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Absolute partial and total electron-impact ionization cross-sections of the CCl_2F_2 molecule

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Abstract

A study of the partial ionization cross-sections (ICSs) of the set of ions produced by electron-impact dissociative ionization on halomethane CCl_2F_2 and a sample of the kinetic energy distribution (KED) for the ejected $CClF_2^+$ ion are reported. Collision experiments were carried out by crossing at right angle two pulsed beams, a supersonic halometane beam and an electron beam with energies in the range from 0 to 100 eV. The ions generated were removed by an appropriate electric field and further characterized in a double focusing time-of-flight mass spectrometer. The $CClF_2^+$ cation is the fragment ion with the largest partial ICS in the range of electron energies studied, followed by Cl^+, CF_2^+, CF^+, CCl_2F^+, CCl^+, $CClF^+$, C^+, F^+, Cl_2^+ and $CCl_2F_2^+$ and some doubly charged ions with smaller intensities. The total ICS curve as a function of the electron-impact energy was obtained by adding up the partial ICS of all the ion fragments. A comparison is made with the computed cross-sections by the binary-encounter Bethe (BEB), the Deutsch and Märk (DM), and the modified-additivity-rule (MAR) methods. The experimental results agree best with the DM formalism.

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1. Introduction

The knowledge of the electron ionization cross-sections (ICSs), of halomethanes in the energy range 0–100 eV is crucial for the modeling and optimization of industrial plasmas [1]. In this range of electron energies most of the precursors' excited electronic states and dissociative ionization channels are accessible, and the cross-section curves reach their maxima. Dichlorodifluoromethane, CCl_2F_2 is a widely employed compound used to create reactive etching species in semiconductor processing plasmas and in other plasmas. Furthermore, the photodissociation of CCl_2F_2 in the earth stratosphere yields Cl atoms, which are known to deplete the ozone layer [2]. The long residence lifetime of CCl_2F_2 in the upper atmosphere makes it an important greenhouse gas.

Previous studies of low-energy electron ICS, dissociative ionization and temperature-dependent attachment on the CCl_2F_2 precursor have been reviewed and discussed by Christophorou et al. [3]. Total ICSs were measured at a few electron energies by Beran and Kevan [4] employing the total ion current method and at many more energies by Pejcev et al. [5]. Recently,

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Bart et al. [6] have reported the total ICS of a series of perfluorinated hydrocarbons and small halocarbons, including CCl_2F_2. Contributions to the total ICS from individual bonds were also determined and the experimental data compared with ionization efficiency curves calculated using the DM and BEB models. Partial ICSs were reported by Leiter et al. [7]. Their total ICS curve is markedly different from the one determined by the total ion current method. The emission of neutral and excited ion fragments generated by 0–500 eV electron collisions have also been analyzed [8]. The most significant emission features arise from the CCl ($A^2\Delta$–$X^2\Pi$), CCl^+ ($A^1\Pi$–$X^1\Sigma^+$) and CF_2 (A–X) transitions.

This work reports a detailed study of the partial ICS curves of the ions produced by electron-impact on CCl_2F_2 for energies up to 100 eV. The sum of the partial cross-sections to yield the total ICSs was also determined. Partial ICSs are compared to those of Leiter et al. [7] and the total ICS curve with that of Leiter et al. [7], Pejcev et al. [5] and Beran and Kevan [4]. A comparison is also made with cross-sections computed by the binary-encounter Bethe (BEB), the Deutsch–Märk (DM), and the modified-additivity-rule (MAR) methods.

2. Experimental results

The experimental set-up and the method to measure the partial ICSs are described elsewhere [9,10] and only a brief account will be given here. A pulsed supersonic molecular beam generated by expansion of a mixture of Ar seeded with CCl_2F_2 is crossed at right angle with a pulsed electron beam (0.5 eV FWHM and 10 μA electron intensity) in the ionization region of a lineal double focusing time-of-flight mass spectrometer (R.M. Jordan). The ions produced by the electron collisions are extracted by the electric field produced by a negative voltage pulse applied to a grid or plate and directed with the aid of electrostatic lenses through the 86.5 cm long flight tube towards the multichannel plate (MCP) detector placed at the tube end. The response of the MCP (C-07001, 18 mm diameter) is sent to a digital oscilloscope and to a computer for further analysis and storage.

