Excited Chlorine Atoms Produced from Photodissociation of Cl₂ with Vacuum Ultraviolet Radiation

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Photodissociation of Cl₂ molecules in the wavelength region smaller than 110 nm produces strong emissions in the ultraviolet and the vacuum ultraviolet as observed previously. We show in this paper that the vacuum ultraviolet emission results from generation of electronically excited chlorine atoms, and the ultraviolet emission from molecular chlorine. That the parent state responsible for this process is a triplet state is discussed.

I. INTRODUCTION

The higher excited states of chlorine molecules have recently received much attention. By means of synchrotron radiation the absorption spectrum in the 105-140 nm wavelength region has been determined. The spectrum consists of prominent features due to both Rydberg states and ion-pair states. The fluorescence originating from these states is quite strong as discussed in these publications. Theoretical calculations on the higher excited states of chlorine molecule have also been recently published by Peyerimhoff and Buenker and Grein et al. They provide useful guidance for the interpretation of experimental data. In general the agreement between the theoretical calculations and the experimental results is quite good.

The ground state of the chlorine molecule has the electron configuration:

\[ (\sigma_g 3s)^2(\sigma_g 3s)^2(\sigma_g 3p)^2(\pi_u 3p)^2(\pi_u 3p)^4 \]

briefly written as \((a,)^6 (\pi_u)^4(\pi_u)^4\). The excitation of the \(\pi_u\) electron into higher Rydberg orbitals 4\(\pi\), \(1^1\Sigma_u^+\) state and \(4\pi\alpha(2^1\Sigma_u^+)\) produced strong emissions in the ultraviolet (UV, \(\lambda > 200\text{nm}\)) and vacuum ultraviolet (VUV, \(\lambda < 200\text{nm}\)) region as discussed in Ref. 1-3.
Møller et al. investigated extensively the nature of the $1 \Sigma^+_u$ excited state.

As shown in Ref. 1, the excitations of Cl$_2$ at wavelengths above the ionization threshold at 108 nm produce strong vuv and uv emissions. Because the emission was observed at excitation wavelengths smaller than about 110 nm, by considering the energy which is insufficient to produce the chlorine atoms in the $2 \Sigma$ excited state for the emission at 134.7 nm, these authors ruled out the possibility of the $2 \Sigma^+ \rightarrow 3 \Pi$ transition. It was also found that the UV emission depends quadratically on the pressure of molecular chlorine. The excitation spectrum for this fluorescence process is shown in Fig. 1.

![Excitation spectrum](image)

**FIG. 1** Excitation spectrum to produce uv and vuv emission from Cl$_2$ from Ref. 1

It is the purpose of this report to unravel the nature of the sources for UV and VUV emission generated by exciting Cl$_2$ at wavelengths above the ionization limit. In general excitation of a gas with photon energy greater than the ionization threshold leads mainly to ionization process. In contrast, the case for molecular chlorine indicates that the fluorescence process is dominant.

**II. EXPERIMENTAL**

A fast flow system was constructed for this experiment. This system consists of a stainless steel fluorescence cell connected with one inch pyrex tubing for gas inlet and control of the process. The fluorescence cell was painted black inside to eliminate stray light. A light source and detector were attached to this cell. VUV light generated by a microwave-discharged argon lamp produced emissions at 106.6 and 104.8 nm from resonant transitions of argon atoms. A LiF crystal was generally used as the lamp window to separate the discharge gas from the chlorine gas, but occasionally this window was removed to increase the
VUV intensity because LiF window is known to have a transmission limit near 104 nm. According to the literature, the intensity of the 106.6 nm light is weaker at low pressure than the 104.8 nm light. Fluorescence produced from the excitation of Cl₂ was dispersed with a VUV monochromator (Acton VM502) combined with a photomultiplier tube (PMT). The monochromator was isolated from the system by a magnesium fluoride window. Two types of photomultiplier tubes were used: one for the VUV (Hamamatsu R1459) which measures light with wavelength smaller than 200 nm and one for the UV-visible (EM1 model 9789QB) which is sensitive to light in the wavelength range 160-650 nm. As the VUV photomultiplier tube has a MgF₂ window, it can detect light of wavelength only greater than 115 nm. This tube is capable of detecting emissions from Cl atoms but not monitoring the lamp emission at 106.6 or 104.8 nm. Photon signals were processed by a preamplifier, amplifier, and ratemeter/counter and recorded by a X-Y recorder and microcomputer. The experimental setup is shown in Fig. 2.

FIG. 2 Schematic diagram for the experimental setup.

Traces of molecular chlorine of about 20 mtorr entered into the flow system through the Pyrex tube and were carried by nitrogen or argon. The total pressure in the system was about 1 torr controlled by a mechanical pump with flow capacity of 500 liters per minute (Welch 1397).

