

## Low-energy electron scattering from halomethanes: IV. $e\text{-CF}_2\text{Cl}_2^*$

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**Abstract.** Differential cross sections are presented for vibrationally elastic and inelastic  $e\text{-CF}_2\text{Cl}_2$  scattering in the energy range 0.5–10 eV. All four low-lying  $\sigma^*$  valence type resonances are observed in the measurements. The hitherto unidentified  $B_1$  ( $\text{C-F } \sigma^*$ ) resonance has been located at 5.0–5.5 eV. A quite selective excitation of  $\text{CF}_2$  and  $\text{CCl}_2$  stretching modes is observed corresponding to the respective valence character of the resonance and in agreement with the symmetry selection rules. Resonance-enhanced vibrational excitation is found to be most pronounced in the totally symmetric resonances of symmetry type  $A_1$ . The results are discussed in comparison with dissociative attachment experiments. Below 1 eV, similar to the other molecules in this series ( $\text{CF}_4$ ,  $\text{CF}_3\text{Cl}$ ), direct scattering leads to strong excitation of stretching modes according to their IR activity.

### 1. Introduction

Among the molecules of the present series,  $\text{CF}_2\text{Cl}_2$  has the lowest symmetry ( $C_{2v}$ ) with only twofold axes and, consequently, only non-degenerate symmetry types. Thus, we have the full number of nine different vibrational modes and expect four different valence type resonances. The resonances have been studied in electron transmission experiments by Burrow *et al* (1982) and by Jones (1986), and three resonant structures are observed at approximately 1.0 eV, 2.5 eV and 4.0 eV. In *ab initio* SCF calculations on the neutral molecule, Burrow *et al* find the energetic order of the unoccupied orbitals to be  $a_1$  ( $\text{C-Cl } \sigma^*$ ),  $b_2$  ( $\text{C-Cl } \sigma^*$ ),  $a_1$  ( $\text{C-F } \sigma^*$ ),  $b_1$  ( $\text{C-F } \sigma^*$ ) and attribute the observed resonances to the lowest three of these molecular orbitals. The energetic difference of the two ( $\text{C-F } \sigma^*$ ) orbitals is estimated to be around 1 eV, and this suggests a placement of the highest valence resonance at around 5 eV. Jones observes a weak shoulder at 6.0 eV, but hesitates in assigning it to the  $B_1$  ( $\text{C-F } \sigma^*$ ) resonance.

The investigation of the specific decay channels provides a more detailed picture of the resonances than can be obtained from the total cross section. In particular from the study of resonance-enhanced vibrational excitation, one can expect further experimental evidence on the symmetries and energetic positions of the resonances. Due to the non-degeneracy of the symmetry species, the selection rules are more restrictive than in the previously studied cases ( $\text{CF}_4$ : Mann and Linder 1992b, paper II;  $\text{CF}_3\text{Cl}$ :

\* This work represents part of the doctoral thesis of A Mann.

Mann and Linder 1992c, paper III), and only totally symmetric modes are expected to be excited.

Dissociative attachment with mass and energy analysis of the fragment ions has been studied by Illenberger and co-workers (Illenberger *et al* 1979, Illenberger 1982, for a review see Oster *et al* 1989). Measurements on electron transmission, dissociative attachment, and electronic threshold excitation have been reported by Verhaart *et al* (1978) for impact energies up to 15 eV. Absolute cross sections for electron attachment are given by McCorkle *et al* (1980); the 'electron scavenging properties' have been studied with ECR techniques by Schumacher *et al* (1978). In this context, one should also mention the experiments of Dispert and Lacmann (1978) on negative-ion formation in collisions between potassium atoms and  $\text{CF}_{4-n}\text{Cl}_n$ .

The possible use of gas mixtures containing  $\text{CF}_2\text{Cl}_2$  as gaseous dielectrics has motivated several studies on the properties of an electron swarm in neat  $\text{CF}_2\text{Cl}_2$  gas as well as in  $\text{N}_2$ - $\text{CF}_2\text{Cl}_2$  mixtures (Novak and Fréchette 1985, Okabe and Kouno 1985, Fréchette 1987). These calculations are based on the Boltzmann equation and need reliable cross sections as input data. While absolute integral cross sections are known for attachment and ionization, only crude estimates are possible for elastic scattering and vibrational excitation (Hayashi 1987). These uncertainties are a major problem for the intended tailoring of gas mixtures, and the results of the present work are expected to allow more precise calculations of the swarm properties.

Among the halocarbons,  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$  have attracted considerable attention as being important for the depletion of the stratospheric ozone layer (Rowland and Molina 1975) and the increased absorption of infrared radiation ('greenhouse effect', e.g. Ramanathan *et al* 1987). As they are chemically inert and have a low solubility in water, the probably most important sink is the photolysis by UV radiation ( $\lambda < 200$  nm) in the stratosphere. The cross sections for interaction with low-energy electrons are several orders of magnitude larger, but the density of electrons is small in the stratosphere and electron interactions are generally not regarded as primary processes in the atmosphere (Rowland and Molina 1975). Nevertheless, with respect to the importance of these molecules, any information about the molecular properties and possible interactions is desirable.

