Quantum yield of Cl* ($^2P_{1/2}$) production in the gas phase photolysis of CCl$_4$ in the ultraviolet

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Abstract. In this paper, we have probed the dynamics of chlorine atom production from the gas phase photodissociation of carbon tetrachloride at 222 and 235 nm. The quantum yield, $\boldsymbol{f}^*$ of Cl* ($^2P_{1/2}$) production has been determined by probing the nascent concentrations of both excited ($^2P_{1/2}$) and ground state ($^2P_{3/2}$) chlorine atoms by suitable resonance-enhanced multiphoton ionization (REMPI) detection schemes. Although at the photolysis wavelengths the absorption of carbon tetrachloride is weak, significant amounts of Cl* are produced. Surprisingly, the quantum yield of Cl* production does not follow the absorption spectrum closely, which gives rise to the possibility of an indirect dissociation mechanism present in CCl$_4$ along with direct dissociation at these ultraviolet wavelengths.
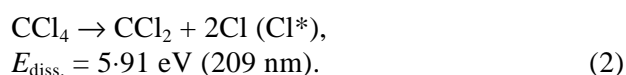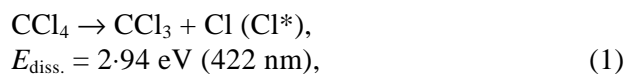
Keywords. Ultraviolet photolysis; carbon tetrachloride; gas phase; resonance enhanced multiphoton ionization; quantum yield.

1. Introduction

Photolysis of carbon tetrachloride (CCl$_4$) and chlorine-substituted hydrocarbons in the ultraviolet is important to investigate not only for their ability to produce active chlorine atoms upon decomposition when exposed to ultraviolet (UV) and vacuum ultraviolet (VUV) radiation in the upper atmosphere which can enter the cycle for ozone destruction but also to understand the C–Cl bond dissociation dynamics in chlorinated hydrocarbons. A large volume of CCl$_4$ is used as organic solvent for many purposes and it thus possesses large ozone depletion potential in the stratosphere.[1] Photolysis of CCl$_4$ has been studied at several vacuum ultraviolet wavelengths, since it absorbs[2] strongly between 125 and 150 nm. In CCl$_4$, the strongest absorption band which is a doublet, arises due to two split Rydberg transitions on the chlorine atom. A weak absorption band with a maximum around 182 nm due to the $\boldsymbol{s}^* \leftarrow n$ transition centred on the C–Cl bond is also present in CCl$_4$. This molecule, however, does not exhibit any appreciable absorption in the ultraviolet.

Vacuum ultraviolet photodissociation of carbon tetrachloride has been carried out by several workers. Matsumi *et al*[3] measured the Cl*/Cl branching ratio at 157 and 193 nm and found the percent Cl* produced in the process to be small. They later modified the branching ratio upward after calibrating the resonance enhanced multiphoton ionization signal from the Cl and Cl* atoms appropriately.[4] They found that the relative quantum yield of Cl* production, $\boldsymbol{f}^*([Cl^*]/([Cl] + [Cl^*]))$ from CCl$_4$ is 0·23 at 193 nm and less than 0·13 at 157 nm. In a recent measurement Taketani *et al*[5] have reported the relative quantum yield, $\boldsymbol{f}^*$ to be 0·32 at 193 nm. Hanf *et al*[6] studied the absolute quantum yield of the chlorine atom production from CCl$_4$ at 193 and 135 nm by following the Doppler profiles of Cl*($^2P_{1/2}$) and Cl atoms. They found that at both the photolysis wavelengths the absolute quantum yield for chlorine production is higher and concluded that the two decay channels corresponding to one C–Cl and two C–Cl bond breaking are operative at these wavelengths. This is also consistent with the original photolysis pathways suggested by Rebbert *et al*[7], which are

$$CCl_4 \rightarrow CCl_3 + Cl \ (Cl^*),$$
$$E_{diss.} = 2\cdot94 \text{ eV (422 nm)}, \tag{1}$$

