IVR and Dissociation in the S1 State of Jet-Cooled Benzonitrile-H_2O

Kenji Sakota, Kaori Nishi, Kazuhiko Ohashi, and Hiroshi Sekiya*
Department of Molecular Chemistry, Graduate School of Science, Kyushu University,
6-10-1, Hakozaki, Higashi-ku, Fukuoka 812-8581

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The $S_1 \rightarrow S_0$ dispersed fluorescence spectra of jet-cooled benzonitrile-H_2O 1:1 complex have been measured by exciting various vibronic levels. The binding energy of the complex has been estimated to be $1187 < D_0 < 1644$ cm^{-1}. No sign of intramolecular charge transfer has been observed.

Benzonitrile forms stable complexes with various species in a supersonic jet. The hydrogen bonded complex of benzonitrile with water has been extensively studied in its ground state and electronically excited state with different spectroscopic techniques.[1-7] Much attention has been paid to model the solvation process and its possible influence on charge transfer reactions. The structures of the benzonitrile-H_2O 1:1 complex in the S_0 and S_1 state have been studied in detail by using microwave[1-3] and electronic spectroscopy.[2] The structure of benzonitrile-H_2O is planar, and the hydrogen bond forms a ring-like structure.[1-3]

In the present work, we have measured the dispersed fluorescence spectra of benzonitrile-H_2O by exciting the states up to 1887 cm^{-1} to investigate the intracluster vibrational energy redistribution (IVR) and dissociation processes. Kobayashi et al. investigated the excited-state dynamics of the complexes of benzonitrile with various species.[4-6] However, detailed results on benzonitrile-H_2O have not been reported. Recently, Mordzinski et al. reported the observation of a broad feature underlying many sharp features in the dispersed fluorescence spectra of benzonitrile and tolunitrile.[8] The broad feature was ascribed to emission originating from intramolecular charge transfer (CT) reaction. However, no other experimental data which support the occurrence of a CT reaction in benzonitrile have been reported. The effects of the binding of H_2O on the CT emission in benzonitrile have been examined.

The experimental apparatus used was essentially the same as that described previously.[9] A few drops of water were introduced into the nozzle housing. A continuous stream of helium at 2.5–4.0 atm pressure was passed over room-temperature samples, and the mixture of benzonitrile, water, and helium was expanded into the chamber with a pulsed nozzle (General Valve 0.5 mm diam.). The $S_1 \leftarrow S_0$ fluorescence excitation spectrum of benzonitrile-H_2O in a free jet was probed with an excimer laser pumped frequency doubled dye laser (Lumonics EX-600 and HD-300). The dispersed fluorescence spectrum was measured with an f=85 cm monochromator (Spex 1402). The spectral resolution in the dispersed fluorescence spectrum was 50 cm^{-1}.

In the fluorescence excitation spectrum, the origin band of benzonitrile-H_2O was observed at 36442 cm^{-1}, which is 70 cm^{-1} red-shifted with respect to the origin band of benzonitrile. This shift is in good agreement with a reported value of 71 cm^{-1}.[5] The bands due to the intermolecular modes have not been observed, suggesting that the geometry of the complex does not significantly change upon photoexcitation.

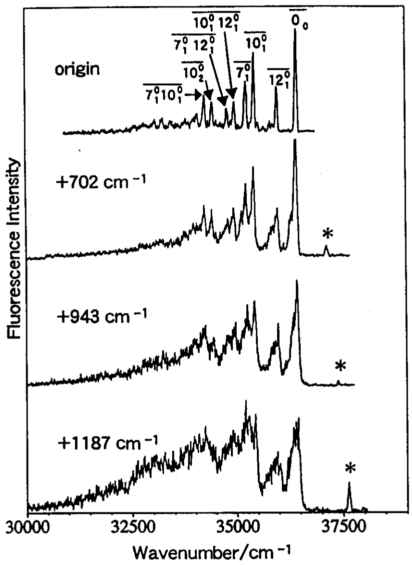

Figure 1. Dispersed fluorescence spectra of benzonitrile-H_2O following the excitation of the bands at the origin, +702, +943, and +1187 cm^{-1}. The asterisks indicate scattered laser light.

Figure 1 shows the dispersed fluorescence spectra of benzonitrile-H_2O measured by exciting the bands at the origin, 702 (11^1), 943 (10^1), and 1187 cm^{-1} (7^1). The assignments for the upper states are given in the parentheses.[4,5] The vibronic patterns in the dispersed fluorescence spectra of benzonitrile substantially depended on the excited vibronic state due to the appearance of the resonance fluorescence. In contrast, the vibronic patterns in the spectra of benzonitrile-H_2O are similar to each other although the bandwidths substantially increase with the excess energy. This indicates that emission observed by the excitation at 702, 943, and 1187 cm^{-1} is originating from the vibrationally redistributed states of the complex.