The experimental conditions have been described before (Mann and Linder 1991a, paper I). In a crossed-beam apparatus, differential cross sections for elastic and vibrationally inelastic scattering are measured with an energy resolution of  $\Delta E \sim 25$  meV. Additional complications arise in the case of  $\text{CF}_2\text{Cl}_2$  which we attribute to the production of  $\text{CF}_2\text{Cl}$  radicals in near-thermal e- $\text{CF}_2\text{Cl}_2$  collisions. We observe a reduced lifetime of the filament and a lower stability of the spectrometer, resulting in somewhat higher possible errors for the cross sections of the present system.

## 2. Elastic scattering

In figure 1, we present energy spectra for vibrationally elastic e- $\text{CF}_2\text{Cl}_2$  scattering at  $\vartheta = 60^\circ$  and  $\vartheta = 90^\circ$ . Similar to the results for  $\text{CF}_3\text{Cl}$ , a pronounced minimum appears below 1 eV which is interpreted as a Ramsauer-Townsend minimum in the elastic channel superimposed by considerable rotational excitation due to the permanent dipole moment of  $\text{CF}_2\text{Cl}_2$  (0.5 D). At  $\vartheta = 90^\circ$ , the cross section is remarkably constant between 1 and 10 eV. The present results are compared with some earlier measurements of Rohr (1979). The two spectra at  $\vartheta = 60^\circ$  agree in their general shape; the differences

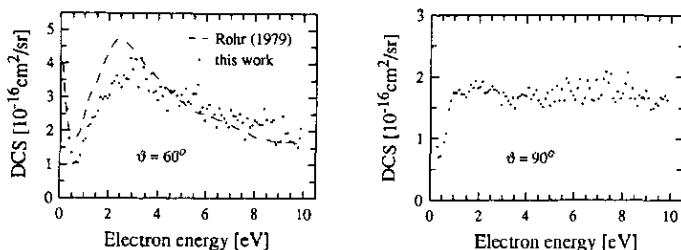


Figure 1. Energy spectra for elastic  $e\text{-CF}_2\text{Cl}_2$  scattering at  $\vartheta = 60^\circ$  and  $\vartheta = 90^\circ$ .

are attributed to difficulties in the control of the transmission. Regarding the fact that both sets of data are independently given in absolute units, the agreement is satisfactory within the estimated error bars of 30–50%.

Angular spectra for five different collision energies are depicted in figure 2. Scattering in forward direction becomes more and more important with increasing collision energy. At  $\vartheta = 50^\circ$ , the medium-energy spectra show a local maximum (2.5 eV, 4.0 eV) or a shoulder (6.0 eV). All curves practically coincide at  $\vartheta = 90^\circ$ . A compilation of the measured cross section values is given in table 1.

The integral elastic cross section depicted in figure 3 is obtained by extrapolating the measured DCS, weighted by  $\sin \vartheta$ , towards  $0^\circ$  and  $180^\circ$ . This procedure has been described in paper I. The elastic cross section shows none of the structures which appear in the total cross section (Jones 1986). These structures must therefore be attributed to inelastic processes and appear exposed in the total inelastic cross section which is obtained as the difference of the two before-mentioned cross sections. The resonance at  $E = 1$  eV gives a remarkably strong cross section for the inelastic channels ( $\sim 2 \times 10^{-15} \text{ cm}^2$ ) which equals the value for elastic scattering at this energy. The Born dipole approximation (BDA) for total vibrational excitation, indicated by the solid line in figure 3, accounts only for a minor part of this value. Even at its maximum, the BDA cross section reaches only about  $1 \times 10^{-15} \text{ cm}^2$  which is, however, comparable to the maximum values in the case of  $e\text{-CF}_4$  and  $e\text{-CF}_3\text{Cl}$ . Further structures in the inelastic cross section appear at 2.5 eV, 4 eV, 6 eV and 9 eV, the latter energy lying above the threshold for electronic excitation (7.0 eV, Doucet *et al* 1973). These structures will be discussed in more detail below in connection with the results for the individual inelastic channels.

