International Journal of Mass Spectrometry 277 (2008) 57–61

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Anion formation by electron impact from CF_4

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ARTICLE INFO

Article history:
Received 25 March 2008
Received in revised form 11 May 2008
Accepted 13 May 2008
Available online 20 May 2008

Dedicated to Prof. E. Illenberger on his 65th birthday.

Keywords:
Carbon tetrafluoride
Dissociative electron attachment
Ion pair formation
Electron impact

ABSTRACT

Anion formation by electron impact from CF_4 has been studied experimentally in the range 0–30 eV electron energy. F^- and CF_3^- anions were observed while F_2^- ions, if any, were below the detection limit. The resonance peaks for F^- and CF_3^- were measured to be 6.5 and 7.1 eV, respectively. Only F^- is produced via the ion pair formation channel and the yield varies monotonically with energy above the threshold.

1. Introduction

Carbon tetrafluoride (CF_4) is an important gas (also known as R14) used by the semiconductor industry for dry etching. It is also used by the industry in the production of plastic foams, discharge switches, etc. It is a green house gas and accumulates in the atmosphere [1]. As the plasma processes result in fragmentation of the molecule by various collisional processes resulting in various neutrals, cations and anions, it is necessary that these basic processes [2] are well understood to exploit them for proper use while using this gaseous compound. Of the many species that react with CF_4 either in a plasma medium or in the earth's atmosphere are the electrons available in copious quantities over a wide range of energies. It is therefore essential that reactions with electrons are studied in detail. A detailed compilation of electron CF_4 interactions has been compiled by Christophorou et al. [3,4]. The production of negative ions by electron interaction was first studied by Dibeler et al. [5]. Since then MacNeil and Thynne [6], Harland and Franklin [7], Wang et al. [8], Illenberger's group in Berlin [9–12], Christophorou and co-workers [13], Srivastava and co-workers [14] and Le Coat et al. [15] have studied anion formation from CF_4 by electron impact by the process of dissociative electron attachment (DEA). Anions are also produced by the ion pair formation channel, which was first studied by Ahnell and Koski [16], and later by Srivastava and co-workers [14] and Mi et al. [17]. The ion pair production channel due to photon impact has been studied in fair detail by Mitsuke et al. [18] where they observe F^- as the only negative ion formed by this process. The structure of CF_4 has been determined experimentally by Brodersen [19] to be of tetrahedral (T_d) symmetry with a bond length of 1.3151 Å. However, there are very few calculations [20–23] on the CF_4^- anion, with the most recent being that of Gutsev and Adamowicz [24], therefore theoretical prediction of the fragment anion dissociation channels are not available.

Of the different groups that have reported the formation of anions, Iga et al. [14] is the only one in the literature where they observe F_2^- formation both in the DEA channel with a resonance peak at 6.8 eV and also in the ion pair formation channel. Though clear structures are reported in the F^- anion yield function as a function of photon energy, Iga et al.'s data for the same channel as a function of electron energy appears smooth. In addition, the resonance energies for both F^- and CF_3^- reported by different groups are not in full agreement. To resolve these issues, experiments were conducted on CF_4 to elucidate the resonance energies for the formation of F^- and CF_3^- via the DEA process, to check if F_2^- is formed by electron impact, whether structures could be measured in the ion pair formation channel and if CF_3^- is formed via the ion pair production channel.

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doi:10.1016/j.ijms.2008.05.014

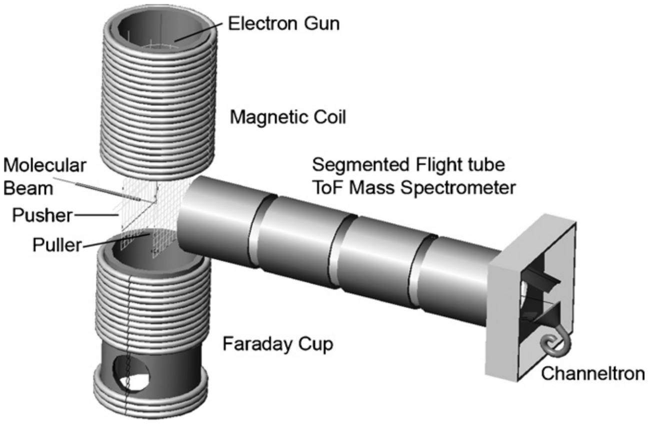

Fig. 1. Schematic of the experimental setup.

