International Journal of Mass Spectrometry 192 (1999) 205–214

Electron-transfer and neutral-loss reactions in collisions of CF_3^{2+} with argon

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Received 21 January 1999; accepted 19 March 1999

Abstract

We have recorded the relative intensities of the product ions formed following collisions of CF_3^{2+} with Ar at collision energies between 1.8 and 4.4 eV in the centre of mass frame. These experiments show that electron-transfer and neutral-loss reactions dominate the ion yield. The neutral-loss reaction produces CF_2^{2+} whilst the electron-transfer reactions produce CF^+ and CF_2^+ together with Ar^+. The variation of the neutral-loss ion yield with the collision energy provides a first estimate for the bond energy of the weak CF_2^{2+}–F bond as 58 kJ mol^{-1}. Unrestricted Hartree Fock/second order Moller-Plesset ab initio calculations indicate that the ground state of CF_3^{2+} adopts a C_{2v} equilibrium geometry. Complete active space self-consistent field/multireference configuration interaction calculations of the electronic states of CF_3^+ at the C_{2v} geometry of the dication have also been performed. Using these calculated state energies, together with Landau-Zener theory, to try to rationalise the electron-transfer reactivity, it appears likely that at least two electronic states of CF_3^{2+} are present in the dication beam. The ground state of CF_3^{2+} is predicted to react via electron transfer to form predominantly CF_2^+. An excited state of CF_3^{2+} lying approximately 5 eV above the ground state is hence required to explain the presence of CF^+ ions that we observe in the experiments. (Int J Mass Spectrom 192 (1999) 205–214) © 1999 Elsevier Science B.V.

Keywords: Electron transfer; Dication; Landau-Zener; Ion–molecule reaction; Ab initio

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1. Introduction

Molecular doubly charged ions (dications) are highly energy-rich and reactive metastable species that are the subject of an increasing number of experimental and theoretical investigations [1–3]. As with any poorly characterised species, the majority of these experimental investigations have concentrated on probing the properties of molecular dications in an isolated environment. However, attention has recently focused on the reactivity of molecular dications following collisions with neutral species [4–13].

In general, the majority of small molecular dications are thermodynamically unstable with respect to a corresponding pair of singly charged ions. Hence, many of the electronic states of small molecular dications rapidly undergo unimolecular charge separation:

$$CF_2^{2+} \rightarrow CF^+ + F^+ \tag{1}$$

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PII S1387-3806(99)00093-7

However, despite these thermodynamic constraints, most small molecular dications possess at least one long-lived (metastable) electronic state due to a barrier in the pathway to the charge-separation asymptote. Quite frequently, these metastable states can be populated in an ionizing transition from the associated neutral molecule, allowing the production of molecular dication beams with intensities suitable for collision studies.

Early experiments to investigate the reactivity of molecular dications involved colliding doubly charged ions formed by nondissociative double ionization of stable molecules (e.g. CS_2^{2+}, CO^{2+}) with atomic targets [14–18]. These experiments revealed a rich electron-transfer reactivity [Eq. (2)], which was rationalised using a simple model based on Landau-Zener theory [11], accompanied by dicationic charge-separation [Eq. (3)] induced by collisional energy transfer,

$$CO_2^{2+} + Ar \rightarrow CO_2^{+} + Ar^{+} \tag{2}$$

$$CO_2^{2+} + Ar \rightarrow CO^{+} + O^{+} + Ar \tag{3}$$

Later experiments explored the reactivity of fragment dications (e.g. CF_2^{2+}, SiF_2^{2+}), formed by dissociative double ionization of stable molecules, in collisions with atomic targets [19–21]. These experiments found a similar electron-transfer reactivity to that observed for conventional dications (CS_2^{2+}, CO^{2+}), together with a propensity for the dications to lose neutral species upon collisional excitation [20,22]

$$CF_3^{2+} + Ar \rightarrow CF_2^{2+} + F + Ar \tag{4}$$

More recent experiments, involving collisions between dications and molecular targets, have revealed that molecular dications can undergo true "chemical" reactions involving the formation of new bonds [9,12,23].

This article presents an investigation of the product ions formed following collisions of CF_3^{2+} with Ar. We study the relative yields of the electron-transfer reactions and also investigate the collision-energy dependence of the neutral-loss reactions. The latter aspect of the investigation allows us to estimate the first C–F bond energy in CF_3^{2+}.

