Photochemistry of Cyanogen Chloride
in the 40 - 120 nm Region

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In the vacuum UV photodissociation of ClCN, $CN(B^2\Sigma^+)$ and $CN(A^2\Pi_i)$ are produced as excited photofragments and subsequent CN(B-X) and CN(A-X) emissions have been observed in the UV and visible region and in the near infrared region, respectively. For the wavelength range shorter than 105 nm, little has been known about the high-lying electronic states of ClCN because of the lack of a radiation source available for the photoabsorption measurements. In the present study, by taking advantage of the window-less experimental configuration at BL2A of UVSOR, absolute cross section for the formation of CN(B) are determined in the wavelength range 40-120 nm. The relative cross section for the $CN(A^2\Pi_i)$ production was also measured. In the 90-120 nm region, the photoabsorption spectrum and photoexcitation spectrum have been measured by use of an Ar gas filter, instead of a LiF window, which was mounted in front of the absorption cell, in order to eliminate the secondary light of a incident SOR beam. Typical pressure of Ar in the gas filter was 270 mTorr. For the measurement in the 40-90 nm region, any gas was not introduced to the gas filter.

The electronic configuration of ClCN in the ground electronic state is[2]

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(3\sigma)^2(2\pi)^4; {}^1\Sigma^+.$$
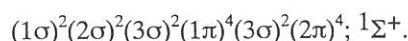
The first ionization potential (IP) of ClCN is reported to be 99770 cm^{-1} (100.2 nm) for the production of ClCN$^+$ in the $^2\Pi_{1/2}$ manifolds. The second IP associated with the $^2\Sigma^+$ ionic state is located at 111300 cm^{-1} (89.8 nm). In Fig. 1, the absolute cross section is plotted against the excitation wavelength in the range 30-150 nm, respectively. A broad, structureless continuum was observed below 90 nm, above the second IP. Numerous peaks have been observed in the wavelength region $\lambda > 90$ nm. The absorption peaks, in the 90-100 nm region have been assigned to the transitions to the super-excited states. These super-excited states have been associated with the Rydberg series converging to the second IP. As a result, almost absorption bands below the second IP can be assigned to the Rydberg transitions converging to these first and second IPs or intravalence transitions.

The absolute cross section for the production of CN(B) was determined by a comparison of the intensity of the CN(B-X) emission produced in the photodissociation of HCN.[3] The quantum yield was calculated as the

ratio of the emission cross section to the absorption cross section.　As shown in Fig. 2, the quantum yield for the production of CN(B) takes maximum value　~0.13 at 119 nm.　It appears that the dominant photodissociation channels in the wavelength region $\lambda > 119$ nm lead to the production of CN fragments in $X^2\Sigma^+$ and/or $A^2\Pi_i$ states.　As shown in Figs. 2 and 3, the cross section for the production of excited CN fragment decreases drastically down around 100 nm, due provably to the preferential operation of ionization in the energies above the first ionization potential.

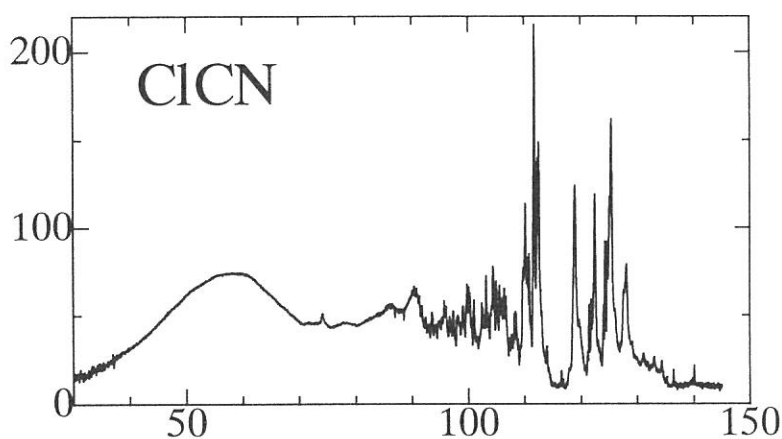Fig.1　The absorption cross sections of ClCN in the 30-150 nm region. The spectral solution was 0.1 nm.

