

Photoionisation Cross Sections of Chlorine Atoms and Molecules at 584 Å*

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Abstract

A recently developed modulation method is used to obtain cross sections for the photoionisation of ground state neutral to ground state ionic, atomic and molecular chlorine *relative* to that of the $\text{HCl}^+(\text{X}^2\Pi_{1/2,3/2}) \leftarrow \text{HCl}(\text{X}^1\Sigma^+)$ transition at the He I α wavelength. With the known absolute cross section of the latter process, determined by (e, 2e) coincidence spectroscopy, the present experiments provide *absolute* photoionisation cross sections of the $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}(\text{}^2\text{P})$ and $\text{Cl}_2^+(\text{X}^2\Pi_{g,1/2,3/2}) \leftarrow \text{Cl}_2(\text{X}^1\Sigma_g^+)$ transitions. Relative cross sections, previously determined for the transitions to the additional Cl and Cl_2 ionic states accessible with He I α radiation, are used to obtain absolute cross sections for the $\text{Cl}^+(\text{}^1\text{D}_2, \text{}^1\text{S}_0) \leftarrow \text{Cl}(\text{}^2\text{P})$ and $\text{Cl}_2^+(\text{A}^2\Pi_{u,1/2,3/2}, \text{B}^2\Sigma_g^+) \leftarrow \text{Cl}_2(\text{X}^1\Sigma_g^+)$ ionisation processes.

1. Introduction

Photoionisation cross sections have been the subject of numerous theoretical and experimental investigations in the last few decades. In theoretical descriptions of the photoionisation process, proper characterisation of the final state, consisting of an ion interacting with the leaving electron, is no trivial matter. This holds especially in UV photoelectron (PE) spectroscopy, where the electrons, liberated in the photoionisation process, have relatively low kinetic energies. Because of the complexity of the problem, attention was at first focused on the calculation of cross sections for the noble gases (Dalgarno 1952; Cooper 1962), which at low photon energies only give rise to a spin-orbit coupled doublet ^2P final ionic state. Subsequent improvements, incorporating among others core relaxation, many body effects, interchannel coupling and pair excitation effects, yielded consistent values for the calculated photoionisation cross section over a wide energy range (Starace 1970; Swanson and Armstrong 1977*a*, 1977*b*) which compare well with values available from experiment. By now the photoionisation process of closed shell atoms is fairly well understood.

More recently the emphasis has shifted towards the more challenging problems of ionisation of open shell atoms. Atomic chlorine, which is adjacent to the well-studied argon atom in the periodic table, served as a test case in many recent theoretical investigations (Conneely *et al.* 1970; Starace and Armstrong 1976; Cherepkov and Chernysheva 1977; Brown *et al.* 1978; Lamoureux and Combet Farnoux 1979;

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Manson *et al.* 1979; Brown *et al.* 1980; Fielder and Armstrong 1983; Shahabi *et al.* 1984). These calculations indicate that the final state interchannel interactions are dominant in the electron correlations. In open shell atoms, removal of a single electron gives rise to several ionic states. For example, ionisation from the chlorine 3p subshell yields a Cl^+ ion with $^3\text{P}_{2,1,0}$, $^1\text{D}_2$ and $^1\text{S}_0$ final ionic states. These states are mixed in the presence of the photoelectron, hence the coupling between the different final state channels should be treated carefully (Fielder and Armstrong 1983). The calculations further show that interchannel coupling effects on the cross section are most important near the ionisation threshold. However, complete lack of relevant experimental data has clearly prohibited the much desired comparison between theory and experiment.

Due to the reduced symmetry of the problem, calculation of photoionisation cross sections of molecules is an even more complicated matter. However, a theoretical study concerning HCl, a molecule relevant to the present study, has been published (Faegri and Kelly 1982), which gives absolute cross sections for the $2\pi^{-1}$ and $5\sigma^{-1}$ ionisations that compare well (within 10%) with experimental HCl cross sections measured by (e, 2e) spectroscopy around 21.2 eV (Daviel *et al.* 1984).

