the CF₃ radical calculated using state-averaged natural orbitals and the $(1a' \dots 6a' 1a'' 2a'')^{16}$ $(7a' \dots 13a' 3a'' \dots 7a'')^{17}$ CAS-CI model. The ground state dipole moment calculated using state-averaged NOs is 0.51 Debye,

State		configuration	N	E
C_{3v}	C_s			
X^2A_1	X^2A'	$1a_1^2 \dots 10a_1^2 1e^4 \dots 5e^4 1a_2^2 6a_1$	28329	-336.2903
A^2A_2	A^2A''	$6a_1^{-1} 2a_2^1$	28299	7.91
B^2E	$2^2A'$	$6a_1^{-1} 7a_1^1$	28329	8.66
	$2^2A''$	$6a_1^{-1} 3a_2^1$	28299	8.66
2^2E	$3^2A'$	$6a_1^{-1} 8a_1^1$	28329	9.72
	$3^2A''$	$6a_1^{-1} 4a_2^1$	28299	9.72

Table 6.4: The total ground X^2A_1 state energy (in Hartree) and vertical excitation energies (in eV) for the CF₃ target states generated using model 3 (see text for details) and state-averaged natural orbitals at equilibrium geometry. Also given are the dominant configuration of each state in C_{3v} and the number of configurations N in CI expansion.

which is close to the experimental value 0.43 ± 0.07 Debye (Butkovskaya et al 1979).

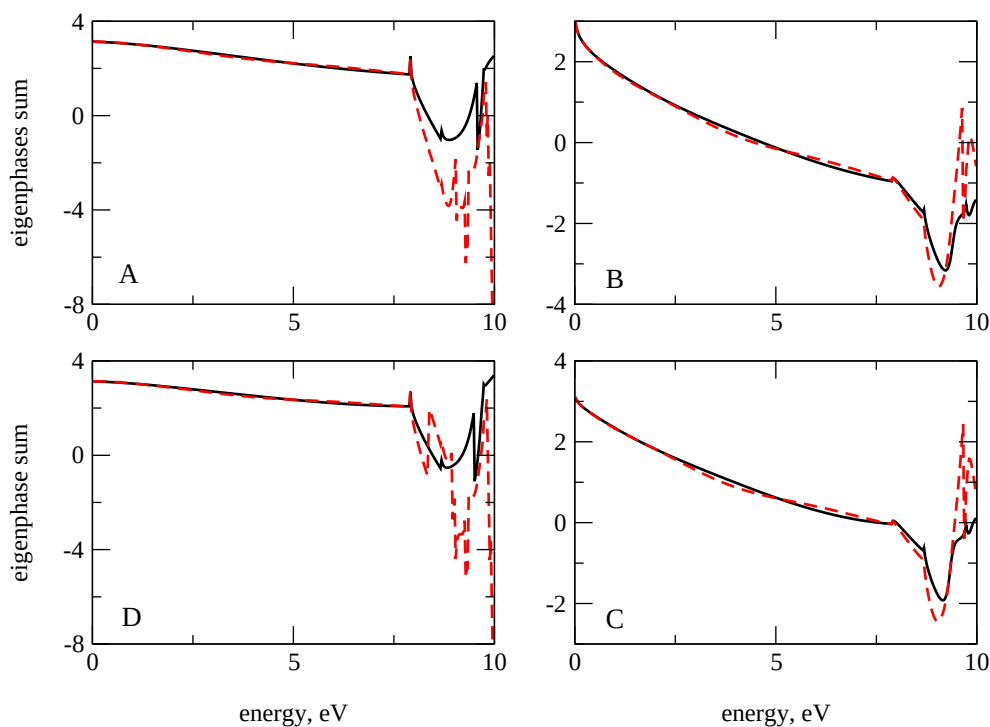


Figure 6.1: Eigenphase sums (in rad) for the $^1A''$ (A), $^1A'$ (B), $^3A'$ (C) and $^3A''$ (D) total symmetries of the CF_3 plotted at $a = 10 a_0$ (solid lines) and $a = 13 a_0$ (dashed lines).

