

Thermal Electron Attachment to SF₆ and CFCl₃

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Abstract

Measurements of the attachment rate for thermal electrons to SF₆ and CFCl₃ have been made using the Cavalleri electron-density sampling technique. The largest single source of error was shown to be uncertainty in the composition of the gas mixtures used in the experiments which contained <10 ppm of the attaching gases. By paying special attention to this problem, the overall uncertainty in the attachment rates was reduced to less than $\pm 3\%$.

1. Introduction

The need to identify gases that can serve as efficient electron scavengers in a number of applications (see e.g. Christophorou 1980) has led to a detailed study of attachment processes in a wide range of gases. Among this group are the compounds SF₆ and CFCl₃ for which the attachment cross sections are comparable with the theoretical upper limit for thermal electron capture. Recently Ajello and Chutjian (1979) determined the shape of the attachment cross sections for these molecules in the range of electron energies ϵ between 0 and 200 meV. These relative cross sections were subsequently normalized by Chutjian (1981, 1982) using experimental data for the attachment rate constants k_{at} for thermal electrons and the relation

$$k_{\text{at}} = (2/m)^{\frac{1}{2}} \int_0^{\infty} \epsilon S \sigma'_{\text{at}}(\epsilon) f(\epsilon) d\epsilon,$$

where $f(\epsilon)$ is the (normalized) Maxwellian energy distribution function corresponding to the gas temperature, m is the electron mass, $\sigma'_{\text{at}}(\epsilon)$ is the unnormalized cross section, and S is the normalizing factor.

Unfortunately there is a very large spread in the values of the attachment rate constants reported for both SF₆ and CFCl₃ (see Table 1). Moreover, almost without exception, the values quoted are unaccompanied by an error estimate so that the choice of 'best' values is somewhat arbitrary. An examination of the results in some of the papers reveals a scatter of at least $\pm 10\%$ while, as can be seen from Table 1, the differences between the results of various authors are very much larger.

Many of the previous determinations are based on data derived from measurements with a nonzero value of E/N (electric field strength/gas number density) in which the energy of the electron swarm is necessarily above thermal, although the

departure from thermal equilibrium may be small. In such cases an accurate knowledge of the electron-energy distribution function is required in order to unfold the attachment cross section and hence calculate the thermal attachment rate. In the present work the attachment rate for thermal electrons has been measured directly. The overall uncertainty in our measured values is estimated to be less than 3% which represents a considerable improvement on previous measurements. A preliminary account of this work has been given by Crompton *et al.* (1982).

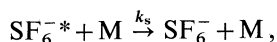
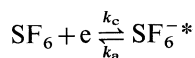
Table 1. Summary of results for the attachment rate constant for thermal electrons in SF₆ and CFCI₃ obtained in previous investigations

Results of the present work are shown for comparison			
k_{at} (10^{-7} cm ³ s ⁻¹)	T (K)	Buffer	Reference
SF ₆			
2.89×10^{-6}	300	Xe	Hasted and Beg (1965)
3.85×10^{-1}	300	C ₂ H ₄	Compton <i>et al.</i> (1966)
2.7	300	He	Young (1966)
2.42	300	10% CH ₄ , 90% Ar	Chen <i>et al.</i> (1968)
3.82×10^{-5}	380	C ₇ H ₁₄	Freeman (1968)
2.13	300	Various	Davis and Nelson (1970)
2.21	289	He	Fehsenfeld (1970)
2.2	300?	C ₃ H ₈	Fessenden and Bansal (1970)
2.70	298	N ₂	Christophorou <i>et al.</i> (1971)
2.79	298	C ₂ H ₄	Christophorou <i>et al.</i> (1971)
2.8	298	10% CH ₄ , 90% Ar	Ayala <i>et al.</i> (1981)
2.27 ± 0.07	295	N ₂	Present work
CFCI ₃			
1.1	300	N ₂	Blaunstein and Christophorou (1968) ^A
1.0	298	Ar	Schumacher <i>et al.</i> (1978)
0.12	298	N ₂	McCorkle <i>et al.</i> (1980)
2.43	298	N ₂	McCorkle <i>et al.</i> (1982)
2.37 ± 0.07	295	N ₂	Present work

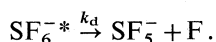
^A Derived from Lee (1963).