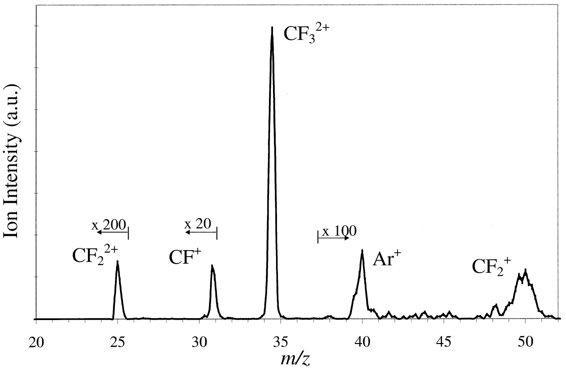

Fig. 1. Representative mass spectrum recorded after the interaction of a beam of CF_3^{2+} ions with Ar atoms at a collision energy of 3.3 eV in the centre-of-mass frame.

2. Experimental

The apparatus used in the investigations reported in this article has been described in detail before [10]. Briefly, the molecular dication of interest is mass selected, using a velocity filter, from the positive ions produced in an electron-impact ionization source. To produce CF_3^{2+} we utilise the dissociative double ionization of CF_4 by 150 eV electrons. The resulting dication beam is decelerated, using an electrostatic decelerator, to the required collision energy and then encounters an effusive beam of Ar. These collisions take place in the source region of a time-of-flight mass spectrometer (TOFMS), which is used to identify and quantify the charged products of the interactions. A section of a typical mass spectrum is shown in Fig. 1.

We are careful to maintain the number density of the neutral collision partner such that single collision conditions exist in the source region of the TOFMS [24]. This is confirmed by a linear dependence of the product ion yields on the neutral gas pressure. Mass spectra recorded in the absence of the neutral collision partner are used, as described below, to correct the product ion mass spectra for impurity ions. These impurity ions may arise from imperfect operation of the velocity filter or dication collisions with background gas.

In this work the ionic products following collisions between CF_3^{2+} and Ar were monitored at centre-of-mass collision energies from 1.8 to 4.4 eV. The centre-of-mass collision energy is calculated using the initial dication velocity, which is known from the beam potential, and assuming that the velocity of the neutral molecule is negligible with respect to the velocity of the dication. Given that the neutrals are admitted as an effusive beam and that the dication beams have energies between 3 and 12 eV in the laboratory frame, this approach is perfectly satisfactory.

As shown in Sec. 3, when the mass spectra are corrected for any impurity ions in the dication beam, we clearly see that CF_2^{2+}, CF^+, CF_2^+, and Ar^+ ions result from bimolecular encounters of CF_3^{2+} with Ar.

3. Theory

As is discussed in Sec. 4, our experimental results indicate that CF_3^{2+} principally reacts with argon by losing a neutral F atom [Eq. (4)] or via electron-transfer. Such electron-transfer reactions can, as illustrated in Eq. (2), be nondissociative and populate stable states of CF_3^+. Alternatively [as shown in Eq. (5)], dissociative electron-transfer may occur. The detailed mechanism of this reaction has recently been elucidated by elegant angular scattering measurements [25], confirming the previous assumption that unstable states of the parent monocation, in this case CF_3^+, are initially populated following electron-transfer. These unstable states subsequently dissociate to form fragment ions such as CF_2^+ or CF^+:

$$CF_3^{2+} + Ar \rightarrow CF_3^{+*} + Ar^+ \rightarrow CF_2^+ + F + Ar^+ \tag{5}$$

In previous work, the electron-transfer reactivity of molecular dications has been rationalised using a simple model based on the Landau-Zener theory [17]. In order to apply this model to the CF_3^{2+}/Ar collision system we need to know the electronic state energies of CF_3^{2+} and CF_3^+ at the geometry at which the electron-transfer reaction occurs. As CF_3^{2+} is the reactant species, we assume the geometry of the electron-transfer reaction is that of the equilibrium geometry of the ground state of CF_3^{2+}. Unfortunately, the electronic and structural data required for this analysis are not available in the literature and we have been forced to calculate the required energetics ab initio. Sec. 3.1 describes our ab initio methodology and is followed by a description of how these energetic data are used in the Landau-Zener algorithm to model the electron-transfer reactions of CF_3^{2+}.

