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Electron collisions with the CF_2 radical using the *R*-matrix method

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Abstract

The *R*-matrix method is used to treat electron collisions with the molecular radical CF_2. These calculations concentrate on obtaining low-energy (less than 10 eV) elastic and excitation cross sections of the six lowest-lying electronically excited states of the CF_2 molecule. These states have symmetry $^3B_1$, $^1B_1$, $^3A_2$, $^1A_2$, $^3B_2$ and $^1B_2$ and vertical excitation energies in the range 2.44–10 eV. Two shape resonances of $^2A_1$ and $^2B_1$ symmetries are found at 5.61 and 0.95 eV respectively. Calculations which stretch one C–F bond show that the $^2B_1$ resonance becomes bound at a bond length beyond 3.2 a_0. No other bound CF_2^- states are found.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The etching of wafers using molecular plasmas has driven many of the advances in the miniaturization of computer components. In these plasmas so-called feedstock gases are bombarded with electrons to produce chemically active molecular radicals and ions. It is these species which are responsible for the etching. Many of the processes that occur in these plasmas are both poorly characterized and poorly understood, which provides a significant impediment for the construction of reliable models of the etching process (Kushner 1996). Such models are essential if further advances are not to be constrained by lack of scientific understanding (Makabe 2001).

Environmental demands have led to the investigation of the CF_3I and C_2F_4 molecules as possible feedstock gases. When bombarded with electrons these systems fragment into various CF_x radicals, about which little is known. In particular, there appears to be essentially no information available on how these radicals interact with low-energy electrons.

In this paper we investigate collisions of (sub 10 eV) electrons with the CF_2 radical. To our knowledge there has been no previous theoretical work on this problem and the only experimental study dealt only with impact ionization (Tarnovsky *et al* 1993). CF_2 radicals are highly reactive and therefore difficult species to work with in the laboratory. This makes

theoretical approaches, provided they are reliable, an attractive source of information. In this work we use the UK R-matrix codes (Morgan *et al* 1998) and methods which have recently been benchmarked in a series of calculations (Baluja *et al* 2000, 2001a, 2001b) on Cl_xO_y radicals. In particular, studies on the electron-rich OClO radical gave excellent agreement with experiment over a range of energies (100 meV–6 eV).

2. Method

2.1. General theory

The R-matrix method is used to study the electron collisions with the molecular radical CF_2. This method (Burke and Berrington 1993, Morgan *et al* 1998) is based on splitting coordinate space into two regions by a sphere of radius a centred on the centre of mass of the molecule. The R-matrix sphere, chosen to be 10 a_0 in this work, contains all the charge cloud of the target. The interaction between the electron and the target molecule have different features in the inner region and outer region. Inside the R-matrix sphere the scattering electron lies within the molecular charge cloud and exchange and electron–electron correlation are taken into account using quantum chemistry methods. In the outer region these effects are assumed to be negligible and only long-range multipolar interactions between the scattering electron and the target are included.

In the inner region the total wavefunction describing scattering of an electron by an N-electron molecule is (Burke and Berrington 1993)

$$\Psi_k^{N+1} = A \sum_I \Psi_I^N(x_1, \ldots, x_N) \sum_j \xi_j(x_{N+1}) a_{Ijk} + \sum_m \chi_m(x_1, \ldots, x_N, x_{N+1}) b_{mk} \tag{1}$$

where A is the anti-symmetrization operator, x_n is the spatial and spin coordinate of the nth electron, ξ_j is a continuum orbital spin-coupled with the scattering electron and a_{Ijk} and b_{mk} are variational coefficients determined by our program. The first summation runs over all CI target states and gives terms known as 'target + continuum' configurations. The second summation runs over configurations χ_m, where all electrons are placed in target molecular orbitals. These configurations are generally described as 'L^2'.

The general application of the R-matrix method to polyatomic molecules employing the UK polyatomic R-matrix code has been described in the literature (Morgan *et al* 1998, Tennyson and Morgan 1999). The application of these codes to electron collisions with Cl_xO_y radicals was described by Baluja *et al* (2000, 2001a, 2001b).

2.2. Target representation

The equilibrium geometry of CF_2 was measured by microwave and absorption spectroscopy (Powell and Lide 1966, Kirchhoff *et al* 1973, Charo and De Lucia 1982, Mathews 1966, Mathews 1967). According to these studies the CF_2 molecule belongs to the C_{2v} symmetry group, the C–F bond length is 1.304 Å and the angle FCF is 104.8° at equilibrium. The calculations on the geometry of CF_2 performed recently (Russo *et al* 1992, Schwartz and Marshal 1999) are in a good agreement with these experimental results.