2. Experiment

Attachment of thermal electrons to SF₆ proceeds via a two-step process:



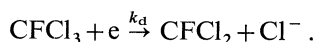
where M is a second molecule of any kind. Alternatively,



The electron-capture rate constant is given by k_c , the rate constant for auto-detachment by k_a , and the rate constants for stabilization and dissociation by k_s and k_d respectively. Although there has been some controversy about the lifetime of the excited state against autodetachment (see e.g. Odom *et al.* 1975; Ajello and Chutjian 1979) the lowest value reported ($\approx 10^{-5}$ s) is long compared

with the lifetime against dissociation, or the collision time at pressures ≥ 1 kPa. This means that the attachment process leading to the production of SF_6^- is effectively two body with a rate coefficient of k_e . Under the conditions of our experiment there is evidence from other work (Fehsenfeld 1970) that the alternative channel leading to the formation of SF_5^- can be ignored (see Section 4).

For the case of CFCl_3 the potential-energy curve for the parent negative ion is purely repulsive in the Franck-Condon region and the molecule undergoes dissociative attachment:



The rate coefficient for this reaction is therefore also a two-body coefficient.

Thus, for both compounds the attachment collision frequency ν_{at} is proportional to the gas number density N , and $k_{\text{at}} = \nu_{\text{at}}/N$. In our experiments the reaction rate was found to be proportional to pressure for both compounds, confirming that the attachment process is effectively or actually two body in both cases.

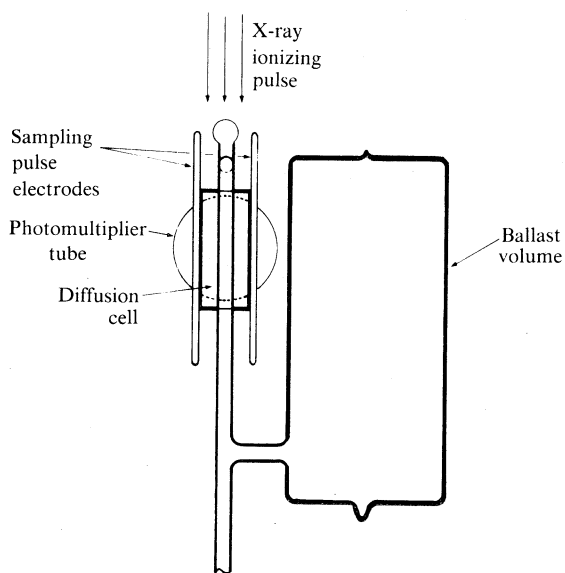


Fig. 1. Schematic diagram of the apparatus. The components shown are situated in a light-tight enclosure with the axis of the photomultiplier tube normal to the plane of the paper. The pulsed (triode) X-ray tube is external to the enclosure, the X-rays being transmitted through a thin beryllium window.

The principle of the measurement is based on the Cavalleri electron-density sampling method (Cavalleri 1969; Gibson *et al.* 1973). The apparatus is shown in Fig. 1. Electrons are produced in the cylindrical cell of known dimensions by an X-ray flash of a few μs duration. Initial electron populations are of the order 10^3 or less. A relative measure of the residual electron population after a time delay t is found by applying an r.f. field for a short time interval by means of electrodes external to the cell. The r.f. pulse, of about $1 \mu\text{s}$ duration, causes each free electron to initiate a local avalanche. The total photon flux received by the