2. Experimental

The experiments were carried out in crossed beam geometry and under single collision conditions. The schematic of the experimental setup [25] is depicted in Fig. 1. The electrons are produced by a Pierce type electron gun and guided into the interaction region and further into the Faraday cup, by a low-magnetic field ~50 G produced by a pair of Helmoltz coils (which are ultra high-vacuum compatible). The electrons interact with an effusive beam of CF_4 (Alfa gas with certified 99.995% purity used without any further purification). The uninteracted electrons reach the Faraday cup placed on the other side of the interaction region. The ions produced by the interaction of the electrons are pushed by a repeller into a homemade time-of-flight (ToF) mass spectrometer for mass analysis. The interaction region is flanked by the repeller plate on one side and a high-transparency molybdenum mesh on the other side. The extracted ions that are transmitted through the mesh, fly through a segmented flight tube to a channel electron multiplier detector. The first segment of the flight tube is held at ground potential whereas the other segments are biased such that all the ions which enter the flight tube are focused into the detector. While such an arrangement sacrifices the time resolution, hence the mass resolution, of the mass spectrometer, but it makes sure that all the ions formed even with high-kinetic energies reach the detector. This ensures proper collection and no fragments are missed during the data collection.

The above setup is housed in a vacuum chamber, which is operated at a base pressure of 1×10^{-7} Torr. Molecules of interest are introduced into the interaction region in the vapour phase through a long, narrow capillary of 1.0 mm diameter, protruding a little through the pusher plate into the interaction region. As the time-of-flight mass spectrometer analyzes ions that are sent in temporal bunches, the electron gun is operated in a pulsed mode, with each pulse lasting 200 ns at a repetition rate of 5 kHz. While one of the outputs from the master pulser (SRS model DG535) is used to open the shutter of the electron gun, the second output with an appropriate delay is used to trigger the pusher pulse. The pusher pulse is derived from a variable output pulser (Avtec model AVRH-2-C-PN) which can deliver pulses from 30 to 1800 V with a rise time of 150 ns. The present setup used a pulse, which produced a 275 V/cm gradient for ion extraction. This was found to be adequate to push all the ions, immaterial of its initial kinetic energy, into mass spectrometer ensuring total ion collection. The delay ensured that the scattered electrons were not pushed into the mass spectrometer whereas the expanded ion cloud did not get lost but entered the mass spectrometer for analysis. The third output from the master pulser delayed by a Gate and Delay generator (Tennelec 410A) with a NIM output pulse is used as a start pulse of the time-of-flight setup.

The pulses from the channel electron multiplier were amplified by fast amplifier (CAEN model N412) and after passing though a constant fraction discriminator (Canberra model 2126) reached a multi hit multi channel analyzer (Fast Comtec 7888 card) mounted inside a computer. The card has a minimum pulse pair resolution of 1 ns. This setup helped in analyzing ions of all masses entering the mass spectrometer simultaneously. The electron energy was varied using a programmable power supply controlled via Ethernet. The electron current was simultaneously monitored by a precision electrometer (Kiethley model 6412) with a GPIB computer interface. The whole experiment was controlled as well as the data acquisition was done using a homemade computer program MSMCS. The basic working of this version program [26] is similar to the earlier version [27] while a new bus interface is used and simultaneous analysis of all the ions is possible now. The data acquired is normalized for variation in the electron current, both as a function of electron energy and time.

The electron energy scale for the DEA cross-sections is calibrated using the O^- peak energy values of N_2O molecules [28]. The error in the calibration could be ±0.1 eV. Experiments were repeated several times to ensure reproducibility of results to full satisfaction. For each type of ion the area under the curve over its full width is computed and then plotted as a 1D ion yield curve for further analysis.

3. Results and discussion

The anion formation channels are

$$e^- + CF_4(^1A_1) \rightarrow CF_4{}^{-*} \rightarrow F^-(^1S_0) + CF_3(^2A_1) \qquad (1)$$

$$e^- + CF_4(^1A_1) \rightarrow F(^2P_{3/2}) + CF_3{}^-(^1A_1) \qquad (2)$$

$$e^- + CF_4(^1A_1) \rightarrow F^-(^1S_0) + CF_3{}^+(^1A_1) + e^- \qquad (3)$$

A typical 2D mass spectrum (raw) of the anions formed from CF_4 by electron impact as a function of electron energy is shown in Fig. 2.