$$CCl_4 \rightarrow CCl_2 + 2Cl \ (Cl^*),$$
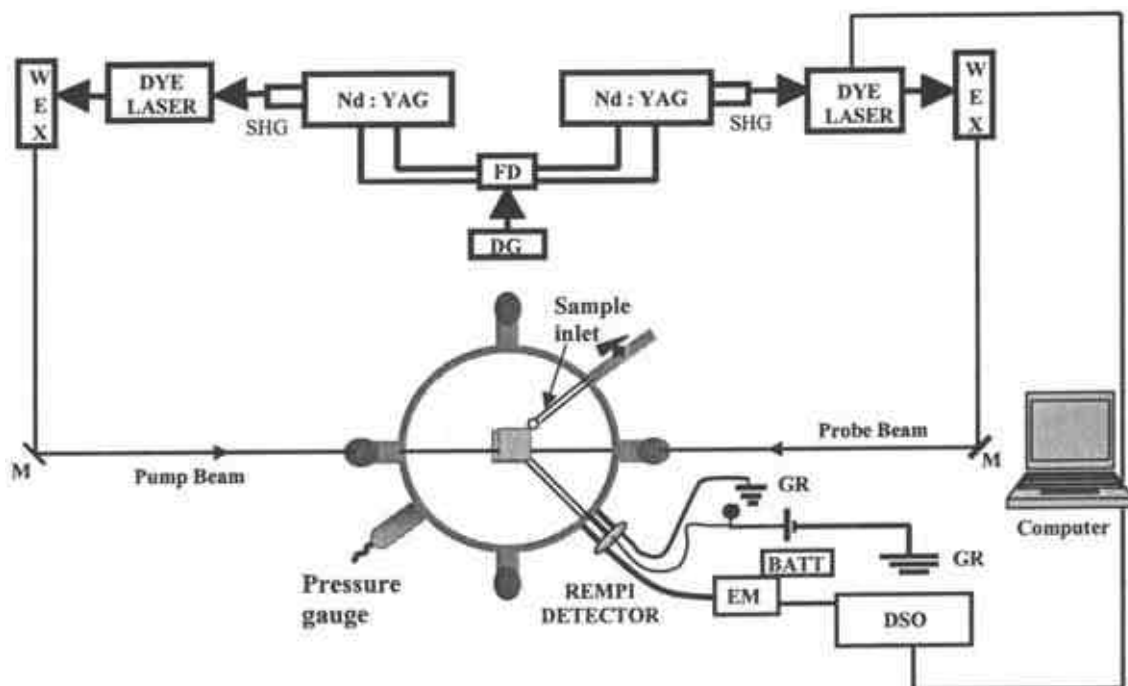$$E_{diss.} = 5\cdot91 \text{ eV (209 nm)}. \tag{2}$$

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Figure 1. Experimental set-up used in our laboratory for photodissociation experiments. WEX: wavelength extender; FD: frequency divider; DG: delay generator; SHG: second harmonic generation; GR: ground; EM: electrometer; DSO: digital storage oscilloscope; W: window; M: mirror; BATT: battery.

At all the vacuum ultraviolet (<200 nm) wavelengths both the channels are accessible. Hanf *et al*[6] showed that the absolute quantum yield is 1·0 at 214 nm and 0·9 at 254 nm. They also indicated that at low laser power only channel (1) is active for one-photon dissociation of CCl_4 at wavelengths > 200 nm.

In this paper, we report the relative quantum yield of Cl* production from the gas phase photodissociation of CCl_4 in the ultraviolet at 222 and 235 nm. At these wavelengths, only the tail of the weak $s* \leftarrow n$ transition is accessible and the energy of the photon is not sufficient to activate the second photolysis channel. Cl and Cl* atoms have been probed by the conventional REMPI detection schemes. The results are compared with those obtained from the vacuum ultraviolet photolysis.