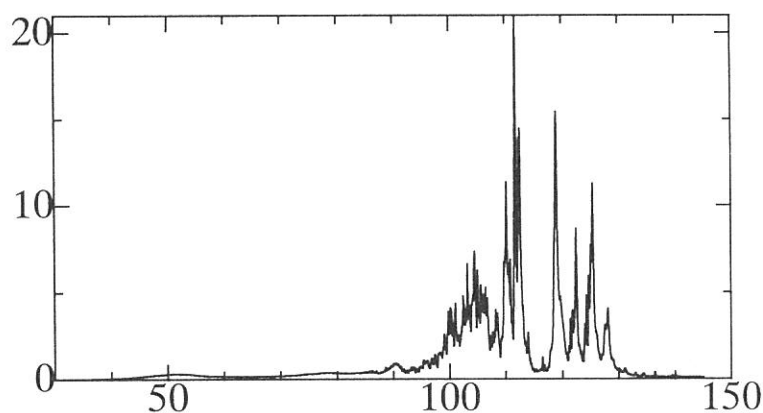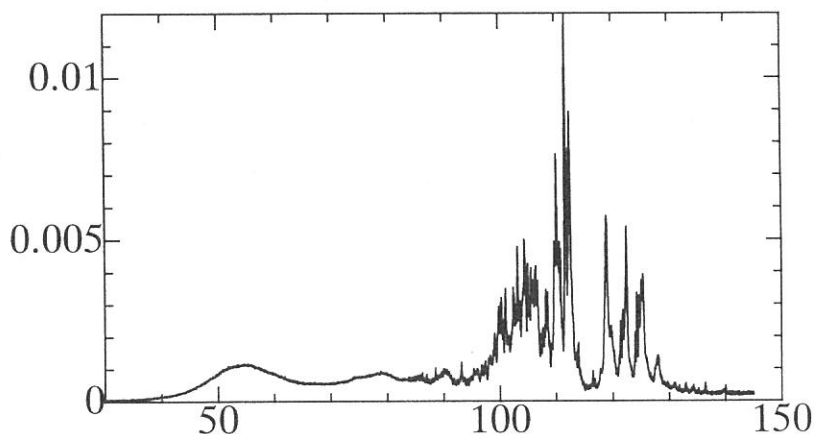Fig.2 Absolute cross section for the production of CN(B) from ClCN.

Fig.3 Absolute cross section for the production of CN(A) from ClCN

Reference

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Dissociative Excitation of HCOOH by Single- VUV and Two- UV Photon at 124 nm Region.