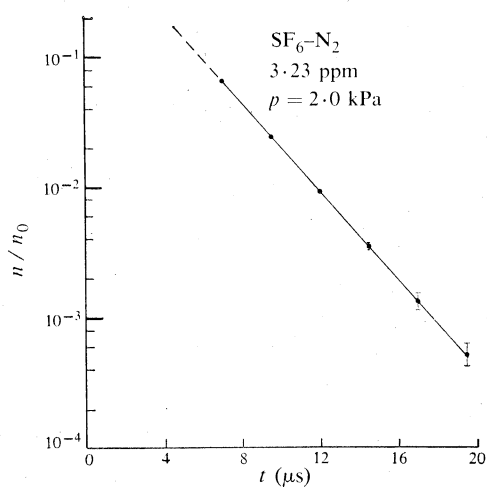


Fig. 2. Exponential decrease in the number of electrons remaining in the cell as a function of time after the X-ray flash.

Fig. 3. Curves of $N\tau^{-1}$ against N^2 for the gas mixtures shown. The slope of the curves is $k_{\text{at}}f$ (see text).

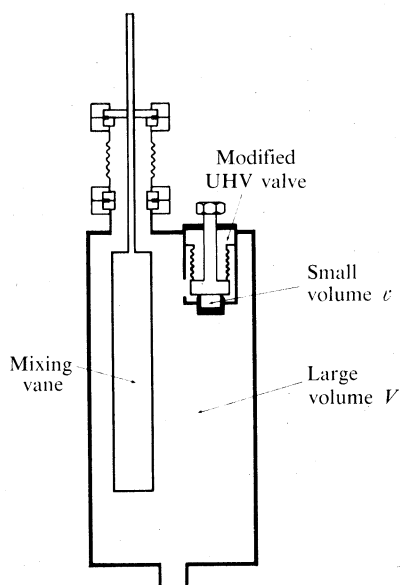
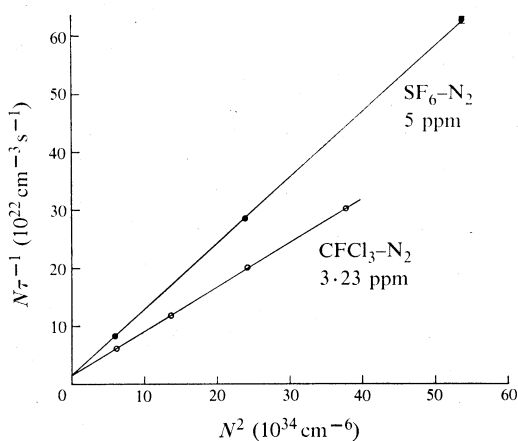


Fig. 4. Schematic diagram of the mixing chamber. The ratio v/V is about 10^{-3} .

photomultiplier viewing the cell is thus proportional to the residual population at the time of application of the r.f. pulse. Measurements of the decay time constant are made by recording the amplitude of the photomultiplier signals corresponding to two different time delays, the delays being alternated to avoid drift. Typically 40 000 shots with a repetition rate of about 1 Hz are made to obtain adequate statistics.

The variation of the electron population within the cell is of the form

$$n(t) = n_0 \exp(-t/\tau),$$

where, in an attaching gas, $\tau^{-1} = D\Lambda^{-2} + v_{at}$. Here D is the diffusion coefficient and Λ is the diffusion length (a function of the geometry of the cell) (see e.g. Huxley and Crompton 1974). The expression for the reciprocal of the attenuation time constant can be rewritten as

$$\tau^{-1} = \tau_D^{-1} + k_{at}[A],$$

where τ_D is the time constant for *free* diffusion, $k_{at} \equiv v_{at}/[A]$ is the rate coefficient for attachment, and $[A]$ is the number density of the gas. Ambipolar diffusion is avoided by using sufficiently small charged particle number densities.