Experimental cross section studies also began with measurements on the noble gases. The most difficult step is concerned with the normalisation of measured values to an absolute cross section scale. Many different experiments were designed to determine the absorption coefficient appearing in the well-known Lambert–Beer absorption law:

$$I = I_0 \exp(-kx), \quad (1)$$

where k (cm^{-1}) is the absorption coefficient, x (cm) is the length of the absorption path and I_0 and I are the incident and transmitted light intensities. Pressure or position dependent measurements of total ion or electron current as well as photon beam intensity measurements were performed. Photoionisation and photoabsorption cross sections obtained in this way are almost identical at the He I α wavelength where the quantum yield of photoionisation is virtually unity since competitive processes such as Auger electron emission, autoionisation or resonant photoabsorption are well known to be insignificant. The absorption coefficients can be converted into cross sections through division by the Loschmidt number (Lee and Weissler 1955). These methods all involve measurements of experimental parameters; in order to obtain accurate absolute cross sections, measurements of either particle densities in a flow system or photon beam intensities or photoionisation efficiencies in combination with photoelectron collection and detection efficiencies have to be determined (Lee and Weissler 1955; Wainfan *et al.* 1955; Samson 1964; Rustgi 1964; Samson 1969; Madden *et al.* 1969; Samson and Gardner 1974; West *et al.* 1974). These experimental parameters in general cannot be measured with high precision. For transient species in particular such an approach would lead to difficulties that cannot easily be overcome.

The abovementioned problems accompanying the normalisation procedure for measured cross sections can be avoided if (e, 2e) and (e, e + ion) coincidence scattering experiments in combination with Thomas–Reiche–Kuhn sum rule arguments are invoked. Scattering cross sections, obtained in this way from energy loss spectroscopy, can be compared with photoabsorption cross sections within the Born approximation in the limit of zero momentum transfer (Brion and Hamnett 1981; Backx and van der Wiel 1974). Application of this method reduces the experimental demands to constant

particle density in the impact region. The scattering experiments must be performed over a wide range of energy losses to ensure correct application of the sum rule in the cross section normalisation. Although the experiment requires time-consuming coincidence measurements, many successful applications on stable molecules have been reported (Brion and Thomson 1984). Because of the long term stability in the particle density required, the scattering method cannot be applied easily to the cross section determination of transients. Due to such problems only very few experimental cross sections of short-lived species are available to date.

Recently we developed a new modulation method which can produce accurate *relative* photoionisation cross sections (van der Meer *et al.* 1985). Application of this new method to H_2 and D_2 provided cross sections σ_{H_2} relative to σ_{H} , and σ_{D_2} relative to σ_{D} . With the exactly calculated H and D atomic cross sections, *absolute* H_2 and D_2 cross sections were obtained without the need to measure photon flux and particle densities. In the present work this modulation method is extended to the determination of the photoionisation cross section of the chlorine atom relative to that of its stable precursor HCl. Using the absolute value for the HCl cross section available from (e, 2e) experiments, absolute Cl photoionisation cross sections are presented. In addition similar information on molecular chlorine is obtained.

2. Experimental

The PE spectrometer was especially designed to minimise the ill effects of reactive species on the transmission and spectral resolution of the spectrometer and has been described in detail elsewhere (van Lonkhuyzen *et al.* 1981; Grabandt *et al.* 1984). Unpolarised He I α resonance radiation (584 Å) was produced by a d.c. discharge lamp. Photoelectrons were collected at 90° with respect to the incident photon beam and analysed according to their kinetic energies with an electrostatic deflection analyser. Because photoelectron detection at the magic angle was not possible with the apparatus, information on asymmetry parameters β for each observed PE band was necessary. For the cross section measurements, a modulation method was used which was originally developed to extract weak signals of transients from a spectrum dominated by strong bands of stable precursor molecules (van Lonkhuyzen and de Lange 1982, 1984*a*, 1984*b*). In the modulation experiment, a gas flow of suitable precursors was passed through a microwave discharge. The discharge power, and consequently the transient signal, was square-wave modulated. In order to ignite the discharge reliably a pretriggering method (van Lonkhuyzen and de Lange 1982) was employed. Alternating gas packets consisting of either solely precursor molecules (discharge-off) or a mixture of both precursor molecules and transients (discharge-on) entered the ionisation region. Spectra obtained in both modulation phases were recorded virtually simultaneously and stored in separate buffers of a computer memory.

