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To cite this article: P J M van der Burgt and J W McConkey 1991 *J. Phys. B: At. Mol. Opt. Phys.* **24** 4821

J. Phys. B: At. Mol. Opt. Phys. 24 (1991) 4821–4830. Printed in the UK

Metastable fragment production by electron-impact dissociation of CF_4

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Received 6 June 1991, in final form 13 August 1991

Abstract. Time-of-flight detection of neutral metastable fragments has been applied to the study of electron-impact dissociation of CF_4 molecules. The time-of-flight distributions indicate that a number of distinct processes are involved in the production of metastable fragments. Excitation functions for these processes have been measured up to 400 eV. The results presented are compared with other studies of fragmentation of CF_4 and indicate that fragmentation into an excited CF_3^+ ion and an excited F atom is a prominent process.

1. Introduction

Fluorine-containing molecules have recently attracted increasing interest, because of their use in the plasma etching of semiconductors and in glow discharges. Progress in these fields will benefit from a more detailed understanding of the atomic and molecular collision processes involving these molecules. The production of neutral and charged fragments by electron impact dissociation is very relevant in this context. Neutral fluorine atoms are the active species in the etching, whereas heavier molecular fragments are believed to be responsible for contamination and damage of the etched surfaces. Also fluorine-containing molecules are significant in the catalytic destruction of ozone in the stratosphere, because of free fluorine atoms formed by photodissociation.

In recent years one of the research programs of this laboratory has focused upon electron-impact dissociation of several fluorine-containing molecules, such as SF_6, CF_4, CF_3H, CCl_2F_2 and CCl_3F. Studies of metastable fragment production (Corr *et al* 1987, Allcock and McConkey 1978) and vacuum ultraviolet emissions (Wang and McConkey 1989, Wang *et al* 1989) have been reported recently. This report focuses on the production of metastable fragments by electron impact on CF_4.

CF_4 has been the topic of a number of previous investigations. Ma *et al* (1991) and Stephan *et al* (1985) have reported absolute partial electron-impact ionization cross sections for a number of fragment ions, and relative abundances of positive and negative fragment ions have been measured by Dibeler *et al* (1956). Studies of optical emission following electron impact have been performed in different wavelength regions: 50–130 nm, Wang *et al* (1989); 200–600 nm, van Sprang *et al* (1978), Aarts (1985) and Blanks and Becker (1987); 600–800 nm, van Sprang *et al* (1978) and Blanks

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0953-4075/91/224821+10$03.50

et al (1987). Other important information comes from electron-impact energy-loss studies by King and McConkey (1978), Harshbarger and Lassettre (1973) and Harshbarger *et al* (1972) and from measurement of the total dissociation cross section by Winters and Inokuti (1982). Photofragmentation of CF_4 has been studied by Codling *et al* (1991) and Curtis and Eland (1985). Morgan (1991) has reviewed electron impact cross sections for CF_4 that are of importance to plasma processing modelling. Considering the recent interest in CF_4 it is quite timely to perform a study of dissociative production of neutral fragments.

2. Experiment

The apparatus used in these studies is very similar to the apparatus used by Corr *et al* (1987). A pulsed electron beam intersects, at right angles, a gas beam of CF_4 molecules effusing from a single hypodermic needle. A metastable detector, comprising of two high-transparency grids followed by a channeltron is mounted at right angles to both the electron beam and the gas beam. The cone of the channeltron is at 100 mm distance from the intersection of both beams. The grid closest to the channeltron is biased positively and the channeltron cone is biased negatively to prevent the detection of charged particles. The grid closest to the intersection of both beams is kept at ground potential to keep a field-free time-of-flight path.

