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CRDS 法による塩素錯体検出

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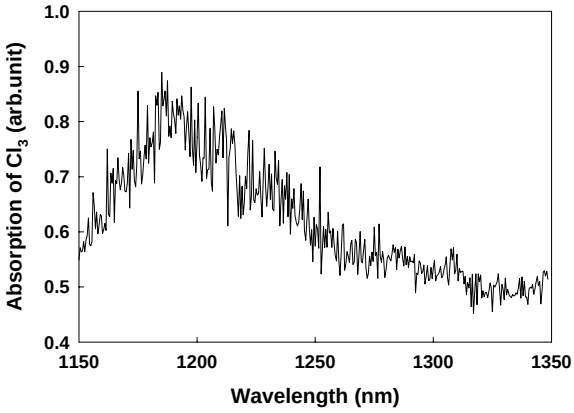
We have reported the direct observation of the weakly bound Cl-M (M = Cl_2, O_2, RI, CH_3SCH_3) complexes using cavity ring-down spectroscopy (CRDS) in low temperature and moderate pressure conditions. Theoretical calculations confirmed the present experimental results. The bond lengths and bond energies for Cl-M are summarized in Table 1.

[Cl-Cl_2] We have firstly reported the broad absorption of Cl_3 radicals in the near IR region using cavity ring-down spectroscopy with an OPO laser. The mechanism for Cl atom reaction with Cl_2 is:



$$Cl + Cl_2 + M \underset{\leftarrow}{\overset{\rightarrow}{}} Cl_3 + M \qquad (1, -1)$$

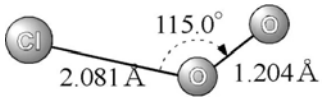
$$Cl_3 + Cl \rightarrow 2Cl_2 \qquad (2)$$

The pressure and temperature dependence of the formation of Cl_3 was experimentally investigated. The rate constants of reaction 2 were determined. The equilibrium rate constants of reactions 1, -1 were determined theoretically as well as the ground state structure of Cl_3. We concluded that the Cl-Cl_2 complex is of a van der Waals complex type. The Cl-Cl_2 bond dissociation energy is determined to be 0.9 kcal mol^{-1} [1]

[Cl-O_2] The equilibrium constants for the formation of ClOO from Cl and O_2 are experimentally measured at 212 – 245 K.

$$Cl + O_2 \underset{\leftarrow}{\overset{\rightarrow}{}} Cl\text{-}O_2 \qquad (3)$$

A van't Hoff plot analysis yields $\Delta H_r = 4.8 \pm 1.5$ kcal mol^{-1}. The bond dissociation energy is determined to be 4.67 ± 0.06 kcal mol^{-1} based on the third-law analysis of the present and previously reported temperature dependence of the equilibrium constants.[2] The reaction of ClOO



with NO was also investigated to determine the reaction branching ratios at $T = 213$ K.[3]

$$Cl\text{-}O_2 + NO \rightarrow ClNO + O_2 \quad (4)$$
$$\rightarrow ClO + NO_2 \quad (5)$$

[Cl-IR] The visible absorption spectra of RI-Cl (R = CH_3, C_2H_5, C_3H_7, C_4H_9, CH_2I, CH_2Br, CH_2Cl, *cyclo*-C_6H_{11}, C_6H_5, C_6F_5, *p*-$CH_3C_6H_4$) were firstly observed in the gas phase. Those complexes do not react with O_2 at $T < 263$ K. The complex formation occurs via the charge transfer mechanism since the absorption intensity is well correlated with the ionization potential of the corresponding RI.[4,5]

[Cl-S(CH_3)$_2$] The complex formation of Cl atom with CH_3SCH_3 was observed in the UV region.[6] The following rate constants and structure of the complex are determined.

$$Cl + CH_3SCH_3 + M \underset{\leftarrow}{\rightarrow} Cl\text{-DMS} + M \quad (6a, -6a)$$

$$Cl + CH_3SCH_3 \rightarrow HCl + CH_3SCH_2. \quad (6b)$$

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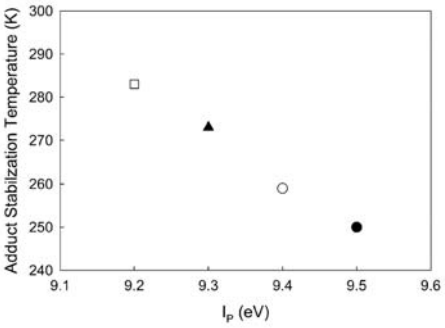

Table 1 Summary of Cl-M complexes

Cl-X	Bond length (Å)	Bond energy D_0 (kJmol^{-1})
Cl-Cl_2	3.6	3.6 [a]
Cl-OO	2.1	19.5 [b]
CH_3I-Cl	2.9	59.0 [c]
C_6H_5I-Cl	2.9	56.5 [d]
CH_3S(-Cl)CH_3	2.6	74.1 [e]

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