6.3 Scattering Model

Scattering calculations were carried out on the six states of the CF_3 , presented in table 6.4. In all calculations the continuum orbitals, describing the incident electron, were represented by the Gaussian Type Orbitals (GTOs) of Faure et al. (2002) of up to g ($l \leq 4$) partial waves for both $a = 10 a_0$ and $13 a_0$. Previous calculation on the CF_2 (chapter 5) showed that these continuum orbitals give better results than the orbitals of Nestmann & Peyerimhoff (1990) or those of Sarpal et al. (1996). In order to test the stability of the model 3, scattering calculations were performed for two R-matrix radii $a = 10 a_0$ and $13 a_0$. The continuum GTOs were orthogonalized to the state-averaged NOs and among themselves using the symmetric orthogonalization procedure. During this process any continuum GTOs which correspond to very small eigenvalues of the overlap matrix (less than 2×10^{-8} for $a = 10 a_0$ and 2×10^{-9} for $a = 13 a_0$) were discarded.

For scattering energies below 8 eV both calculations give very similar answers, see figure 6.1. The final calculations used the R-matrix radius $a = 10 a_0$ 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 a 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 (Chu & Dalgarno 1974). CF_3 is a symmetric top molecule with the ground state dipole moment lying along z axis. The rotational constants calculated using the rigid experimental geometry are $B = 0.3525$ and $C = 0.18288 \text{ cm}^{-1}$.

The range of scattering energies was restricted to energies below 10 eV, as this is the range covered by the electronic states included in present calculations. Resonance positions and widths are normally found by fitting the eigenphase sum to a Breit-Wigner profile (Tennyson & Noble 1984).

6.4 Cross sections and bound states

Elastic cross sections were calculated at equilibrium geometry of the CF_3 using two values for the R-matrix radii. Figure 6.2 compares total elastic cross sections with added Born correction and the same cross section without Born correction calculated using $a = 10 a_0$. Those obtained using $a = 13 a_0$ 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 CF_2 , both of which support rich low energy resonant structures. In order to check if this is model dependent, the scattering calculations for target model 4 using $a = 10 a_0$ were also performed. 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 (see figure 6.3). The absence of any low-lying resonances means that CF_3 will not undergo dissociative electron attachment.

All scattering calculations do show the presence of a bound state of the $^1\text{A}_1$ symmetry at

