

Absolute total cross sections for the scattering of low energy electrons by CCl_4 , CCl_3F , CCl_2F_2 , CClF_3 , and CF_4

Robert K. Jones^{a)}

Chemistry Department, Indiana University, Bloomington, Indiana 47405

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Absolute total electron scattering cross sections were measured with a time-of-flight electron transmission spectrometer for incident electron energies ranging from 0.6 to 50 eV. The halomethanes studied exhibit low energy structure which can be associated with electron capture processes. Comparisons are made with recent experiments and calculations.

INTRODUCTION

The low energy electron scattering cross sections for many small molecules exhibit pronounced structure that has been associated with electron capture processes.^{1,2} Because of the paucity of experimental studies and scattering calculations, many fundamental questions remain unanswered about the nature of the anion states involved in these resonances in electron scattering by the chlorofluoromethanes. Reliable measurements of the electron scattering cross sections are prerequisite to understanding these electron capture processes.

Low energy electron scattering measurements of the halogenated methanes also have practical applications. Since low energy electron reactions are involved in the energy deposition scheme of ionizing radiation with matter,³ studies of these low energy reactions can lead to a more complete understanding of the atmospheric chemistry of the freons. Some of the halogenated methanes have also been investigated for use as gaseous dielectrics in high voltage equipment. Their breakdown voltages are strongly influenced by their large electron attachment cross sections.^{4,5} Basic data on electron scattering and electron attachment and detachment processes, which are valuable in tailoring gaseous dielectrics, is at present limited for these molecules.

The results of absolute measurements of the total electron scattering cross sections (TCS) for CCl_4 , CCl_3F , CCl_2F_2 , CClF_3 , and CF_4 are presented here. The measurements were made with a time-of-flight electron transmission spectrometer with an energy range from 0.6 to 50 eV.

EXPERIMENTAL PROCEDURE AND ERROR ANALYSIS

The apparatus employed for these measurements has been described in earlier publications reporting measurements of the total cross sections of helium,^{6(a),6(b)} molecular hydrogen,⁷ and methane.⁸ Significant modifications were made between the earliest work on helium and the measurements of methane; however, the specifics of the experiment and error analysis were identical for the present measurements and the methane measurements.

The apparatus consisted of a pulsed electron source in line with a 38 cm gas sample cell and a microchannel plate

electron detector. The total cross section at each energy was determined from the attenuation of the electron intensity as it passed through the sample cell. The total cross section (Q) was related by the Beer-Lambert relationship to the unattenuated electron intensity measured when the sample cell was evacuated, I_0 ; the electron intensity attenuated by the sample gas, I ; the number density of the gas, n ; and the cell length, l :

$$Q = \frac{1}{nl} \ln \frac{I_0}{I}.$$

The source emitted electrons with energies ranging from 2 keV to thermal energies. A sharp peak in its intensity occurred at 2 keV and a very broad structureless maximum occurred between 1 and 50 eV. The source was pulsed every 4 μs and the intensity was regulated to keep the count rate at the detector less than 2500 counts per second. Electron energies were determined from their flight time from the source to the detector. The energy resolution (ΔE) for these measurements was dependent primarily on the timing resolution of the processing electronics (~ 3 ns). Its energy dependence is given by

$$\Delta E = 0.0080 E^{3/2} \text{ (in eV)}.$$

The experimental procedure involved collecting the electron transmission spectrum as a function of electron energy with the cell evacuated for 100 to 200 s. The sample gas was then admitted to the cell and the attenuated transmission spectrum was recorded for 200 to 800 s. This cycle was repeated for 6 to 24 h and the data was averaged over time. The sample gas pressure was continuously recorded and averaged over time. The data were corrected for instrument dead time effects, background noise in the detector and variations in the intensity of the electron source.

Five measurements of the cross section of CF_4 were made with sample pressures ranging from 0.3 to 0.6 mT. Three measurements were made of cross sections of each of the remaining molecules with sample pressures between 0.2 and 0.4 mT. No systematic deviations between measurements larger than what was indicated by the error analysis were observed.