Figure 2 shows the dispersed fluorescence spectra measured by exciting the bands at 1644, 1668, and 1887 cm^{-1}, respectively. The bandwidths in these spectra are remarkably narrower than those in the spectrum at 1187 cm^{-1}. In addition, the frequencies of the bands are in good agreement with those of the benzonitrile monomer. These findings indicate that benzonitrile-H_2O dissociates only to the vibrationless level of the bare molecule. The binding energy of the S_1 complex has been estimated to be $1187 < D_0 < 1644$ cm^{-1}. The lower limit is obtained on the assumption that the dissociation rate of the complex is faster than the radiative decay rate for the excitation at the 1187 cm^{-1} state. To our knowledge, the binding energy of benzonitrile-H_2O has not been determined.

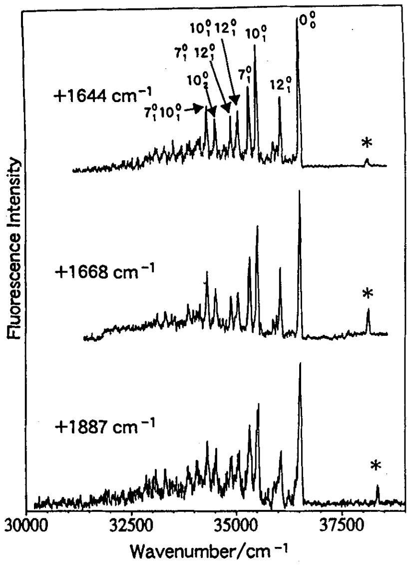

Figure 2. Dispersed fluorescence spectra of benzonitrile produced from the dissociation of benzonitrile-H_2O measured by the excitation of the bands at +1644, +1688, and +1887 cm^{-1}. The asterisks indicate scattered laser light.

The broadening of the bands in the dispersed fluorescence spectra in Figure 1 can be explained by the IVR. The rate for IVR increases with the excess energy since the state density of the van der Waals mode increases with the excess energy. The rates for IVR in the S_1 state of benzonitrile-H_2O must be much faster than the radiate decay rate (~2x10^7 s^{-1}).[5] As a result, fluorescence is observed only from the vibrationally redistributed states following the excitation to the states with the excess energy less than 1187 cm^{-1}. In the states above the binding energy, the dissociation of the complex occurs and provides emission of the bare molecule. The IVR and dissociation processes in the S_1 state have been studied extensively in several complexes such as *p*-difluorobenzene-Ar[10] and aniline-CH_4.[11,12] However, the excited-state dynamics is not well understood for the complexes containing the aromatic chromophore and H_2O. The benzonitrile-H_2O complex is a good system to investigate the IVR and dissociation processes by various techniques since highly excited vibronic states are easily accessible by photoexcitation.

The concept of twisted intramolecular charge transfer introduced by Grabowski et al. is now widely accepted for the interpretation of the dual fluorescence in *N*,*N*-(dimethylamino)benzonitrile (DMABN).[13,14] Recently, an alternative model has been proposed to elucidate the CT emission from benzonitrile, 4-aminobenzonitrile, and DMABN on the basis of the calculations with the CASPT2/DZP method.[15] In this RICT (rehybridization intramolecular charge transfer) model the bending of the cyano group is the intramolecular coordinate that leads to the stabilization of the CT state by the rehybridization from sp to sp^2 of the carbon atom in the cyano group due to an extra charge transferred from the ring. The CT emission due to intramolecular CT reaction has been observed only in polar solvents.[13,14] It is expected that the binding of H_2O to the CN group significantly stabilizes the CT state, which facilitates the energy transfer from the S_1 state to the CT state and provides a red-shifted broad feature in the emission spectrum. The wavelengths of a broad feature in benzonitrile-H_2O should be longer than those of the monomer. At higher excess energy the energy transfer from the excited S_1 state to the RICT state may become faster, and the relative intensity of the CT emission to the resonance emission may increase. Contrary to our expectation, no red-shifted broad feature is observed in the dispersed fluorescence spectra of benzonitrile-H_2O as is clear from Figures 1 and 2. Very recently, we have measured the dispersed fluorescence spectrum of benzonitrile at much higher resolution (16–25 cm^{-1})[16] than a resolution of 55 cm^{-1} employed previously.[8] The broad feature in the emission spectrum of benzonitrile previously ascribed to the RICT emission was almost completely resolved into a lot of sharp features.[16] Our results on benzonitrile-H_2O and benzonitrile do not support the observation of dual emission from benzonitrile.

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