The electron gun is built out of a tungsten filament, Wehnelt cylinder, anode and six aperture lens elements (Karras 1988). Electrons are extracted from the filament using a Pierce extraction stage consisting of a Wehnelt cylinder with negative potential and a positive anode with an aperture of 1 mm diameter. A second skimming aperture removes excessively divergent electrons. Five equally spaced lens elements with apertures of 7.6 mm (the last element at ground potential) focus the electron beam through the interaction region into the Faraday cup. The electron gun is mounted inside a cylinder kept at ground potential. The Faraday cup consists of an inner element in an outer tube. Measurements of the current on both Faraday cup elements indicate that the electron beam gradually diverges at decreasing incident energies below 100 eV, but the total current is constant down to 12 eV. The performance of the electron gun has been verified by measuring excitation functions for metastable helium atoms and metastable nitrogen molecules.

The electron beam is pulsed by applying a pulse to the Wehnelt cylinder of a width of 0.5 or 1 μs and a repetition rate of 9 kHz. Faraday cup currents of the order of 100 nA (integrated) are used. Without a gas beam the pressure in the vacuum chamber is 2.9×10^{-7} Torr, whereas pressures of about 5×10^{-6} Torr are recorded when the CF_4 beam is turned on.

Data accumulation is controlled by a fast multichannel scaler (Gillen 1988) consisting of two 40 MHz 24 bit counters, a memory bank of 512 channels (3 byte words), and a 6502 microprocessor. Both counters are alternately accumulating counts and routing their contents to memory. The microprocessor controls the set-up of the counters, the display and the RS232 serial communication port. Dwell times varying from 200 ns to 5 s per channel can be used. After completion of a sweep through all channels the scaler is triggered either externally or internally after a specified delay period. Serial communication is used to transfer the accumulated spectrum to a personal computer for further analysis. The scaler can be set either manually through controls on the front panel or by sending commands via the serial port. An oscilloscope with

intensity modulation input is hooked up to the scaler to display the accumulated spectrum.

Time-of-flight spectra are recorded by externally triggering the multichannel scaler, synchronously with the electron beam pulse. In this type of measurement dwell times of 200 ns per channel are used, resulting in a time-of-flight range of 102 μs. This range is sufficient in studies of CF_4 because no significant signal is detected at longer flight times.

Excitation functions are measured using a time-to-pulse-height converter, started by the electron beam pulse and stopped by pulses from the channeltron. Events within a time window set on the time-to-pulse-height converter result in output pulses which are accumulated by the multichannel scaler. The multichannel scaler (now operated with a dwell time of 0.5 s per channel and triggered internally) produces a ramp voltage used to increase the incident electron energy. The energy scale is calibrated by examining the threshold excitation of the 2^3S metastable state of helium (using an electron pulse repetition rate of 1.6 kHz). This also indicates that the energy spread in the electron beam is about 0.8 eV FWHM.

3. Results

3.1. Time-of-flight spectra and kinetic energy distributions

Time-of-flight spectra for five different electron energies are shown in figure 1. All spectra are taken using electron pulses of 0.5 μs width and a repetition rate of 9 kHz. The origin of the time-of-flight scale is determined by a prompt peak produced by radiative decay of excited fragments. Apparently some of the fragments decay in their flight towards the detector, producing a trailing edge on the prompt peak (not shown in figure 1). Wang *et al* (1989) also found indications for long-lived species produced by electron impact dissociation of CF_4. The most prominent features in the time-of-flight spectra are a peak at 16 μs, and a second peak of faster fragments coming up at energies above 100 eV. A few spectra have been taken for flight times up to 500 μs. No significant features are observed except for a weak and broad distribution around 160 μs at energies of 40 eV and lower, which we attribute to a small amount of nitrogen molecules present in the vacuum chamber.

Kinetic energy distributions are obtained by using the transformation given by equations (3) and (4) of Smyth *et al* (1973) and are shown in figure 2. The distributions shown cover a range from 9 to 74 μs. As the transformation involves a factor t^3 a large number of data points are transformed into a narrow region of small fragment energies. In order to avoid the clutter of points in this region the transformation is performed numerically using equal energy steps of 0.1 eV. The baseline level of background counts used in the transformation is obtained by delaying the detector pulses 5 μs after the multichannel scaler is triggered.