In these experiments with SF_6 and CFCl_3 the attachment rate constant is so large that it is not possible to work with samples of the pure gas. For example, at a pressure of 0.5 kPa, which is about the minimum pressure that can be used, the time constant would be of the order of 10^{-10} s. Consequently it is necessary to work with mixtures of the attaching gas in a buffer gas with concentrations of the attaching component of a few ppm. If the number density of the buffer gas is N and the fractional concentration of the attaching gas is denoted by f ($\equiv [A]/N$), then the expression for τ^{-1} in the mixture becomes

$$\tau^{-1} = \tau_D^{-1} + k_{at}fN. \quad (1)$$

Fig. 2 shows a typical decay curve for a mixture of 3.23 ppm of SF_6 in N_2 at a pressure p of 2.0 kPa. It can be seen that the decay accurately obeys the expected exponential form.

Experimental data can be taken and analysed in two ways. From equation (1) it follows that, if τ_D is known, the rate coefficient can be determined from a measurement of the decay time constant at a single pressure. The diffusion time constant τ_D can be determined from a separate experiment in pure N_2 since the diffusion loss is entirely determined by the nitrogen at these low concentrations (<10 ppm) of attaching gas. In many of our experiments the diffusion term was less than 10% of the attachment term so that errors in the determination of τ_D are relatively unimportant. The diffusion term was never more than 30% of the attachment term under any of our experimental conditions.

Alternatively the rate coefficient can be determined from data recorded at several pressures. If equation (1) is multiplied by N we get

$$N\tau^{-1} = N\tau_D^{-1} + k_{at}fN^2$$

and, since $N\tau_D^{-1}$ is a constant, a plot of $N\tau^{-1}$ against N^2 should yield a straight line of slope $k_{at}f$. This is illustrated in Fig. 3 where the expected linearity can be seen. The values obtained for k_{at} using this procedure are in excellent agreement with those obtained by the first method.

An analysis of errors (see Section 3) shows that the largest source of uncertainty is likely to be in the determination of the mixture composition. Consequently we constructed a mixing chamber, shown in Fig. 4, which consists of a small volume situated within a larger volume and isolated by a valve. The ratio of the two volumes is approximately 1000:1 and was determined to better than 0.5%. The pressure gauge used to determine filling pressures for these volumes can measure pressure ratios of 200:1 or less with an uncertainty of better than 0.2%. This combination means that mixtures could be made with concentrations of the minor constituent as low as 5 ppm with an uncertainty of <0.75%. By using a two-step process, mixtures could be made containing less than 1 ppm of the minor constituent whose composition was known to the same order of accuracy. All mixtures were agitated prior to use with the vane shown in Fig. 4. The repeatability of the measurements over a period of several weeks showed that the mixture concentration was stable.

Because of the large discrepancies between various values of the attachment rate published in the literature we made mixtures of CFCl_3 in N_2 using a variety of techniques which would lead to concentrations above or below the nominal values if either adsorption or desorption of CFCl_3 to the walls of the chamber was significant. We found no difference in the results and conclude that adsorption and desorption are not significant processes in our experiments.

The large discrepancy between our initial results for CFCl_3 and the attachment rate coefficient for CFCl_3 given by McCorkle *et al.* (1980) prompted us to make measurements using gas taken from two cylinders of CFCl_3 . Both cylinders were specified as containing CFCl_3 with a purity of 99.9% in the liquid phase. We found that the vapour phase in both contained an appreciable quantity of nitrogen which we removed by repeatedly freezing a sample with liquid nitrogen and pumping off the remaining gas. However, even after this 'distillation' process there were large inconsistencies in the results for samples taken from the two cylinders. This was eventually traced to the fact that the first cylinder contained a significant amount of CF_2Cl_2 for which the attachment rate constant has been measured to be more than two orders of magnitude lower (McCorkle *et al.* 1980). Mass spectrometric analysis of the gas from the second cylinder gave a cracking pattern consistent with pure CFCl_3 . In succeeding work, gas from only this cylinder was used, and purified by the procedure described above.

