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# Direct observation of the $D'\ 2_g(^3P_2)$–$A'\ ^3\Pi(2_u)$ system for $Cl_2$ by laser induced fluorescence spectroscopy: Determination of the absolute position of the $A'$ state

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## Abstract

In a discharged supersonic jet of $Cl_2$, transitions of the $D'\ 2_g(^3P_2)$–$A'\ ^3\Pi(2_u)$ system for $^{35}Cl_2$ were observed directly by laser induced fluorescence spectroscopy. By a discharge in $Cl_2$, the $Cl_2$ molecules were populated into the $A'$ state, which is a metastable and optically forbidden state, from the $X\ ^1\Sigma_g^+(0_g^+)$ state. An ultraviolet laser radiation excites the molecules to the $D'$ ion-pair state. A set of Dunham parameters for the $A'$ state is determined from a global least-squares fitting for 59 vibronic bands with $v'' = 0$–$7$. In the fitting, the previously reported data, $T(v)$ and $B(v)$ for the $v = 14$ and 15 bands of the $A'$ state [T. Ishiwata, A. Ishiguro, K. Obi, J. Mol. Spectrosc. 147 (1991) 300–320], were included. $Y_{00} = 57295.723(5)\ \mathrm{cm}^{-1}$ of the $D'$ state [J.-H. Si, T. Ishiwata, K. Obi, J. Mol. Spectrosc. 147 (1991) 334–345] was also included in the global fitting in order to determine the absolute position of the $A'$ state. The determined parameters of the $A'$ state are $Y_{00} = 17171.506(14)$, $Y_{10} = 255.915(85)$, $Y_{20} = -4.465(70)$, $Y_{30} = -8.7(23)\times10^{-2}$, $Y_{40} = 6.3(35)\times10^{-3}$, $Y_{50} = -4.9(26)\times10^{-4}$, $Y_{60} = 1.43(69)\times10^{-5}$, $Y_{01} = 0.16282(15)$, $Y_{11} = -2.363(68)\times10^{-3}$, $Y_{21} = -5.01(93)\times10^{-5}$, and $Y_{31} = -3.01(36)\times10^{-6}$ (in $\mathrm{cm}^{-1}$ and one standard deviations of the fit in parentheses). The absolute position of the $A'$ state is determined with good accuracy.

*Keywords:* $Cl_2$; Dunham parameters; $A'$ state; $D'$ state; Valence state; Metastable; LIF

## 1. Introduction

$Cl_2$ is one of the typical diatomic halogen molecules, which has been studied extensively. A large number of electronic states have therefore been observed for $Cl_2$, and detailed spectroscopic constants have been reported [1]. In 1922 Angerer showed a presence of a strong emission of $Cl_2$ near 258 nm [2]. The transition has been historically known as the *E*–*B* band of the pure halogens [3,4]. Bondybey and Fletchar have observed this state by a matrix isolation study [5]. They suggested that $A'$ might be the lower state of the strong emission system which peaks near 258 nm. In 1987 Tellinghuisen and Chakraborty have reexamined the emission [6] with a tesla discharge, and identified the band to the $D'\ 2_g(^3P_2)$–$A'\ ^3\Pi(2_u)$ system. In 1988, Tellinghuisen et al., observed and analyzed rotationally resolved spectra of this system and reported spectroscopic constants of $A'$ and $D'$ [7]. However, the constants are not sufficiently accurate because they did not observe bands with $v'' = 0$ and 1 in their high resolution spectra.

In the early 1990s, Ishiwata and co-workers studied many electronic states of $Cl_2$ by an optical–optical double resonance (OODR) technique. In these experiments, they found heterogeneous couplings of the $A\ ^3\Pi(1_u)$ state with other valence states, $A'\ ^3\Pi(2_u)$, $B\ ^3\Pi(0_u^+)$, and $B'\ ^3\Pi(0_u^-)$ [8]. Although transitions from valence to ion-pair states occur according to the $\Delta\Omega = 0$ selection rule for parallel transitions, Ishiwata et al., were able to observe a lot of ion-pair states through the perturbed $A$ state using OODR

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spectroscopy. They have thus determined a large number of spectroscopic constants for not only the valence state, $A$, but also the ion-pair states, $E\ 0_g^+(^3P_2)$, $\beta\ 1_g(^3P_2)$, $D'\ 2_g(^3P_2)$, $1_g(^3P_1)$, and $0_g^-(^3P_1)$ at high accuracy [9–13]. However, in the case of the lowest excited valence state, $A'$, which is the $\Omega = 2$ component of a $^3\Pi$ multiplet, there have been few efforts to determine the spectroscopic constants for the state, because it is difficult to observe the $A'$ state.