3.1. Ab initio methodology

Ab initio calculations have been performed using the GAUSSIAN98 [27] and MOLPRO96.4 [28] program suites. All calculations were carried out at the unrestricted Hartree-Fock level with the correlation consistent valence triple zeta basis set of Kendall *et al*. [29]. The geometry of the $^2B_2$ ground state of CF_3^{2+} was calculated using GAUSSIAN98, electron correlation being included at the MP2 level. The electronic states of CF_3^+ at the ground state geometry of CF_3^{2+} were then calculated using the state-averaged complete active space self-consistent field/multireference configuration interaction (CASSCF/MRCI) [30–33] approach implemented in MOLPRO. The active space for the CASSCF calculations comprised the nine highest occupied molecular orbitals (i.e. 18 electrons) and the four lowest unoccupied molecular orbitals. The energies of the lowest three roots of the singlet and triplet states of each of the four spatial symmetries of C_{2v} were calculated.

3.2. Reaction window theory

As described in Sec. 2, mass spectra were recorded following collisions between CF_3^{2+} ions and Ar target molecules at centre-of-mass collision energies between 1.8 and 4.4 eV. In order to explain the relative yields of the electron-transfer reactions in this collision system we employ an algorithm based on the Landau-Zener theory [34–36].

A detailed description of the Landau-Zener theory and its implementation in dication/neutral collisions is provided elsewhere [11]. Briefly, the electron-transfer is considered to occur at an avoided crossing between diabatic reactant and product potential energy curves. As the system passes twice through the curve crossing, the probability P for an electron-transfer reaction occurring is given by

$$P = 2\delta(1 - \delta) \tag{6}$$

where δ is the probability of the collision system remaining on the same diabatic curve on a pass through the crossing point, and can be calculated using the Landau-Zener equation:

$$\delta = \left(\frac{-\pi|H_{12}|^2}{2\hbar|V'_p - V'_r|v}\right) \tag{7}$$

As shown in Eq. (7), δ is a function of $|H_{12}|$, the electronic coupling matrix element between the two states, $|V'_p - V'_r|$, the difference in the slopes at the curve crossing of the diabatic curves representing the reactant and product potentials and v, the relative radial velocity at the curve crossing. For our dication–neutral systems, we model the reactant potential V_r purely as polarization attraction and the product potential V_p solely as the coulombic repulsion between the product singly charged ions. To place these two potentials on the same scale we require the reaction exothermicity ΔE for populating given electronic states of the product ions ($CF_3^+ + Ar^+$) from given electronic states of the reactant species ($CF_3^{2+} + Ar$). To evaluate the reaction exothermicity ΔE, given the shortage of relevant experimental thermodynamic data for this collision system, we require ab initio calculations of the relative energies of the electronic energy levels of CF_3^{2+} and CF_3^+ at the equilibrium geometry of CF_3^{2+}. Then, using this value of ΔE we have

$$V_p = e^2/4\pi\epsilon_0 r \tag{8}$$

$$V_r = -e^2\alpha/2\pi\epsilon_0 r^4 + \Delta E \tag{9}$$

Using these potentials we can then evaluate the curve-crossing radius, $|V'_p - V'_r|$ and, for a given impact parameter and collision energy, the relative radial velocity. $|H_{12}|$ is estimated using the empirical equations of Olson *et al.* [26] which have been used by several authors and have proved reliable in this role in recent studies [11,17,19,20]. Given the above parameters we can then evaluate the electron-transfer cross section for forming the electronic state of the product ions for which we derived the exothermicity by integrating P with respect to the impact parameter b between $b = 0$ and the maximum value of b for which the collision reaches the crossing radius.

As has been discussed previously, the above theoretical approach is approximate [11,20]. Most importantly it neglects any anisotropy in the potential surfaces. However, in the past this model has proved highly successful in the semiquantitative rationalisation of the product ion yields from molecular dication electron-transfer reactions. This success is principally due the fact that electron-transfer occurs efficiently at significant interspecies separations where the model potentials provide a good approximation to the real potential energy surfaces. Indeed, as has been noted before [11,20], the scarcity of data on both the energetics and potential energy surfaces of the reactant molecular dications and the interaction potentials between the reactants preclude a more rigorous approach.