There have also been a several calculations that derive the singlet–triplet energy splittings of CF_2 (Russo *et al* 1992, Garcia *et al* 1996, Cai 1993). They were carried out at different levels. Only Cai (1993) studied the seven low-lying electronic states of the CF_2 radical using multireference single and double excitation configuration interaction (MRSDCI) calculations with a triple zeta (TZ + 2P) basis set. The adiabatic excitation energies for these states,

Table 1. Excitation energies (in eV) and dipole moments (in debye) for the CF_2 target states generated using a CASCI model with state-averaged pseudo-natural orbitals at equilibrium geometry. Also given are the dominant configurations of each state and the number of configurations N in C_{2v} symmetry.

State				This work		Theory	Observed
C_{2v}	C_s	Configuration	N	Δ	μ	Δ[a]	Δ
$X\ ^1A_1$	X^1A'	$(1a_1^2\cdots 6a_1^2)1b_1^2(1b_2^2\cdots 4b_2^2)1a_2^2$	4067		0.448		
$^3B_1$	$^3A''$	$1b_1^{-1}7a_1$	5826	2.49	0.47	2.42	2.46[b]
$^1B_1$	$^1A''$	$1b_1^{-1}7a_1$	3858	5.42	0.38	4.64	4.62[c]
$^3A_2$	$^3A''$	$1b_1^{-1}5b_2$	5811	9.06	0.31	6.31	
$^1A_2$	$^1A''$	$1b_1^{-1}5b_2$	3843	9.11	0.31	6.52	7.84[d]
$^3B_2$	$^3A'$	$4b_2^{-1}7a_1$	5802	9.52	0.32	7.76	

[a] From Cai (1993).
[b] From Koda (1978, 1979, 1982).
[c] From Mathews (1967).
[d] From Carter and Goddard (1988).

calculated by Cai, are shown in table 1. In our calculations we derive the vertical excitation energies, which are normally larger then the adiabatic ones.

Our calculations on CF_2 used the 6-311G* Gaussian basis set (11s5p/4s3p). We cannot use a very large (diffuse) set as it will extend outside the *R*-matrix box. We performed several test calculations using smaller basis sets (DZP, 6-31G, 6-311G, TZ). These basis sets gave a poor representation of the target properties, particularly the ground state dipole moment. The 6-311G* basis set gives a satisfactory compromise between the singlet–triplet energy gap and dipole moment which are both in good agreement with the experimental values. We then used this basis set in all scattering calculations reported here.

In order to get good target properties we used complete active space configuration interaction (CASCI) wavefunctions where the orbitals were represented by state-averaged pseudo-natural orbitals (NO) obtained from 'all single and double' configuration interaction (CI) calculations for all target states. A state-averaging of NOs was performed through averaging of density matrices. In the averaging procedure we included the $^1A_1$, $^3B_1$, $^1B_1$ and $^3A_2$ states with a maximum weight given to the first excited state as this model gave better target properties.

Our final CASCI calculations were divided into six core electrons and 18 valence electrons. The core electrons were frozen in doubly occupied molecular orbitals $1a_1$, $2a_1$, $2b_1$. The complete active space consists of 18 electrons that were allowed to move freely between 15 molecular orbitals: $3a_1$, $4a_1$, $5a_1$, $6a_1$, $7a_1$, $1b_1$, $2b_1$, $1b_2$, $2b_2$, $3b_2$, $4b_2$, $5b_2$ and $1a_2$. Table 1 compares ground state dipole moment and vertical excitation energies for the states considered in our calculation with data available in the literature.

The ground state dipole moment of 0.448 D, calculated using our model, is in a good agreement with the experimental value of Kirchhoff and Lide (1973) 0.469 ± 0.026 D and with 0.44 D calculated by Russo *et al* (1992).

At non-equilibrium geometries the CF_2 molecule belongs to the C_s point group. In C_s the lowest four molecular states are labelled $^1A'(\tilde{X})$, $^3A''$, $^1A''$, $^3A'$ respectively. The ground state electronic configuration CAS can be written as $(1a'\ 2a'\ 3a')^6\ (4a'\ldots 12a'\ 1a''\ldots 3a'')^{18}$. For the calculation of target properties in this case we used the same model as for the one described for equilibrium geometry. The electronic state energies as a function of changing one C–F bond are plotted in figure 1.