The procedure used to estimate all the errors and the magnitude of most of the contributing errors were the same for the present measurements and an earlier work on methane.⁸ However, the magnitudes of the errors due to pressure

^{a)} Present address: National Bureau of Standards, Washington, D. C. 20234.

TABLE I. Estimated maximum error (coherent sum) and most probable error (incoherent sum) in the measured total cross sections.

	CCl ₄	CCl ₃ F	CCl ₂ F ₂	CClF ₃	CF ₄
<i>E</i> < 4.0 eV					
Incoherent sum	+ 3.3% - 3.3%	+ 2.8% - 2.8%	+ 4.6% - 4.6%	+ 4.1% - 4.1%	+ 2.3% - 2.3%
Coherent sum	+ 7.8% - 7.8%	+ 6.6% - 6.6%	+ 10.0% - 9.9%	+ 9.0% - 9.0%	+ 5.3% - 5.2%
4.2 eV < <i>E</i> < 15.0 eV					
Incoherent sum	+ 3.5% - 3.0%	+ 3.3% - 2.8%	+ 4.5% - 4.2%	+ 2.9% - 2.4%	+ 3.3% - 3.0%
Coherent sum	+ 8.7% - 6.8%	+ 7.9% - 6.1%	+ 10.2% - 8.6%	+ 7.9% - 6.2%	+ 8.7% - 7.2%
16.0 eV < <i>E</i> < 25.0 eV					
Incoherent sum	+ 4.1% - 3.0%	+ 3.8% - 2.7%	+ 4.9% - 4.2%	+ 3.5% - 2.2%	+ 3.4% - 2.1%
Coherent sum	+ 9.3% - 6.5%	+ 8.5% - 5.8%	+ 11.0% - 8.5%	+ 8.1% - 5.4%	+ 7.5% - 4.9%
26.0 < <i>E</i> < 50.0 eV					
Incoherent sum	+ 7.8% - 3.3%	+ 7.4% - 2.9%	+ 7.9% - 4.6%	+ 7.4% - 2.6%	+ 7.4% - 2.8%
Coherent sum	+ 14.3% - 7.2%	+ 13.0% - 6.2%	+ 15.8% - 9.4%	+ 13.1% - 6.2%	+ 12.6% - 5.7%

gradients in the sample cell, impurities in the sample gas, scattering of high energy electrons from the edges of the apertures near the detector, and the experimental reproducibility were dependent upon the sample gas. The total estimated errors in the measured cross sections are listed in Table I. The incoherent sum was obtained by adding directly all systematic errors that could act in only one direction (to either raise or lower the magnitude of the measured cross section); this sum was squared, added to the sum of the squares of all other systematic and random errors and the square root was taken of the total. This incoherent sum represents the most probable error in the measured values. The coherent sum, which acts as an estimated maximum error, consists of a direct sum of all contributing systematic and random errors. Separate sums were found for errors that act to raise and lower the measured cross sections.

Errors in the energy scale were evaluated with respect to their effect on the magnitude of the measured cross section and were included in the above mentioned error sums. The incoherent sum of the energy scale errors are also listed in Table II to indicate the overall reliability of the energy scale.

RESULTS AND DISCUSSION

The measured absolute total electron scattering cross sections for CCl₄, CCl₃F, CCl₂F₂, CClF₃, and CF₄ are pre-

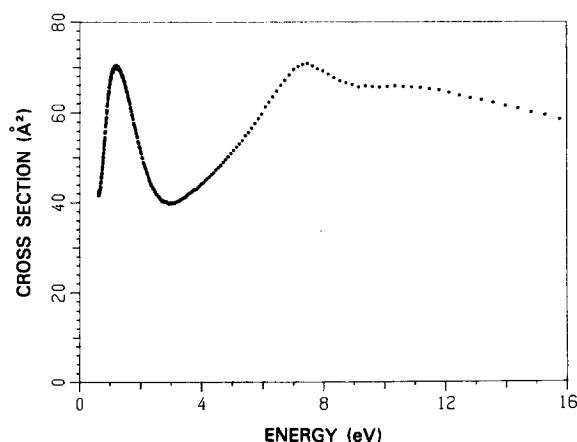
TABLE II. Estimated accuracy of the energy scale and energy resolution (eV).

