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Fluorescence Excitation Spectra and Quantum Yield in Vacuum Ultraviolet Photodissociation of CF_3CN

Dock-Chil CHE, Toshio KASAI,* Hiroshi OHOYAMA, Keiji KUWATA,
Mitsuhiko KONO,[†] Kiyohiko TABAYASHI,[†] and Kosuke SHOBATAKE[†]
Department of Chemistry, Faculty Of Science, Osaka University, Toyonaka, Osaka 560
[†]Department of Functional Molecular Science, The Graduate University for Advanced Studies, and Institute for Molecular Science, Myodaiji, Okazaki 444

The fluorescence excitation spectra of CN(A,B→X) and CF_3 ($2A'_1 \rightarrow 1A''_2$) and the quantum yield for the CN(B) radical formation were measured in the photodissociation of CF_3CN in 105-135 nm. The quantum yield for the CN(B) radical formation was found to be only a few percent. The similarity in the excitation energy dependence of CN(B→X) and of CN(A→X) indicated a common dissociation mechanism via the 3s Rydberg state of CF_3CN for both states.

A variety of the spin manifold in transition affords useful comparison between photoexcitation and the collisional excitation with the metastable rare-gas atoms, and it especially provides an insight into the electronic excited states of reactant molecule leading to dissociation.[1-3)] Based on the similarity observed in the orientational dependences, the existence of a common excited state of CF_3CN which leads to the CN(A) and CN(B) radical formations was proposed in the $CF_3CN + Ar(^3P)$ reaction.[4)] To fill out the lack of data on the fluorescence excitation spectra and the quantum yield for the CF_3CN molecule, and to make comparison with the collisional excitation available, photodissociation of CF_3CN was carried out in the wavelength region of 105-135 nm. The VUV-light source was used at BL-2A beam line in UVSOR facility of Institute for Molecular Science, Okazaki.[5)] The wavelength resolution of the exciting light was set as 3.0 Å for improving the S/N ratio. The sample gas at 30 mTorr continuously flows into the absorption cell with four openings of LiF windows along the two central axes of the cell. The reagent gas was irradiated by the VUV light in the middle of the cell. The absorption cross section was measured by attenuation method with an optical length of 12 cm. The transmitted light and the emissions from the product radicals were measured as a function of the excitation wavelength by three sets of photon-counting units with R585 photomultipliers. A band-pass filter(SWPF 300) centered at 300 nm was used for isolating the $CF_3(2A'_1 \rightarrow 1A''_2)$ emission. A low-pass filter(HOYA O-58) with 580 nm cut-off wavelength was used for the CN(A→X) emission. Since the $CF_3(2A'_1 \rightarrow 1A''_2)$ emission was found to be very small as compared with the CN(B→X) emission, no filter was used for isolating the CN(B→X) emission. The quantum yield of the CN(B) radical formation was determined by comparative measurement of the OH(A→X) emission of water under the given experimental conditions.[6]

Figure 1 shows the absorption spectrum of CF_3CN and the fluorescence excitation spectra of the product radicals by VUV-light excitation. The maximum energy available from the metastable argon atom is shown by the arrow of Ar* for the comparison purpose with collisional excitation. The locations of the main two peaks of the absorption spectrum were found to coincide with those in the literature where the peaks were assigned as the $7a_1 \rightarrow 3s$ and/or $2e \rightarrow 3s$ Rydberg transitions.[7] The fluorescence excitation spectra of CN(B→X) and CN(A→X) are shown by Δ and ●, respectively.

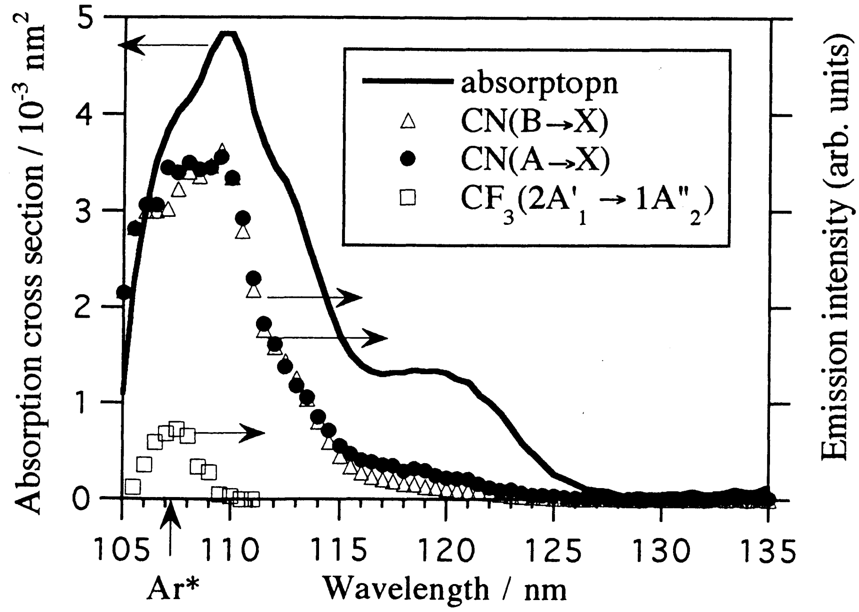

Fig. 1. The absorption spectrum of CF_3CN and the fluorescence excitation spectra of CN(B→X), CN(A→X), and $CF_3(2A'_1 \rightarrow 1A''_2)$. The emission intensity, the vertical axis on the right is arbitrary on each spectrum. The arrow of Ar* shows the wavelength corresponds to the maximum energy available in the CF_3CN + Ar(^{3}P) reaction.