Relative cross sections were derived from the ratio of the intensity decrease of the precursor signal to the intensity gain of the transient bands on switching the microwave discharge on, as shown in detail in the next section. In the present experiments HCl (>99%, Matheson) and Cl_2 (5% in helium, BOC) were subjected to a 2.45 GHz microwave discharge. The discharge was applied in a 15 mm o.d. alumina tube coated with boric acid. Dissipated microwave power typically amounted to 75 W in the HCl discharge and 85 W in the Cl_2 discharge. The modulation frequency was 2.5 Hz in all experiments and pressure in the discharge tube was estimated at 0.1–1

mbar (1 bar = 10^5 Pa). To enhance the reliability of the pretriggering, a trace of neon (c.p. >99.99%, Matheson) was added. The discharge tube was connected to a pyrex 13 mm o.d. inlet tube, coated with halocarbon wax to minimise wall recombination reactions. From the pyrex tube the gas was pumped into a brass inner ionisation chamber which was mounted on the lamp head cylindrically around the photon beam and acted as a Faraday cage. This shielding limited the influence of contaminants formed in the discharge on the spectral drift and resolution and transmission of the analyser. The transport time from the discharge zone to the ionisation region was estimated at 15 ms.

In order to monitor the transmission in the spectral region under consideration, spectra of the $O_2^+(X^2\Pi_g) \leftarrow O_2(X^3\Sigma_g^-)$ band were recorded regularly. With the absolute intensities measured by Gardner and Samson (1976), the transmission function could be evaluated. The hemispherical analyser generally discriminates against electrons with kinetic energies less than about 5 eV. In the spectral region of the present measurements (around 10 eV kinetic energy) the transmission was expected to be almost constant, which was confirmed by intensity determination of the vibrational features of the oxygen first band. The spectral positions were calibrated against the well-known ionisation energies (IE) of the $HCl^+(X^2\Pi_{1/2,3/2}) \leftarrow HCl(X^1\Sigma^+)$, $Cl^+(^3P_{2,1,0}) \leftarrow Cl(^2P)$ and $Cl_2^+(X^2\Pi_{g,1/2,3/2}) \leftarrow Cl_2(X^1\Sigma_g^+)$ transitions (Rabalais 1977; de Leeuw *et al.* 1978).

3. Theory

Relative photoionisation cross sections can in principle be derived from intensity measurements in PE spectra. A detailed description of the factors determining the experimental integrated PE intensities has been given in a previous paper (van der Meer *et al.* 1985). Briefly these factors can be divided into two categories. The first category consists of parameters depending on spectrometer design and light source, the second consists of quantities related to the compounds studied. Since in our approach the spectra were recorded under virtually identical circumstances in both phases of the modulation experiment, the apparatus dependent parameters are almost identical and hence do not influence relative cross section values. The species related parameters are the photoionisation cross section σ and the dimensionless asymmetry parameter β which for unpolarised light appears in the intensity expression as a $1 - \frac{1}{4}\beta_i(3\cos^2\theta - 1)$ factor (Manson and Dill 1978). In the present experimental setup with $\theta = 90^\circ$ this reduces to a $(1 + \frac{1}{4}\beta_i)$ dependency. Photoionisation cross sections are proportional to the squared electric dipole transition matrix element and can change considerably with the wavelength of the ionising radiation. Asymmetry parameters β_i ($-1 \leq \beta_i \leq +2$) are in general also a function of the photon energy.