The kinetic energy distributions must be interpreted with some care, because the transformation assumes that atomic fluorine fragments are detected. Contributions could be present due to metastable C, CF or F_2 fragments. Absence of structures at longer flight times indicates that neutral fragments of higher mass are not produced in significant amounts. The metastable detector is able to detect those metastable species with excitation energies greater than the work function of the channel electron multiplier (estimated to be about 8 V by Brunt *et al* (1978)). Consequently C ^{1}D and C ^{1}S metastable atoms are not detected, but F(3s) $^4P_{5/2}$ metastable atoms at 12.73 eV

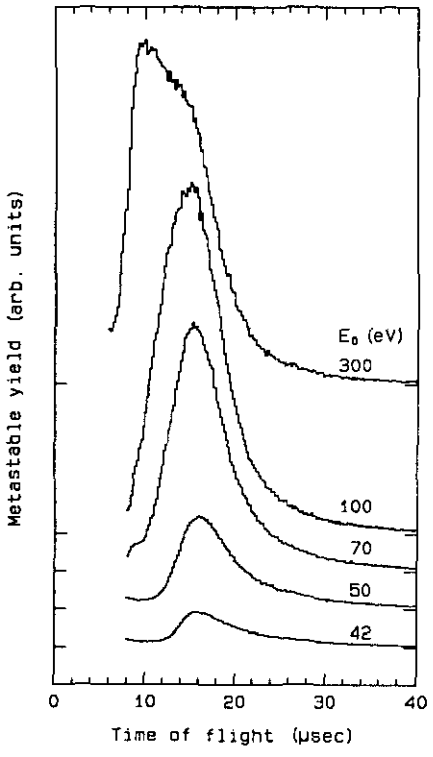

Figure 1. Time-of-flight spectra for metastable fragments obtained at the incident electron energies indicated. Vertical scales are comparable to within 20%.

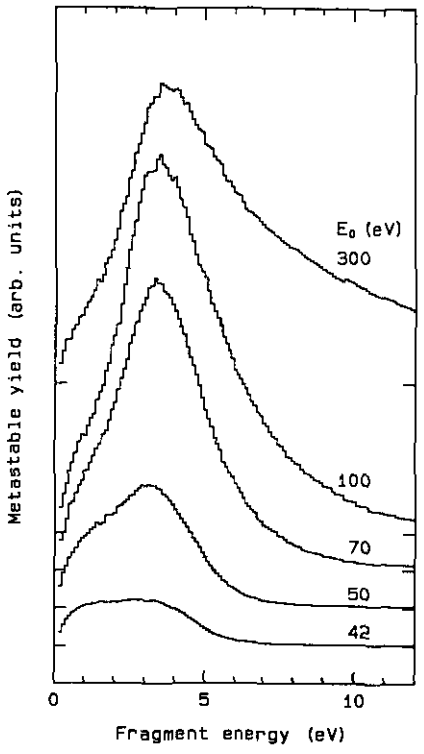

Figure 2. Kinetic energy spectra obtained from the spectra in figure 1, assuming the detected metastable fragment is F. The spectra cover a range from 9 to 74 μs and the time-of-flight path is 100 mm.

have a sufficiently long lifetime (Gruzdev 1971) to reach the detector. Fluorine and carbon atoms in long-lived Rydberg states can be detected as well. Although these states lie above the conduction band of the surface, the presence of adsorbed contaminations on the surface prevents tunnelling of the excited atomic electron to a vacant state in the metal. Also in this situation ejected electrons can be produced by Auger de-excitation of the metastable atoms (Hart *et al* 1989).

Note that the fragments have a wide range of kinetic energies. The time-of-flight spectrum at 300 eV indicates that the fastest fragments at 7 μs have energies up to 20 eV.