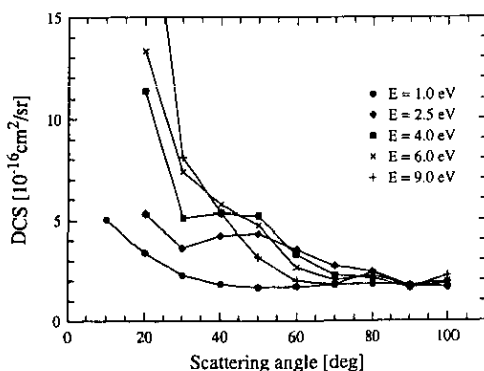
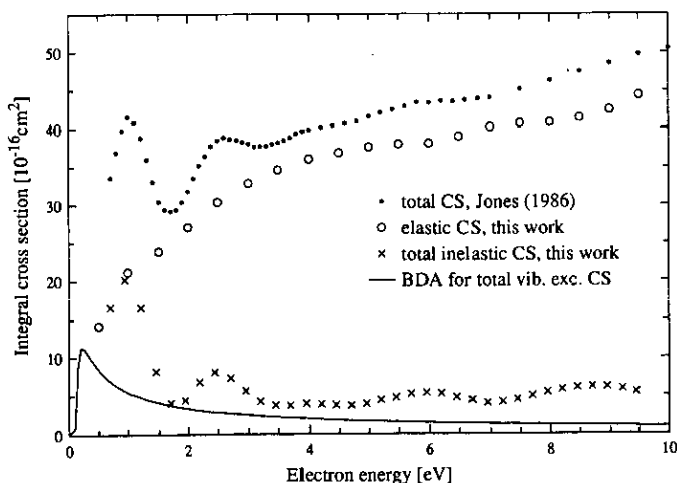


Figure 2. Angular spectra for elastic  $e\text{-CF}_2\text{Cl}_2$  scattering at different collision energies.

**Table 1.** Differential cross section  $d\sigma/d\Omega$  ( $10^{-16}$  cm<sup>2</sup> sr<sup>-1</sup>) for elastic e-CF<sub>2</sub>Cl<sub>2</sub> scattering. The experimental errors are estimated to about 30% and up to 50% for small energies and angles.

Energy (eV)	Scattering angle (deg)								
	20	30	40	50	60	70	80	90	100
0.5	3.98	3.07	2.20	1.67	1.21	0.80	0.79	0.80	0.73
1.0	3.38	2.27	1.80	1.67	1.69	1.79	1.83	1.76	1.65
1.5	2.62	2.34	2.39	2.74	2.58	2.40	2.30	1.71	1.61
2.0	3.48	2.92	3.29	3.67	3.18	2.69	2.48	1.73	1.60
2.5	5.30	3.61	4.21	4.33	3.55	2.73	2.44	1.73	1.67
3.0	7.39	4.25	4.83	4.71	3.68	2.59	2.32	1.69	1.74
3.5	9.57	4.73	5.14	4.97	3.55	2.42	2.19	1.66	1.80
4.0	11.38	5.11	5.34	5.20	3.30	2.29	2.12	1.66	1.87
4.5	12.23	5.52	5.57	5.35	3.11	2.22	2.11	1.66	1.89
5.0	13.13	5.99	5.78	5.28	2.99	2.18	2.12	1.69	1.89
5.5	13.52	6.57	5.83	5.03	2.86	2.12	2.16	1.73	1.91
6.0	13.32	7.37	5.74	4.76	2.66	2.03	2.24	1.76	1.96
6.5	13.93	8.25	5.79	4.53	2.49	1.93	2.35	1.78	2.04
7.0	15.46	8.57	5.86	4.35	2.38	1.86	2.47	1.80	2.10
7.5	16.83	8.43	5.74	4.14	2.30	1.81	2.52	1.81	2.13
8.0	18.26	8.14	5.55	3.81	2.23	1.81	2.48	1.77	2.13
8.5	20.23	8.02	5.44	3.48	2.14	1.82	2.46	1.71	2.15
9.0	22.31	8.10	5.32	3.17	1.98	1.81	2.41	1.65	2.24
9.5	24.56	8.07	5.23	3.01	1.83	1.75	2.35	1.59	2.49



**Figure 3.** Comparison of various integral cross sections for e-CF<sub>2</sub>Cl<sub>2</sub> scattering. The total inelastic cross section is obtained as the difference between the total cross section (Jones 1986) and our integral elastic cross section. Also shown is the Born dipole approximation (BDA) for the total vibrational excitation cross section (sum of  $\nu_1$ ,  $\nu_2$ ,  $\nu_4$ ,  $\nu_6$ ,  $\nu_8$ ).

In the context of figure 3, we mention that our absolute values are obtained by normalizing the sum of the elastic and inelastic cross section at a certain collision energy to the total cross section of Jones (1986). We have chosen  $E = 1.8$  eV as the normalization point, because at this energy the contributions from resonant processes are small. The procedure has been described in detail in papers I and II.