If a microwave discharge is applied in HCl, the molecules will partly dissociate into H and Cl atoms. Under the assumption that neither the precursor nor the discharge products react with wall coatings and that recombination of atoms does not yield products other than HCl, it follows that the number of HCl molecules dissociated is equal to the number of either H or Cl atoms reaching the photoionisation region. The numbers of H and Cl atoms are equal under the above assumptions. However, due to the large difference between photoionisation cross sections of H and Cl atoms at the He I α wavelength, relative intensities measured with respect to the small H atom signal are plagued with large uncertainties because of insufficient counting statistics. This problem can be largely avoided by comparison of Cl

atom and HCl intensities both originating from species with cross sections of the same order of magnitude. Considering only the $\text{HCl}^+(\text{X}^2\Pi_i) \leftarrow \text{HCl}({}^1\Sigma^+)$ and $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}({}^2\text{P})$ transitions, the stoichiometry leads to the following simple relation for the measured intensities:

$$\frac{\Delta I_{\text{HCl}^+(\text{X}^2\Pi_i)}}{(1 + \frac{1}{4}\beta_{\text{HCl}^+(\text{X}^2\Pi_i)})\sigma_{\text{HCl}^+(\text{X}^2\Pi_i)}} = \frac{I_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})}}{(1 + \frac{1}{4}\beta_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})})\sigma_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})}}, \quad (2)$$

where $\Delta I_{\text{HCl}^+(\text{X}^2\Pi_i)}$ signifies the intensity decrease of the $\text{HCl}^+(\text{X}^2\Pi_i) \leftarrow \text{HCl}({}^1\Sigma^+)$ transition in going from the discharge-off to discharge-on spectrum, $I_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})}$ is shorthand notation for the intensity of the $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}({}^2\text{P})$ transition in the discharge-on spectrum, and the σ and β parameters carry similar labels. With the β values available in the literature (Carlson *et al.* 1983*b*; Fielder and Armstrong 1983) this equation can easily be converted to give the cross section ratio for both transitions. Using the $\text{HCl}^+(\text{X}^2\Pi_i) \leftarrow \text{HCl}({}^1\Sigma^+)$ absolute cross section from (e, 2e) experiments (Daviel *et al.* 1984), (2) reduces to an equation with one unknown (i.e. $\sigma_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})}$).

Unfortunately, in our experimental setup a slight recombination of Cl atoms into molecular chlorine was observed. Taking this recombination into account, equation (2) is replaced by

$$\begin{aligned} \frac{\Delta I_{\text{HCl}^+(\text{X}^2\Pi_i)}}{(1 + \frac{1}{4}\beta_{\text{HCl}^+(\text{X}^2\Pi_i)})\sigma_{\text{HCl}^+(\text{X}^2\Pi_i)}} &= \frac{I_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})}}{(1 + \frac{1}{4}\beta_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})})\sigma_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})}} \\ &+ \frac{2I_{\text{Cl}_2^+(\text{X}^2\Pi_{g,i})}}{(1 + \frac{1}{4}\beta_{\text{Cl}_2^+(\text{X}^2\Pi_{g,i})})\sigma_{\text{Cl}_2^+(\text{X}^2\Pi_{g,i})}}, \end{aligned} \quad (3)$$

where the symbols have the same meaning as in (2). This is an equation with two unknowns ($\sigma_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})}$ and $\sigma_{\text{Cl}_2^+(\text{X}^2\Pi_{g,i})}$) and hence the problem cannot be solved unless another relation between these cross sections can be determined. In an additional Cl_2 modulation experiment the cross section ratio for the $\text{Cl}_2^+(\text{X}^2\Pi_{g,i}) \leftarrow \text{Cl}_2({}^1\Sigma_g^+)$ and $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}({}^2\text{P})$ transitions can be obtained. With similar assumptions as above the stoichiometry then leads to the following expression (see also van der Meer *et al.* 1985):

$$\frac{2\Delta I_{\text{Cl}_2^+(\text{X}^2\Pi_{g,i})}}{(1 + \frac{1}{4}\beta_{\text{Cl}_2^+(\text{X}^2\Pi_{g,i})})\sigma_{\text{Cl}_2^+(\text{X}^2\Pi_{g,i})}} = \frac{I_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})}}{(1 + \frac{1}{4}\beta_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})})\sigma_{\text{Cl}^+(\text{}^3\text{P}_{2,1,0})}}. \quad (4)$$

By combining the results from independent HCl and Cl_2 modulation experiments, and using experimental β values for Cl_2 (Carlson *et al.* 1983*a*), absolute photoionisation cross sections for the $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}({}^2\text{P})$ and $\text{Cl}_2^+(\text{X}^2\Pi_{g,i}) \leftarrow \text{Cl}_2({}^1\Sigma_g^+)$ transitions can finally be extracted from equations (3) and (4).