During the course of experiments with mixtures of CFCl_3 in N_2 we observed a certain degree of variability from run to run and a tendency for the time constant to decrease significantly from a high initial value at the start of each run. A normal run would consist of, say, 40 000 individual density samplings which were subdivided into 20 groups. For each group the sums of the signal amplitudes recorded for each of the two delay times (1000 for each) were formed and used to calculate 20 separate determinations of the time constant which were then averaged to produce the final result. We observed that the first of these determinations was often higher than the remaining 19. This was particularly evident when we changed the gas sample in the cell; or reduced the pressure of the sample, but not evident if we simply repeated a run under identical conditions. In order to explain this behaviour we ran all the usual diagnostic checks but failed to resolve the problem. Eventually, however, a chance observation led us to the explanation which we subsequently verified.

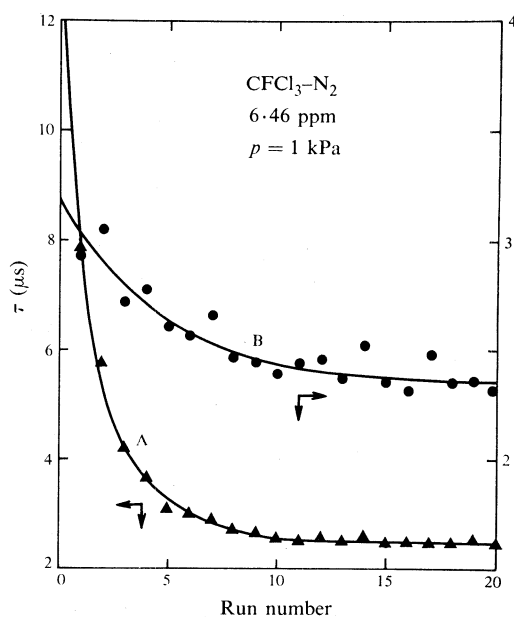


Fig. 5. Time dependence of the measured time constant in a $\text{CFCl}_3\text{-N}_2$ mixture after subjecting the sample to 40 large r.f. pulses (curve A) and 5 large r.f. pulses (curve B). Each run occupies approximately 4.5 min.

Under normal experimental conditions the dissociation of CFCl_3 in the initial attachment reactions, and subsequent reactions that take place during the density sampling using the r.f. pulse, cause negligible destruction of CFCl_3 as shown by the invariance of the results with time when the results were repeated with the same sample. However, if a sample of CFCl_3 in N_2 is subjected to an abnormally large r.f. sampling pulse a significant amount of CFCl_3 is apparently dissociated, thereby changing the composition of the gas mixture in the cell. If now a series of measurements of the time constant is made with a normal r.f. sampling pulse amplitude, the results show a time dependence due to mixing of the CFCl_3 depleted mixture in the cell with the original mixture in the ballast volume (see Fig. 1). This is best illustrated with reference to Fig. 5 where we show the measured time constant as a function of time after subjecting a sample to either 40 large r.f. sampling pulses (curve A) or 5 large r.f. sampling pulses (curve B). The time dependence is clearly evident, and the asymptotic values are somewhat higher than the expected values, confirming our explanation. It should be noted that the total number of r.f. pulses used in taking one of these curves is only about 5000 compared with our normal runs having a total of 40 000. This accounts for the poor statistics in the data shown in Fig. 5.

The reason why we observed similar effects in our normal experimental runs is as follows. The establishment of the appropriate r.f. pulse amplitude at the start of each new experimental run with a fresh gas sample normally involves the application of at least one, and often several, abnormally large pulses to the sample; and because of a characteristic of the program that controls the experiment,

an abnormally large pulse is automatically applied at the commencement of each experiment at a lower pressure unless special precautions are taken. In repeat runs with the same sample of gas *at the same pressure* this can be avoided. Thus, no anomalous results were observed whenever the experiments were repeated; they were always observed when the pressure of a given sample was reduced, and often observed when a new sample was used. The time scale for the mixing of the gas in the cell with the gas in the ballast volume, as indicated by the results shown in Fig. 5, is the reason why only the first of the 20 determinations of the time constant in a normal experimental run is affected, the mixing being almost complete within the time required for this determination.