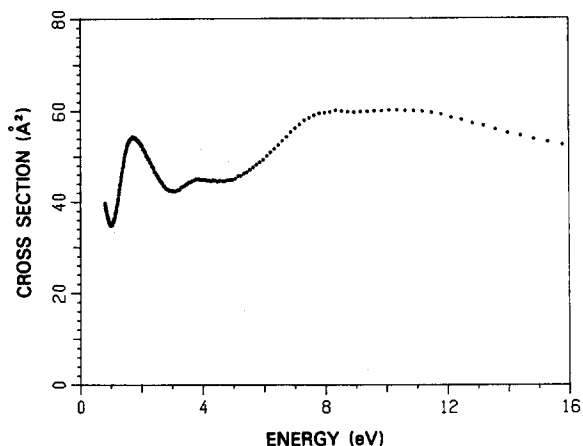
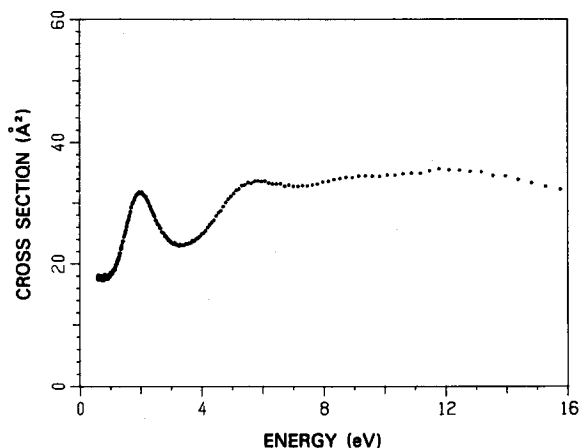
	<i>E</i> < 4.0 eV	4.2–15 eV	16–25 eV	26–50 eV
Most probable error	± 0.02	± 0.09	± 0.18	± 0.49
Energy resolution	0.06	0.46	1.0	2.8

sented graphically for energies below 16 eV in Figs. 1 through 5 and in tabular form up to 50 eV in Table III. The figures present the weighted average of a number of experiments on each sample; the weighting factors were based on the signal-to-noise ratio in each experiment. The table of cross section values was obtained by linearly interpolating the experimental values to predesignated energies and then finding the weighted averages.

The positions of the low energy peaks in the total cross sections are presented in Table IV. The uncertainties in the positions are estimates of the accuracies with which the peak positions were read from plotted data.

The total cross sections of the chlorinated halomethanes presented here exhibit similar structure at low energies. In all cases a single large peak occurs below 2.5 eV in the energy range of this study. This is followed by generally smaller less

FIG. 1. The total electron scattering cross section of CCl₄.

FIG. 2. The total electron scattering cross section of CCl_3F .FIG. 4. The total electron scattering cross section of CClF_3 .

pronounced peaks at higher energy. A broad maximum occurs around 10 eV followed by a monotonic decrease in cross section with increasing energy up to the energy limit of the experiment at 50 eV. The CF_4 cross section, by contrast, displays a very broad shoulder around 3.6 eV and a peak at 8.9 eV followed by a very broad maximum around 25 eV, with a monotonic decrease at higher energy.

Dominant peaks in the cross sections for electron scattering by molecules for incident electron energies below the electronic excitation threshold are commonly attributed to elastic shape resonances. A number of methods have been employed to analyze low energy electron resonances in polyatomic molecules.^{1,9,10} In principle, the direct approach of calculating the electron scattering cross section is clearly the most satisfactory approach to obtain quantitative information; however, the paucity of scattering calculations on molecules of the complexity of the substituted methanes discussed here has limited this approach to the assignment of scattering resonances.