2. Experiment

The photolysis experiments were carried out in a flow cell (figure 1) using that experimental arrangement described elsewhere.[8] Carbon tetrachloride was maintained at a constant pressure between 5 and 500 microtorr in a stainless steel chamber being pumped continuously by a diffusion pump backed by a mechanical pump. The resulting chlorine atoms in the ground and spin-orbit excited states were detected by REMPI schemes reported in the literature[9,10] using a parallel-plate homemade detector. The pump and probe lasers were overlapped in a counter-propagating alignment between the two detector electrodes inside the chamber. The pump wavelength at 222 nm was generated by mixing the doubled dye output at 280 nm with the fundamental of the YAG laser at 1064 nm in a KD*P crystal. The probe wavelength at 235 nm is generated by mixing doubled dye output at 305 nm with the YAG laser fundamental in a KD*P crystal. The incident power at 222 nm was typically 1 mJ/pulse, whereas the probe laser power at 235 nm was <1 mJ/pulse. For the 235 nm photolysis, the same pulse that photolysed the molecule was used for probing. The delay between the pump and the probe lasers was kept at ~100 ns. Low photolysis laser power was maintained throughout to avoid multiphoton dissociation. The output from the ion detector was collected through a homemade electrometer, amplified, averaged over 50 laser shots and digitized in a storage oscilloscope.
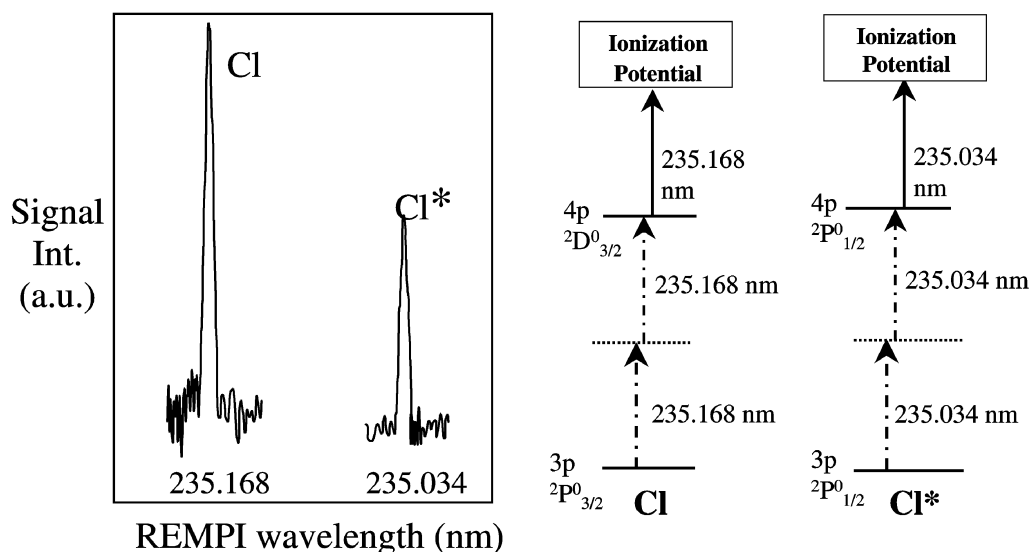
Figure 2. REMPI spectra and scheme for Cl and Cl* atoms. The spectra were obtained at 222 nm dissociation of CCl_4.

Table 1. Cl* quantum yield from CCl_4 at different wavelengths.

$f*$ at wavelength (nm)				
222	235	266	280	~304
0.35 ± 0.03	0.22 ± 0.02	ND	ND	ND

ND = not detected

3. Results and discussion

REMPI spectra for Cl and Cl* were recorded by scanning the probe laser across the $(2 + 1)$ ionization lines of Cl (235·168 nm), and Cl* (235·034 nm). The relative quantum yield of Cl*, $f* = N(Cl*)/[N(Cl) + N(Cl*)]$, was determined directly from the REMPI signal (figure 2) intensity and is listed in table 1. The ratio of the measured REMPI signals from Cl [$S(Cl)$] and Cl* [$S(Cl*)$] may be expressed as,

$$\frac{N(Cl)}{N(Cl*)} = \frac{S(Cl)}{S(Cl*)} \frac{F(Cl)}{F(Cl*)} \frac{s(Cl)}{s(Cl*)} \frac{s(CCl_4)}{s*(CCl_4)}, \qquad (3)$$