Once the cause of the problem had been found we took great care to avoid any large-amplitude sampling pulses and have since taken up to 400 000 shots under a variety of different conditions with no evidence of this effect. Using samples of different concentration at pressures from 1 to 2.5 kPa we obtained values of the attachment rate coefficient having a maximum difference of $\pm 1\%$. There was no evidence of a similar effect with the $\text{SF}_6\text{-N}_2$ mixtures.

Table 2. Sources of experimental error in the electron-density sampling technique used in the present work

Source	Estimate	Source	Estimate
Errors in p and T	$<0.5\%$	Determination of τ_D	$<2.3\%^A$
Non-linearity in detection chain	$<0.5\%$	Mixture composition	$<1\%$
Statistics	$<0.5\%$		

^A Contributing $<1\%$ to error in k_{at} —see text.

3. Estimates of Experimental Error

Table 2 lists the sources of error and their estimated values. Remembering that at most the error in τ_D contributes only 1% to the error in the attachment rate, we see that the *arithmetic* sum of the estimated error is $\sim 3\%$.

In SF_6 , measurements were made with mixtures containing 1.00, 2.10, 3.23, 5.00 and 10.0 ppm of SF_6 at pressures of 0.5, 1.0, 2.0 and 3.0 kPa; in CFCl_3 , mixtures containing 3.23 and 6.46 ppm of CFCl_3 were used at pressures of 1.0, 1.5, 2.0 and 2.5 kPa. By placing a limit of $\pm 0.07 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ on the rate constant for each gas we can include all results recorded at all pressures for all mixtures. We therefore regard our error bounds of $\pm 3\%$ on the final results as somewhat conservative.

4. Results and Discussion

The values for the attachment rates of thermal electrons to SF_6 and CFCl_3 at 295 K are $(2.27 \pm 0.07) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and $(2.37 \pm 0.07) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ respectively.

Our result for SF_6 is in good agreement with the value of $2.2 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ obtained by both Fehsenfeld (1970) and Fessenden and Bansal (1970) (Table 1) but is significantly lower than the value of $(2.8 \pm 0.3) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ obtained more recently by Ayala *et al.* (1981). This somewhat higher value was also

obtained by Young (1966)* and Christophorou *et al.* (1971). The average value obtained by Davis and Nelson (1970) ($2.13 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$) is not significantly different from our value, while the value obtained by Chen *et al.* (1968) lies about midway between the two sets of values.

While we are unable to explain the reason for the two sets clustering around 2.2 and $2.7 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, we feel confident of our value and error assessment as they apply to the conditions of our experiment. The low level of ionization produced by the X-ray pulse (see Section 2) and the independence of the results on the experimental parameters, which were varied through wide limits, make it reasonable to assume that the SF_6 molecules had vibrational populations corresponding to the gas temperature. The absence of an imposed electric field means that, in principle, the electrons were in thermal equilibrium with the gas. Two factors could invalidate the assumption of thermal equilibrium: inadequate thermalization following the initial ionization by the X-ray pulse, and attachment cooling (Crompton *et al.* 1980). The linearity of the exponential decay of the electron population (see Fig. 2) and the invariance of the measured attachment rate constant with a change in the total gas pressure indicate adequate thermalization. It also seems that attachment cooling was not significant. When the attachment is two body (i.e. dissociative attachment) or, as in the present case, saturated three body, attachment cooling could affect the electron-energy distribution function, and hence the interpretation of the results in terms of a thermal Maxwellian distribution, without the effect showing up through an anomalous pressure dependence as in the experiments of Crompton *et al.* (1980). In such cases the attachment and energy-exchange collision frequencies vary linearly with pressure so that the energy distribution function may be distorted by the selective loss of electrons through attachment yet remain invariant with pressure. In the present case, however, such an effect is likely to be small, even though the ratio of the attachment frequency to the energy-exchange collision frequency in our experiments is about the same as that in the experiments of Crompton *et al.* First, the buffer gas used was nitrogen for which the energy-exchange rate under comparable conditions is about ten times that for oxygen. The data of Crompton *et al.* clearly demonstrate the much greater effectiveness of nitrogen as a thermalizing agent. Second, and more significantly, the monotonic decrease of the attachment cross section for SF_6 with increasing energy (Chutjian 1981) is in sharp contrast with the (broad) resonance structure of the cross section for non-dissociative attachment in O_2 . This means that the attachment collision frequency in SF_6 is only a weak function of energy, with the result that electrons are removed from the thermal swarm at approximately equal rates at all energies, in contrast to the selective removal of electrons in the neighbourhood of the 90 meV resonance in oxygen. Attachment cooling is thus not expected to be a significant process. This conclusion is borne out by the independence of the measured attachment rate constant on mixture composition. By varying the composition the ratio of attachment to energy-exchange collision frequency can be conveniently varied. In our experiments the ratio was varied by a factor of 10, but no significant variation in the rate constant was observed.