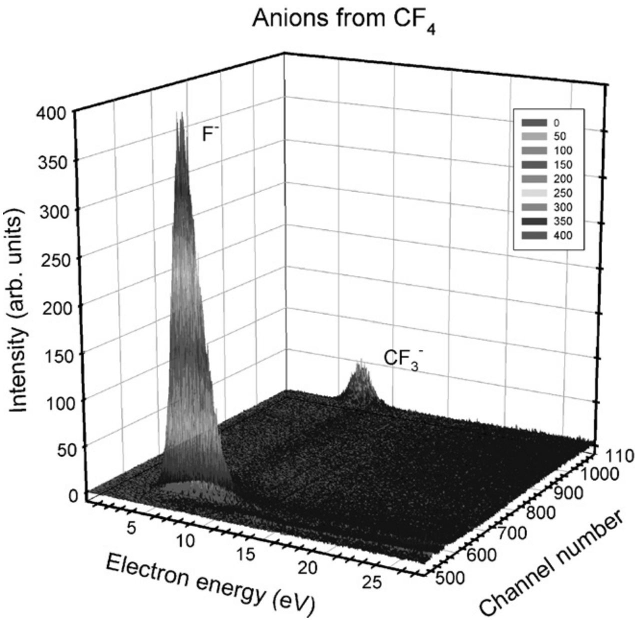

Fig. 2. 2D plot of the raw data of the yield of various anions as a function of electron energy.

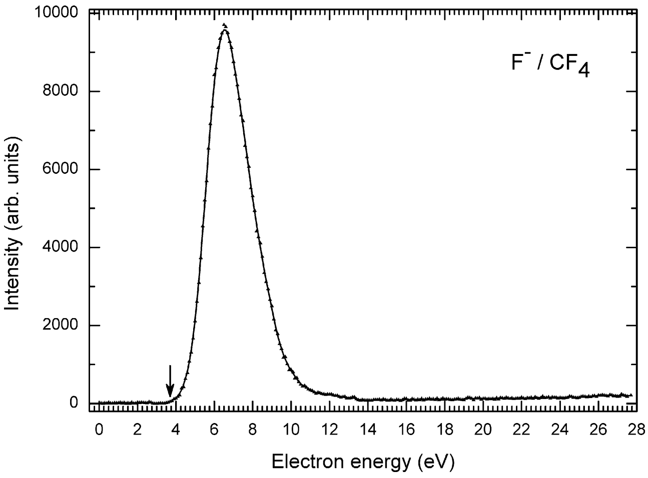

Fig. 3. F^- yield curve, normalized to electron current, as a function of electron energy.

The two main peaks correspond to F^- and $CF_3{}^-$. A detailed analysis of this spectrum was done by summing over the channels, after subtracting the background and normalizing it with respect to the electron current, which correspond to F^-, $F_2{}^-$ and $CF_3{}^-$ ions, and these are shown in Figs. 3–5, respectively. As the whole data corresponding to all the ions that are formed by this reaction is acquired simultaneously, any fluctuations that could arise, say between F^- and $F_2{}^-$ data sets, in which intensity of one fragment is very high compared to the other is completely nullified, giving full credibility to the data that is collected.

It is obvious from Fig. 4 that in the region where $F_2{}^-$ ions are expected, based on the mass calibration done, that any possible signal due to formation of $F_2{}^-$ ions does not get above the noise level. Iga et al. [14] is the only group which has reported observation of $F_2{}^-$ from CF_4, with a peak cross section 2.17% of F^-, i.e., a ratio of 1 to 46 for $F_2{}^-/F^-$. With total ion collection and good sensitivity, our experiments should have detected $F_2{}^-$ ions. Attempts to collect data over long periods to look for small signatures of $F_2{}^-$ also yielded negative results. This means that the $F_2{}^-/F^-$ ratio from our measurements is <0.0016. Iga et al. do not specify the purity of the gas used in their experiments. Therefore, the observation of $F_2{}^-$ by them could possibly be attributed to either purity of the gas used by them or some experimental conditions.

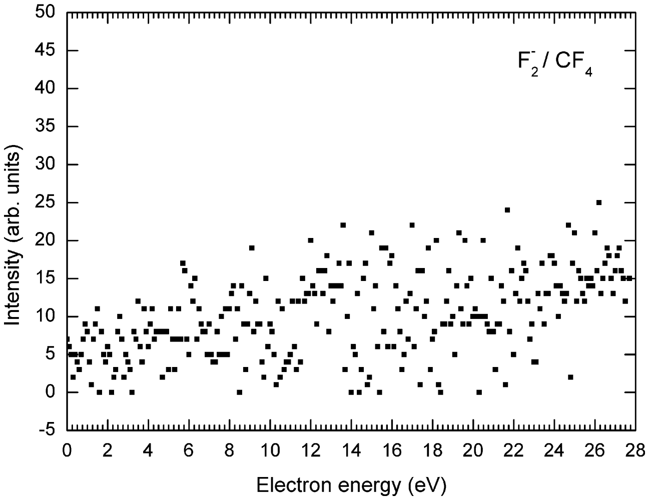

Fig. 4. $F_2{}^-$ yield curve, normalized to electron current, as a function of electron energy.