### 3. Vibrational excitation

Before discussing the energy loss spectra and the excitation functions for vibrational excitation, we wish to recall the basic principles of the selection rules for resonant vibrational excitation as originally formulated by Wong and Schulz (1975). The matrix element for a transition from the ground state  $\chi_0$  (symmetry type  $\Gamma_{\chi_0}$ ) to the final state  $\chi_f$  (symmetry type  $\Gamma_{\chi_f}$ ) is written in the form  $\langle \chi_f | G | \chi_0 \rangle$ . The symmetry type  $\Gamma_G$  of the propagator  $G$  is obtained by forming the symmetric product of the representation of the resonant orbital. The transition matrix element is different from zero only if the direct product  $\Gamma_{\chi_f} \times \Gamma_G \times \Gamma_{\chi_0}$  contains the totally symmetric species ( $A_1$  in the present point group  $C_{2v}$ ). As the ground state  $\chi_0$  belongs to  $A_1$ , only vibrational modes with  $\Gamma_{\chi_f} \subseteq \Gamma_G$  will be excited. In the present case, the symmetric product of all symmetry species gives  $A_1$ . Thus  $G$  has always  $A_1$  symmetry independent of the symmetry type of the resonance and, according to the selection rules, only excitation of vibrational modes with  $A_1$  symmetry is allowed. Wong and Schulz also introduced a second (weaker) mechanism, the so-called distorted-resonance process, in which a component of  $A_1$  symmetry is admixed to the original symmetry of the undistorted resonance. In this way, also modes with the same symmetry type as the resonant orbital can be excited, although with weaker intensity.

In figure 4, several energy loss spectra are shown with impact energies corresponding to the structures observed in the total and the total inelastic cross section. In the following discussion we will proceed on the assumption that these structures approximately correspond to the energetic positions of the expected four valence type resonances mentioned in the introduction. A survey of the normal modes of CF<sub>2</sub>Cl<sub>2</sub> is given in table 2. The modes  $\nu_1$  and  $\nu_6$  (symmetric and asymmetric CF<sub>2</sub> stretch) are close in

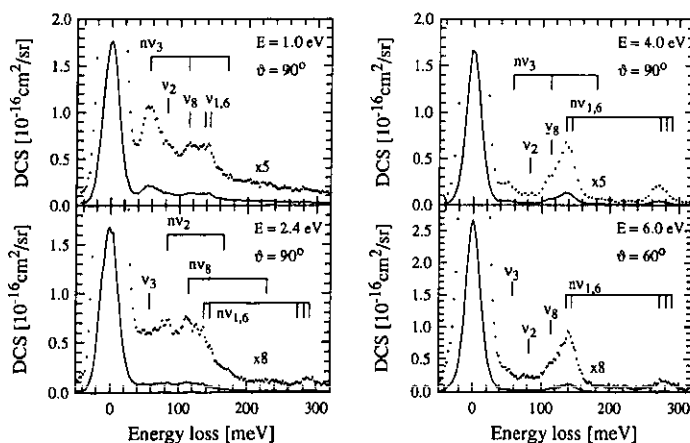


Figure 4. Energy loss spectra for  $e$ -CF<sub>2</sub>Cl<sub>2</sub> scattering at  $\theta = 90^\circ$  ( $60^\circ$ ) and different collision energies.

**Table 2.** Vibrational modes of  $\text{CF}_2\text{Cl}_2$  (point group  $C_{2v}$ ,  $\Gamma_1 = 4A_1 + A_2 + 2B_1 + 2B_2$ ) with respective energies and symmetry types (from Herzberg 1945, Sverdlov *et al* 1974). All modes are Raman allowed. The value of the sum of the squared dipole matrix elements  $M_n^d$  ( $e^2 a_0^2$ ) (see paper II) is given with the IR-active modes (Bishop and Cheung 1982).

Mode	$E$ (meV)	Nuclear motion	Symmetry	Activity
$\nu_1$	136.1	$\text{CF}_2$ symmetric stretch	$A_1$	IR (0.0168)
$\nu_2$	82.7	$\text{CF}_2$ bending	$A_1$	IR (0.0011)
$\nu_3$	56.6	$\text{CCl}_2$ symmetric stretch	$A_1$	
$\nu_4$	32.5	$\text{CCl}_2$ bending	$A_1$	IR (0.0006)
$\nu_5$	39.9	torsion	$A_2$	
$\nu_6$	144.7	$\text{CF}_2$ asymmetric stretch	$B_1$	IR (0.0107)
$\nu_7$	55.3	$\text{CF}_2$ -plane rocking	$B_1$	
$\nu_8$	114.4	$\text{CCl}_2$ asymmetric stretch	$B_2$	IR (0.0207)
$\nu_9$	53.9	$\text{CCl}_2$ -plane rocking	$B_2$	

energy and can be separated only in the overtone region. On the other hand, the  $\text{CCl}_2$  stretching modes  $\nu_3$  and  $\nu_8$  differ considerably in energy, but here it is impossible to distinguish between  $2\nu_3$  and  $\nu_8$ .