Chlorine gas obtained from Matheson with a stated purity of 99.9%. Argon and nitrogen were supplied by San-Fu with purity 99.99%.
III. RESULTS

Excitation of Cl$_2$ by the Ar discharge lamp produced strong VUV emissions as measured with our solar-blind PMT. Dispersion of the emission spectrum showed that the emission centred mainly about 139 nm but with a small signal at 135 nm as shown in Fig. 3.

From the spectroscopic data$^{8,9}$, we found that the emission was produced from the electronically excited quartet state of the chlorine atom with the electron configurations $(3\sigma^2)(3\pi)^{-} (4\sigma^4)(4\pi^4)$ for the 139 nm group and $(3\pi^2)(4\sigma^4)(4\pi^4)$ for the 135 nm. The energy levels of atoms chlorine are shown in Fig. 3.

The energy required to produce these excited states is thus:

$$\text{Cl}, + \text{hv} \rightarrow \text{Cl}^*(^2\Pi) + \text{Cl}^*(^4\Pi_{1/2}) \quad E = 11.40 \text{ eV} (108.8 \text{ nm})$$

$$\text{Cl}^*(^4\Pi_{3/2}) \quad E = 11.47 \text{ eV} (108.1 \text{ nm})$$

$$\text{Cl}^*(^4\Pi_{5/2}) \quad E = 11.51 \text{ eV} (107.7 \text{ nm})$$

$$\text{Cl}^*(^4\Pi_{3/2}) \quad E = 11.68 \text{ eV} (106.1 \text{ nm})$$

$$\text{Cl}^*(^4\Pi_{1/2}) \quad E = 11.76 \text{ eV} (105.4 \text{ nm})$$

Evidently the 106.6 nm line is responsible for the production of the excited states in the first group at 138 nm, while the 104.8 nm line for the second group at 135 nm.

The authors in Ref. 1 did not consider the production of quartet states as a possible channel. Because coupling of the electronic angular momenta in the Cl atom is inter-
The UV emission spectrum of Cl₂, in which Dᵢ - Aᵢ and Dᵢ - A transitions are tentatively assigned.

mediate between L-S and J-J coupling, the ⁴P - ²P transition is partially allowed. The transition probability for each of these multiplets is shown in Table I.

TABLE I. Wavelengths and Einstein coefficients for ²P and ⁴P transitions*

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Upper state</th>
<th>Lower state</th>
<th>A_{ki} (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>133.57</td>
<td>²P₁/₂</td>
<td>²P₃/₂</td>
<td>1.74x10⁸</td>
</tr>
<tr>
<td>135.16</td>
<td>²P₁/₂</td>
<td>²P₃/₂</td>
<td>3.23x10⁸</td>
</tr>
<tr>
<td>134.72</td>
<td>²P₃/₂</td>
<td>²P₃/₂</td>
<td>4.19x10⁸</td>
</tr>
<tr>
<td>136.35</td>
<td>²P₁/₂</td>
<td>²P₃/₂</td>
<td>7.5x10⁷</td>
</tr>
<tr>
<td>138.97</td>
<td>⁴P₅/₂</td>
<td>²P₃/₂</td>
<td>2.3x10⁵</td>
</tr>
<tr>
<td>137.95</td>
<td>⁴P₃/₂</td>
<td>²P₃/₂</td>
<td>1.1x10⁷</td>
</tr>
<tr>
<td>139.65</td>
<td>²P₁/₂</td>
<td>²P₃/₂</td>
<td>1.5x10⁶</td>
</tr>
<tr>
<td>137.31</td>
<td>⁴P₁/₂</td>
<td>²P₃/₂</td>
<td>2.9x10⁵</td>
</tr>
<tr>
<td>138.99</td>
<td>²P₁/₂</td>
<td>²P₃/₂</td>
<td>1.7x10⁶</td>
</tr>
</tbody>
</table>

* Quoted from Ref. 8

The UV emission reported in Ref. 1 was found to originate from the transition Dᵢ - Aᵢ and possibly other systems. However, the signal was not very strong. The assignment could...
not be unambiguously made. Part of the emission spectrum is shown in Fig. 4.

IV. DISCUSSION

The ground state of Cl₂ molecule is \( ^1\Sigma^+_g \). The higher electronic states of this molecule were assigned in Ref. 1 for wavelengths greater than about 110 nm. The states at wavelengths shorter than 110 nm are not well understood. The excited state corresponding to the production of the excited chlorine atom should be a singlet \( ^2\Pi \) or \( ^2\Sigma \); if the selection rule is obeyed. Because spin conservation may not hold rigidly, as in the case of the Cl atom, the triplet upper state should also be considered.