Once the $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}({}^2\text{P})$ and $\text{Cl}_2^+(\text{X}^2\Pi_{g,i}) \leftarrow \text{Cl}_2({}^1\Sigma_g^+)$ cross sections have been placed on an absolute scale it is possible to derive absolute cross sections for the ionisations to excited states of the ions (${}^1\text{D}_2$, ${}^1\text{S}_0$ for Cl^+ ; $\text{A}^2\Pi_{u,i}$ and $\text{B}^2\Sigma_g^+$ for Cl_2^+) from previously determined relative band intensities (Kimura *et al.* 1978; Carlson *et al.* 1983*a*).

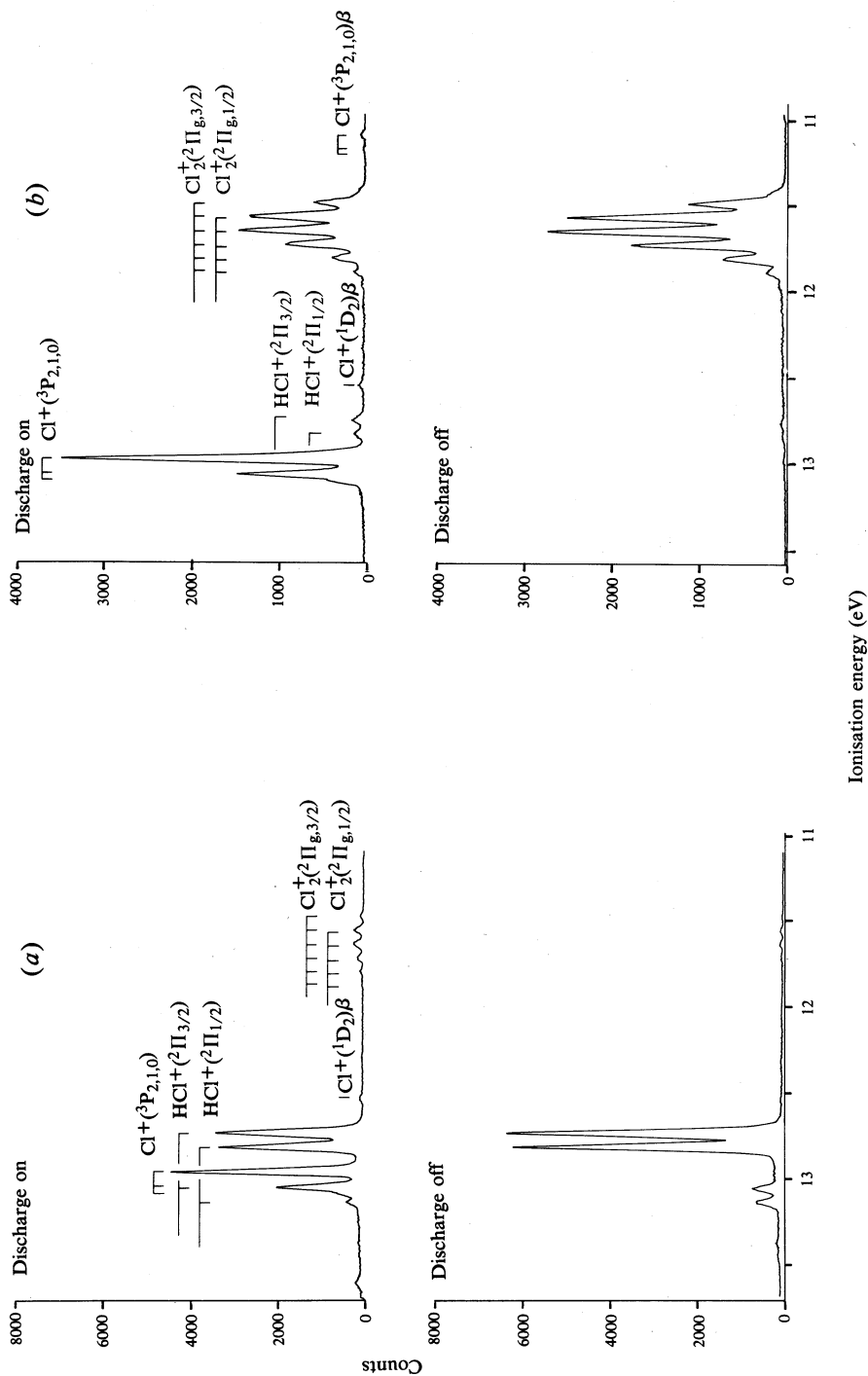


Fig. 1. Modulation spectra at 584 Å of (a) HCl and (b) Cl₂. The upper traces correspond to the discharge-on period and the lower traces to the discharge-off period of the experiment.

4. Results and Discussion

Typical sections of both discharge-on and discharge-off spectra obtained in the HCl modulation experiment are shown in Fig. 1a. The discharge-off spectrum solely exhibits PE bands due to the $\text{HCl}^+(\text{X}^2\Pi_{1/2,3/2}, v'=0, 1) \leftarrow \text{HCl}(\text{X}^1\Sigma^+, v''=0)$ transition. In the discharge-on spectrum $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}(\text{}^2\text{P})$ peaks appear clearly in the 13 eV region. Weak $\text{Cl}_2^+(\text{X}^2\Pi_{g,i}) \leftarrow \text{Cl}_2(\text{}^1\Sigma_g^+)$ transitions can also be distinguished on the low IE side of the spectrum. The $\text{Cl}^+(\text{}^1\text{D}_2)\beta$ peak is caused by ionisation of ground-state Cl atoms to the $^1\text{D}_2$ excited ionic state by the He I β 'impurity' line in the light source. Apart from small