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Dissociative excitation of HCOOH was studied by single- VUV photon absorption at 124.5 nm with SR source, and by two- UV photon absorption at 249 nm with KrF laser. Nascent rotational and vibrational (V/R) state distributions of $OH(A^2\Sigma^+)$ produced via the photodissociation, HCOOH + $nh\nu$ (n=1, 2) $\rightarrow$ HCO + $OH(A^2\Sigma^+)$ were determined by computer simulation analysis of the dispersed fluorescence spectra. The internal state distributions were found to be of the relaxed type, and rotational distribution could be approximated by a Boltzmann distribution.(Fig.I) One- VUV photon excitation gave the best-fit rotational temperature $T_r(v'=0)$= 3000 K and vibrational population ratio $N_{v'=1}/N_{v'=0}$=0.14, while two- UV photon excitation showed $T_r(v'=0)$=2000 K with $N_{v'=1}/N_{v'=0}$=0.12. Possible mechanisms for the OH(A) formation by both excitation sources were examined based on simple theoretical models. The degree of internal excitation is not consistent with a direct dissociation on a repulsive surface, and a dissociation from a long-lived intermediate state, neither. The formation of $OH(A\Sigma^+)$ is interpreted as dissociation of an electronically excited intermediate state leading to the formation of OH(A)+CHO, populated competitively via an electronic predissociation process. The substantially different V/R distributions observed are dependent on the excited precursor state initially accessed, and may result from the constraint in the competing predissociation step that follows.
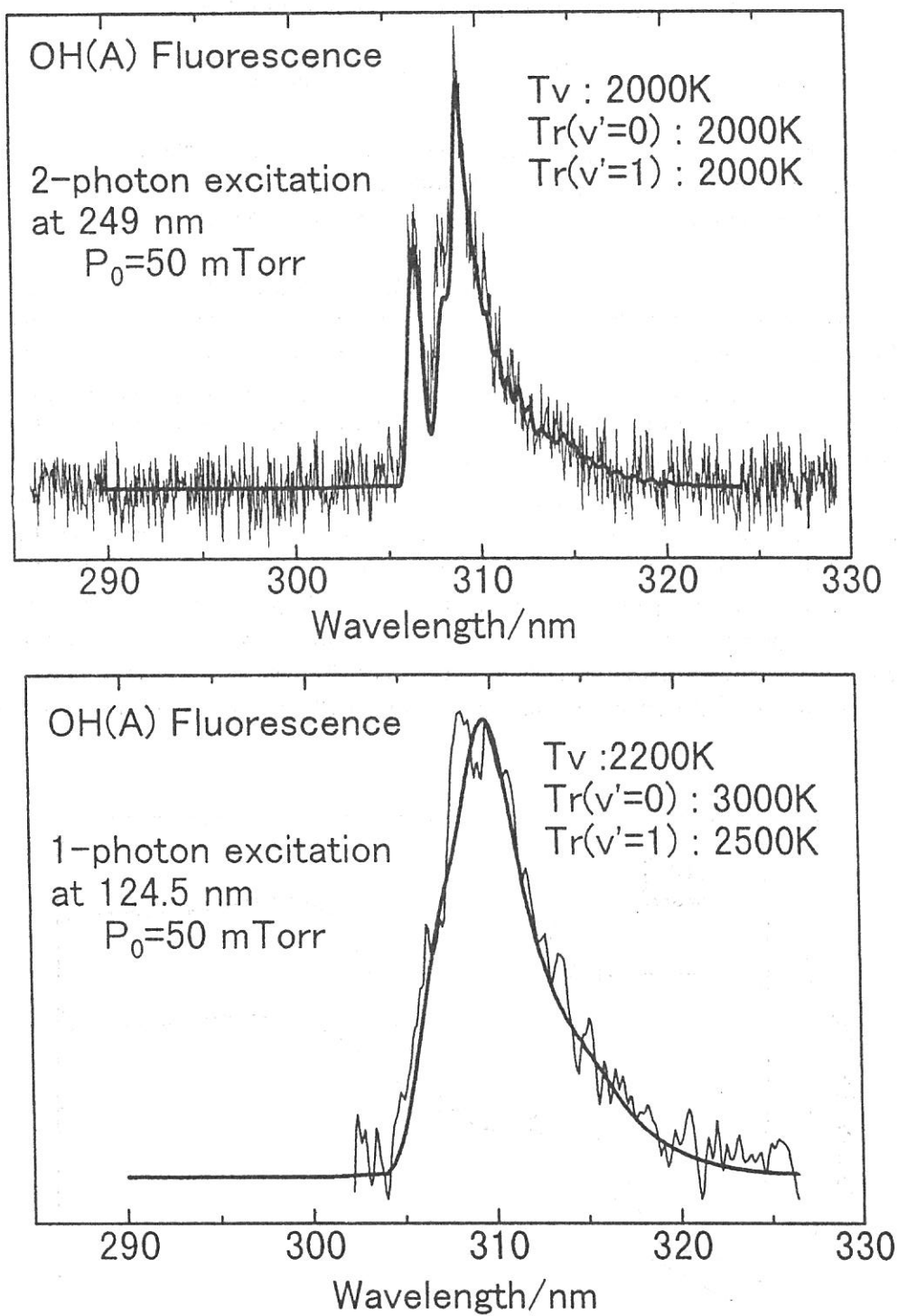
OH(A) Fluorescence

Tv : 2000K
Tr(v'=0) : 2000K
Tr(v'=1) : 2000K

2-photon excitation
at 249 nm
P_0=50 mTorr

Wavelength/nm

OH(A) Fluorescence

Tv :2200K
Tr(v'=0) : 3000K
Tr(v'=1) : 2500K

1-photon excitation
at 124.5 nm
P_0=50 mTorr

Wavelength/nm

Fig. I.   Experimetal and computer simulated spectra of OH(A-X) produced
with one-VUV and two-UV photon excitation of HCOOH at 124.5 nm.
Upper spectrum; spectral resolution was 0.83 nm.
Lower spectrum; spectral resolution was 2.4 nm.