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

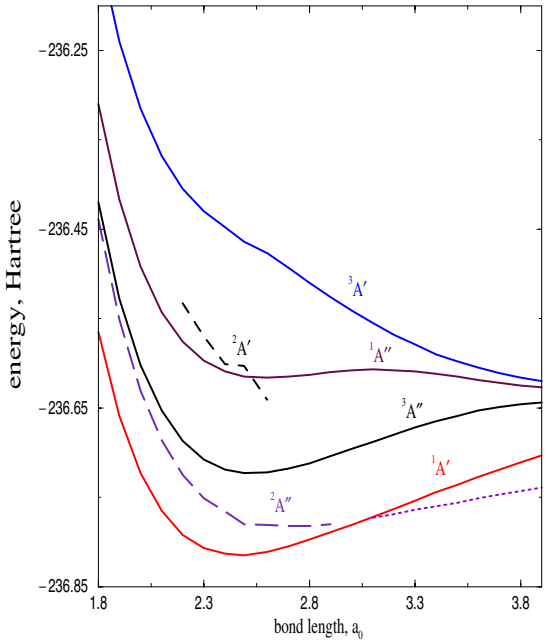

Figure 1. Electronic state energies of CF_2 as a function of changing one C–F bond, solid curves. The dashed curves represent the CF_2^- resonance energy curves; the dotted curve below the ground state curve represents the CF_2^- bound state curve. Curves are labelled using C_s point group symmetries.

2.3. Scattering model

Our scattering calculations included the seven states given in table 1. In all calculations the continuum orbitals describing the scattered electron were represented by Gaussians (GTO) centred on the centre of gravity of CF_2. The test calculations were performed using several continuum basis sets: Nestmann and Peyerimhoff's (1990) original continuum orbitals of up to f ($l \leqslant 3$) partial waves, continuum orbitals of Sarpal *et al* (1996) and orbitals of Faure *et al* (2001) up to g ($l \leqslant 4$) partial waves. Our final calculations used continuum orbitals of Faure *et al* (2002) as these gave the highest and smoothest eigenphase sums.

The elastic scattering cross section of static molecules with a permanent dipole moment is formally divergent. It is well known that 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 and Dalgarno 1974). The calculated rotational constants for the CF_2 molecule in the C_{2v} point group are 2.8295, 0.4028 and 0.3525 cm^{-1}. The dipole moment of CF_2 lies along the C_{2v} symmetry axis which we take as the z axis. The CF_2 molecule is an asymmetric top with an asymmetry parameter value of -0.96, so, to a good approximation we can treat it as a symmetric top.

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

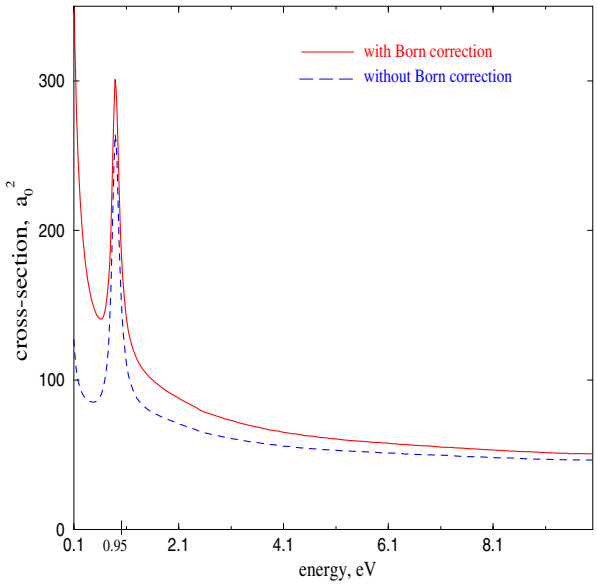

Figure 2. Total elastic cross section for the molecule CF_2 at equilibrium geometry. The dashed curve represents the cross section without Born correction. The solid curve represents the cross section with added Born correction.

3. Results

3.1. Elastic scattering

Elastic cross sections were calculated at different geometries. Previous *R*-matrix calculations on electron-OClO (Baluja *et al* 2001b) give generally excellent agreement with experimental measurements but shows disagreement between Born-corrected cross sections and the experimental values at energies below 100 meV. At the very low energy, the calculated cross sections do not reproduce the sharp minimum observed in the experiments. Field *et al* (2000) suggest that this structure is due to interference effects between rotational (and other) channels. Neither Baluja *et al* or our model includes rotational coupling.

The resulting elastic cross sections for CF_2 are shown in figure 2. Figure 3 gives the 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 $^2B_1$ symmetry ($^2A''$ in C_s). At equilibrium geometry this resonance has position and width of 0.95 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 1 and 4, respectively.