Partial ICSs were normalized relative to either Ar (40 amu) or Kr (83.8 amu) as reference gases, depending on the mass of the ion and in order to avoid mass discrimination effects in the extraction and the flight tube regions. Before supersonic expansion the reference and target gases were stored in a stainless steel cylinder at a stagnation pressure of 3 bar (MKS-baratron 750B, 1% accuracy). Absolute partial ICS of a product ion is obtained by comparing the signal intensity of the ion and an appropriate reference gas of known absolute ICSs, Ar^+ or Kr^+ ions in our case [11,12]. Errors in partial ICSs are estimated to be <10% [10] for ions with masses comparable with those of Ar or Kr, and higher (<15%) for lighter ions, where the large velocities and their kinetic energy distribution (KED) preclude a complete focusing of the ions on the MCP detector.

For reasons of comparison the electron-impact total ICSs have been computed by the BEB [13], the DM [14] and the MAR methods [15]. Although the BEB and DM methods include some type of additivity, they do not represent additivity rules but include orbital energies, whose ab initio values may be computed with the GAUSSIAN 98W package [16]. In this paper the computations were conducted at the MP2/6-31G* level. The basis set was chosen after checking that enlargement in size does not lead to an improvement of the total ICS curves. However, a net improvement of total ICS is attained [9] by taking the experimental first ionization energy instead of the computed one.

3. Results and discussion

3.1. Partial ionization cross-sections

The ions with a sizable electron-impact partial ICSs of the CCl_2F_2 molecule include $CClF_2^+$, Cl^+, CF_2^+, CF^+, CCl_2F^+, CCl^+, $CClF^+$, C^+, F^+, Cl_2^+ and $CCl_2F_2^+$. Their ICSs vs. the electron-impact energies below 100 eV are plotted in Fig. 1. Other ions and doubly charged ions such as CCl_2^+, CCl_2F^{2+}, $CClF_2^{2+}$,