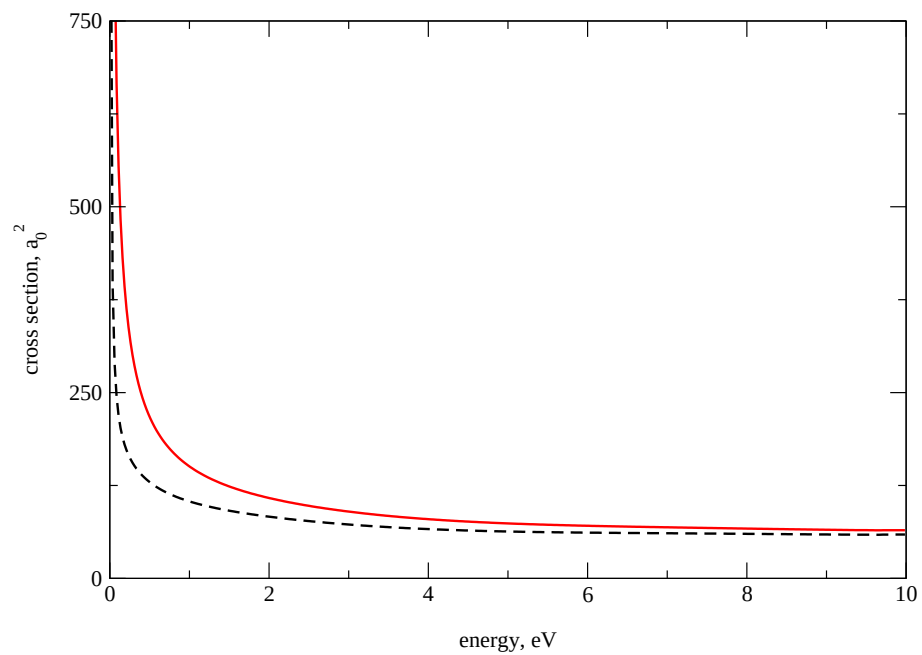


Figure 6.2: Total elastic cross section for molecule CF_3 at equilibrium geometry calculated using $a = 10 a_0$. Dashed line represents the cross section without Born correction. Solid line represents the cross section with added Born correction.

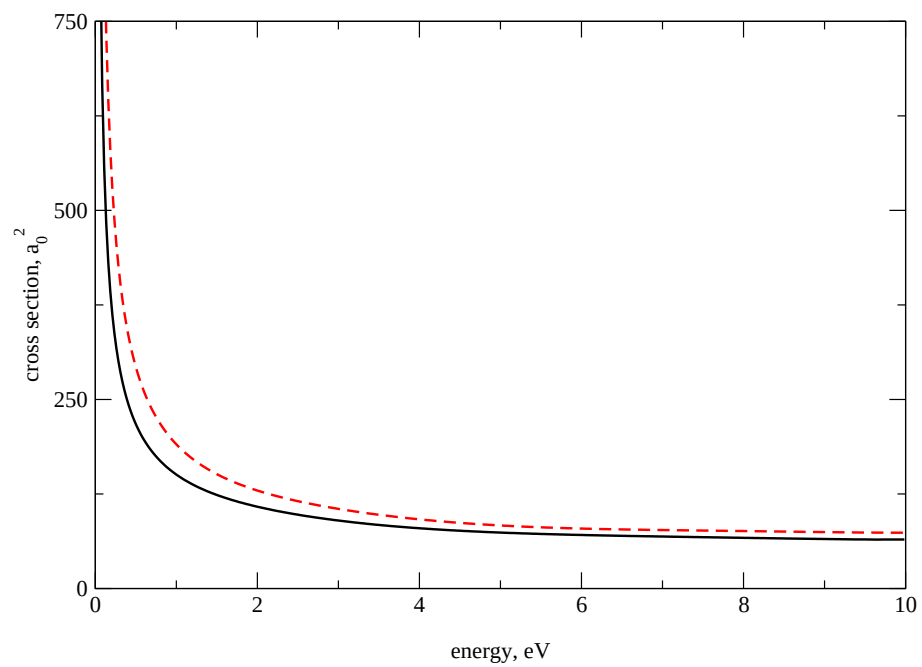


Figure 6.3: Total elastic cross section with added Born correction for the CF_3 for the models 3 (solid line) and 4 (dashed line) plotted at equilibrium geometry.