Except for the similarity of the spectra at 4.0 eV and 6.0 eV, the dominant features are significantly different in each of the spectra shown in figure 4. In the  $A_1$  ( $\text{C-Cl } \sigma^*$ ) resonance at 1.0 eV, the most prominent energy loss is assigned to the excitation of  $\nu_3$ . The modes  $\nu_7$  and  $\nu_9$  are very close in energy, but can be disregarded with respect to their symmetry and nuclear motion. Besides  $\nu_3$ , structures corresponding to  $2\nu_3/\nu_8$  and  $\nu_{1,6}$  appear and, in addition, a  $\nu_2$  signal is visible in the wing of the  $\nu_3$  peak. The predominance of the  $\nu_3$  excitation is clearly in accordance with the ( $\text{C-Cl } \sigma^*$ ) character of the resonance. The simultaneous appearance of  $\text{CF}_2$  bending and stretching excitations ( $\nu_2$  and  $\nu_{1,6}$ ) is very similar to the corresponding observation for the  $A_1$  ( $\text{C-Cl } \sigma^*$ ) resonance in  $e\text{-CF}_3\text{Cl}$  scattering (see paper III) and may be explained in a similar way, namely that the charge distribution of the ( $\text{C-Cl } \sigma^*$ ) orbital reaches beyond the C atom into the  $\text{CF}_2$  part of the molecule and thus induces  $\text{CF}_2$  bending and stretching motions. This excitation behaviour found in both  $e\text{-CF}_3\text{Cl}$  and  $e\text{-CF}_2\text{Cl}_2$  scattering seems to be characteristic of the  $A_1$  ( $\text{C-Cl } \sigma^*$ ) type resonance.

In the  $A_1$  ( $\text{C-F } \sigma^*$ ) resonance at 4.0 eV, the excitation of  $n\nu_{1,6}$  is clearly the dominating process in accordance with the ( $\text{C-F } \sigma^*$ ) character of the resonance. The excitation of  $\nu_3$  and  $2\nu_3/\nu_8$  is only weakly indicated. As shown in figure 5, a remarkably strong overtone excitation is observed in this resonance. At the higher energy losses, it is possible to distinguish between  $\nu_1$  and  $\nu_6$  with the result that  $\nu_1$  (and its overtones) appears to be the dominant excitation. This observation is in agreement with the selection rules discussed above. The spectrum shown in figure 5 represents another example of the pronounced mode selectivity which can be found in electron-impact vibrational excitation of polyatomic molecules.

Comparing the influence of the  $A_1$  ( $\text{C-Cl } \sigma^*$ ) and  $A_1$  ( $\text{C-F } \sigma^*$ ) resonances on vibrational excitation, there are some common properties, but also certain differences. These resonances of symmetry type  $A_1$  are the dominant features in the excitation functions as shown below (see figure 6). In either case, the dominant excitation corresponds to the respective valence character of the resonance, i.e.  $\nu_3$  in the  $A_1$  ( $\text{C-Cl } \sigma^*$ ) resonance and  $\nu_1$  in the  $A_1$  ( $\text{C-F } \sigma^*$ ) resonance. However, the strong coupling with the other side of the molecule, leading to the excitation of  $\text{CF}_2$  bending

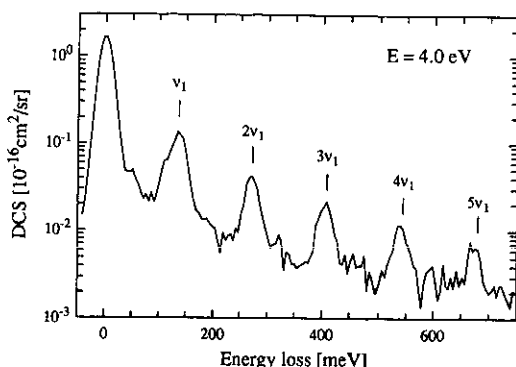


Figure 5. Energy loss spectrum for  $e$ -CF<sub>2</sub>Cl<sub>2</sub> scattering at  $E = 4.0$  eV and  $\vartheta = 90^\circ$ . The indicated energy loss values of  $n\nu_1$  do not include anharmonicities.

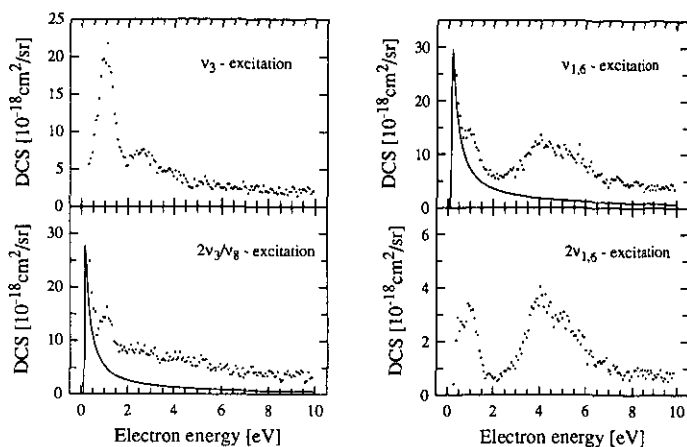
and stretching motions, is only observed in pronounced form for the  $A_1$  (C-Cl  $\sigma^*$ ) resonance. On the other hand, the pronounced overtone excitation is only found for the  $A_1$  (C-F  $\sigma^*$ ) resonance and not observed in a similar way for the  $A_1$  (C-Cl  $\sigma^*$ ) resonance.

