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On the partial ionization cross-sections for CF_4 by use of the pulsed-electron-beam time-of-flight method

M.R. Bruce and R.A. Bonham

Department of Chemistry, Indiana University, Bloomington, IN 47405 (USA)

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Abstract

Recent measurements of the absolute partial ionization cross-sections for CF_4 by two different experimental approaches are in generally good agreement except for the cross-sections for production of the doubly charged ions CF_3^{2+} and CF_2^{2+} which were in serious disagreement. We have recently remeasured the Ar^{2+}/Ar^+ ratio using the pulsed-electron-beam time-of-flight method and have uncovered several problems which caused a revision of our earlier work. Here we report a similar study for the CF_4 molecule. Although one of the three error sources in the case of Ar was found to be unimportant in the case of CF_4, the main error, insufficient ion impact energy on the front surface of the detector, leads to an upward revision of most of our previous cross-sections. Our new results range from 5–15% larger than our previous values for the partial cross-sections. These results are in even better agreement with those reported by H. Poll, C. Winkler, D. Margreiter, V. Grill and T.D. Märk [Int. J. Mass Spectrom. Ion Processes, 112 (1992) 1], except for the CF_3^{2+}/CF_3^+ and CF_2^{2+}/CF_3^+ cross-section ratios which are approximately a factor of two higher than those of Poll et al. The cause of this remaining discrepancy is unknown.

Keywords: CF_4; ionization cross-sections; time of flight; electron impact.

Introduction

Recently Poll et al. [1] have published a revision of results reported earlier on the absolute partial ionization cross-sections for CF_4 [2] which brought their results into excellent agreement with results from our laboratory [3] except for the partial ionization cross-sections for CF_3^{2+} and CF_2^{2+} which were 3–4 times larger in our work. We have recently undertaken a careful analysis of possible sources of uncertainty in the use of the pulsed-electron-beam time-of-flight method for both Ar [4] and CF_4. The results of this study for CF_4 will be reported here.

Correspondence to: R.A. Bonham, Department of Chemistry, Indiana University, Bloomington, IN 47405, USA.

Experiment

This work is mainly concerned with the partial ionization cross-section ratios relative to CF_3^+ and as such only those error sources that were considered to have the possibility of influencing the ratio values were investigated [4]. The details of the apparatus have been given elsewhere [5]. All measurements reported here were made at an electron impact energy of 100 eV. Briefly, the apparatus consists of two identical flight tube assemblies at 180° to each other with opposing potentials. Positive ions are extracted from the point of intersection of an electron pulse and an effusive gas jet and are subsequently accelerated down one flight tube assembly while electrons and negative ions are extracted down the other assembly. The separation between the two flight tube assemblies is 12 mm.

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Each assembly consists of a 25 mm long extraction cylinder with 91.7% transparent gold meshes covering each end followed 6 mm away by a 150 mm long drift cylinder with the same grids covering each end. Six mm further on, the flight tube assembly is terminated by a 40 mm diameter microchannel plate (MCP) detector. Typically, 40 ns wide electron pulses are used at a 20 kHz pulse repetition rate with a d.c. equivalent beam current in the sub-pico ampere range. Extraction fields up to 167 V cm^{-1} are turned on about 10 ns after the incident electron pulse has passed through the scattering region. Voltages up to 1000 V are used on the drift section. The ion impact energy on the detector surface for singly charged ions was usually around 2.3 keV with doubly charged ions having twice that energy. The output from the MCP was amplified and passed through a constant fraction timing discriminator (CFD) which was then fed into the first of eight stop inputs of a cascaded time-to-digital convertor. The TDC has a 1 ns timing resolution and a dynamic range of 16 ms.

The error sources dealt with in this study have been summarized in ref. 4. The parameter involved in each case was varied over the same range indicated in Table 1 of ref. 4. Of the error sources investigated in the case of Ar that were found to be significant only the dependence on the discriminator threshold setting and the ion impact energy were found to significantly influence the results for CF_4. Surprisingly the dependence of the ratios of double to singly charged species on background gas pressure was found to be rather insignificant. A more detailed presentation of our results for the main error sources follows.

CFD threshold effect

This problem has already been discussed in refs. 3 and 4. Briefly, the problem arises in our case because we accelerate all ions through the same potential field. This means that doubly charged ions hit the front surface of our MCP detector at twice the energy of singly charged species and as a result have pulse height distributions with maxima shifted to higher pulse height. If the threshold level is set too high, counts from the singly charged pulse height distribution are lost at a faster rate than those from the doubly charged distribution and the observed ratio becomes too large. This effect was investigated in ref. 3 for the case of CF_4 where it was established that the threshold values used to obtain our reported results did not suffer significantly from this error source.