It is worth repeating that to construct the product and reactant potentials we require the energy difference between the products (e.g. $CF_2^+ + F + Ar^+$) and reactants ($CF_3^{2+} + Ar$). As was explained previously, since no energetic information is available for the CF_3^{2+}/CF_3^+ electron-transfer system we have calculated the relevant electronic energy levels ab initio.

4. Results and data analysis

4.1. Experimental

When the raw ion intensities from the mass spectra are corrected [10–13], using mass spectra recorded in the absence of any collision gas, for the presence of the small number of F_2^+ and CF^+ impurity ions present in the ion beam, we clearly see that the only ions formed in bimolecular encounters are CF_2^{2+}, CF^+, CF_2^+, and Ar^+. A typical set of background corrected ion intensities confirming this conclusion are shown in Table 1, together with their associated experimental uncertainties.

The identities of these product ions immediately

Table 1
Background corrected product ion intensities [in arbitrary units (au)] recorded following collisions of CF_3^{2+} with Ar at a collision energy of 3.3 eV in the centre of mass frame; the number in parentheses gives the uncertainty in the last figure of the product ion intensity

Product ion	CF_2^{2+}	CF^+	Ar^+	CF_2^+	F_2^+
Intensity (au)	64 (7)	161 (36)	170 (14)	201 (14)	−1 (26)

allow considerable insight into the reactivity of the CF_3^{2+}/Ar collision system. The observed CF_2^{2+} product ion can only be formed as a result of collision-induced neutral loss:

$$CF_3^{2+} + Ar \rightarrow CF_2^{2+} + F + Ar \tag{10}$$

The relative yield of CF_2^{2+} in the background corrected mass spectra, as a function of the centre-of-mass collision energy, is shown in Fig. 2 and clearly indicates the threshold for CF_2^{2+} formation is approximately 0.6 eV.

The CF_2^+ and CF^+ product ions that we detect can be formed by either dissociative electron-transfer [Eq. (5)] or collision-induced charge separation:

$$CF_3^{2+} + Ar \rightarrow CF_2^+ + F^+ + Ar \tag{11}$$

However, the absence of any F^+ signal in our mass spectra eliminates the possibility of collision-induced charge separation as the source of CF_2^+ and CF^+. Hence, we assign these ions as the products of dissociative electron-transfer reactions. Indeed, the formation of just CF^+ and CF_2^+ ions from CF_3^{2+} following electron-transfer has been reported before [23].

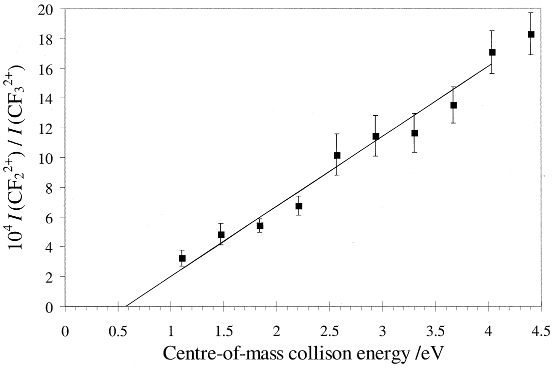

Fig. 2. Variation of the ion intensity of CF_2^{2+}, relative to the number of unreacted dications, as a function of collision energy following collisions of CF_3^{2+} with Ar. The line is a least-squares fit to the data.

Having identified the principal reactive channels in the CF_3^{2+}/Ar collision system, we now focus on the details of the reactivity exhibited. An investigation of the mechanism of the electron-transfer reactions requires the extraction of the true relative ion yields from the mass spectra and, hence, a consideration of the ion detection efficiency.

Relative ion intensities: As described in Sec. 4.1, the product ion intensities that result from the CF_3^{2+}/Ar encounters are obtained by adjusting the raw ion intensities in the mass spectrum for any background ion contribution. With our dication beams such corrections are small. However, when we wish to consider the relative intensities of the product ion signals we must consider the possibility that mass discrimination effects may mean that these background corrected signals do not exactly represent the true ion yields.