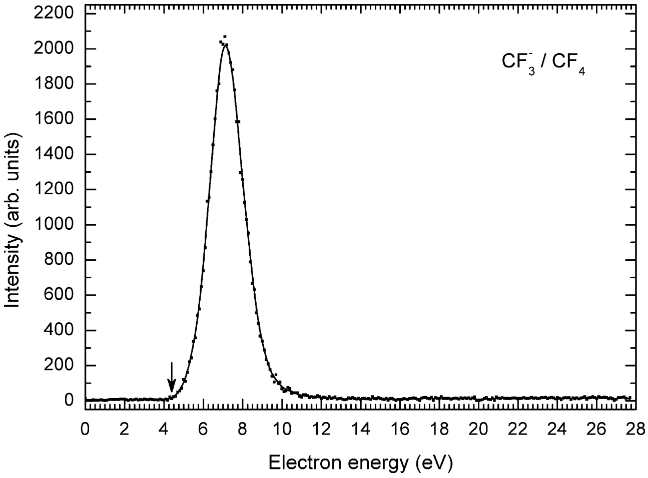

Fig. 5. $CF_3{}^-$ yield curve, normalized to electron current, as a function of electron energy.

The F^- ion yield curve is shown in Fig. 3. The measured threshold for its formation is 3.7 eV and the resonance peak is at 6.5 eV. The measured threshold and peak values along with the literature values are given in Table 1. The high-energy part of the curve tails a little beyond 13 eV. Illenberger group's measurements [9–12] done with an electron beam of width 70 meV shows a possible overlap of two resonances, however, with the electron energy width of 0.5 eV in our experiments, we observed only one resonant peak at 6.5 eV. The observation of a single peak and the energy is similar to all other measurements reported till now [5,6,8,13] except that of Iga et al. [14] who observe a single peak at 7.6 eV while their threshold is at an energy of 4.6 eV. They do not state any reason for the shift in the resonance peak energy compared to earlier measurements. The error in our peak energy measurements is estimated to be ±0.1 eV and the resonance peak value is in consonance with most earlier measurements. Our lower value of appearance energy is probably due to the larger energy spread in the electron beam that gives rise to an energy tail with high-energy electrons.

The threshold for F^- formation via the ion pair production channel (Eq. (3)), is 12.29 eV based on the appearance energy of $CF_3{}^+$ (15.69 eV) [29] and the electron affinity of F (3.399 eV) [30] atoms. Ion pair formation studies by Mitsuke et al. [18] by photon interaction shows the threshold to be 13.19 eV with many structures beyond this energy, the prominent being at 13.90, 15.77 and ~21 eV. The 13.90 eV structure is the strongest and the width of the resonance peak extends from 13.2 to 14.94 eV. These resonant peaks have been attributed to $^1T_2$, $^1A_1$ and $^1T_2$ $CF_4{}^{**}$ Rydberg states. In the current experiments we looked for resonant structures in the

Table 1
Appearance energies (AE) and their peak energies of F^- and $CF_3{}^-$ ions from CF_4 formed by electron impact

	F^-		$CF_3{}^-$	
	AE	Peak	AE	Peak
MacNeil and Thynne [6]	4.7	–	5.4	–
Dibeler et al. [5]	4.5	–	–	–
Wang et al. [8]	4.8	6.5	5.6	7.1
Scheunemann et al. [12]	4.5	6.7	4.7	7.7
Spyrou et al. [13]	4.5	6.7	5.1	7.1
Iga et al. [14]	4.6	7.6	5.5	7.8
Present work	3.7	6.5	4.4	7.1

ion pair formation region of F^-. However, there is only a monotonic increase in the intensity of F^- as function of electron energy beyond 13 eV and no structure that is discernible beyond the fluctuations were measurable. The measurements by Iga et al. [14] also do not report any structures. It is very likely that the structures not being observed may be due to the differences in the way the photons and electrons interact with target molecules as well as due to the electron energy spread being 0.5 eV both in our experiments and that of Iga et al., as well as due to the ion yield through this channel being low. High-resolution electron impact studies would help to resolve this.