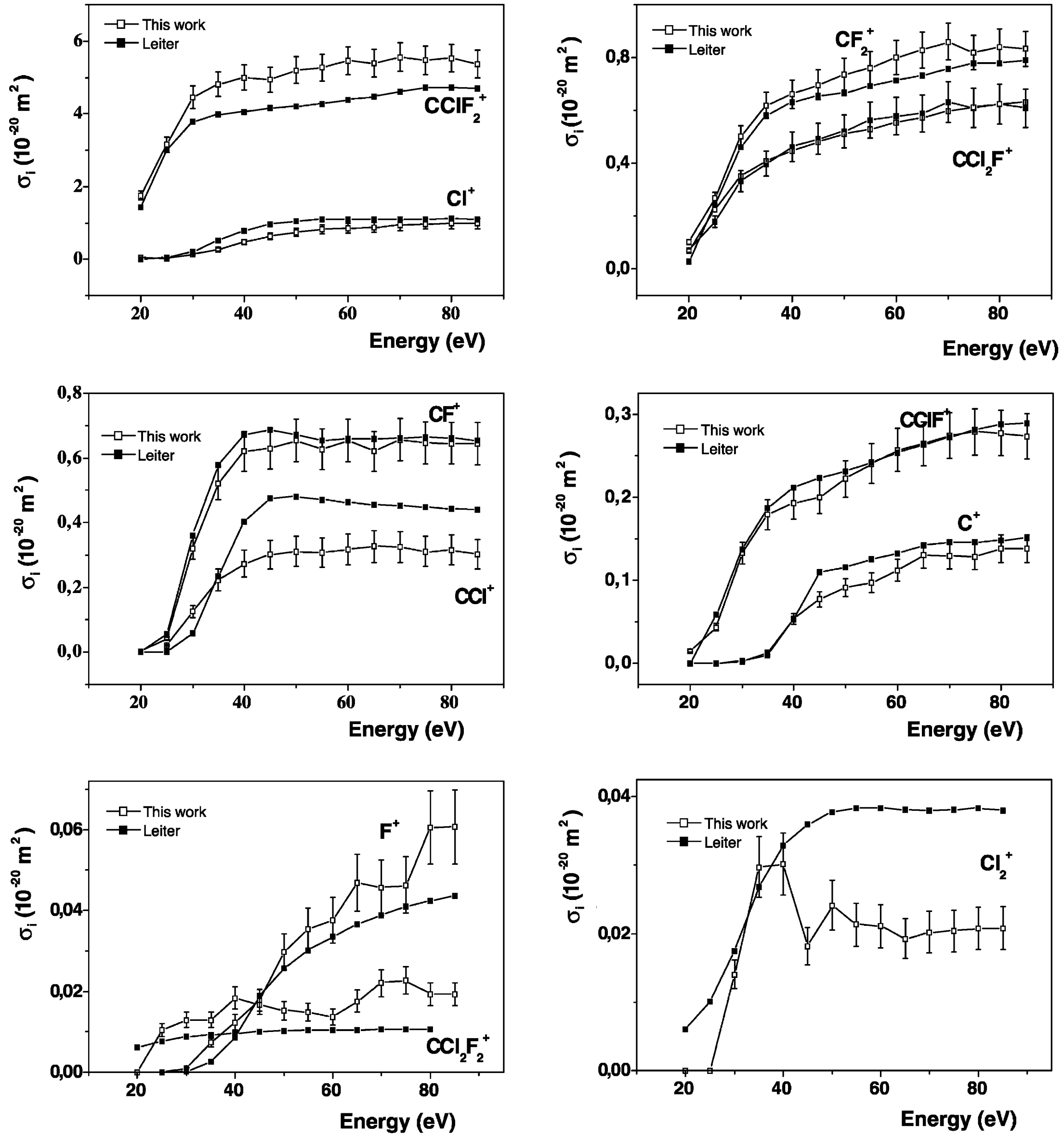

Fig. 1. Partial ionization cross-sections (ICSs) of the $CClF_2^+$, Cl^+ CF_2^+, CF^+, CCl_2F^+, CCl^+, $CClF^+$, C^+, F^+, Cl_2^+ and $CCl_2F_2^+$ ions produced by electron collisions up to 100 eV with CCl_2F_2 molecule. References within the figure: (■) Leiter et al. [7], (□) this work.

CCl_2^{2+}, CCl^{2+} and Cl^{2+}, have partial ICS lower than 10^{-22} m^2 and are barely observed. Their contribution to the total ICS is insignificant. A detailed list of the partial ICS of the major ions is given in Table 1.

The ICSs curves for the Cl^+, CF_2^+, CCl_2F^+, CF^+ and $CClF^+$ ions are in excellent to good agreement, within the experimental errors, with those of Leiter et al. [7] (Fig. 1). The discrepancies for C^+ and F^+ are small, in spite of the difficulty of measuring small ICSs. However, the cross-section curves for $CClF_2^+$, CCl^+, $CCl_2F_2^+$ and even more for Cl_2^+ ions have significant differences, apparently not related to the KED

Table 1
Partial and total ionization cross-sections of ions produced by electron-impact on CCl_2F_2 (cross-sections are in 10^{-20} m^2 units)

Energy (eV)	$CClF_2^+$	Cl^+	CF_2^+	CF^+	CCl_2F^+	CCl^+	$CClF^+$	C^+	F^+	Cl_2^+	$CCl_2F_2^+$	Total
20	1.751	0.019	0.079	–	0.073	0.009	–	–	–	–	–	1.931
25	3.061	0.042	0.215	0.078	0.191	0.019	0.052	–	–	–	0.014	3.672
30	4.281	0.176	0.479	0.328	0.337	0.082	0.146	0.005	0.001	0.009	0.019	5.863
35	4.679	0.349	0.614	0.522	0.399	0.183	0.191	0.022	0.005	0.022	0.017	7.003
40	4.848	0.536	0.655	0.604	0.456	0.274	0.208	0.059	0.017	0.028	0.023	7.708
45	4.894	0.667	0.673	0.616	0.472	0.302	0.211	0.078	0.021	0.029	0.020	7.983
50	5.068	0.795	0.725	0.627	0.504	0.301	0.230	0.098	0.029	0.032	0.020	8.429
55	5.211	0.838	0.753	0.619	0.540	0.301	0.249	0.099	0.033	0.032	0.021	8.696
60	5.317	0.893	0.787	0.641	0.554	0.319	0.255	0.109	0.038	0.029	0.019	8.961
65	5.359	0.901	0.821	0.625	0.573	0.317	0.257	0.122	0.048	0.026	0.023	9.072
70	5.473	0.963	0.859	0.650	0.603	0.331	0.277	0.131	0.050	0.023	0.023	9.383
75	5.342	0.957	0.831	0.632	0.587	0.316	0.278	0.132	0.053	0.026	0.023	9.177
80	5.350	0.979	0.846	0.631	0.595	0.321	0.289	0.138	0.058	0.025	0.019	9.251
85	5.206	0.976	0.848	0.622	0.580	0.315	0.274	0.139	0.058	0.022	0.022	9.062