signals due to H and H_2 in the spectra no evidence for other products is found. In order to measure the $\text{Cl}^+(\text{}^3\text{P}_{2,1,0})$ intensity reliably in the HCl modulation spectra, the intensity of the underlying $\text{HCl}^+(\text{X}^2\Pi_{1/2,3/2}, v'=1) \leftarrow \text{HCl}(\text{X}^1\Sigma^+, v''=0)$ ionisation should be subtracted. This intensity was estimated from the corresponding $v'=0$ band by using the $(v'=0)/(v'=1)$ ratio deduced from the discharge-off spectrum.

Fig. 1b contains similar spectra recorded in the Cl_2 modulation experiment. The discharge-off spectrum only contains signals due to ionisation of precursor Cl_2 molecules. In the discharge-on spectrum $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}(\text{}^2\text{P})$ bands appear, whereas the Cl_2 band intensity is reduced. The presence of weak $\text{HCl}^+(\text{X}^2\Pi_{1/2,3/2}) \leftarrow \text{HCl}(\text{X}^1\Sigma^+)$ bands indicates that a minor part of the Cl atoms generated in the discharge reacts with the wall coating to produce traces of HCl in the gas flow. Because the cross section and β parameter for this HCl transition are known, correction can be made for this reaction. Again ionisations of ground-state atomic chlorine to excited ionic states by He I β radiation are observed. No evidence for production of other species is found. All displayed spectra were accumulated in 10 scans of 410 s each. Experimental band intensities were corrected for spectrometer transmission effects which were found to be unimportant in view of the narrow energy region considered.