(BL2A)

Fundamental Absorption Spectra of Solid HBr

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Absorption spectra have been obtained for solid HBr films deposited on LiF single crystals at liquid nitrogen temperature(-177°C) in the 5–10 eV region. The base pressure of the sample chamber was 2×10^{-6} Torr. The absorption measurements were carried out warming the sample from -177°C to -82°C. The preliminary result is shown in Fig. 1. The thin and thick curves show the spectra for the samples as deposited(-177°C) and at -118°C, respectively. The optical density of the spectrum at -118°C is larger than that at -177°C. This may be due to the contamination of the sample with residual gases. Both spectra show broad spectral shapes, which are not found in gaseous HBr showing complicated vibronic structures [1]. This feature is different from that in usual molecular crystals, in which the spectral profile of the individual molecule remains well. Two peaks around 6.5eV became clearer in the sample at -118°C than in the sample as deposited. The energy separation of the peaks is 0.5eV, which corresponds to the spin-orbit splitting of Br^- ion. These peaks are regarded as excitonic peaks. The electronic structure of solid HBr seems not to resemble that of gaseuos HBr, but to resemble to those of NaBr crystal[2] and solid Kr[3] though the excitonic peaks in solid HBr are not as sharp as those in these materials.
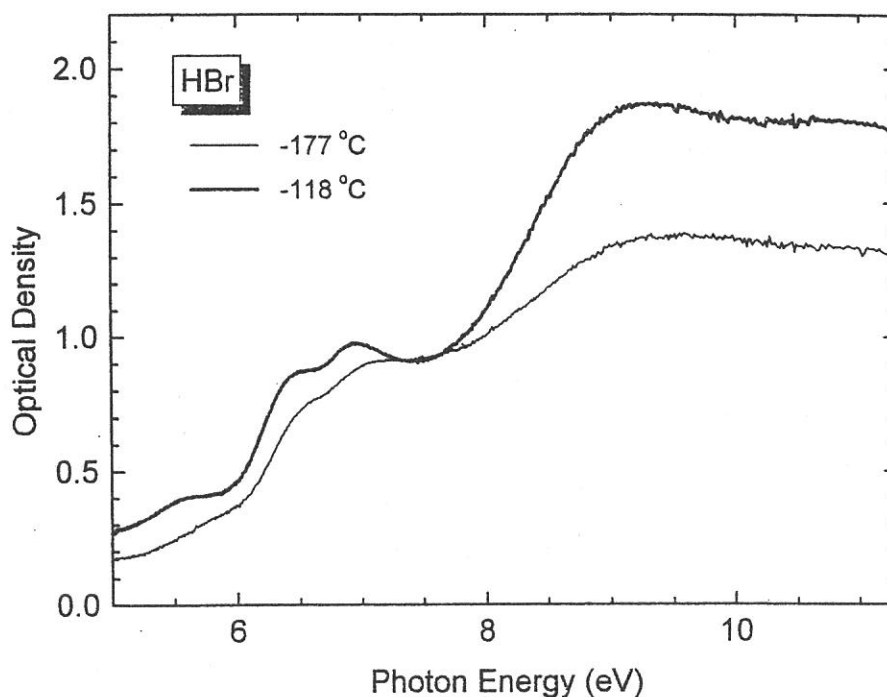

Fig.1 Absorption spectra of solid HBr.

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2. J. E. Eby, K. J. Teegarden and D. B. Dutton, Phys. Rev. **116** (1959) 1099.
3. G. Baldini, Phys. Rev. **128** (1962) 1562.