Photodissociation spectroscopy of cyanogen halides in the extreme vacuum ultraviolet region

Kazuhiro Kanda [a,*], Mitsuhiko Kono [b], Kosuke Shobatake [c], Toshio Ibuki [d]

[a] *Laboratory of Advanced Science and Technology for Industry, University of Hyogo, Kamigori, Hyogo 678-1205, Japan*
[b] *Research School of Physical Sciences and Engineering, The Australian National University, Canberra, ACT 0200, Australia*
[c] *Department of Materials Chemistry, School of Engineering, Nagoya University, Chikusa-ku, Nagoya 464-8601, Japan*
[d] *Faculty of Education, Kyoto University of Education, Fushimi-ku, Kyoto 612-8522, Japan*

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Abstract

Photodissociation of cyanogen halides, ClCN, BrCN and ICN, was investigated using synchrotron radiation. The absolute cross-sections for the photoabsorption and the production of $CN(B^2\Sigma^+ - X^2\Sigma^+)$ emission were determined in the wavelength range of 50–180 nm (200,000–55,000 cm^{-1}). The observed photoabsorption spectra displayed congested structures, indicating the presence of a number of Rydberg states in the energy region under the second ionization potential. No structures were observed beyond the second ionization potential. The quantum yield for the $CN(B^2\Sigma^+)$ production first increased with excitation energy and then suddenly decreased at the excitation wavelength corresponding to the opening of the ionization channel.
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1. Introduction

Photodissociation of cyanogen halides has long been the subject of extensive research as a benchmark reaction in the study of photodissociation of triatomic molecules. In the photoabsorption/photoexcitaion spectra of cyanogen halides, XCN (X = Cl, Br and I), numerous peaks have been observed in the vacuum UV region around 10 eV. Several researchers have attempted to assign these peaks, however, their results have not always been consistent [1–4]. In our previous work, spectral assignments of absorption bands of XCN in the >105 nm region were established by optical polarization measurement of fragment $CN(B^2\Sigma^+ - X^2\Sigma^+)$ photoemission which was produced by photoexcitation using a linear polarized synchrotron radiation (SR) light source [5–7]. However, the first and second ionization potentials (IPs) of XCN, where Rydberg series, were observed in the absorption spectra in the <105 nm region. Therefore, spectroscopic

information obtained near the IPs is undoubtedly important for the assignment of Rydberg transitions.

In the present work, photodissociation of XCN was investigated in the extreme vacuum ultraviolet region of 50–180 nm (200,000–55,000 cm^{-1}) using SR. The photoabsorption and absolute cross-sections for the CN(B–X) emission observed in the photodissociation process of XCN were also determined.

2. Experimental

The measurements were carried out at the BL2A stage of UVSOR in the Institute for Molecular Science, Japan. The experimental procedure was described in Ref. [5]. The SR provided by a 0.75 GeV electron storage ring was dispersed by a 1 m Seya-Namioka monochromator (Hitachi, SNM-2). The instrumental resolution was estimated to be ≈0.1 nm full width at half maximum from the spectral width of the atomic absorption line of Kr at 123.6 nm. The wavelength reading of the monochromator was calibrated against the known spectral positions of the absorption bands of H_2O [8]. The

* Corresponding author. Tel.: +81 791 58 0476; fax: +81 791 58 0242.
 E-mail address: kanda@lasti.himeji-tech.ac.jp (K. Kanda).

uncertainty in the calibrated wavelength was estimated to be ± 0.03 nm.

The higher order light from the monochromator was reduced by three methods with reference to the excitation wavelength. In the 105–180 nm region (95,000–55,000 cm^{-1}), incident light was introduced into the reaction cell through a LiF window (LiF window configuration), as in previous studies [5–7]. For the measurements in the wavelength region shorter than 105 nm, a gas-filter was mounted in front of the reaction cell instead of using a LiF window (window-less configuration) [9]. In the wavelength region 80–120 nm (125,000–84,000 cm^{-1}), the gas-filter was filled with ≈ 300 mTorr of Ar to reduce higher order stray light. In the 50–90 nm (200,000–112,000 cm^{-1}) region, incident light was directly introduced into the reaction cell without using any gas in the gas-filter. The effective pass length of the reaction cell was 12.3 cm and the sample pressure in the cell was typically 15–45 mTorr (1 Torr = 133.322 Pa).