The energy loss spectrum at  $E = 2.4$  eV, which has to be seen as representative of the  $B_2$  (C-Cl  $\sigma^*$ ) resonance, shows the excitation of several modes without any of them being particularly dominating. With the limited resolution of the present experiment, a rather flat spectrum is obtained with energy losses between 30 and 150 meV. As well CCl<sub>2</sub> stretching modes ( $\nu_3$  and  $2\nu_3/\nu_8$ ) as CF<sub>2</sub> bending and stretching modes ( $\nu_2$  and  $\nu_{1,6}$ ) appear to be excited. The former are in accordance with the valence character of the resonance, but only  $\nu_3$  and  $2\nu_3$  agree with the selection rules. The excitation of the latter may be explained by a similar picture as for the  $A_1$  (C-Cl  $\sigma^*$ ) resonance.

The energy loss spectrum at  $E = 6.0$  eV, which has been taken according to the broad structure observed at this energy in the total inelastic cross section, is very similar to the one at  $E = 4.0$  eV and allows no special conclusions. Measurements at other energies reveal that the character of the energy loss spectra does not change significantly for collision energies between 4 and 7 eV; only the inelasticity is decreasing continuously. The question about the assignment of the  $B_1$  (C-F  $\sigma^*$ ) resonance must therefore be postponed until the discussion of the excitation functions.

One further feature observed in the energy loss spectrum at  $E = 1.0$  eV may be worth noting. After a step at  $\Delta E \sim 150$  meV, the intensity is reduced, but the excitation cross section is still in the order of  $5 \times 10^{-18}$  cm<sup>2</sup> sr<sup>-1</sup>. The spectrum shows no structure in this region, and it is not clear to which processes these energy losses can be attributed. This unspecific excitation at higher energy losses, together with the missing overtone excitation, seems to be characteristic of the  $A_1$  (C-Cl  $\sigma^*$ ) resonance and may be connected with the low-energy crossing of the potential surfaces of the molecular ground state and the lowest negative-ion state, but relatively little is known about these potential surfaces (see e.g. Disper and Lacmann 1978).

In figure 6, we present some measured excitation functions at  $\vartheta = 90^\circ$  for several energy loss processes. The positions of the three lowest resonances at 1.0 eV, 2.5 eV, and 4.0 eV are readily found again in these excitation functions. In particular, the 4.0 eV resonance, which was only weakly indicated in the total inelastic cross section, appears quite pronounced here. There remains the question of the fourth resonance



**Figure 6.** Excitation functions for the most important energy loss processes in  $e\text{-CF}_2\text{Cl}_2$  scattering at  $\theta = 90^\circ$ . The full lines represent the Born dipole cross sections for the excitation of  $\nu_{1,6}$  and  $\nu_8$ .

which is of  $B_1$  ( $\text{C-F } \sigma^*$ ) type. In the excitation functions of  $\nu_{1,6}$  and  $2\nu_{1,6}$ , one may recognize a shoulder on the high-energy side of the 4.0 eV resonance. Since there is no evidence of a further structure in the excitation functions and since this type of measurement is expected to be more sensitive concerning the identification of resonances than total and integral cross sections, we identify the observed shoulder with the missing  $B_1$  ( $\text{C-F } \sigma^*$ ) resonance and assign it to an energy value of 5.0–5.5 eV. The predominant excitation of the  $\nu_1$  mode (including overtones) observed in this energy range is in accordance both with the ( $\text{C-F } \sigma^*$ ) character of the resonance and with the symmetry selection rules. One also understands the fact that the energy loss spectra do not change in character over the collision energy range of the two overlapping  $A_1$  ( $\text{C-F } \sigma^*$ ) and  $B_1$  ( $\text{C-F } \sigma^*$ ) resonances.

Some further details may be discussed concerning the excitation functions. The full lines shown in figure 6 indicate the excitation cross sections calculated by the Born dipole approximation (BDA) as described in paper II. Regarding the IR-active modes, the strong increase of the cross section below 1 eV is roughly described by the BDA. At higher impact energies, the Born dipole cross sections are substantially below the experimental values.

In measuring these excitation functions for polyatomic molecules, the usual difficulties arise with the unambiguous assignment of the measured intensity at a certain energy loss value to one particular excitation process because of possible contributions from nearby energy loss processes. We will discuss two examples. In the excitation function ascribed to the symmetric  $\text{CCl}_2$  stretching mode  $\nu_3$ , the two ( $\text{C-Cl } \sigma^*$ ) resonances at 1.0 eV and 2.5 eV are clearly pronounced. This fact, combined with the valence character of these resonances and the symmetry selection rules, allows us to assign the main portion of the measured excitation cross section below 3 eV to  $\nu_3$  excitation instead of  $\nu_7$  or  $\nu_9$  which nearly coincide with  $\nu_3$  in energy. For impact energies above 3 eV we have no arguments for a distinction between  $\nu_3$ ,  $\nu_7$  and  $\nu_9$ .