3.2. Appearance potentials and excitation functions

A number of excitation functions have been measured for a variety of time-of-flight windows. All excitation functions have been measured using electron pulses of 1 μs width. A typical data accumulation time for one excitation function is 24 h. Three excitation functions are displayed in figure 3. Onsets are identified in this figure. Because a number of different dissociation processes are contributing to the yield of metastables, the excitation functions exhibit sharp increases in slope at one or more energies corresponding to the thresholds of the contributing dissociation processes. These onsets have been located by drawing straight line segments (or curved line segments with decreasing slope) in the graphs (not shown in figure 3). The identification

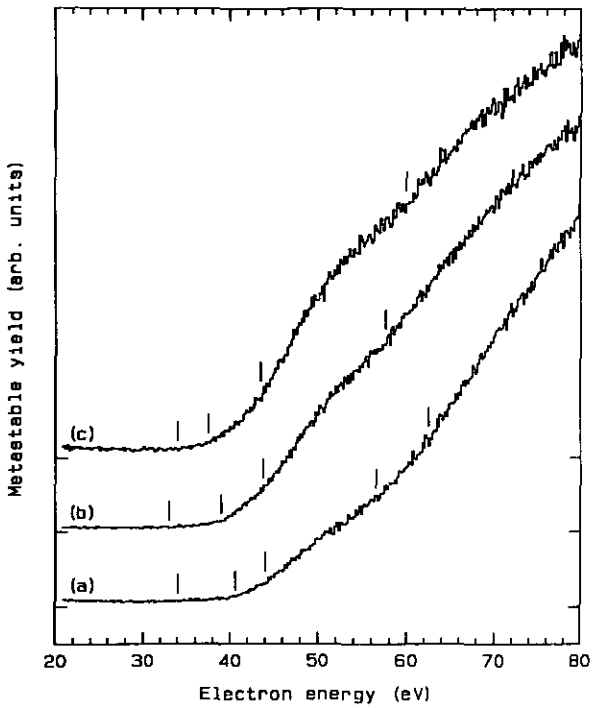

Figure 3. Excitation functions measured for different fragment kinetic energies: 4.7–5.5 eV (*a*), 3.1–3.9 eV (*b*) and 2.1–2.9 eV (*c*). Marks indicate the onsets of dissociation processes. *Vertical scales are not comparable.*

of onsets is difficult and in many cases only possible by extending the vertical scale of the graph. Even in data with good statistics an onset at a higher energy results in a small increase superimposed on a large signal from lower thresholds, and is only indicated by a minor inflection in the accumulated counts. We estimate the error in the onset energies to be about 0.5 eV for well defined onsets, and about 1 eV or more for onsets in the threshold region (poor statistics) and onsets indicated by a minor inflection.

A plot of fragment kinetic energies against appearance potentials (location of onsets on a calibrated energy scale) is shown in figure 4. Assuming a fluorine atom is detected as a result of a two-fragment break-up (and no internal energy is carried off in the other fragment) the slope of appearance potentials against fragment energies follows from conservation of momentum (see Allcock and McConkey 1978):

$$S = m(CF_3)/m(CF_4) = 0.78. \tag{1}$$

In case of a two-fragment break-up with detection of F_2 a slope of 0.39 is obtained in plots such as in figure 4.

For dissociation of polyatomic molecules molecular fragments with different amounts of rotational and vibrational excitation might be produced, or multiple fragmentations may occur. These situations complicate the relation between appearance potentials and fragment energies (see the review by Freund 1983). In the first situation, if a constant fraction of the excess energy is converted into translational motion, again a constant slope is obtained. In the second situation, two or more undetected fragments are produced with varying kinetic energy, and a vertical slope is obtained.