A more common approach, which is much more manageable computationally, has been to relate the energy of the observed resonances to the calculated energies of the unoccupied valence molecular orbitals of the neutral molecules. This latter approach assumes the unoccupied valence orbitals of the neutral molecule closely approximate the orbitals

occupied by the incident electron in the temporary anion state formed at resonance. This assumption is partially justified by the fact that, since the formation time and often the anion lifetime are shorter than the vibrational period, the geometry of the molecule is unchanged during the electron capture process.

Intrinsic to this latter approach is the consideration of valence molecular orbitals only. Consequently it has not been useful in illuminating resonances associated with electron capture in nonvalence orbitals. Shape resonances of this type have been proposed for several of the halomethanes.^{10,11} The orbitals have been characterized as diffuse with much of their electron density outside of the internuclear region.⁹

Resonances observed in dissociative attachment measurements have also been used to aid in the assignment of low energy resonances.¹⁰ The dissociative attachment process can be understood as an electronic transition in the Franck-Condon region from the ground state of the molecule plus a free electron to a discrete anion state, followed by dissociation of the anion. The energy of the peak in the electron attachment cross section corresponds to the vertical attachment energy (VAE), which is the vertical distance between a minimum in the potential energy surface of the ground state of the molecule and the potential energy surface for the anion that is formed. It should be noted that the VAE, which

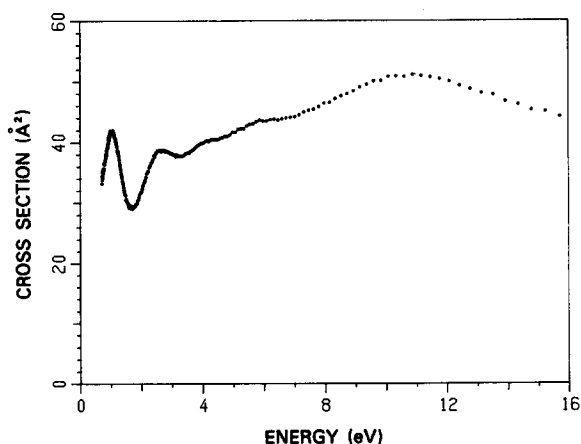
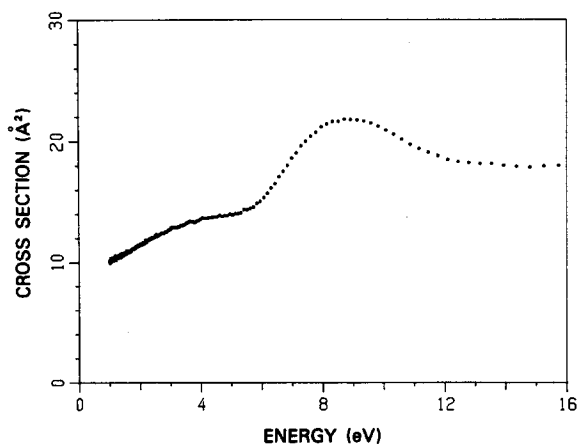
FIG. 3. The total electron scattering cross section of CCl_2F_2 .FIG. 5. The total electron scattering cross section of CF_4 .

TABLE III. Absolute total electron scattering cross sections for some halomethanes (\AA^2).