The absolute cross-section for the production of CN(B) in the 105–180 nm region obtained in the LiF window configuration was scaled to an absolute value by comparing with the intensity of the CN(B–X) emission produced in the photodissociation of HCN, for which the absolute emission cross-section has been reported [10]. The scaling procedure for obtaining the absolute emission cross-section from the emission intensity and relative optical responses of the detection systems was described in Ref. [5]. The relative uncertainty in the emission cross-section was estimated to be $\approx 10\%$. The emission cross-section of CN(B–X) in the 50–105 nm region obtained in the window-less configuration was determined by comparing the intensity of the CN(B–X) emission with that observed in the LiF window configuration.

3. Results and discussion

The outer molecular orbital (MO) configuration of cyanogen halides in the ground state can be written as

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi)^4(4\sigma)^2(2\pi)^4; \quad {}^1\Sigma^+$$

by photoelectron spectroscopy studies [11–14]. Briefly, a 2π orbital originated from the in-phase combination of the p orbital of the halogen atom and the π bonding orbital of the CN group. This band system was split by spin–orbit coupling into a lower energy $X^2\Pi_{3/2}$ component and a higher energy $X^2\Pi_{1/2}$ component. The first IPs were 99,770 cm^{-1} (ClCN: $X^2\Pi_{3/2}$), 95,820 cm^{-1} (BrCN: $X^2\Pi_{3/2}$), 97,350 cm^{-1} (BrCN: $X^2\Pi_{1/2}$), 88,160 cm^{-1} (ICN: $X^2\Pi_{3/2}$) and 92,500 cm^{-1} (ICN: $X^2\Pi_{1/2}$). The 4σ orbital is regarded primarily as a lone pair localized on the nitrogen atom. The second IPs were 111,300 cm^{-1} (ClCN: $A^2\Sigma^+$), 109,530 cm^{-1} (BrCN: $X^2\Pi_{3/2}$) and 106,200 cm^{-1} (ICN: $A^2\Sigma^+$). The 1π orbital was the out-of-phase combination of the p orbital of the halogen atom and the π bonding orbital of the CN group. The third IPs were 124,000 cm^{-1} (ClCN: $B^2\Pi_{3/2}$), 116,100 cm^{-1} (BrCN: $B^2\Pi_{3/2}$), 107,300 cm^{-1}
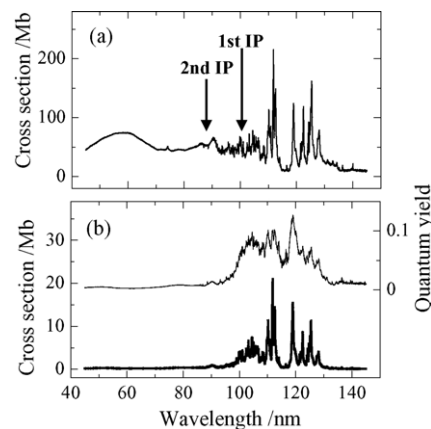

Fig. 1. (a) Photoabsorption cross-section of ClCN. (b) Absolute cross-section (thick line) and quantum yield (thin line) for the production of CN($B^2\Sigma^+$) from the photodissociation of ClCN in the 50–140 nm region.

(ICN: $B^2\Pi_{3/2}$) and 108,430 cm^{-1} (ICN: $B^2\Pi_{1/2}$). The IP of XCN decreased with the effective nuclear charge of the halogen atom. The molecular conformations of XCN and XCN$^+$ indicated by these band systems have also been reported to be linear [11–14].

Panel (a) in Figs. 1–3 show the absolute absorption cross-sections of ClCN, BrCN and ICN, respectively, against the excitation wavelength in the range of 50–180 nm. The spectral features and positions of the absorption bands observed in the present study were in good agreement with those reported previously [1–4]. Panel (b) in Figs. 1–3 show absolute cross-sections and quantum yields, plotted for the CN($B^2\Sigma^+$) produced in the photodissociation of ClCN, BrCN and ICN, respectively. The excitation spectrum of CN(B–X) emission from XCN was observed by Macpherson and Simons [3] in the >125 nm region (<79,400 cm^{-1}) and by Poliakoff et al. [15] in the >110 nm region (<90,900 cm^{-1}); however, absolute cross-sections were not determined in these studies. The present measurement with higher spectral resolution not only reproduces their results but also reveals the existence
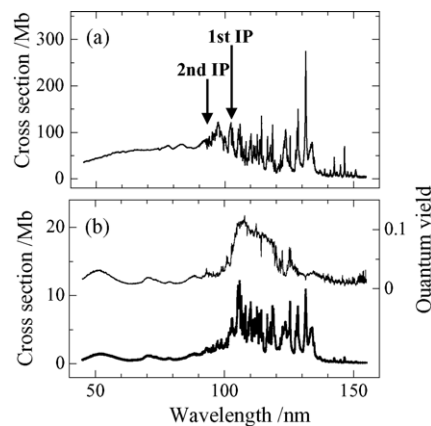