Another example to illustrate these problems is given by the  $2\nu_3/\nu_8$  excitation function. The strong increase below 0.5 eV is certainly due to direct excitation of the IR-active mode  $\nu_8$ . A small peak appears at the energy of the  $A_1$  ( $\text{C-Cl } \sigma^*$ ) resonance



and can safely be attributed to the excitation of the  $2\nu_3$  mode. A corresponding contribution of  $2\nu_3$  excitation can be expected from the B<sub>2</sub> (C-Cl  $\sigma^*$ ) resonance at 2.5 eV. Towards higher energies, the spectrum shows considerable excitation without any further structure; the cross section is larger than for  $\nu_3$  excitation. Most probably, one has strong  $\nu_8$  excitation by some direct scattering mechanism which is not adequately described by the BDA at these higher energies, but at least part of the signal may also be due to contributions from the wing of the  $\nu_{1,6}$  excitation. Some of these problems can be solved by an improved experimental resolution. In general, however, the selective mechanisms, which are operative under certain conditions, contribute more effectively to producing a clear-cut picture of the excitation processes in these complex systems.

#### 4. Comparison with dissociative attachment

Within the series CF<sub>4-n</sub>Cl<sub>n</sub>, the electron affinity (EA) is increasing with the number of Cl atoms. The CF<sub>2</sub>Cl<sub>2</sub> molecule is at the border between negative and positive EA values. The vertical EA is still negative as demonstrated by the electron transmission experiments (Burrow *et al* 1982, Jones 1986) and the results of the present work. For the adiabatic EA, a positive value of 0.4 eV has been calculated by Preston and Kaufman (1977) and has been confirmed experimentally by Dispert and Lacmann (1978). These latter authors have detected the stable CF<sub>2</sub>Cl<sub>2</sub><sup>-</sup> anion in K-CF<sub>2</sub>Cl<sub>2</sub> collisions.

Electron impact with CF<sub>2</sub>Cl<sub>2</sub> leads exclusively to fragment ions. The various dissociative attachment processes have been studied in detail by Illenberger and co-workers (Illenberger *et al* 1979, Illenberger 1982). The results are compiled in table 3. Some further weak structures are observed in several negative-ion production channels above 8 eV, but these are not related to the presently discussed processes and will not be considered here. The processes can be grouped according to their energy positions into one group of low-energy processes (0.55 and 0.65 eV) and a second group with processes between 2.85 and 3.1 eV. It seems not clear, if the two peaks at 3.55 and 3.9 eV have to be regarded as an extra group or if they belong to the second group around 3 eV.

**Table 3.** Negative-ion production in  $e$ -CF<sub>2</sub>Cl<sub>2</sub> scattering. The values for the heat of reaction  $\Delta H_0$  are taken from Illenberger (1982). The energetic positions of the maxima in the negative-ion yield curves and the corresponding relative intensities are from Illenberger *et al* (1979) and Illenberger (1982).

Ion	Neutral fragment(s)	$\Delta H_0$ (eV)	$E$ (eV)	Rel. int.
Cl <sup>-</sup>	CF <sub>2</sub> Cl	0.0	0.55	50
Cl <sub>2</sub> <sup>-</sup>	CF <sub>2</sub>	0.3	0.65	0.7
FCI <sup>-</sup>	CFCI	2.3	2.85	1
Cl <sup>-</sup>	CF <sub>2</sub> + Cl	2.1	3.0	1
F <sup>-</sup>	CFCI <sub>2</sub>	1.5	3.1	6.5
Cl <sub>2</sub> <sup>-</sup>	CF <sub>2</sub>	0.3	3.1	0.3
CFCI <sub>2</sub> <sup>-</sup>	F	2.7	3.55	2
Cl <sup>-</sup>	CFCI + F	3.8	3.9	1

The low-energy processes with their C-Cl bond breaking character are readily assigned to the  $A_1$  (C-Cl  $\sigma^*$ ) resonance at 1.0 eV. As observed before (see papers II and III), the energetic position of the resonance is lower in dissociative attachment than in vibrational excitation. In the series  $CF_{4-n}Cl_n$ , the cross section for negative-ion production is found to increase with growing Cl substitution. For  $CF_2Cl_2$ , an absolute cross section for low-energy  $Cl^-$  production of  $3.4 \times 10^{-16} \text{ cm}^2$  has been given by McCorkle *et al* (1980). From the results of the present work, we estimate the cross section for resonant vibrational excitation at 1.0 eV to be still larger by about a factor of 4. From the relative size of the cross sections as well as the energetic shift of the resonance position, we conclude that the branching ratio for the decay of the  $A_1$  (C-Cl  $\sigma^*$ ) resonance is still in favour of autodetachment.