From 14 independent Cl_2 modulation runs the cross section ratio for the $\{\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}(\text{}^2\text{P})\}/\{\text{Cl}_2^+(\text{X}^2\Pi_{g,i}) \leftarrow \text{Cl}_2(\text{}^1\Sigma_g^+)\}$ transitions was determined to be 0.538 ± 0.027 . Combining a series of 15 independent HCl runs and these Cl_2 modulation runs, the cross section ratio for the $\{\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}(\text{}^2\text{P})\}/\{\text{HCl}^+(\text{X}^2\Pi_i) \leftarrow \text{HCl}(\text{X}^1\Sigma^+)\}$ ionisations was determined to be 0.753 ± 0.020 . In addition a cross section ratio of 1.404 ± 0.073 was derived for the $\{\text{Cl}_2^+(\text{X}^2\Pi_{g,i}) \leftarrow \text{Cl}_2(\text{}^1\Sigma_g^+)\}/\{\text{HCl}^+(\text{X}^2\Pi_i) \leftarrow \text{HCl}(\text{X}^1\Sigma^+)\}$ ionisations. Absolute experimental cross section values for these transitions were determined from a combination of our relative cross section results with absolute HCl cross sections obtained by Daviel *et al.* (1984). The uncertainty in the σ values from (e,2e) measurements (10%) is in fact the main cause for the relatively large errors quoted in the present experimentally determined cross sections. Experimental cross sections of transitions to higher ionic states are deduced by utilising our absolute values for the first band, the corresponding β parameters (Fielder and Armstrong 1983; Carlson *et al.* 1983a) and previous relative measurements (Kimura *et al.* 1978; Carlson *et al.* 1983a).

A summary of relevant literature data and our present experimental results are presented in Tables 1–3. In Table 1 recent β and σ literature values at 584 Å for Cl, Cl_2 and HCl are given. In Table 2 theoretical Cl cross section data are summarised and compared with the present absolute σ determination, while Table 3 gives a

Table 1. Recent β and σ values at 584 Å

Ionic state	β	σ (relative)	σ (absolute)
$\text{Cl}_2^+(\text{X}^2\Pi_{g,i})$	0.723 ^A	100 ^{A,B}	13.8 ^C
$\text{Cl}_2^+(\text{A}^2\Pi_{u,i})$	1.303 ^A	81 ^{A,B}	11.2 ^C
$\text{Cl}_2^+(\text{B}^2\Sigma_g^+)$	0.200 ^A	33 ^{A,B}	4.6 ^C
$\text{Cl}^+(\text{}^3\text{P}_{2,1,0})$	0.66 ^D	100 ^E	
$\text{Cl}^+(\text{}^1\text{D}_2)$	0.31 ^D	54 ^E	
$\text{Cl}^+(\text{}^1\text{S}_0)$	0.47 ^D	11 ^E	
$\text{HCl}^+(\text{X}^2\Pi_i)$	1.22 ^F		26.12 ^G
$\text{HCl}^+(\text{A}^2\Sigma^+)$	0.51 ^F		14.71 ^G

^A Experimental values from Carlson *et al.* (1983 *a*). ^B Accurate relative values, normalised on the $\text{Cl}_2^+(\text{X}^2\Pi_{g,i})$ band and corrected for asymmetry parameters from Carlson *et al.* (1983 *a*). ^C Absolute values are uncertain by a factor of ≈ 2 and are given in Mb (1 Mb = 10^{-18} cm²) (Carlson *et al.* 1983 *a*). ^D Theoretical β values from Fielder and Armstrong (1983). ^E Experimental values from PE experiments at 90°, not corrected for asymmetry parameters (Kimura *et al.* 1978). ^F Experimental values from Carlson *et al.* (1983 *b*). ^G Experimental values from Daviel *et al.* (1984).

Table 2. Photoionisation cross sections for the $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}, \text{}^1\text{D}_2, \text{}^1\text{S}_0) \leftarrow \text{Cl}(\text{}^2\text{P})$ ionisations

Cross sections are given in Mb at 584 Å. Relative values are scaled to the $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}(\text{}^2\text{P})$ transition. All values are corrected for asymmetry parameters (see Table 1)