Fig. 2. (a) Photoabsorption cross-section of BrCN. (b) Absolute cross-section (thick line) and quantum yield (thin line) for the production of CN($B^2\Sigma^+$) from the photodissociation of BrCN in the 50–160 nm region.
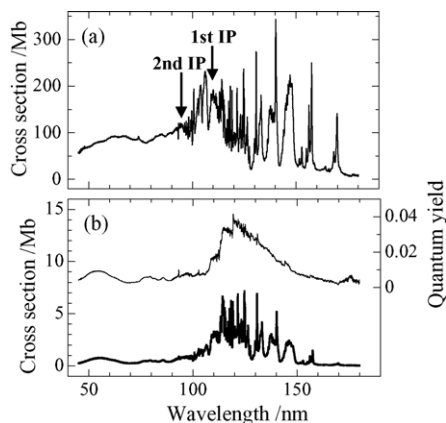
Fig. 3. (a) Photoabsorption cross-section of ICN. (b) Absolute cross-section (thick line) and quantum yield (thin line) for the production of $CN(B^2\Sigma^+)$ from the photodissociation of ICN in the 50–180 nm region.

of an abundance of tiny structures in the <125 nm region (>80,000 cm^{-1}).

The observed photoabsorption and photoexcitation spectra displayed congested structures, indicating the presence of a number of Rydberg and high-lying valence states in the energy region under the first IP. In addition, several peaks were observed between the first and second IPs. These peaks indicate Rydberg states, which are super-excited states, congesting to the second IP. No structures were observed beyond the second IP. Assignments of the photoabsorption spectra of ClCN, BrCN and ICN in the wavelength region of 105–180 nm obtained by polarization anisotropy of fragment $CN(B^2\Sigma^+–X^2\Sigma^+)$ emission were described in Ref. [5–7], respectively. Our preliminary assignments in the wavelength region of 50–105 nm were reported in Ref. [16–18] and full assignments are going to be listed in Ref. [19]. Recently, Holland and Shaw [20] reported assignments of highly excited states of XCN in the photoionization spectra. They assigned peaks in the region beyond the second IP to the transition from the 3σ orbital. However, these peaks could not be observed in the photoabsorption spectra and $CN(B^2\Sigma^+–X^2\Sigma^+)$ photoexcitation spectra in the present work. Other assignments almost agreed with their assignments.

The absolute absorption cross-sections of XCN were <300 Mb in the 50–180 nm region. They increased slightly with an increasing atomic number of the halogen atom. The maximum absolute emission cross-sections for $CN(B^2\Sigma^+)$ produced in the photodissociation of ClCN, BrCN and ICN were 22, 12 and 8 Mb, respectively. The emission cross-sections for $CN(B^2\Sigma^+)$ decreased with an increasing atomic number of the halogen atom. The quantum yield for the production of CN(B), Γ_B, was calculated as the ratio of the emission cross-sections to the absorption cross-sections. As shown in panel (b) in Figs. 1–3, Γ_B increased with excitation

energy below the first IP. The maximum values of Γ_B were ≈ 0.13, ≈ 0.11 and ≈ 0.04 for the photodissociation of ClCN, BrCN and ICN, respectively. It appears that the dominant photodissociation channels, in the region below the first IP, lead to the production of CN fragments in the $X^2\Sigma^+$ and/or $A^2\Pi_i$ states. Γ_B suddenly decreased in the wavelength region corresponding to the opening of the ionization channel of XCN. However, several small peaks resulting from the fluorescence from the Rydberg states converging to the second IP were observed in the excitation wavelength region within the first and second IPs.

Acknowledgments

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