Recently Kokh et al., have reported potentials of the ion-pair states using ab initio calculations considering the spin-orbit coupling [14]. They have also reported radiative characteristics of these states; especially dipole transition moments connecting various ion-pair states with low-lying valence states. As a result, they have succeeded in explaining the experimental results reported previously.

In the present experiment, we have observed the direct transition of the $D'$–$A'$ system using a laser induced fluorescence (LIF) spectrometer in combination with a pulsed-discharge nozzle (PDN). $Cl_2$ molecules are populated to the metastable $A'$ state by discharging $Cl_2$ in the PDN. A probe laser then excites the molecules to the $D'$ state. We were able to determine the spectroscopic constants and the RKR-potential of the $A'$ state for $^{35}Cl_2$.

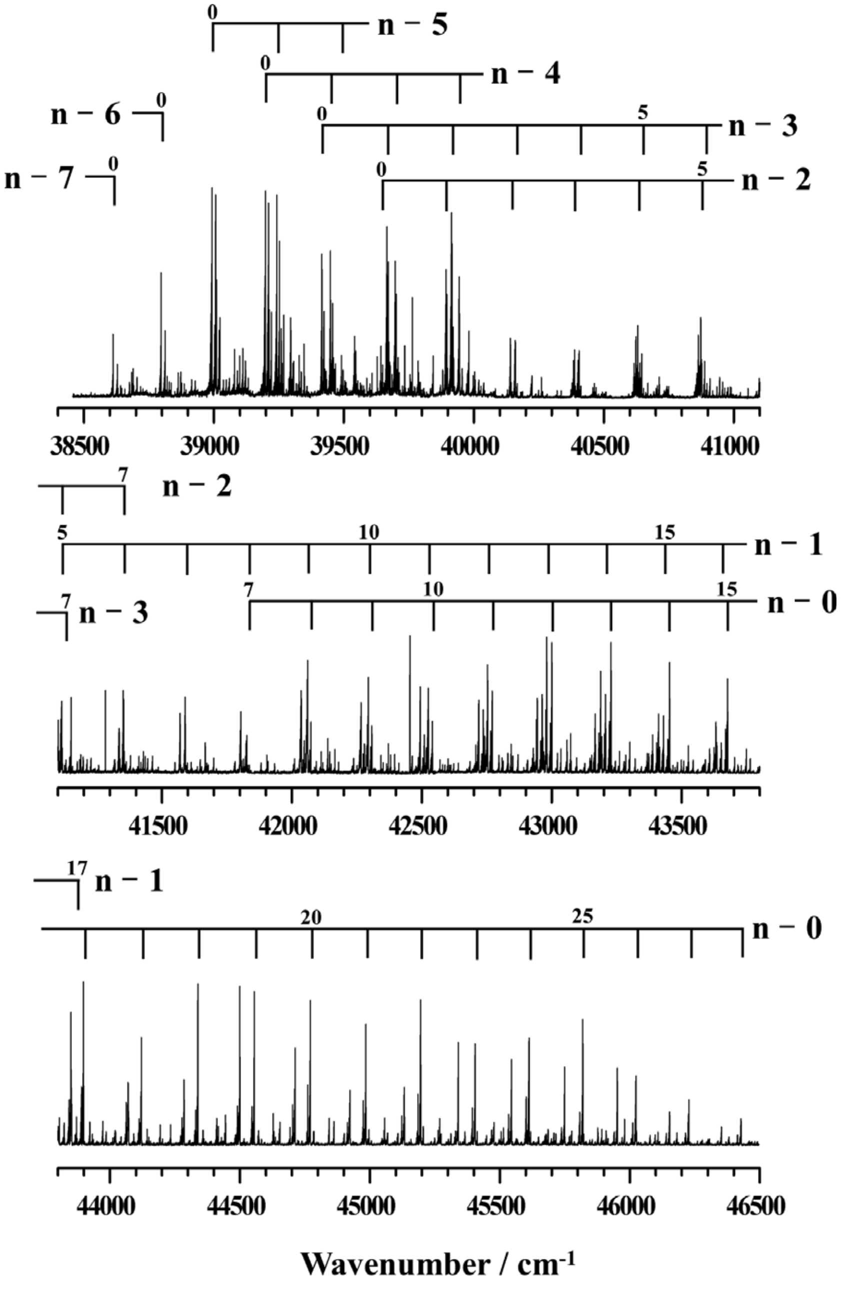

Fig. 1. LIF excitation spectrum of $Cl_2$. Vibrational assignments are shown in the solid lines ($v'$–$v''$). The observed spectrum is very complex because of the existence of three isotopomers ($^{35}Cl_2$, $^{35}Cl^{37}Cl$, and $^{37}Cl_2$) and two systems ($D'$–$A'$ and $\beta$–$A$).