If a reaction occurs during the collision of the dication with the neutral target, the dynamics of the reaction may result in a significant release of kinetic energy. Each reaction channel may have a different average kinetic energy release (KER) and a different distribution of kinetic energy releases. This KER, which is released in the centre-of-mass frame, changes the translational energy of the reaction products in the laboratory frame. Hence, the different product ions may well have different velocities across the source region of the TOFMS. Owing to these different transverse velocities, the product ions may travel different transverse distances as they fly down the TOFMS to reach the multichannel plate (MCP) detector. Those ions with larger transverse kinetic energies in the laboratory frame will travel a greater distance away from the central axis of the TOFMS than less energetic product ions. Owing to this effect, the length of the source region in the direction of the ion beam which is imaged onto the MCP detector varies with the total kinetic energy of the product ion. Hence, the background corrected ion count must be further adjusted, to allow for this potential discrimination, to yield the true relative ion intensities.

In principle, the transverse velocity of the product ions in the laboratory frame can be calculated, given the value of the KER for the reaction and the laboratory-frame collision energy using basic kinematics. This approach involves assuming, as has been shown recently to be the case for CF_2^{2+}/D_2 [25], that dissociative electron-transfer involves the population of unstable states of CF_3^+ which subsequently dissociate to form CF^+ or CF_2^+ with an energy release negligible in comparison to that of the coulombic repulsion between the Ar^+ and the parent CF_3^+ ion. Unfortunately, no data concerning the values of the KER for the electron-transfer reactions between CF_3^{2+} and Ar are available in the literature. However, product-ion KER distributions have been determined for the electron-transfer channels in the CF_2^{2+}/D_2 collision system [9]. Given the lack of any other information, we have used the mean KER value for the CF_2^{2+}/D_2 collision system to correct our experimental ion intensities for the CF_3^{2+}/Ar system. We do not feel that using this datum is a major approximation, as undoubtedly the KER of the electron-transfer channels in both collision systems is dominated by the coulombic repulsion between the singly charged product ions. In fact, the relative correction factors we will calculate are not a strong function of the KER, supporting this approach. To use these representative KER values to determine the average product ion velocity we also assume that the dynamics of the collision system predominantly involve forward scattering. Again, this is an assumption, but angularly resolved investigations indicate that forward scattering is the dominant reaction mechanism in dication electron-transfer reactions [4,9,25]. After using the representative KER values to determine the product ion velocities, the following correction formula is applied to the background corrected ion intensities I to give the true relative ion intensities R for CF_2^+ and CF_3^+:

$$\frac{R_{CF^+}}{R_{CF_2^+}} = \frac{I_{CF^+}}{I_{CF_2^+}} \frac{L_{CF_2^+}}{L_{CF^+}} \frac{v_{CF^+}}{v_{CF_2^+}} = \alpha \frac{I_{CF^+}}{I_{CF_2^+}} \tag{12}$$

Table 2
Correction factors α calculated by using Eq. (12) for the relative detection efficiency of CF_2^+ and CF^+ and the resulting relative ion intensities $R(CF^+)/R(CF_2^+)$ derived from the background corrected experimental data

E_{COM} (eV)	α	$R(CF^+)/R(CF_2^+)$
4.4	0.59	0.65
4.0	0.62	0.57
3.7	0.64	0.72
3.3	0.66	0.53
2.9	0.68	0.51
2.6	0.71	0.31
2.2	0.73	0.57
1.8	0.75	0.51

The derivation of this formula has been described in the literature before [10] and, as described above, its use requires the KER of the reaction to calculate the velocity v of a product ion transverse to the axis of the TOFMS and the geometry of the apparatus to determine the length L of the TOFMS source region imaged onto the detector for an ion with this velocity. Calculating α for the collision energies employed in this work (Table 2) we see that our detection efficiency varies only slightly (12%) over the collision energies employed in this work and we always discriminate slightly against detection of the CF_2^+ ion. This discrimination arises as the velocity of both the CF_2^+ and CF^+ ions across the source region is determined by the initial velocity of the CF_3^{+*} ion, the primary product of the electron-transfer reaction. Hence, the heavier CF_2^+ ion has a larger transverse kinetic energy and is less efficiently detected. Correcting our background corrected ion intensities using the values of α (Table 2) yields the relative intensities also listed in Table 2 and plotted in Fig. 3. In Fig. 3 we see that within our error limits the relative cross sections for forming CF_2^+ and CF^+ are in an approximate ratio of 2:1 and do not vary significantly with the collision energy.