3.2. Bound state

CF_2 has an equilibrium dipole moment of 0.44 D. Our calculations show that CF_2 does not have any bound states at its equilibrium geometry. With increasing C–F bond length the $^2B_1$ ($^2A''$) resonance energy curve approaches the ground state energy curve. As one C–F bond length is

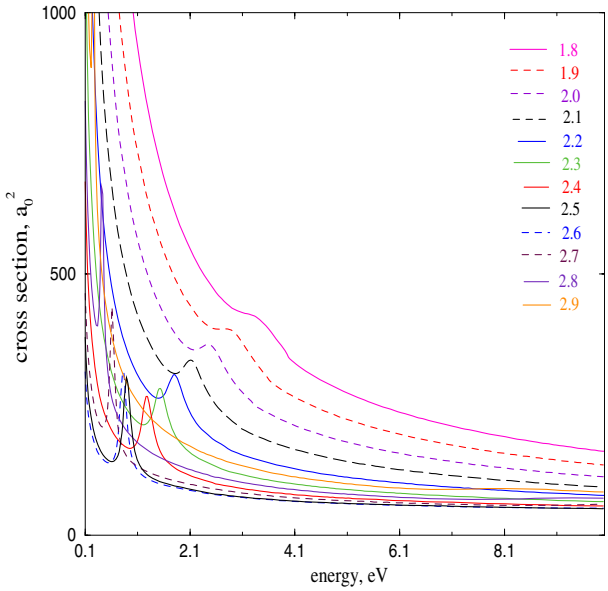

Figure 3. Total elastic cross sections for the molecule CF_2 plotted at different C–F bond lengths (from 1.8 to 3.0 a_0).

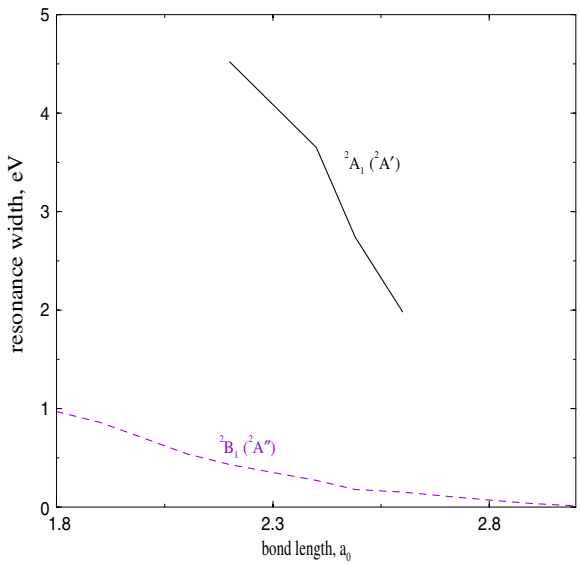

Figure 4. Resonance width as a function of C–F bond length. The solid curve represents the width of the shape resonance of $^2A_1$ ($^2A'$) symmetry. The dashed curve represents the width of the shape resonance of $^2B_1$ ($^2A''$) symmetry.

increased to 3.2 a_0, this resonance becomes bound (see figure 1). At larger bond lengths the energy of the bound state was calculated from the scattering wavefunctions using the program BOUND (Sarpal *et al* 1991). The $^2B_1$ ($^2A''$) resonance thus displays the classic behaviour one would expect of resonance supporting dissociative attachment. Asymptotically the resonance

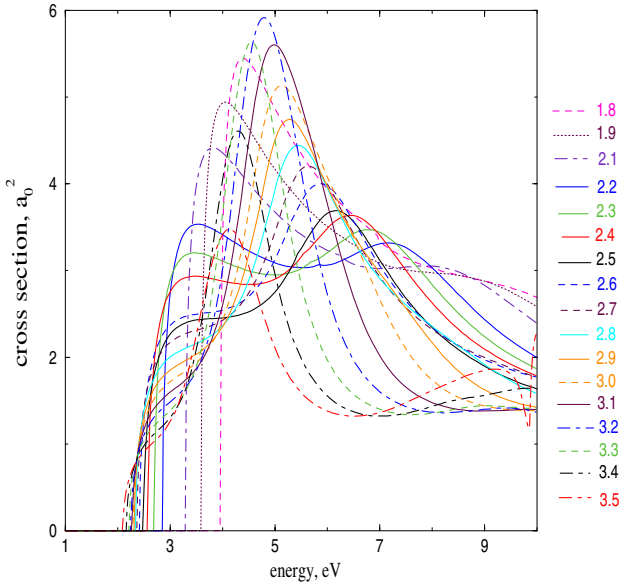

Figure 5. Total cross sections for electron impact excitation of lowest excited state $^3B_1$ ($^3A''$ in C_s) plotted at different C–F bond lengths (from 1.8 to 3.5 a_0).

dissociates to $CF(^2\Pi) + F^-(^1S)$ which one would therefore expect to be a major product of low-energy electron collisions with CF_2.