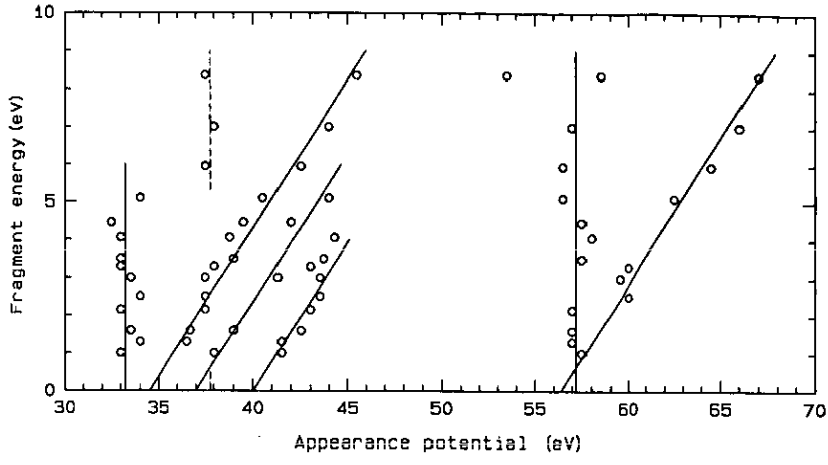

Figure 4. Plot of appearance potentials against fragment kinetic energies, assuming the detected metastable fragment is F. The lines with slope 0.78 are due to two-fragment dissociations producing metastable F atoms and the vertical lines indicate multiple fragment dissociations (see text).

Figure 4 shows that four series of appearance potentials follow straight lines that closely match the predicted slope for a two-fragment break-up producing metastable fluorine atoms. Three series of appearance potentials with vertical slope indicate that multiple fragmentation processes also occur. No indication is found for a two-fragment break-up producing F_2 molecules.

4. Discussion of fragmentation processes

It is clear from figure 4 that a number of different dissociation processes contribute to the yield of metastables. Definitive identification of the processes involved is difficult in view of the great many possible channels. However, using literature values for dissociation and ionization energies, we are able to make a few positive identifications. Ionization energies for various molecular fragments are tabulated by Rosenstock *et al* (1977), and dissociation energies can be obtained from enthalpies of formation listed by Chase *et al* (1985). Fluorine and carbon Rydberg atoms (denoted by F(R) and C(R) in the equations below) have energies close to their ionization energies of 17.4 eV and 11.3 eV, respectively.

Four series of onsets in figure 4 indicate two-fragment break-ups with dissociation limits at 34.5, 37.0, 40.0 and 56.4 eV. Because fragmentation into an excited F atom and a neutral CF_3 molecule would have a dissociation limit at 23.0 eV, these onsets must be due to processes leading to excited CF_3^+ fragments. In photoemission studies of electron impact dissociation of CF_4 Blanks and Becker (1987) observed an intense continuum emission around 285 nm, which they attributed to excited CF_3^+ ions. The relevant reaction processes are:

$$e + CF_4 \rightarrow CF_3^+ + F(R) + 2e \tag{2}$$

$$e + CF_4 \rightarrow CF_3^{+*} + F(3s)\,{}^4P_{5/2} + 2e \tag{3}$$

$$e + CF_4 \rightarrow CF_3^{+*} + F(R) + 2e. \tag{4}$$

Using the dissociation energy $CF_4 \rightarrow CF_3 + F$ (5.6 eV, Chase *et al* 1985), the ionization energy of CF_3 (9.2 eV, Rosenstock *et al* 1977), and the excitation energy of CF_3^{+*} (estimated 5-8 eV by Blanks and Becker 1987), one obtains dissociation limits of 32.2 eV, 32.5-35.5 eV and 37.2-40.2 eV for the reactions (2), (3) and (4), respectively. The limits for the reactions (3) and (4) are in good agreement with the limits we observe at 34.5 and 40.0 eV. The limit observed at 37.0 eV may also be due to reaction (4), as Rydberg atoms may be produced within a small range of excitation energies below the ionization threshold. The observed limit at 56.4 eV is likely due to a dissociation process producing multiply-ionized and excited molecular fragments.