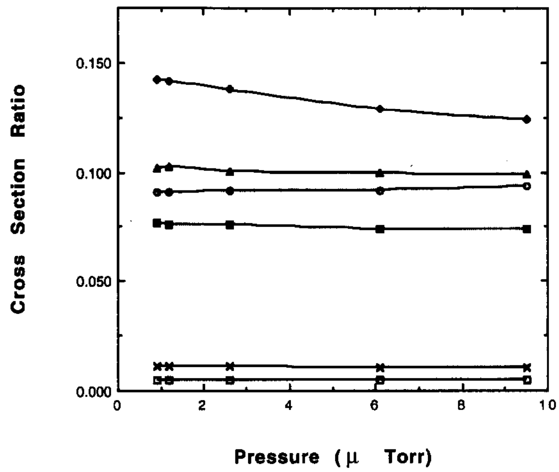

Fig. 1. Variation of the X/CF_3^+ ratios as a function of the background gas pressure where X includes all ions other than CF_3^+. All data for Figs. 1–3 were taken at an electron impact energy of 100 eV. The symbols used to denote the various ions are: ■: C^+/CF_3^+; ◇: F^+/CF_3^+; ×: CF_2^{2+}/CF_3^+; ▲: CF^+/CF_3^+; □: CF_3^{2+}/CF_3^+; ○: CF_2^+/CF_3^+.

Pressure effects

The effect on the ratio of each partial ionization cross-section to the CF_3^+ cross-section as a function of the background gas pressure is shown in Fig. 1. Unlike the Ar case where the Ar^{2+}/Ar^+ ratio was sensitive to pressure we find no serious correction in this case. We can only surmise that the ion/molecule cross-sections are much smaller, possibly because symmetric charge exchange, which has a large cross-section in the case of Ar, cannot occur in the case of CF_4. In any event this was not a problem in our earlier work because of the low pressures used [3]. Note that of all the ratios plotted

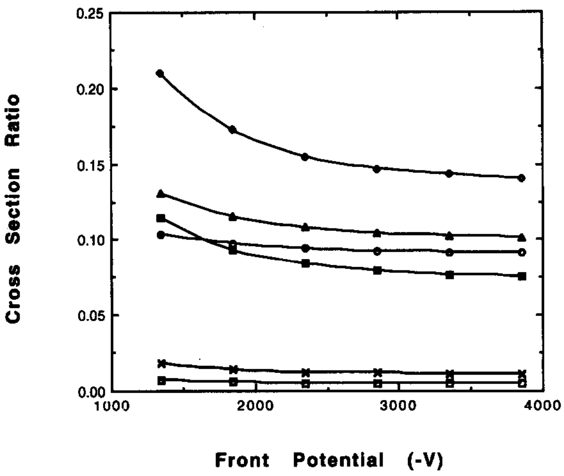

Fig. 2. Variation of the X/CF_3^+ ratios as a function of the negative voltage applied to the front surface of the MCP. As in Fig. 1, X varies over all ions other than CF_3^+ and the symbols used for the various ions are defined in the caption to Fig. 1.

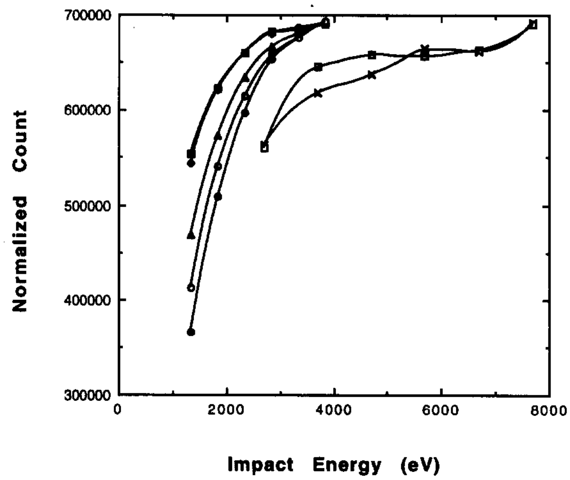

Fig. 3. Comparison of the relative detection efficiencies for all the ions as a function of the ion impact energy in electronvolts. All curves were matched at 4000 V. The symbols used to denote the various ions are: ●: CF_3^+; ■: C^+; ◇: F^+; ×: CF_2^{2+}; ▲: CF^+; □: CF_3^{2+}; ○: CF_2^+.

as a function of pressure, the only one which shows any indication of a pressure effect is the F^+/CF_3^+ ratio; this indicates that F^+ has a larger ion/molecule cross-section than CF_3^+, although the CF_3^+ cross-section is not significantly different from those for the other ions.

Ion impact energy on the front surface of the MCP

In Fig. 2 the ratios of the cross-sections for all ionic species relative to the CF_3^+ cross-section are shown as a function of the MCP front surface potential which is essentially the ion impact energy of the singly charged species with the doubly charged species having twice that energy. This is the major source of error in our previous work since we used a front surface potential on our MCP of only 2300 V. It appears necessary to use front surface potentials of at least 3500 V and preferably higher if possible.