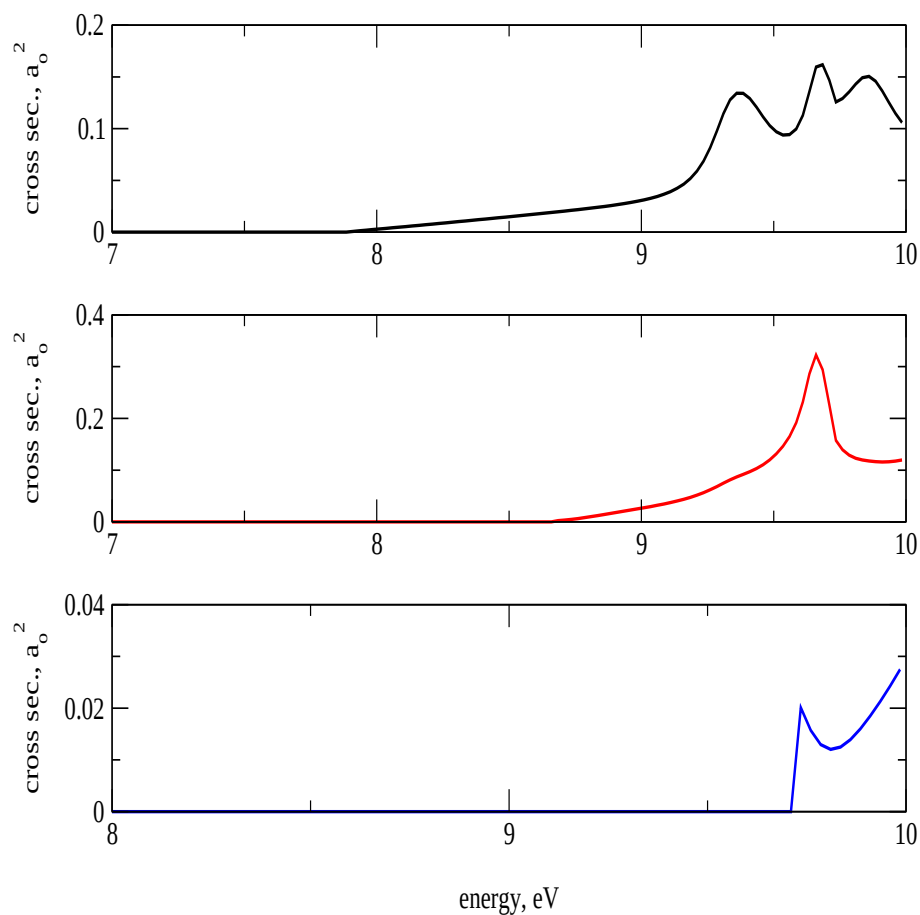


Figure 6.4: Top graph: electron impact excitation cross section with added Born correction for the excitation of the first excited $^2\text{A}_2$ state of the CF_3 . Middle graph: cross section with added Born correction for the transition into the second excited ^2E state. Bottom graph: cross section for the transition into the third excited ^2E state. States are labelled in C_{3v} molecular symmetry group.

the equilibrium geometry of CF_3 . The vertical binding energy of this state, estimated from pure bound state calculations, is about 0.6 eV.

Figure 6.4 presents the electron-impact excitation cross sections from the ground X^2A_1 state to the first, second and third excited states of the CF_3 in C_{3v} point group. The states $2^2A'$ and $2^2A''$, and $3^2A'$ and $3^2A''$ in C_s 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 $0.15 a_0^2$. 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.

6.5 Summary

The first study of low-energy electron collisions with the CF_3 molecular radical were performed. 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 (Morgan et al. 1998), using MOLPRO CASSCF NOs which give satisfactory target parameters when compared to the more comprehensive MRCI calculations. All 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.

Present calculations show the absence of any low-lying resonances which means that CF_3 will not undergo dissociative electron attachment. This can make a significant effect on surface chemistry during the etching.

Conclusions

7.1 Summary of results

Electron collisions with the CF_x radicals are studied in the low energy region (< 10 eV) using the UK molecular R-matrix codes and the target models which give satisfactory target parameters (eg. vertical excitation energies and the ground state dipole moment). Particular emphasis is given to resonances in the energy region below 5 eV as such low-lying resonances can become bound and then dissociate.

Target calculations employed different strategies for the three radicals considered in the present study. Thus, the CF target was modelled using natural orbitals and an approach where target molecular orbitals are divided into core, valence and Rydberg in order to treat the $\text{A } ^2\Sigma^+$ Rydberg state. The Rydberg molecular orbitals were constructed from single-excitation configuration interaction (CI) calculations with one electron excited into a separate Rydberg orbital space (Cooper & Kirby 1987). The target parameters generated using this approach are in good agreement with the theoretical and experimental values. The profiles of the potential energy curves of the CF show satisfactory agreement with the larger MRCI calculations of Petsalakis (1999).

The target parameters for the CF_2 were calculated using natural orbitals and are also in good agreement with the available experimental and theoretical values. The first potential

energy curves for the CF_2 were calculated in the course of this work.