The ion yield via the CF_3^- ion formation channel is shown in Fig. 5. The threshold is measured to be at 4.4 eV and the resonance peak at 7.1 eV. Again, the lower threshold in our measurements is due to the larger energy spread of the interacting electrons. The resonance peak value matches with that of Wang et al. [8] and Spyrou et al. [13], where as Scheunemann et al. [12] and Iga et al. [14] report higher values (see Table 1). Though our values do not match that of Iga et al., it is difficult to evaluate the difference between the present measurements and that of Scheunemann et al. as there is very little disagreement in the F^- channel. Though detailed kinetic energy release measurements for both the anion exit channels have been reported by Le Coat et al. [15], they do not report kinetic energy integrated values for the resonance peaks. No CF_3^- ions could be observed via the ion pair production channel supporting all the earlier measurements carried out either by electron impact or photon impact.

The ion yield curves of F^- and CF_3^- from our measurements indicate that the ratio of F^-/CF_3^- to be 4.8 where as that of Iga et al. [14] is 3.86. Considering that the experimental setups are similar, it is surprising that the ratios are not close. One of the possibilities for this difference could be due the purity of the gas used by Iga et al. [14].

CF_4 belongs to the T_d point group and its electronic structure [24] is $\ldots 4a_1^2$, $3t_2^6$, $1e^4$, $4t_2^6$, $1t_1^6$ $(^1A_1)$. Our geometry optimization calculations on CF_4 at the CCSD level carried out using 6–311++G* basis set with the help of Gaussian 03 [31] package shows that CF_4 has tetrahedral symmetry with a C–F bond length of 1.3193 Å which is very close to the experimental value [19] of 1.3151 Å supporting the quality of our calculations. The first three LUMOs are $5a_1$, $5t_2$, $6t_2$. The additional electron goes into the $5a_1$ orbital leading to the formation of the lowest state of CF_4^-. It also indicates that the LUMOs are anti bonding, which is the likely reason that F^- and CF_3^- are formed easily. In addition, the vertical electron affinity is negative (−1.78 eV) in the T_d symmetry. Mann and Linder's [32] electron scattering measurements and the angle dependent kinetic energy measurements of Le Coat et al. [15] indicate that the resonant states involved has T_2 and T_1 symmetries, respectively. Purely going by the electronic configurations, this is likely to correspond mainly to $\ldots 4a_1^2$, $3t_2^6$, $1e^4$, $4t_2^6$, $1t_1^6$, $5t_2^1$ and $\ldots 4a_1^2$, $3t_2^6$, $1e^4$, $4t_2^6$, $1t_1^5$, $5a_1^2$ electronic configurations, respectively.

4. Summary and conclusions

The experiments done in total ion collection mode does not show any measurable F_2^- ions formed by electron impact in the range 0–25 eV. The literature values for the peak of F^- ions range from 6.5 to 7.6 eV, with many values from different groups bring around 6.5 eV and our measurement gives a value of 6.5 eV. The threshold values vary from 3.7 to 4.8 eV, with many values close to 4.5 eV. Our low-threshold value could be due to the energy spread [25] of 0.5 eV in the electron beam. Similarly, for CF_3^- resonance peak, the literature values range from 7.1 to 7.8 eV with three values being 7.1 eV and our present measurements value is 7.1 eV. Due to the very slow decrease in the resonant part of the F^- formation and due the gradual increase in the ion pair formation channel no specific threshold for the ion pair formation could be determined. Again, due to the low signal to noise ratio, structures in the F^- ion pair formation channel could not be seen like the ones observed by Mitsuke et al. [18] by photon interaction at similar energies. It would be good to repeat these measurements with high-resolution electron beams and with total ion collection to explore if structures in the F^- channel could be reproduced similar to photon interaction.

The computed vertical electron affinity of CF_4 turns out to be negative (−1.78 eV) in the T_d symmetry instead of 0 eV as predicted by Gutsev and Adamowicz [24] as our calculations are done at a more accurate CCSD level of theory instead of MP4 level.

Acknowledgements

The authors wish to thank T.S. Anantakrishnan for his help on MSMCS data acquisition software. They also thank Satej T. Tare and Yogesh V. Upalekar for the dedicated technical support. Thanks are also due to Kinjalk Lochan for the wholehearted assistance with the experiments.

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