In Fig. 3 we show the ion count rates for all ionic species separately as a function of ion impact energy where all the ion count rates have been matched at 4000 V MCP front plate potential. Note that in terms of the ion impact energy the singly charged species reach their maximum values at lower impact energies than the doubly charged species. This suggests that if both ion currents were to be measured at the same energy and if that energy were less than 4 keV then the observed ratios would be too small. The situation is reversed in our case where all ions are accelerated through the same potential field as is shown in the plot of the ratio against the MCP front face potential (Fig. 2) which leads to a ratio that is too large if the impact energy is too small.

Conclusions

Our new results are essentially the same as those we have reported earlier [3] except that the ratios of doubly to CF_3^+ charged species has decreased. At an electron impact energy of 100 eV both the CF_3^{2+}/CF_3^+ and CF_2^{2+}/CF_3^+ ratios are approximately a factor of two larger than those of refs. 1 and 2. We have no definite idea as to the nature of the remaining difference. A remote possibility, since the two experiments differ dramatically in the length of time it takes to detect an ion after it has been formed, is that the doubly charged ions are metastable with a lifetime on the order of 10 μs. Such an

TABLE 1

Corrected absolute electron-impact ionization cross-sections for CF_4 taken from Ma et al. [3] (all units are Å^2)

E (eV)	Species						
	CF_3^+	CF_2^+	CF^+	C^+	F^+	CF_2^{2+}	CF_3^{2+}
20	0.423						
25	1.025	0.037					
30	1.701	0.125	0.007				
35	2.250	0.180	0.048	0.004	0.001		
40	2.623	0.193	0.116	0.036	0.021		
45	2.902	0.224	0.186	0.091	0.060	0.002	0.002
50	3.124	0.252	0.219	0.130	0.105	0.004	0.006
55	3.292	0.273	0.238	0.147	0.134	0.006	0.011
60	3.416	0.297	0.287	0.190	0.222	0.011	0.022
65	3.508	0.316	0.329	0.226	0.303	0.017	0.034
70	3.580	0.331	0.351	0.244	0.346	0.020	0.040
75	3.632	0.341	0.359	0.249	0.368	0.022	0.043
80	3.671	0.349	0.363	0.253	0.383	0.023	0.046
85	3.697	0.355	0.370	0.260	0.406	0.025	0.048
90	3.716	0.359	0.380	0.271	0.435	0.026	0.052
95	3.726	0.361	0.391	0.282	0.466	0.027	0.056
100	3.732	0.364	0.402	0.291	0.494	0.028	0.059
110	3.730	0.366	0.414	0.293	0.525	0.028	0.061
120	3.716	0.365	0.417	0.290	0.541	0.029	0.063
130	3.694	0.364	0.413	0.294	0.562	0.030	0.064
140	3.666	0.361	0.406	0.303	0.583	0.032	0.065
150	3.636	0.359	0.400	0.309	0.599	0.033	0.066
160	3.604	0.359	0.399	0.309	0.604	0.033	0.066
170	3.572	0.358	0.397	0.305	0.601	0.032	0.065
180	3.538	0.355	0.394	0.301	0.595	0.032	0.064
190	3.505	0.348	0.387	0.298	0.589	0.032	0.063
200	3.472	0.341	0.380	0.296	0.583	0.033	0.062
250	3.317	0.322	0.351	0.274	0.545	0.030	0.058
300	3.184	0.307	0.329	0.258	0.508	0.025	0.053
350	3.070	0.292	0.304	0.240	0.470	0.022	0.049
400	2.972	0.280	0.286	0.224	0.438	0.020	0.045
450	2.887	0.271	0.267	0.214	0.414	0.019	0.042
500	2.813	0.264	0.253	0.203	0.391	0.018	0.039

effect has been reported in an earlier work on N_2O^+ [6].

The changes suggested by this work are mainly due to the use of too low a value for the impact energy on the front surface of the detector. This effect was looked for in ref. 3 but was not found due to the use of too narrow an ion impact energy on the front face of the MCP. Thus, our previously reported absolute partial ionization cross-section results should all be revised upwards by the amounts: 16% for CF_3^+, 13% for CF_2^+, 9% for CF^+, and 5% for F^+ and C^+. Note that the heavier the mass of the singly charged ion the greater the correction, while there is no measurable correction to apply to the doubly charged ions. For convenience, the revised cross-sections are shown in Table 1. These results are now in even better agreement with recent corrected cross-sections reported by Poll et al. [1].

We have shown that the ratio of doubly charged to singly charged species is especially sensitive to variations in CFD threshold setting and ion impact energy on the detector. In fact it seems reasonable to suggest that the ratio be used as a diagnostic tool for checking on these effects when setting up an experiment. It also seems advisable to measure the pulse height distribution of the ion pulses at the same time that the mass spectrum is recorded since MCP detectors tend to lose gain with time and part of the signal may slip under the CFD threshold setting. A similar effect has also been observed by Syage [7] in the measurement of partial ionization cross-sections for rare gases.

Acknowledgment

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