The lack of data on the CF_3 radical mean that the R-matrix calculations had to be prefaced by *ab initio* CASSCF and MRCI MOLPRO calculations aimed at determining reliable target parameters. The first CASSCF and MRCI vertical excitation energies for CF_3 were calculated. The total ground state energies, obtained using the MOLPRO package and different basis sets, are in good agreement with available data. The quality of the scattering calculations depends on satisfactory representation of the target. In order to get an acceptable CF_3 target model the natural orbitals generated during the MOLPRO CASSCF calculations were first state-averaged using the R-matrix codes and then used in the final target calculation. The target parameters obtained using this strategy are in good agreement with the more comprehensive MRCI calculations.

The elastic cross sections and the excitation cross sections for the CF , CF_2 and CF_3 radicals were calculated. CF_x radicals are polar molecules and the elastic scattering cross section of a static molecules with a permanent dipole moment is divergent. A very large number of partial waves and rotational effects must be included in order to obtain convergent results. States with high l omitted from present calculations were added using a Born correction (Chu & Dalgarno 1974).

The scattering cross sections for CF were calculated at different geometries. Three shape resonances of symmetries $^1\Delta$, $^1\Sigma^+$ and $^3\Sigma^-$ were detected and fitted. Calculations, where a C-F bond was stretched from 1.8 to 3.6 a_0 , show that the resonances $^3\Sigma^-$ and $^1\Delta$ become bound at a bond length beyond 2.5 and 3.3 a_0 respectively. The resonance parameters suggest that the $^1\Sigma^+$ resonance will also become bound, but only at bond lengths larger than those considered here, and may provide a route for dissociative electron attachment (DEA) for this molecule. From the reflexion approximation, the $^3\Sigma^-$ and $^1\Delta$ resonances form vibrationally excited negative ions $(\text{CF}^-)^*$. Approximately 20% of the $^1\Sigma^+$ resonance asymptotically correlates with the excited $\text{C}(^1\text{D}) + \text{F}^-(^1\text{S})$ and the remaining 80% forms $(\text{CF}^-)^*$.

The elastic cross section and the excitation cross sections for the five lowest lying electronically excited states of the CF_2 were calculated. Two shape resonances of symmetries $^2\text{A}_1(^2\text{A}')$ and $^2\text{B}_1(^2\text{A}'')$ were detected and fitted. Calculations, in which one C-F bond was stretched from 1.8 a_0 to 3.7 a_0 with the other C-F distance and the angle CFC held at their equilibrium

values, show that $^2B_1$ ($^2A''$ in C_s) resonance is bound at a bond length beyond $3.2 a_0$. The reflexion approximation suggests that approximately 5% of the $^2B_1$ resonance asymptotically dissociates to $CF(^2\Pi) + F^-(^1S)$ and 95% forms a vibrationally excited negative ion $(CF_2^-)^*$.

Any DEA studies require a proper treatment of vibrational motion which is beyond a scope of the present work. Inclusion of the vibrational motion in the calculations will lower energies of target states and resonances and thus will effect the outcome of electron collisions with the CF and CF_2 radicals. It would be therefore interesting to analyse the $^1\Sigma^+$ (CF) and $^2B_1$ (CF_2) resonance parameters in improved calculations with an inclusion of vibrational motion.

The fact that the CF and CF_2 molecules may attach electrons means that a proportion of the product CF and CF_2 radicals in any plasma reactor may undergo DEA above the surface of the etching wafer. Such negative ions can produce a plasma sheaf above the surface which effects the surface chemistry.

Contrary to the calculations on CF and CF_2 , the present study on CF_3 shows an absence of any low-lying resonances, which means that CF_3 will not undergo dissociative electron attachment.

The absence of any electron attachment to the CF_3 radical, in contrast to CF and CF_2 radicals, 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 (Franklin & Snell 2000, Franklin 2002). 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_2F_6 , and C_4F_8 have been attributed to the presence of anions formed by dissociative attachment (Stoffels et al. 1998), with these 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 feed gas whose main product radical is CF_3 (e.g. CF_3I) with one having CF_2 (e.g. C_2F_4) both in the sheath dynamics and degree of resultant polymerization.