A weak excitation spectrum whose emission was isolated by the 300 nm band-pass filter is shown by □. The emission diminidhes at~100 nm(equivalent to 11.3 eV), and this threshold corresponds to the sum of the dissociation energy of CF_3-CN and the energy gap for the $2A'_1 \rightarrow 1A''_2$ transition of CF_3. Thus the $CF_3(2A'_1)$ radical is expected to be the emitter.[8] The corrected emission intensity of $CF_3(2A'_1)$ is about two orders of magnitude smaller than that of CN(B). This small branching ratio to the CF_3 radical in photodissociation again is consistent with the results obtained in the CF_3CN + Ar(^{3}P) reaction.[4] As seen in the figure the excitation energy dependence of the emissions of CN(B→X) and CN(A→X) turned out to be almost the same, suggesting that both radicals are formed via some common excited state of CF_3CN prior to dissociation. Referring to the assignment of Ashfold and Simons, the common excited state for both radicals can be identified as the 3s Rydberg state/states of CF_3CN. The reaction mechanism via a common excited state was also suggested in the orientational dependences for both products of the CN(A) and CN(B) radicals in the CF_3CN + Ar(^{3}P) reaction.[4)]

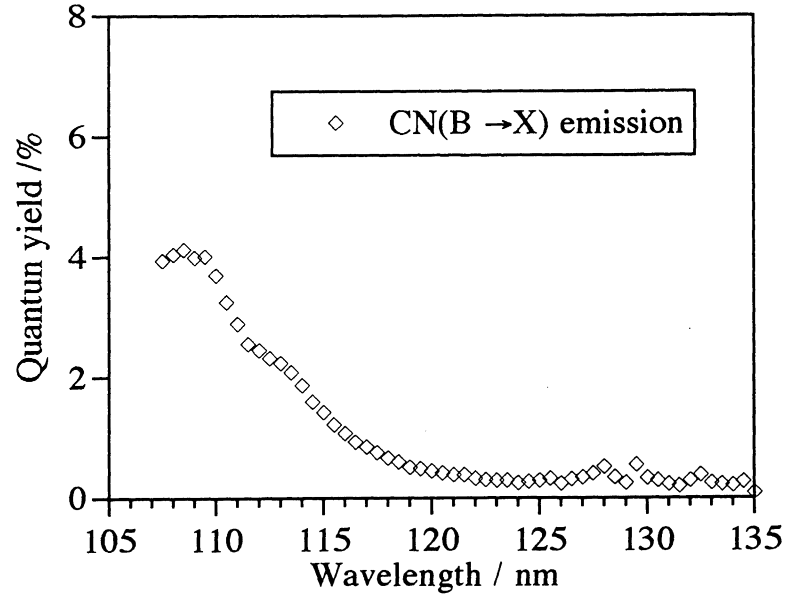

Fig. 2. The quantum yield for the CN(B) radical formation in the photodissociation of CF_3CN.

Figure 2 shows the quantum yield for the CN(B) radical formation, which was determined by the comparative measurement with the OH(A→X) emission of water under the same experimental conditions.[6)] The quantum yield of the CN(A) or $CF_3(2A'_1)$ radical formation was not obtainable because of the difficulty in direct comparison under the different conditions for light detection. It was found that the quantum yield for the CN(B) formation increases with the increase of the excitation energy of the light and it reaches the very small value in the wavelength region longer than 120 nm. The maximum value is about 4 % at 108 nm near the largest peak of the absorption in Fig. 1. The experimental inaccuracy of the quantum yield is estimated to be less than 10% of the indicated values for the points shown in the figure and it becomes worse at the shortest wavelengths because of the weak intensity of the exciting light. It appears that the quantum yield for the CN (B) formation increases in parallel to the excess internal energy of CF_3CN in the excited state as the excitation wavelength becomes shorter. The quantum yield for the CN(A) radical formation could not be obtained, nevertheless it is clear that it should show the same wavelength dependence as that for CN(B) just mentioned above. Because the fluorescence excitation spectra of CN(B) and CN(A) are nearly the same in the relative scale as seen in Fig. 1. The small quantum yield for the CN(B) radical formation seems to reflect a close resemblance to the small branching ratio for the CN(B) formation in the CF_3CN + Ar(^{3}P) reaction.[4)] The similarity in the fluorescence excitation spectra for both states of the CN radical in photodissociation also accords with the orientational dependence for the CN(B) and for the CN(A) radical formation is equal in the CF_3CN + Ar(^{3}P) reaction. Those agreements between the two methods of excitation strongly suggest that the 3s Rydberg state of the molecule plays a common role as a precursor leading to dissociation. This 3s Rydberg state would have a mixed character of the single and the triplet states in nature because the dissociation of CF_3CN undergoes in the same fashion regardless of the different excitation rule on the spin manifold. Alternatively it is plausible that the collisional excitation with the metastable rare-gas atom like in the CF_3CN + Ar(^3P) reaction would be able to behave as a resonance energy transfer like in photoexcitation.

In summary, we have measured for the first time the fluorescence excitation spectra of CN(A→X) and CF_3 ($2A'_1 \rightarrow 1A''_2$), and the quantum yield for the CN(B) radical formation, and confirmed the present absorption spectrum of CF_3CN as the identical spectrum reported earlier by Ashfold and Simons.7) The comparison of the present results with those of the CF_3CN + Ar(^3P) reaction strongly suggests a common dissociation mechanism via the 3s Rydberg state of CF_3CN for the photoexcitation and for the collisional excitation.

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