Regarding nuclear motion, dissociative attachment and vibrational excitation are clearly correlated with each other. The (C-Cl  $\sigma^*$ ) character is evident in both DA decay channels ( $Cl^-$ ,  $Cl_2^-$ ). In vibrational excitation, the  $CCl_2$  symmetric stretch mode  $\nu_3$  is the dominant excitation process. As observed before in the case of  $CF_3Cl$  (paper III), also modes with C-F stretching character are considerably excited in the  $A_1$  (C-Cl  $\sigma^*$ ) resonance. The corresponding DA decay channels ( $F^-$ ,  $CFCl_2^-$ ) are energetically forbidden in this resonance (see table 3).

Next, looking at the group of negative ions formed at around 3 eV, the appropriate precursor is the  $A_1$  (C-F  $\sigma^*$ ) resonance at 4.0 eV. Thus, the energy shift is of the order of 1 eV which appears reasonable. The dominant fragment ion is  $F^-$  in accordance with the (C-F  $\sigma^*$ ) character of the resonance. This character is also expressed in vibrational excitation by the strong and selective excitation of the  $CF_2$  symmetric stretch mode  $\nu_1$ . The DA decay channel  $CFCl_2^- + F$  would also fit into this picture, although it occurs at somewhat higher energy.

The other (weaker) decay channels ( $FCl^-$ ,  $Cl^-$ ,  $Cl_2^-$  around 3 eV;  $Cl^-$  at 3.9 eV) must obviously also be associated with the  $A_1$  (C-F  $\sigma^*$ ) and  $B_1$  (C-F  $\sigma^*$ ) resonances. In these cases, however, the dissociative decay does not correlate with the (C-F  $\sigma^*$ ) character of the resonances and the observed selective excitation of  $CF_2$  symmetric stretch vibrations. A detailed knowledge of the  $CF_2Cl_2^-$  potential surfaces is probably necessary to explain these processes. Similar observations have been made in the case of  $CF_3Cl$  (see paper III).

An interesting consequence of the above assignment consists in the fact that obviously no fragment ions are produced through the  $B_2$  (C-Cl  $\sigma^*$ ) resonance at 2.5 eV. This resonance only shows up in vibrational excitation. A reason could be that the corresponding negative-ion state is correlated with energetically inaccessible fragments, but a definite explanation cannot be given with the present knowledge of  $CF_2Cl_2^-$  potential energy surfaces.

## 5. Conclusions

The main objectives of the present study of low-energy electron scattering from halomethane molecules have been (i) the determination of absolute differential cross sections for vibrationally elastic and inelastic scattering and (ii) the detailed investigation of the underlying mechanisms, especially the role of the resonances. In the energy range from 0.5 to 10 eV, the cross sections for elastic scattering and for excitation of the most important vibrational modes are presented. The importance of the intermediate

negative-ion states in the inelastic processes (vibrational excitation, dissociative attachment) is again evident in the case of  $\text{CF}_2\text{Cl}_2$ . Resonance-enhanced vibrational excitation is found to be most pronounced in the totally symmetric resonances of symmetry type  $A_1$ . The main features concerning the observed selectivity in both decay channels can be described with simple electron-location and symmetry arguments. A more detailed knowledge of the relevant potential energy surfaces seems necessary for some other effects such as the unspecific excitation in the 1.0 eV resonance or the apparent lack of negative-ion production in the 2.5 eV resonance.

In the 1.0 eV resonance, the inelastic cross section reaches the size of the elastic cross section and attains a value of about  $20 \times 10^{-16} \text{ cm}^2$ . A rough estimate for a partitioning of this value into the different contributions yields cross sections of  $\sim 12 \times 10^{-16} \text{ cm}^2$  for resonant vibrational excitation,  $\sim 5 \times 10^{-16} \text{ cm}^2$  for direct vibrational excitation, and  $\sim 3 \times 10^{-16} \text{ cm}^2$  for dissociative attachment. All inelastic cross sections are getting much smaller for impact energies above the range of this resonance, and elastic scattering becomes the dominant process.

The low-energy  $e$ - $\text{CF}_2\text{Cl}_2$  scattering shows several similarities to the  $e$ - $\text{CF}_3\text{Cl}$  system. In both cases, the elastic cross section exhibits a Ramsauer-Townsend minimum with a certain socle attributed to rotational excitation. The direct excitation mechanism is important below  $\sim 1$  eV for all stretching modes except the symmetric C-Cl stretch mode. In the first resonance which is of  $A_1$  (C-Cl  $\sigma^*$ ) type in both cases, the symmetric C-Cl stretching modes are excited together with  $\text{CF}_2$  ( $\text{CF}_3$ ) bending and C-F stretching motions. Also, the unspecific excitation at higher energy losses is observed in this resonance for both molecules. In contrast, the (C-F  $\sigma^*$ ) resonances are much more specific with respect to the halogen bond involved; they nearly exclusively lead to excitation of C-F stretching modes with several overtones. It would be interesting to see this behaviour confirmed by calculations on the negative-ion potential energy surfaces.

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