Regarding the results presented here it is important to note some results obtained by other researchers. Mass spectrometry studies (Dibeler *et al* 1956, Stephan *et al* 1985, Ma *et al* 1991) show that CF_3^+ is the dominant charged species produced by electron impact on CF_4. Studies of photoemissions produced by electron impact of CF_4 (Wang *et al* 1989, Blanks *et al* 1987) show that the strongest emissions are due to neutral excited fluorine atoms. As noted earlier, Blanks and Becker (1987) attributed an intense continuum emission around 285 nm to excited CF_3^+ ions. These observations are consistent with our present observation of two-fragment break-up processes. Also Codling *et al* (1991) observed two-fragment dissociations. They report an onset at 37.6 eV for the production of CF_3^+ and F^+ by photodissociation of CF_4. Assuming a kinetic energy release of 5 eV near threshold they conclude that both fragments depart in their ground electronic states. Extending their work, Ma *et al* (1991) (Bonham 1991) obtained an onset at 36.0 eV for the production of $CF_3^+ + F^+$ by electron impact on CF_4 and estimate 3.6 eV excess energy near threshold. Our measurements show that fluorine fragments of less than 1 eV (total kinetic energy release less than 1.3 eV) are produced near threshold, possibly indicating that part of the signals detected by Codling *et al* (1991) and Ma *et al* (1991) are due to excited CF_3^+ with low kinetic energy. Ma *et al* (1991) compare their absolute dissociative ionization cross section with the total dissociation cross section of Winters and Inokuti (1982), showing that dissociative ionization is a dominant process for electron impact above 30 eV. All these observations indicate the importance of electron impact dissociation of CF_4 into excited CF_3^+ and excited F.

Two series of onsets with vertical slopes at 33.2 eV and 57.2 eV indicate total fragmentation of CF_4. Allcock and McConkey (1978), using a Rydberg ionizer and mass spectrometer, obtained vertical slopes when they detected carbon Rydberg atoms produced by total fragmentation of CCl_2F_2. The onset at 33.2 eV could therefore very well be due to metastable carbon atoms, produced by the reaction:

$$e + CF_4 \rightarrow C(R) + 4F + e \tag{5}$$

however, the onset could also be due to metastable fluorine atoms produced by:

$$e + CF_4 \rightarrow C + F(3s)\,{}^4P_{5/2} + 3F + e \tag{6}$$

$$e + CF_4 \rightarrow CF_2^+ + F(3s)\,{}^4P_{5/2} + F + e. \tag{7}$$

Using the dissociation energies for $CF_4 \rightarrow C + 4F$ and $CF_4 \rightarrow CF_2 + 2F$ (20.4 eV and 9.4 eV, Chase *et al* 1985), and the ionization energy of CF_2 (11.8 eV, Rosenstock *et al* 1977), one obtains dissociation limits of 31.7 eV, 33.1 eV and 31.9 eV for the reactions (5), (6) and (7), respectively. Indication of a third series of onsets with a vertical slope at 37.8 eV could be due to F(R) produced by a process equivalent to (6) with a calculated dissociation limit of 37.8 eV.

A multitude of possible assignments exist for the vertical onset observed at 57.2 eV. A possibility is fragmentation into $C^+ + 2F(3s)\,{}^4P_{5/2} + 2F$ with a calculated threshold at 57.1 eV, however we do not observe a related fragmentation into $C^+ + F(3s)\,{}^4P_{5/2} + F(R) + 2F$ (61.8 eV calculated threshold). Codling *et al* (1991) and Ma *et al* (1991) (Bonham 1991) obtained onsets for the production of $C^+ + F^+$ at 62.0 eV and 63.0 eV, respectively, but these onsets cannot be compared with our work because both groups estimate an excess energy of about 15 eV near threshold.