* The value of $3.1 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ reported by Mahan and Young (1966) is stated by Fessenden and Bansal (1970) to be the result of an incorrect analysis of Young's original data. For this reason it was omitted from Table 1.

The experimental data for electron attachment to CFCl_3 are relatively sparse. Apart from the anomalously low value obtained by McCorkle *et al.* in 1980, the reason for which is now understood (see McCorkle *et al.* 1982), there was, until very recently, reasonable agreement between the values measured in several laboratories using different techniques. However, our value and the latest value of McCorkle *et al.* (1982), which are in good agreement, are more than twice as large as the earlier values. Our comments with respect to the reliability of our value are similar to those for SF_6 .

Finally we comment on the application of these data to the normalization of attachment cross sections as carried out by Chutjian (1981, 1982). Chutjian has pointed out that the 'line-shapes' determined by Ajello and Chutjian (1979) refer to the production of one species of ion only (SF_6^- and Cl^- in their experiments), whereas the attachment rate constants determined in our experiments and those of McCorkle *et al.* refer to *all* attachment processes. There is thus a potential problem in a normalization procedure based on these non-specific rate constants.

In the case of SF_6 there appears to be no problem if one accepts the evidence from Fehsenfeld's (1970) flowing afterglow experiments. At room temperature the ratio of SF_5^- to SF_6^- ion concentrations was found to be $\sim 10^{-4}$ so that negligible error arises from normalizing in this way. For CFCl_3 the situation is not so clear-cut. From a comparison of the shape of the cross section for the formation of Cl^- obtained by Ajello and Chutjian (1979) with the cross section for *all* processes found by McCorkle *et al.* (1982), it appears that an additional process may exist having a threshold energy in the vicinity of 80 meV and a broad maximum in the cross section at about 180 meV. In order to calculate the error in the normalization that would result from such a process, we have assumed a constant value of 30 \AA^2 for the cross section above a threshold energy of 80 meV.* We find that such a process would contribute only about 2% to the overall rate coefficient and conclude that such a process, if it exists, does not invalidate the normalization unless its threshold occurs at significantly lower energy.

Acknowledgments

The authors acknowledge with thanks the work of R. Hegerberg, K. Nygaard and A. G. Robertson during the early part of this investigation. They also wish to thank M. T. Elford and D. E. Boyd for helpful discussions on the manuscript.

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* The shapes of the cross sections determined by Ajello and Chutjian (1979) and by McCorkle *et al.* (1982) are not in good agreement below 80 meV, and the evidence for the onset of a new process at 80 meV is no longer as strong as in Chutjian's (1981) paper (see Chutjian 1982). The pronounced change in slope of the McCorkle *et al.* cross section at this energy, which is not evident in the Chutjian cross section, is the basis for the assumption used in our calculations.

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