Energy	CCl_4	CCl_3F	CCl_2F_2	CClF_3	CF_4
0.6	41.76			17.67	
0.7	44.59		33.58	17.83	
0.8	51.70	39.75	36.91	17.81	
0.9	60.39	36.02	39.78	17.72	
1.0	66.36	34.80	41.54	18.03	10.23
1.1	69.24	36.33	40.80	18.93	10.31
1.2	70.26	39.46	38.82	19.74	10.35
1.3	69.53	43.92	35.98	21.09	10.42
1.4	68.18	47.67	33.06	22.93	10.63
1.5	66.44	51.27	30.47	25.04	10.74
1.6	63.67	53.34	29.39	27.20	10.87
1.7	60.72	53.99	29.18	29.42	11.00
1.8	57.48	53.97	29.41	30.67	11.11
1.9	54.81	53.40	30.46	31.62	11.30
2.0	51.98	52.57	31.82	31.77	11.40
2.1	49.27	51.36	33.48	31.49	11.46
2.2	47.13	49.96	35.19	30.80	11.65
2.3	45.02	48.66	36.46	29.62	11.90
2.4	43.62	47.43	37.76	28.49	11.93
2.5	42.28	45.95	38.50	27.18	12.17
2.6	41.39	44.85	38.68	26.27	12.16
2.7	40.51	43.85	38.65	25.22	12.32
2.8	40.26	42.86	38.50	24.53	12.40
2.9	39.94	42.56	38.28	23.93	12.53
3.0	39.94	42.46	38.04	25.54	12.65
3.1	39.94	42.39	37.67	23.39	12.79
3.2	40.23	42.64	37.73	23.14	12.86
3.3	40.55	43.24	37.74	23.15	12.91
3.4	40.94	43.60	38.00	23.06	13.02
3.5	41.35	44.02	38.20	23.27	13.08
3.6	42.06	44.42	38.52	23.38	13.25
3.7	42.49	44.73	38.83	23.75	13.30
3.8	42.96	45.04	39.34	23.92	13.22
3.9	43.42	44.98	39.68	24.26	13.39
4.0	44.20	44.94	39.86	24.82	13.51
4.2	45.46	44.79	40.17	25.94	13.60
4.4	46.65	44.79	40.41	27.07	13.64
4.6	48.12	44.69	40.68	28.51	13.79
4.8	49.62	44.86	40.96	30.05	13.85
5.0	51.28	44.97	41.59	31.24	13.95
5.2	52.86	45.75	42.13	32.21	14.05
5.4	54.60	46.47	42.50	32.98	14.30
5.6	56.28	47.41	42.91	33.35	14.42
5.8	58.22	48.50	43.44	33.68	14.74
6.0	60.14	49.53	43.38	33.66	15.14
6.2	62.28	50.89	43.62	33.42	15.76
6.4	64.19	52.17	43.57	33.26	16.39
6.6	66.12	53.54	43.76	33.28	17.21
6.8	67.80	54.93	43.93	32.98	17.84
7.0	69.49	56.18	44.07	32.88	18.61
7.5	70.81	58.56	45.18	32.98	20.11
8.0	69.17	59.60	46.32	33.62	21.19
8.5	67.18	59.97	47.44	34.13	21.55
9.0	66.06	59.71	48.52	34.39	21.73
9.5	65.83	59.92	49.73	34.58	21.54
10.0	65.70	60.09	50.47	34.67	20.89
10.5	65.82	60.10	50.67	34.86	20.26
11.0	65.57	59.95	50.87	35.05	19.56
11.5	65.19	59.60	50.52	35.46	18.98
12.0	64.65	58.78	49.97	35.65	18.54
12.5	63.73	57.97	49.05	35.51	18.26
13.0	63.05	57.00	48.20	35.28	18.16
13.5	62.35	56.10	47.67	34.76	18.07
14.0	61.53	55.12	46.54	34.52	17.96
14.5	60.84	54.41	45.80	33.84	17.88
15.0	59.96	53.57	45.09	33.22	17.89
16.0	58.36	52.18	43.94	32.27	18.06
17.0	57.01	50.77	43.00	31.74	18.17
18.0	55.80	49.66	42.30	30.82	18.39
19.0	54.59	48.62	41.13	30.54	18.67

TABLE III (continued).

Energy	CCl ₄	CCl ₃ F	CCl ₂ F ₂	CClF ₃	CF ₄
20.0	53.38	47.86	40.31	29.97	19.03
21.0	52.33	47.00	39.88	29.90	19.28
22.0	51.17	45.90	39.15	29.57	19.53
23.0	50.31	45.54	38.88	29.65	19.73
24.0	49.60	44.74	38.33	29.31	20.00
25.0	48.99	44.23	38.03	29.06	20.13
27.5	47.65	42.81	36.89	28.38	20.04
30.0	46.04	41.59	36.26	27.65	19.94
32.5	44.77	40.51	34.99	27.14	19.79
35.0	43.51	39.29	34.23	26.45	19.77
37.5	42.73	38.46	33.42	26.15	19.72
40.0	41.33	37.66	32.94	25.70	19.74
45.0	40.11	36.28	31.78	25.20	19.58
50.0	38.99	35.31	31.14	24.34	19.44