4.2. Theoretical

Our ab initio calculations indicate that the $^2B_2$ ground state of CF_3^{2+} has a "T" shaped C_{2v} geometry,

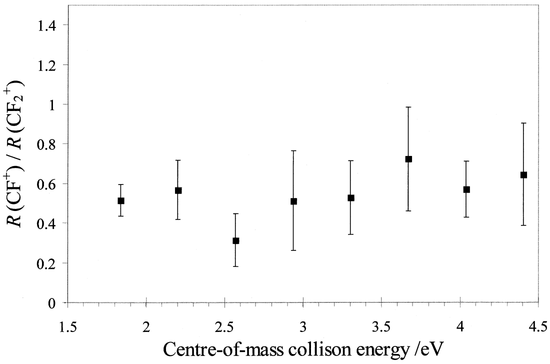

Fig. 3. Variation of the relative ion intensity of the CF^+ and CF_2^+ product ions, as a function of collision energy, following collisions of CF_3^{2+} with Ar.

illustrated in Fig. 4, with one long and two short C–F bonds. This structure and its total energy (−335.90 Hartree) are in excellent agreement with very recent calculations of Hrusak et al. (total energy = −335.93 Hartree) [37].

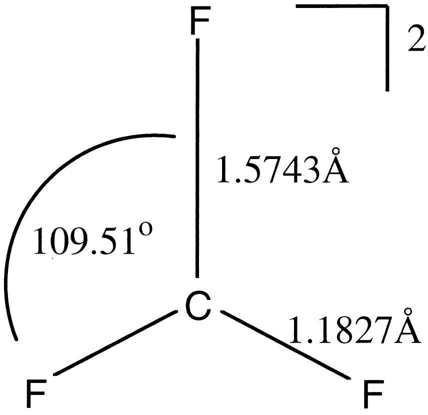

Fig. 4. The calculated geometry of the $^2B_2$ ground state of CF_3^{2+}.

Table 3
The energies (eV) of the lowest lying electronic states of CF_3^+ (relative to the energy of the $^1A_1$ ground state in its equilibrium D_{3h} geometry) at the geometry of the $^2B_2$ ground state of CF_3^{2+}

State	Energy (eV)		
$^1A_1$	0.226	7.605	15.766
$^3A_1$	7.205	8.88	13.542
$^1A_2$	7.428	11.475	15.096
$^3A_2$	7.367	11.356	14.823
$^1B_1$	8.625	8.806	14.033
$^3B_1$	8.031	8.831	14.008
$^3B_2$	7.748	11.085	14.715

Since electron transfer will result in the formation of CF_3^+ ions with the geometry of the reactant dication, to apply the Landau-Zener model to our collision system and explain the observed relative yield of CF^+ and CF_2^+ we require the energies of the ground and excited states of CF_3^+ at the dication geometry. Our calculated relative energies of the lowest lying states of CF_3^+ at the ground state geometry of CF_3^{2+} are given in Table 3. Unfortunately it was not possible to converge the state-averaged CASSCF/MRCI calculations for the $^1B_2$ states, but it is very likely that these state energies differ from those of the $^3B_2$ states by an amount similar to the differences between the other singlet and triplet states.

5. Data interpretation and discussion

5.1. Neutral-loss reactivity

Fig. 2 shows the yield of the neutral-loss reaction [Eq. (4)] as a function of the centre-of-mass collision energy. As shown in Fig. 2, linear extrapolation of the CF_2^{2+} yield to the energy axis results in an estimate of the energy required to collisionally dissociate a F atom from CF_3^{2+}. This estimate provides a lower bound on the bond energy as the contribution of any internal excitation in the CF_3^{2+} projectile to breaking the C–F bond is neglected. This estimate of the bond energy (0.57 ± 0.13 eV) indicates, as expected, that the CF_3^{2+} dication possesses one extremely weakly bound (~55 kJ mol^{-1}) fluorine atom.

The C_{2v} geometry of CF_3^{2+} has, as in the case of the isoelectronic BF_3^+ ion [38], been ascribed to a second-order Jahn-Teller distortion [37]. This distortion results in the lowering of the symmetry of the ground state with a lengthening, and consequent weakening, of one of the C–F bonds. However, the neutral-loss reactivity exhibited in the collisional reactions of CF_3^{2+} is not an isolated phenomenon. Neutral-loss reactivity contributes significantly to the product ion yields following bimolecular collisions of a wide variety of perfluorinated dications [20–23].