of the ejected ion (which should be mass-dependent) [17]. Note that even for ions with larger discrepancies, the features of the cross-section shapes are close, as verified for the $CCl_2F_2^+$ ion which at electron energies just over 40 eV levels off and remains constant at larger energies. The small ICS of the $CCl_2F_2^+$ ion reflects the instability of the ion and a marked tendency to dissociate following electron-impact. $CClF_2^+$ and CCl_2F^+ ions have higher ICS, which indicates that the loss of fluorine or chlorine atoms stabilizes the ionic fragment produced. It is worth noting that the ICS curve for the atomic Cl^+ ion is large and second only to that of $CClF_2^+$ ion. The CF_2^+ and CF^+ ions have a high formation yield (Table 1). Both ions and the F^+ ion are known to be efficient etching species in plasma processing [18,19]. The large ICSs for these fluorinated species explain the use of the CCl_2F_2 molecule in plasmas for the microelectronic industry.

3.2. Total ionization cross-sections

The total (counting) ICS at an electron energy was obtained by adding the partial ICSs of the ions produced, and values at a number of electron-impact energies from 0 to 100 eV are shown in the last column of Table 1. A comparison of the total ICS curves obtained and those reported earlier are presented in Fig. 2 [4,5,7]. Beran and Kevan [4] measured the total ICS at three electron collision energies, namely 20, 35 and 70 eV. The cross-section curve reported by

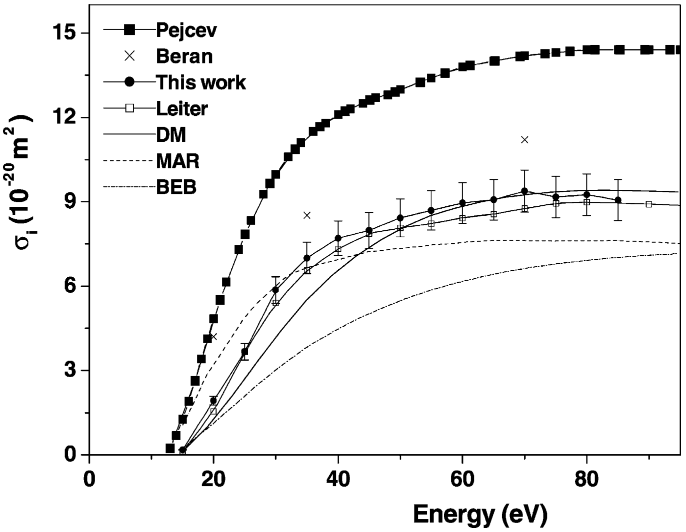

Fig. 2. Total ICS curve following electron-impact on the CCl_2F_2 molecule. The energy of the incident electron was <100 eV. The experimental ICS are indicated as follows: (×) Beran and Kevan [4], (■) Pejcev et al. [5], (□) Leiter et al. [7], (●) this work.

Pejcev et al. [5] is far more detailed and the ICS is significantly larger. Both studies measured the total ICS by recording the total ion current generated at the detector, a method where the extraction region is difficult to determine precisely and where the results are likely to have large errors. Leiter et al. [7] have used a mass selected experimental method similar to that used here and reported a total ICS curve which is only one-half of that of Pejcev et al. [5] and which is in excellent agreement with the curve reported here. It may be thought that the ICSs of Pejcev et al. [5] are unaffected by discrimination of the high-energy ions, that may be lost between the interaction region and the detector. However, for the heavy $CClF_2{}^+$ ion, with a large contribution to the total ICS (Table 1), the discrimination effects cannot explain the discrepancies since heavy ions are released with low KED [10] and are easily focused into the detector. It should be noted that the FWHM of the KED at electron-impact energies of 40 and 70 eV (Fig. 3) are close to 0.5 eV, with the maximum ca. 0.1 eV, and thus comparable to that observed for reference gas Ar to yield Ar^+ ion. Therefore, the $CClF_2{}^+$ partial ICS cannot be larger than that measured in this work, and the values by Pejcev et al. [5] are somehow too high. Similar KED have been observed for other product ions of CCl_2F_2 [17] and thereby the ions are correctly extracted and detected. Furthermore, the simulation with the ‘SIMION 3D’ software [20] confirms the expected low KED. In conclusion, the total ICS curve reported in this work is to be preferred to that of Pejcev et al. [5].