The intensity of the emissions from excited Cl atoms can be estimated according to:

\[
I = \frac{[\text{Cl}^*]}{\tau} = A \cdot [\text{Cl}^*] = A F \sigma_{\lambda} \text{Cl}_2
\]

[photons s⁻¹]

\[
I(138)/I(135) = \frac{A(^4\Pi)[\text{Cl}^* (^4\Pi)]/A(^2\Pi)[\text{Cl}^* (^2\Pi)]}{\sigma_{\lambda} F_{106.6} \text{ Cl}_2}
\]

\[
= \frac{A(^4\Pi)/A(^2\Pi)(F_{106.6} \text{ Cl}_2)}{F_{104.8} \sigma_{\lambda} F_{104.8} \text{ Cl}_2}
\]

in which \( \tau = l/A \) is the radiative lifetime and \( A \) the Einstein coefficient of the excited state given in Table I. The lamp flux \( F \) at the given wavelength is unknown. \( \sigma_{\lambda} \) is the cross-section for the production of the observed emission. The line at 104.8 nm is energetically sufficient to produce the excited states \( \text{Cl}(^2 \Pi) \) and \( \text{Cl}(^2 \Pi) \), but the 106.6 nm line can produce only the excited state \( \text{Cl}(^4 \Pi) \). Here we assume that the cross-sections for the production of \( \text{Cl}(^4 \Pi) \) and \( \text{Cl}(^2 \Pi) \) by the 104.8 nm line are different.

The ratio of the \( A \) coefficients for 134.7 and 137.95 nm is about 38 as determined from values given in Table I. However, the ratio of the intensities at 137.95 and 134.7 nm is about 10, as determined from Fig. 3. Thus the number of \( \text{Cl}(^2 \Pi) \) is produced \( 1/380 \) times smaller than the \( \text{Cl}(^4 \Pi) \). By examination of Fig. 1, one might infer that the cross-section for the production of the excited states at 104.8 nm is much larger than the value at 106.6 nm, the photodissociation process at 104.8 nm lying in the tail of a broad dissociation curve covering the wavelength range 105-1 10 nm. The original experimenters in Ref. 1 did not extend their measurements beyond 105 nm; however our observation does not disagree with the trend of the existing data.

It is possible that the LiF window attenuated the 104.8 nm line so much that the yield of \( \text{Cl}(^2 \Pi) \) was small. However, when experiments were also conducted by removing the LiF window to ensure that 104.8 nm was passed, similar results were obtained.

According to the Wigner correlation rule the molecular states associated with the \( \text{Cl}(^2 \Pi) + \text{Cl}(^4 \Pi) \) are triplet or quintet states of the following symmetry: \( \Sigma^+, \Sigma^-, \Pi, \Pi, \text{A} \), and the molecular states correlated with \( \text{Cl}(^2 \Pi) + \text{Cl}(^2 \Pi) \) are triplet and singlet states of the same symmetries as above. We exclude the quintet state as it severely violates the transition law.
even for the case of \( J J \) coupling (\( \Omega - \Omega \) coupling here). A triplet excited state is therefore likely responsible for the dissociative continuum at 105–1 10 nm.

Theoretical calculations indeed found a \( ^3\Pi_0 \) state that dissociates into \( \text{Cl}(^3P) + \text{Cl}(^4P) \) as shown by Peyerimhoff and Buenker\(^4\). They also showed that this excited state is a Rydberg state of \( \pi_u \rightarrow 4s \) transition with a calculated vertical excitation energy \( 1.3 \text{ eV} \) in excellent agreement with the experimental value.

Lee et al. observed that the UV emission depends quadratically on the gas pressure. This result may be explained as due to the production of the excited molecule \( \text{Cl}_2 \) (\( D' \)) according to the following process:

\[
\text{Cl}_2 + \nu \rightarrow \text{Cl}(^3P) + \text{Cl}^*(^4P)
\]

\[
\text{Cl}^*(^4P) + \text{Cl} \rightarrow \text{Cl} + \text{Cl}^*(D')
\]

The excited \( ^2P \) state of the Cl atom can be eliminated due to its short lifetime (2-3 ns) which could not survive one collision period. Thus the UV emission depends on the chlorine gas pressure quadratically. The energy of the excited quartet state of Cl atom is 8.9 eV whereas the \( D' \) state of molecular chlorine has \( T_J = 7.1 \text{ eV} \). Therefore the energy transfer process is allowed. The \( D' \rightarrow A' \) transition has been discussed by Tellinghuisen and Chakrabarty\(^6\). Other possible transitions are D-A and E-B. Further work using higher resolution is needed to clarify these features.

Therefore the production of an excited Cl atom in the \( ^4P \) state is consistent with the previous observation of strong UV and VUV fluorescence in the photodissociation of Cl, at wavelengths shorter than 110 nm.

VI. CONCLUSION

Using VW radiation generated from an Ar resonance lamp we have identified the UV and VUV emissions produced from molecular chlorine at wavelengths less than about 1 10 nm given in Ref. 1. The \( \text{Cl}(^4P) \) atom provides the strong emission at 137.95 nm. and the subsequent reaction of this excited species with the parent gas to produce excited \( \text{Cl}_2 \) in \( D' \) or \( E' \) excited states produces the UV emission. The excited states responsible for this process have also been briefly discussed.
REFERENCES