Clearly, ab initio investigations of the electronic structure of a variety of the perfluorinated dications would be valuable in determining if Jahn-Teller distortions are always at the heart of the neutral-loss reactivity of dications, or whether, as has been previously proposed [22], large dications consist of a strongly bound dication core (e.g. CF_2^{2+}) together with one or more weakly bound atoms.

5.2. Electron-transfer reactivity

To attempt to explain the relative ion yield of CF_2^+ and CF^+ (Fig. 3) we have used the Landau-Zener algorithm described above, together with our calculated state energies to calculate the cross sections for populating the low lying electronic states of CF_3^+ from the ground state of CF_3^{2+}. However, to transform these calculated electron-transfer cross sections into a prediction of the ion yield we need to know the stability of the CF_3^+ states we populate. Unfortunately again, unlike more common ions (e.g. OCS^+), this information is unavailable. Hence, we are forced to fall back on a series of assumptions that have been used previously to predict the fate of excited states of molecular ions formed in electron-transfer reactions [11,17,19,20]. Specifically, if a CF_3^+ electronic state lies above a thermodynamic dissociation limit we assume that it dissociates to yield those dissociation products on the timescale of the experiment. If the state is at a high enough energy to lie above two dissociation limits, we assume that it dissociates to the closest lying limit. Thus, the population of a CF_3^+ electronic state lying on or above the asymptote for fragmentation into $CF_2^+ + F$ at 5.98 eV [39] (relative to the equilibrium geometry of the 1 $^1A_1$ ground state of CF_3^+ which we use as our energy zero) will result in the observation of CF_2^+ in the product mass spectrum. Similarly, an electronic state of CF_3^+ lying on or above the dissociation asymptote at 9.26 eV [39] will fragment into the $CF^+ + 2F$ channel and a state lying on or above the asymptote at 17.02 eV [39] will fragment into the $C^+ + 3F$ channel resulting in the observation of CF^+ and C^+, respectively, in the product ion mass spectrum.

As shown in Table 4, the cross-section for the population of electronic states that lie above 15 eV, is effectively zero. This arises as the electron-transfer exothermicity for populating such high-lying states is sufficiently small that the curve crossing is highly diabatic and no electron transfer occurs. Hence, we predict that electron-transfer reactions in this system cannot populate any CF_3^+ states lying above the dissociation asymptote to $C^+ + 3F$. Thus, we do not expect to see any C^+ fragments in the product ion mass spectrum, in accordance with our experimental observations. Also, within our error limits, we observe no CF_3^+ signals that result from bimolecular encounters. Again, the data presented in Table 4 are in good agreement with this observation. Table 4 shows that we calculate no significant probability for populating the ground state CF_3^+, the only state that lies below the $CF_2^+ + F$ asymptote at this geometry, by electron transfer.

Experimentally CF_2^+ ions are a significant component of the ion yield (Table 1), and it is clear from the data presented in Table 4 that the CF_3^+ states populated by the electron-transfer reactions of the ground state of CF_3^{2+} all lie below the asymptote for dissociation to $CF^+ + 2F$ but above the dissociation asymptote leading to $CF_2^+ + F$. Hence, we predict a significant CF_2^+ signal in the product ion mass spectrum, as we observe. However, from Table 4 we see that the ground state of CF_3^{2+} has a low probability of populating any excited states of CF_3^+ which lie high enough in energy to dissociate to $CF^+ + 2F$. This is in conflict with our experimental data (Fig. 3) that show that, although CF_2^+ is the dominant product ion, CF^+ is also formed in significant quantities. There are several possible explanations for this disagreement. First, it is possible that the calculated relative energy of the ground state of CF_3^{2+} is in error. We feel this is unlikely, as the energetics from our ab initio calculations agree closely with those of other workers [37]. Indeed, a significant error in the energy (~5 eV) would be required to give the ground state of CF_3^{2+} sufficient energy to populate CF_3^+ states that can dissociate to CF^+ via electron transfer. Second, it may be that the ground state CF_3^{2+} ions in the dication beam are not predominantly at their equilibrium geometry which is where we assume the reaction to occur. However, the estimated pressure in the ion

Table 4
Calculated electron-transfer cross sections σ (in arbitrary units) for populating the low-lying electronic states of CF_3^+ listed in Table 3 from (a) the ground state of CF_3^{2+}, which lies 25.185 eV above the equilibrium geometry of CF_3^+ and (b) an excited state of CF_3^{2+} lying 5 eV higher in energy; the ion predicted to be detected in the mass spectrum following the population of each state is also indicated (see text for details)