corresponds to the resonance energy in total scattering, is associated with a transition in the center of the Franck-Condon region. However, since the geometry of the molecule at the time of electron capture influences the probability of the anion decaying via dissociation, the energy of the peak in the dissociative attachment cross section can be associated with transitions at the edge of the Franck-Condon region. As a

result the center of the resonance in dissociative attachment can be shifted in energy from the center of the resonance in total scattering.

CCl₄

Two low energy peaks were observed in the TCS of CCl₄, at 1.2 and 7.5 eV. The latter, which occurs above the energy of the lowest observed electronic transition around 7 eV,^{12,13} appears to be located on the low energy side of a broad maximum.

The low energy peak was observed at 0.94 eV by Burrow *et al.*¹ in the electron transmission spectrum (ETS). They attributed this peak to the capture of the incident electron in a triply degenerate carbon chlorine antibonding orbital (C-Clσ*) of *t*₂ symmetry. Their assignment was based primarily on a careful comparison of the ETS of a series of halomethanes with the energies of unoccupied molecular orbitals obtained from SCF calculations on the neutral molecules. Burrow *et al.* further state that the VAE to the lower energy ²A₁ ground state anion with the incident electron captured in the *a*₁ C-Clσ* orbital is negative and therefore not observable in electron scattering.

There is experimental and theoretical support for their conclusions. The adiabatic electron affinity and vertical electron affinity have both been calculated for CCl₄ as positive.^{9,14} Dissociative attachment measurements exhibit a large maximum in Cl⁻ production for incident electron energies around zero energy,¹⁵⁻¹⁷ indicating that a repulsive anion potential energy surface intersects the neutral ground state surface in the Franck-Condon region. A second group of peaks in ion production were reported with energies from 0.75 to 1.65 eV.¹⁷ These overlap the peak at 1.22 eV in the total cross section, suggesting that this peak is associated with a higher energy anion state.

Tossell and Davenport employed a MS-Xα method to determine the total electron scattering cross section of CCl₄.^{9(a), 9(b)} Their calculations confirm the valence *t*₂ resonance assignment made by Burrow *et al.* but found the peak in the *t*₂ contribution to the TCS at 1.4 eV. Though the energy of the calculated resonance is in good agreement with the present measurement, the overall shape and magnitude of their calculated cross section do not agree with the measured TCS.

TABLE IV. Peak positions in the halomethanes (eV).

	Peak in TCS	Resonance in dissociative attachment
CCl ₄	1.22 ± 0.06	0.0(Cl ⁻) ^a
		0.75 ± 0.05(Cl ⁻) ^a
		1.1 ± 0.1(Cl ₂ ⁻) ^a
		1.3 ± 0.1(CCl ₃ ⁻) ^a
		1.65 ± 0.1(CCl ₂ ⁻) ^a
CCl ₃ F	7.51 ± 0.04	6.0 ± 0.1(CCl ₂ ⁻) ^a
		> 5.0(Cl ₂ ⁻) ^a
		> 4(Cl ⁻) ^a
		0.0 ± 0.05(Cl ⁻) ^b
		1.6 ± 0.1(Cl ₂ ⁻) ^b
CCl ₂ F ₂	4.0 ± 0.12	3.0 ± 0.2(F ⁻) ^b
		3.3 ± 0.2(CCl ₃ ⁻) ^b
		~ 3(Cl ₂ ⁻) ^b
		1.02 ± 0.02
		0.55 ± 0.1(Cl ⁻) ^b
CClF ₃	2.64 ± 0.06	0.65 ± 0.1(Cl ₂ ⁻) ^b
		2.85 ± 0.2(FCl ⁻) ^b
		3.1 ± 0.2(F ⁻) ^b
		3.55 ± 0.2(CFCl ₂ ⁻) ^b
		~ 3(Cl ⁻) ^b
CF ₄	6.0 ± 0.7 (shoulder)	~ 3(Cl ₂ ⁻) ^b
		1.3 ± 0.2(Cl ⁻) ^b
		3.9 ± 0.2(FCl ⁻) ^b
		4.1 ± 0.2(F ⁻) ^b
		4.2 ± 0.2(CF ₂ Cl ⁻) ^b
CF ₄	2.0 ± 0.4	4.8 ± 0.2(Cl ⁻) ^b
		5.94 ± 0.07
		6.7 ± 0.05(Cl ⁻) ^c
		7.1 ± 0.05(CF ₃ ⁻) ^c
		8.87 ± 0.19