The absence of experimental data on electron – CF_x collisions makes it difficult to benchmark the present study. However, previous R-matrix calculations on low-energy electron collisions with the OCIO radical (Baluja et al. 2001b) gave generally excellent agreement with experimental measurements in the 0.1 eV to 10 eV energy range. At energies below 100 meV, however, the calculated cross sections do not reproduce the sharp minimum observed in the experiments (Field et al. 2000). This structure is almost certainly due to rotational coupling effects not explicitly included in Baluja *et al*'s calculations. Since these effects are also neglected in the present study, the cross sections presented throughout this work can be expected to be reliable only for energies above 0.1 eV.

7.2 Improvements to the calculations

As was emphasised before, the satisfactory representation of the target plays a key role in any scattering calculation. The CF target in this work is represented by Slater type orbitals with added diffuse basis functions in order to represent the $\text{A } ^2\Sigma^+$ Rydberg state. Further, the target molecular orbitals were divided into valence and Rydberg, which were formed using different sets of basis functions, compact and diffuse. Finally, the valence and Rydberg NOs were constructed from the appropriate molecular orbitals employing different strategies. Although, target calculations, performed using this approach, gave good results, the Rydberg orbital space could probably be improved to give better target parameters over the whole range of R values. This also could help to eliminate linear dependence at small R-matrix radii.

The CF_3 radical is an electron rich system and so far the largest molecule treated using the UK R-matrix codes. The CF_3 target is represented using the restricted model with 16 frozen and 17 valence electrons. Such a limited model was required due to computational limitations in the size of the $(N + 1)$ -electron Hamiltonian which could be diagonalized by the *SCATCI* module. The restriction on the size of the Hamiltonian means that the number of ' L^2 ' and target configurations, that could be considered in the expansion of the $(N + 1)$ wavefunction,

has to be also restricted. This may give a poor representation of the target, even though, the CF_3 target parameters obtained during R-matrix calculations are in good agreement with the more complete MRCI calculations. Since that time, improvements to the codes have been made which allow much larger Hamiltonian matrices to be treated and hence also a far greater number of configurations to be considered. These improvements are based on an implementation of the partitioned R-matrix theory, first proposed by Berrington & Ballance (2002) for atomic targets, in the UK molecular R-matrix codes (Tennyson 2003).

Of course, more experimental and *ab initio* work on the CF_x radicals needs to be performed by the scientific community in order to test the results presented here.

7.3 Applications and future work prospects

The calculation of cross sections for the electron collisions with the CF_x radicals in the low energy range has opened up a wide range of possibilities for future calculations and applications. Thus, the dissociative electron attachment cross section can be estimated as 50% of the cross section for excitation of an individual resonance (J. Tennyson, private communication). The DEA cross section as well as dissociation and ionization cross sections are used to determine the ionisation balance within the plasma and thus plasma properties such as the electron energy distribution (N. Mason private communications). The cross section data on CF and CF_2 has already been supplied to collaborators looking at dissociation rates of the CF_x radicals. The electron scattering cross sections presented in this thesis can also be used in plasma simulations (M. Kushner private correspondence) based on different plasma simulation tools such as the Virtual Plasma Equipment Model (Rauf & Kushner 1997).

Calculations performed in this work are expected to give a satisfactory description of the electron – molecule scattering problem only at energies of an incident electron above 100 mV. Below this energy rotational coupling must be taken into account (Field et al. 2000). One of future work prospects is therefore calculations which explicitly include couplings between rotational and other channels. Other possible future calculations include non-adiabatic R-matrix calculations (Schneider et al. 1979, Morgan 1995).

In non-adiabatic R-matrix theory, configuration space is split by a hypersphere defined by

$0 < r \leq a$, where r is the electron-centre of mass distance, and $A_{in} \leq R \leq A_{out}$ (figure 7.1). A_{in} is chosen so as just to exclude the singularity in the potential at the nuclei and A_{out} such that the target vibrational states have negligible amplitude for $R > A_{out}$.