CF_3^{2+} state	Product ion	$\sigma(CF_3^{2+}\ E =$ 25.185 eV)	$\sigma(CF_3^{2+}\ E =$ 30.185 eV)
$1\ ^1A_1$	CF_3^+	0	0
$2\ ^1A_1$	CF_2^+	0.18	0.02
$3\ ^1A_1$	CF^+	0	0
$1\ ^3A_1$	CF_2^+	1.82	0.01
$2\ ^3A_1$	CF_2^+	0	0.42
$3\ ^3A_1$	CF^+	0	0
$1\ ^1A_2$	CF_2^+	0.57	0.02
$2\ ^1A_2$	CF^+	0	15.80
$3\ ^1A_2$	CF^+	0	0
$1\ ^3A_2$	CF_2^+	0.81	0.01
$2\ ^3A_2$	CF^+	0	18.45
$3\ ^3A_2$	CF^+	0	0
$1\ ^1B_1$	CF_2^+	0	0.22
$2\ ^1B_1$	CF_2^+	0	0.34
$3\ ^1B_1$	CF^+	0	0
$1\ ^3B_1$	CF_2^+	0	0.05
$2\ ^3B_1$	CF_2^+	0	0.37
$3\ ^3B_1$	CF^+	0	0
$1\ ^1B_2$	CF_2^+	0.06	0.03
$2\ ^1B_2$	CF^+	0	22.02
$3\ ^1B_2$	CF^+	0	0

source is such that we would expect a significant probability for some vibrational relaxation following ionization and, even if some vibrational excitation is not present, the average geometry of the ground state dications should be well represented by the equilibrium geometry. In addition, since the ions must survive for a flight time of several tens of microseconds before they encounter the neutral beam, it is likely that highly vibrationally excited states of the ground state will predissociate before they reach the interaction region. Indeed, previous investigations of the electron-transfer reactions of polyatomic molecular dications have shown that the observed ions yields are consistent with the dications in the ion beam being well described by the ground state geometry [20]. Third, it is quite possible that the ground state of the dication is not the only electronic state of CF_3^{2+} present ion our ion beam. Indeed, previous studies of perfluorinated dications have provided evidence that excited dication states can exist in ion beams [12,19,25]. Our Landau-Zener model predicts (Table 4) that a metastable CF_3^{2+} state lying 5 eV above the ground state of the dication would react principally to populate CF_3^{2+} states which dissociate to yield CF^+ rather than CF_2^+ or C^+. We feel this latter explanation is the most probable and that our ion beam is composed of CF_3^{2+} ions in both ground and excited states. It is reassuring to note that the Landau-Zener calculations predict no dramatic change in the relative electron-transfer cross sections with collision energy, as observed experimentally.

An obvious, but major, extension to this study would be to calculate the potential energy surfaces of the excited states of CF_3^{2+} to see if, as indicated by the experiments, this ion has a long-lived excited electronic state lying approximately 5 eV above the ground electronic state.

6. Conclusions

This study of the identities and relative intensities of the product ions formed following collisions of CF_3^{2+} with Ar show that electron-transfer and neutral-loss reactivity dominate the product ion yield. The variation of the neutral-loss ion yield with the collision energy provides a first estimate for the bond energy of the weak CF_2^{2+}–F bond as 58 kJ mol^{-1}. Ab initio calculations performed to try and rationalise the yield of the electron-transfer reactions indicate that the ground state of CF_3^{2+} adopts a C_{2v} equilibrium geometry. Using this ab initio calculation, together with calculated energies of the electronic states of CF_3^+ and Landau-Zener theory, we are forced to conclude that at least two electronic states of CF_3^{2+} are present in the dication beam. The ground state of CF_3^{2+} is predicted to react via electron-transfer to form predominantly $CF_2^+ + Ar^+$. An excited state of CF_3^{2+} lying approximately 5 eV above the ground state is, hence, required to explain the formation of CF^+.

Acknowledgements

The authors acknowledge the receipt of a EPSRC studentship for NT and financial support from the

EPSRC, the Central Research Fund of the University of London, the Royal Society, and UCL. They are also grateful for the valuable discussions with Dr. Zdenek Herman made possible by a Royal Society Travel Grant and an award of computing time on the EPSRC's "Columbus/Magellan" central computing facility.

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