^a Reference 17.

^b Reference 21.

^c Reference 25.

Significantly different results were obtained by Bloor *et al.* who also employed a MS- $X\alpha$ method.¹¹ They predicted that the VAE's to both the two lowest anion states with the incident electron in the a_1 and t_2 molecular orbitals are negative, thus making both anion states stable with respect to autodetachment. Nonvalence shape resonances of t_2 and e symmetries were found at 1.74 and 6.3 eV, respectively. Less dominant a_1 and e resonances were also found at 9.4 and 13.3 eV. The magnitude and position of the two lower energy resonances are in good agreement with the present experimental results.

The peak observed in the present experiment at 7.5 eV was beyond the energy limits of the results reported by Tosell and Davenport and Burrow *et al.* but qualitatively correspond to a group of peaks in ion production above 4 eV observed in dissociative attachment,¹⁷ supporting the assignment of this peak as resulting from an electron capture process.

The experiment reported here yields no direct evidence about the orbitals involved in the observed resonances and so cannot resolve the conflicting assignments mentioned above. It should be noted that the unoccupied valence orbital description of the lower energy resonance proposed by Burrow *et al.* does not illuminate the origin of the peak at 7.5 eV, since only two unoccupied valence orbitals are present in CCl_4 ; however, the assignment proposed by Bloor *et al.* does account for all the observed structure in the TCS.

CCl_3F

Two distinct low energy peaks were observed in the TCS of CCl_3F : a large peak at 1.76 eV and a smaller peak at 4.0 eV. As in the case of CCl_4 , there is significant evidence in support of an assignment of these peaks as elastic shape resonances.

MNDO calculations¹⁸ predicted the ordering and dominant bonding nature of the unoccupied valence molecular orbitals: in order of increasing energy, $a_1(\text{C}-\text{Cl}\sigma^*)$, $e(\text{C}-\text{Cl}\sigma^*)$, $a_1(\text{C}-\text{F}\sigma^*)$. Calculations by Chutjian¹⁹ and Peyerimhoff and Buenker²⁰ predict that the 2A_1 ground state potential energy surface of CCl_3F^- crosses the ground state potential energy surface of the neutral near its minimum which results in a VAE very close to zero energy. This is corroborated by dissociative attachment measurements which exhibit a peak in the production of Cl^- at zero energy.^{10,15,21} These indicate that the vertical transition energy to the lowest anion state is close to zero and therefore below the limits of the present experiment.

Illenberger *et al.*²¹ reported a dissociative attachment resonance for the production Cl_2^- at 1.6 eV, and resonances in F^- and CCl_3^- production at 3.0 and 3.3 eV, respectively. A treatment of the low energy peaks in the TCS consistent with dissociative attachment results and the valence orbital approach used by Burrow *et al.* suggests that the lower energy peak is associated with the occupation of the $e(\text{C}-\text{Cl}\sigma^*)$, and the peak at 4.0 eV is associated with the $a_1(\text{C}-\text{F}\sigma^*)$ orbital.