It is interesting to compare the occurrence of onsets presently reported with the onsets observed in excitation functions for ultraviolet and visible emissions. The shapes of the excitation functions shown in figure 3 are qualitatively similar to the excitation functions reported by Wang *et al* (1989), most notably regarding the absence of onsets between 45 and 56 eV. Wang *et al* (1989) observed onsets at 36.0–37.2 eV, 43.1–45.3 eV and 60.3–62.2 eV. These onsets are in good agreement with our observations for fragments with 2–5 eV kinetic energy, which are produced most abundantly. Blanks *et al* (1987) report an appearance potential at 41.0 eV for the 685.6 nm F I transition. This could very well be attributed to reactions similar to (3), (6) and (7) producing excited F(3p) atoms with a few eV kinetic energy. Lacking information about the kinetic energy of the formed fragments, Blanks *et al* (1987) and Wang *et al* (1989) attributed their observed onsets to total fragmentation of CF_4. Our results indicate that total fragmentation indeed occurs, but that two-fragment break-ups are at least equally important. Blanks and Becker (1987) measured an excitation function for the continuum emission around 285 nm, showing a weak onset at 23.1 eV, and a strong onset at 30.4 eV. We do not find any indication of onsets lower than 30 eV, but a weak onset could possibly be obscured by a background of photons at short flight times from in-flight decay of excited fragments.

The two-fragment dissociation processes (3) and (4) discussed above may be understood qualitatively in terms of the core ion model of dissociation (see the review by Freund 1983). In the first step two electrons in the CF_4 molecule are excited to high-Rydberg orbitals, and a third electron is excited to a continuum state and able to escape from the molecule. Next the triply-charged molecular core fragments into a CF_3^{2+} ion and a F^+ ion, and as the fragments separate the two Rydberg electrons both

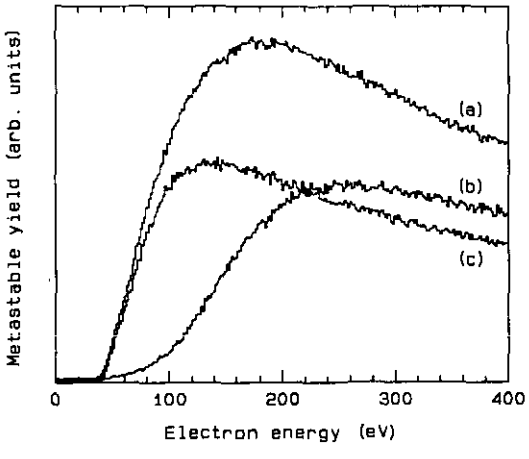

Figure 5. Excitation functions measured for different fragment kinetic energies: all metastables (*a*), 9–18 eV (*b*) and 3.3–4.7 eV (*c*). Vertical scales are not comparable.

end up in excited states of the two fragments. This model would explain why two-fragment break-up processes are observed (figure 4) even though strictly speaking the continuum electron is the third fragment of the CF_4 molecule.

Figure 5 shows an excitation function measured from 0–400 eV using a time-of-flight window wide enough to detect all metastables. Again, the shape of the excitation function is very similar to the excitation functions reported by Wang *et al* (1989) and Blanks *et al* (1987) for photoemission by excited fluorine fragments. Two excitation functions for different time-of-flight windows are also shown. Clearly faster fragments are produced more abundantly at higher electron energies.

5. Conclusions

We have studied the production of metastable fragments by electron impact dissociation of CF_4 molecules. The results show that a number of different processes contribute to the formation of metastable fragments and that very energetic fragments up to 20 eV can be produced. Our results indicate the importance of two-fragment dissociations producing excited fluorine atoms and excited CF_3^+ ions, and also total fragmentation.

Acknowledgments

The authors gratefully acknowledge financial support from the National Sciences and Engineering Research Council of Canada and expert technical assistance from Mr Werner Grewe and Mr Bernard Masse and their staff. The authors are indebted to Dr Jay Corr for discussions. JWMcC acknowledges the hospitality of the Jet Propulsion Laboratory, California Institute of Technology during the period when this manuscript was being prepared for publication.

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