The total ICS curves are compared to computed cross-sections by the BEB [13], DM [14] and MAR [15] methods (cf. Fig. 2). It is readily observed that the DM formalism matches the experimental curve well above 45 eV, with a maximum ICS at 85 eV, close to the experimental value of 80 ± 7 eV (cf. [7]). Our BEB curve and DM calculations are also in accord with Bart et al. [6] BEB calculations and the experimental ICSs. The discrepancies between Bart et al. and the DM calculations presented here are probably due to the levels of calculation used, since Bart’s HF/6-31G level neglects electronic correlation and systematically yields higher ICSs [9]. Although the BEB method is well established for the calculation of total ICSs of molecules consisting of light atoms, it does not provide satisfactory results for the CCl_2F_2 molecule. In our case, the BEB cross-section is low, and reaches a

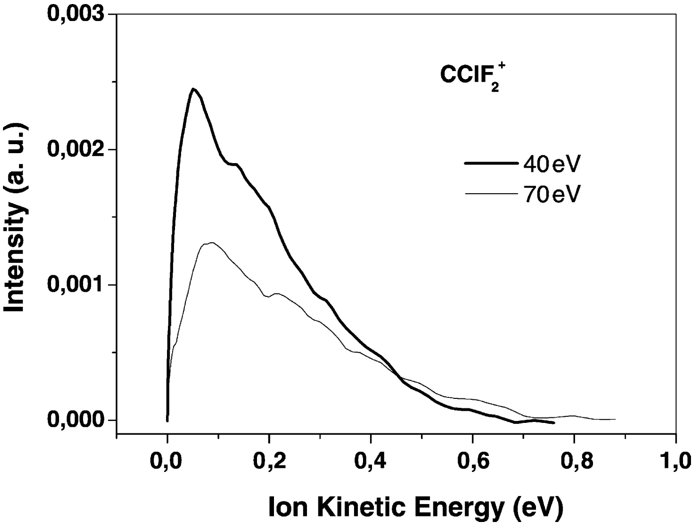

Fig. 3. Nascent kinetic energy distribution (KED) of the $CClF_2^+$ ion produced by electron-impact dissociative ionization of CCl_2F_2. The distributions correspond to electron energies of 70 and 40 eV, respectively.

maximum near 120 eV. It should be pointed out that the BEB method relies on the actual knowledge of the continuum dipole oscillator strength, a magnitude unknown for most atoms and commonly substituted by values of low-mass species, such as H, He and H_2. It seems obvious to argue that the heavier the atoms in the molecule the poorer the assumption. Both BEB and DM methods predict sensible shapes in good agreement with our results over the entire energy range and yield comparable dissociative ionization thresholds. The utility of the DM method to molecules with heavy atoms has been recently verified elsewhere for CF_3Br and CF_3I [21] and also in our laboratory.

The MAR method yields curves with a poor agreement with our data, rising very rapidly in the low electron energy region up to 30 eV and leveling off at higher energies. This level of agreement is poor and in the same trend as those for other molecules [9].

4. Conclusions

A mass selective study of the electron-impact dissociative ICSs of CCl_2F_2 is reported. Partial ICSs curves for electron energies in the range from 0 to 100 eV of the most abundant ions, i.e., $CClF_2^+$, Cl^+, CF_2^+, CF^+, CCl_2F^+, CCl^+, $CClF^+$, C^+, F^+, Cl_2^+ and $CCl_2F_2^+$, have been measured. The total ICS obtained as the sum of the partial ICSs has been compared with the cross-sections calculated by the BEB, DM and MAR methods. Agreement with the BEB cross-section is poorer than with the DM for molecules with atoms of the third row (Cl). The total dissociative ICS and some partial ICS curves are in good agreement with those reported by Leiter et al. [7].

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