Ref. ^A	$\text{}^3\text{P}_{2,1,0}$	Absolute σ values			Relative σ values ^B		
		$\text{}^1\text{D}_2$	$\text{}^1\text{S}_0$	Total	$\text{}^3\text{P}_{2,1,0}$	$\text{}^1\text{D}_2$	$\text{}^1\text{S}_0$
Theoretical results							
1				39 ^C			
2	20.70	7.88	2.44	31.02	100 ^D	38 ^D	12 ^D
3				30			
4				36			
5	21.76	11.87	3.77	37.4	100 ^D	55 ^D	17 ^D
6	23.9	12.6	3.6	40.1	100 ^D	53 ^D	15 ^D
7	17.7 ^E	12.4 ^E	2.1 ^E	32.2 ^F	100 ^F	70 ^F	12 ^F
8	18.9 ^E	10.2 ^E	2.5 ^E	31.5	100 ^G	54 ^G	13 ^G
9	19.5 ^E	13.9 ^E	2.3 ^E	35.7	100 ^G	71 ^G	12 ^G
Experimental results							
10					100	58	11
11	19.7 ± 2.5 ^H	11.4 ± 1.5 ^I	2.16 ± 0.28 ^I	33.3 ± 4.2 ^I			

^A References: 1, Conneely *et al.* (1970); 2, Starace and Armstrong (1976); 3, Cherepkov and Chernysheva (1977); 4, Brown *et al.* (1978); 5, Lamoureux and Combet Farnoux (1979); 6, Manson *et al.* (1979); 7, Brown *et al.* (1980); 8, Fielder and Armstrong (1983); 9, Shahabi *et al.* (1984); 10, Kimura *et al.* (1978); 11, present work.
^B Scaled to the $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}(\text{}^2\text{P})$ band.
^C From Lamoureux and Combet Farnoux (1979); Fig. 3.
^D Determined from absolute partial cross sections.
^E Calculated from absolute total cross section and relative cross section values from the same calculation.
^F Mean of length and velocity calculation; correlation and relaxation are included.
^G Mean of length and velocity calculation.
^H See text.
^I Determined from the experimental $\text{Cl}^+(\text{}^3\text{P}_{2,1,0}) \leftarrow \text{Cl}(\text{}^2\text{P})$ absolute cross section and relative values from Kimura *et al.* (1978).

Table 3. Photoionisation cross sections for the $\text{Cl}_2^+(\text{X}^2\Pi_{g,i}, \text{A}^2\Pi_{u,i}, \text{B}^2\Sigma_g^+) \leftarrow \text{Cl}_2(\text{X}^1\Sigma_g^+)$ transitions at 584 Å

Values are given in Mb and are corrected for asymmetry parameters (see Table 1)

Ref.	$\text{Cl}_2^+(\text{X}^2\Pi_{g,i})$	$\text{Cl}_2^+(\text{A}^2\Pi_{u,i})$	$\text{Cl}_2^+(\text{B}^2\Sigma_g^+)$	Total
Carlson <i>et al.</i> (1983a)	$13.8^{\text{A}} (100)^{\text{B}}$	$11.2^{\text{A}} (81)^{\text{B}}$	$4.6^{\text{A}} (33)^{\text{B}}$	29.6^{A}
Present work	$36.7 \pm 5.5^{\text{C}}$	$29.7 \pm 4.5^{\text{D}}$	$12.1 \pm 1.8^{\text{D}}$	$78.5 \pm 12^{\text{D}}$

^A Absolute values are uncertain by a factor of ≈ 2 due to uncertainties in the calibration procedure (see Carlson *et al.* 1983a).

^B Relative values scaled to $\text{Cl}_2^+(\text{X}^2\Pi_{g,i})$ intensity.

^C See text.

^D Obtained from the $\text{Cl}_2^+(\text{X}^2\Pi_{g,i})$ absolute cross section using relative values from Carlson *et al.* (1983a).

comparison of previous absolute Cl_2 cross section estimates (Carlson *et al.* 1983a) with the present absolute cross section results.

5. Conclusions

The modulation method, used to determine relative cross sections, has been shown to give accurate results when applied to discharges in HCl and Cl_2 . Reliable experimental absolute cross sections at 584 Å were determined for the first time. The main experimental error source in the absolute Cl and Cl_2 cross section values arose from the errors in the absolute (e, 2e) scattering cross section data for HCl (Daviel *et al.* 1984), which were used to put the present relative values on an absolute scale. For the Cl atom no experimental β parameters were available. In this context, extension of our modulation method to allow angle-dependent data acquisition would seem worth while.

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