In this model, configuration space can be split into three distinct regions depending on the outcome of the collision. $r > a$, with the bond length R remaining within the boundary, is equivalent to the electron simply scattering from the molecule. r remaining within the boundary but $R > A_{out}$ is characterized by dissociative attachment. With both $r > a$ and $R > A_{out}$, the molecule dissociates.

The non-adiabatic model includes vibrational functions in the close-coupling expansion. The functions are derived from the potential curves of the R-matrix poles which are tracked as a function of bond length in a series of adiabatic fixed-nuclei calculations. However, in order to calculate the vibrational functions, the diabatic potential of each R-matrix pole (i.e. the potential without avoided crossings) is required. Therefore, if there are sharp avoided crossings between the poles, the pole energies have to be reordered. This procedure has yet to be implemented in the R-matrix codes. One of the future work prospects is therefore a proper treatment of DEA for CF and CF₂ radicals with the inclusion of a vibrational motion.

Applications of the non-adiabatic approximation (Schneider et al. 1979) to nuclear vibration and dissociative attachment have been studied for several diatomic molecules (Morgan 1995). Sarpal et al. (1994) presented a theory for calculations of dissociative recombination and dissociative attachment cross sections applicable for systems with or without curve crossings.

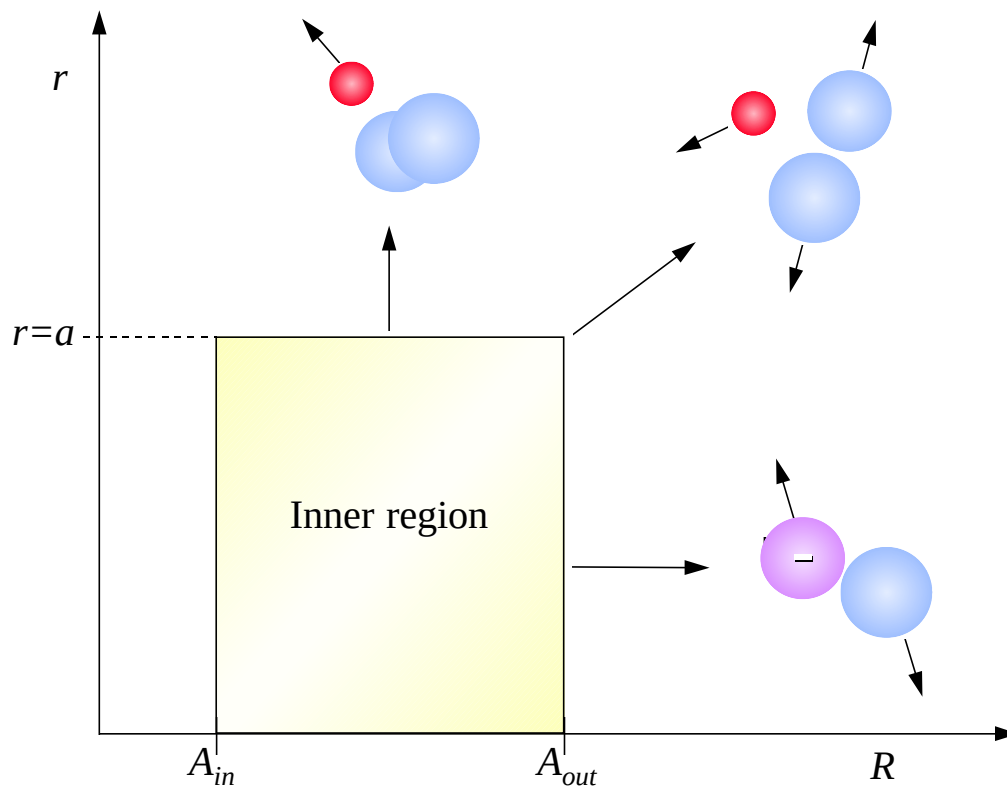


Figure 7.1: Splitting of configuration space in the non-adiabatic model. R is the bond length and r is the the distance of electron from the molecular centre of mass.

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