CCl_2F_2

Two peaks were observed in the total cross section of CCl_2F_2 at 1.02 and 2.64 eV, a shoulder at 4.0 eV, and possibly another weak shoulder around 6 eV. There is good qualitative agreement between the present measurement and the three resonances observed by Burrow *et al.*¹ in the electron transmission spectrum at 0.98, 2.35, and 3.88 eV. They stated that these were associated with the occupation of the three lowest valence molecular orbitals in CCl_2F_2 : the $a_1(\text{C}-\text{Cl}\sigma^*)$, $b_2(\text{C}-\text{Cl}\sigma^*)$, and $a_1(\text{C}-\text{F}\sigma^*)$ orbitals. They do not attribute a resonance to the highest $b_1(\text{C}-\text{F}\sigma^*)$ orbital.

In contrast with CCl_4 and CCl_3F , Burrow *et al.* indicate that the VAE to the lowest anion state is significantly greater than zero. $X\alpha$ calculations reveal a definite trend of decreasing electron affinities with increasing fluorine substitution of the chlorofluoromethanes.¹⁴ A similar trend of increasing energy of the lowest a_1 virtual orbital for this sequence was found from MNDO calculations.¹⁸ Since the a_1 shape resonance occurs close to zero energy in CCl_3F , it is reasonable to expect the transition energy to this anion state to be around 1 eV in CCl_2F_2 .

Burrow *et al.*'s assignments are consistent with dissociative attachment measurements.²¹ Resonances in Cl^- and Cl_2^- production occur at 0.55 and 0.65 eV. A dissociative attachment resonance in FCl^- production occurs at 2.85 eV, which is at slightly higher energy than the electron scattering resonance at 2.64 eV. Peaks in the production of F^- and CFCl_2^- were observed at 3.1 and 3.55 eV, respectively.

Since the shoulder at 6.0 eV is not well defined, occurs close to the electronic threshold at 7.0 eV,²² and dissociative attachment studies do not indicate a resonance near this energy, there is insufficient evidence that this is a shape resonance.

CClF_3

Two peaks in the total cross section of CClF_3 appear below the electronic threshold at 7.1 eV.²² The first peak at 2.0 eV is large and well defined, and a second much broader peak occurs at 5.94 eV. As with the previously mentioned molecules, dissociative attachment measurements indicate that these peaks are associated with electron capture processes.²¹ A description of the orbitals involved can be inferred from published assignments of the other substituted methanes mentioned above, but lacking the results of scattering calculations, any assignment must be viewed as tentative.

A negative electron affinity has been predicted by $X\alpha$ calculations on CClF_3 ,¹⁴ indicating that the lowest energy anion state is accessible by electron scattering. This result is consistent with the trend of decreasing electron affinities with increasing fluorine substitution in this series of molecules, and the theoretically^{14,23} and experimentally²⁴ established negative electron affinity of CF_4 (calculated values are around -0.7 eV). The peak in the TCS at 2.01 eV could be associated with the occupation of the lowest unoccupied valence orbital, the $a_1(\text{C}-\text{Cl}\sigma^*)$. Either of the two higher energy $\text{C}-\text{F}\sigma^*$ unoccupied orbitals of e and a_1 symmetry could then be associated with the higher energy resonance.

CF₄

The broad shoulder around 3.6 eV and peak at 8.9 eV in the TCS of CF₄ result in a much different appearance than the other halomethanes presented above. However, there is evidence suggesting that both features are associated with electron capture processes.

As mentioned above, a number of studies have found that CF₄ has a negative electron affinity. Consequently, the *a*₁ and *t*₂ unoccupied valence orbitals could possibly participate in electron scattering resonances. Tossell and Davenport⁹ calculated the maximum in the *t*₂ contribution to the total electron scattering to occur at 3.2 eV for a carbon fluorine separation of 1.317 Å. However, small changes in the C–F distance resulted in dramatic shifts in the energy of this peak. They state that the vibrational motion of the molecule acts to spread this peak out in energy. This qualitatively agrees with the observed shoulder in this region of the TCS. They further indicate that this is a valence type resonance.

The higher energy structure in the TCS overlaps dissociative attachment resonances for production of F[−] and CF₃[−] at 6.7 and 7.1 eV, respectively,²⁵ suggesting that this peak in the TCS is also associated with an electron capture process.

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