where $s*(CCl_4)$ and $s(CCl_4)$ are the absorption cross sections of carbon tetrachloride at Cl* and Cl [2 + 1] REMPI wavelengths respectively. N is the number density of the halogen atoms, F, the collection efficiency of the ion signals by the detector and $s(Cl)$ and $s(Cl*)$ are the REMPI cross-sections of the ground- and spin-orbit excited chlorine atoms. As in the $s* \leftarrow n$ absorption continuum, absorbance remains more or less constant in a narrow wavelength range (235·168–235·034 nm), we can take the ratio $s(CCl_4)/s*(CCl_4)$ as unity. The ratio of the REMPI cross-sections of Cl* and Cl has been the subject of controversy in recent times and the factor for the REMPI signal calibration has been recommended as $1·06 \pm 0·17$ by Regan *et al.*[11] We considered the collection efficiency of Cl and Cl* as unity throughout. Therefore, in the final analysis, the ratio of the signals $S(Cl)/S(Cl*)$ was multiplied by a factor of 1·06 to get the ratio of the number densities $N(Cl)/N(Cl*)$ and subsequently the quantum yield.

From table 1 it is clear that there is 60% increment in Cl* quantum yield at the dissociation wavelength of 222 nm compared to that of 235 nm. We could not detect any Cl or Cl* signal at longer pump wavelengths. At the wavelengths employed here, Cl* quantum yield is less than 0·5, which indicates that most of the chlorine atoms are produced in the spin-orbit ground state. However, direct dissociation from the excited state should produce more Cl* in this process since the parallel transition which carries most of the transition strength in the $s* \leftarrow n$ transition, correlates to the excited state chlorine atom product. The Cl* quantum yield from CCl_4 as a function of excitation wavelength has been shown in figure 3. As the absorption maximum for CCl_4 is at 182 nm and the spectrum does not extend beyond 200 nm, we do not expect a significant fragmenta-
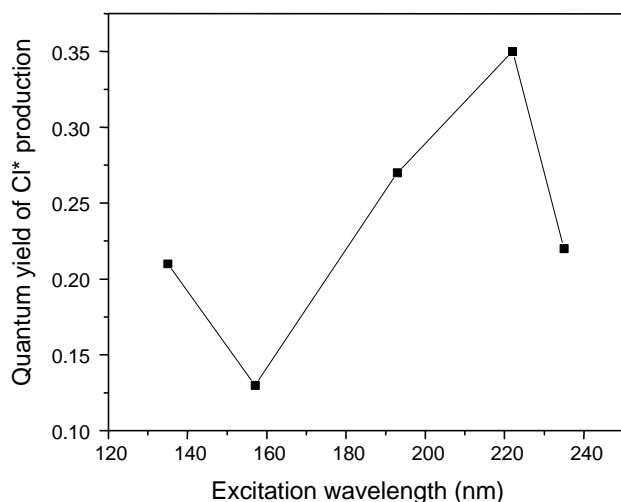
Figure 3. Cl* quantum yield as a function of the dissociation wavelength. Data at 135, 157, and 193 nm are taken from Refs [6, 3].

tion of CCl_4 at a wavelength far from the absorption maximum extending to the ultraviolet. However, the quantum yield does not follow the absorption spectrum closely and reaches a maximum at 222 nm where the absorption is very small. This suggests that the actual dynamics that the molecules undergo in the excited state is not straightforward and the C–Cl bond breaking in this molecule in the ultraviolet is complex. The variation of Cl* quantum yield as a function of excitation wavelength shown in figure 3 bears evidence that an indirect mechanism is operative since in a pure direct dissociation process one would expect the quantum yield for Cl* production to be higher than 0·5 and the dissociation yield to follow the absorption strength.

4. Conclusion

In this paper, we describe Cl* production dynamics from CCl_4 in the red edge of its first absorption band.

We find that both Cl and Cl* fragments are produced at wavelengths longer than 200 nm. When the quantum yield of chlorine production is plotted as a function of excitation wavelength, the presence of an indirect dissociation mechanism is evident. This is perhaps due to the complex motion of the molecule on the excited state potential energy surface.

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