3.3. Inelastic scattering

Figures 5 and 6 presents electron-impact electronic excitation cross section from the 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 and 2.87 eV, respectively. This shape resonance binds the extra electron in the 7 a_1 orbital. It is very broad resonance and could not be detected in our calculations with C–F bond lengths beyond 2.7 a_0 (see figure 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 D at equilibrium geometry. The effect of high partial waves excluded from our calculations was added via a Born correction formula (Chu and Dalgarno 1974). Figure 7 displays the final cross sections for the excitation of $^1B_1$ state. The Born correction is very small and increases with an increase in energy of the incident electron. There are no resonance features apparent in this excitation cross section.

4. Conclusions

We have performed the first study of low-energy electron collisions with the molecule CF_2. The elastic cross section and the excitation cross sections for the six lowest-lying electronically excited states of CF_2 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 singlet–triplet energy splitting and the ground state dipole moment. Our calculations show

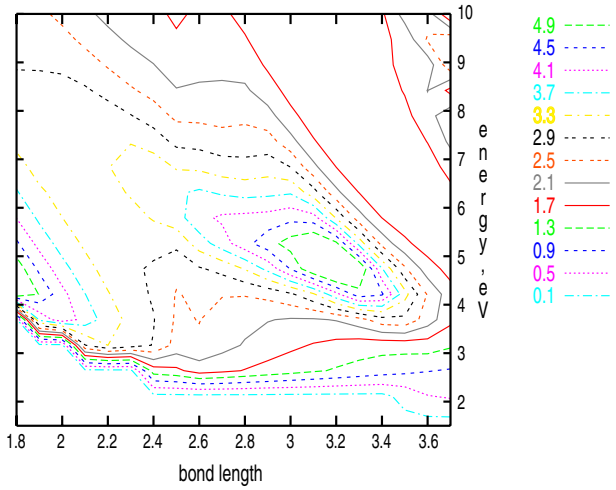

Figure 6. Contour plot of the total cross sections for the excitation of the lowest excited state $^3B_1$ ($^3A''$) plotted at different C–F bond lengths (in a_0) from 1.8 to 3.5 a_0.

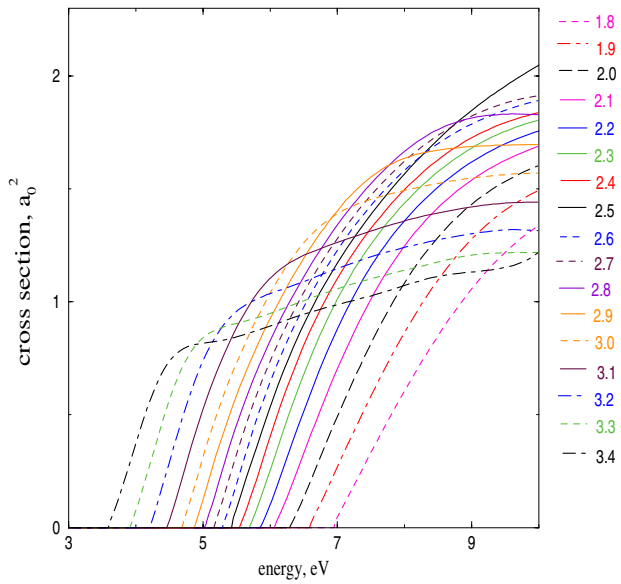

Figure 7. Total cross section for electron impact excitation of the second lowest excited state $^1B_1$ ($^1A''$) plotted at different C–F bond lengths (from 1.8 to 3.4 a_0).

the presence of two shape resonances of symmetries $^2A_1$ ($^2A'$) and $^2B_1$ ($^2A''$) at 5.61 and 0.95 eV respectively. The $^2A_1$ ($^2A'$ in C_s) resonance is broad and short lived. Performing an asymmetric stretch of CF_2 we found that $^2B_1$ ($^2A''$ in C_s) resonance is bound at a bond length beyond 3.2 a_0, providing a route for dissociative attachment in this molecule. Although there is no experimental data on the cross sections for the molecule CF_2, previous studies (Baluja *et al* 2001b) suggest that our elastic cross section should be reliable for energies above 100 meV. Below this energy rotational coupling needs to be explicitly included.

Acknowledgments

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