Gas phase spectroscopy of adrenaline and its hydrated cluster by laser desorption supersonic jet technic

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Neurotransmitters play a crucial role to transmit neural signals by the molecular recognition process, in which the neurotransmitter binds to a specific receptor. Because of the high molecular selectivity, it is often likened as key (neurotransmitter) and lock (receptor). In our real world, keys and locks are solid materials, thus one may expect that the neurotransmitter and the receptor have hard structures. However, it is not the case because they have many C-C single bonds, which can generate many conformers. It is difficult to explain the molecular recognition process from the simple analogy of the real keys and locks. In order to understand the mechanism, it is important to know their possible variety of conformations. The gas phase spectroscopy, particularly the supersonic jet spectroscopy is one of the best methods to investigate conformational landscape. In a supersonic jet expansion, the sample molecules are cooled down to ~ zero K and thus fluctuating conformers are frozen to the potential minima. The frozen conformers can be easily distinguished by the hole-burning (HB) spectroscopy therefore we can clarify the number of stable conformations and their geometrical structures. Here, we investigated conformations of adrenaline (epinephrine), which is one of the most famous neurotransmitter, by laser desorption supersonic jet laser spectroscopy.

The gas phase spectroscopy of adrenaline has already been reported by Çarçabal and co-workers.[1] According to their report, two conformers were observed and both of them are assigned to the conformation stabilized by the hydrogen of the OH group binds to the nitrogen. Although their assignments of two conformers are fine, the S/N of the spectrum was not high enough to conclude whether adrenaline molecule has more conformers or not.

From the above motivation, we re-measured S_1-S_0 REMPI and HB spectra of adrenaline by using advanced laser desorption source with high pressure pulsed nozzle.[2] As can be seen in the REMPI spectrum in figure 1, the S/N of the spectrum is significantly higher than the former report, and thus we can separate the congested vibronic bands clearly. To measure the HB spectra, the probe laser was fixed to the band indicated by dashed lines. The ion signal due to the two-photon ionization of the probe laser reflects the population in the ground state. The burn laser was fired about 1 μs before introducing of the probe laser, and scanned the S_1-S_0 absorption region. When the burn laser is resonant to the transition that originated from the same species as the probe laser was fixed, the ion signal is depleted by the decrease of the population. Then we can observe the S_1-S_0 electronic transition only by a single species.

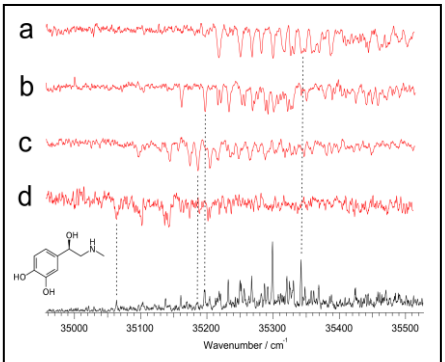

Figure 1. REMPI and UV-UV HB spectra of adrenaline together with its structure

Four different HB spectra were observed (see Figure 1). The spectra in Figure 2a and 2b are the same as in the previous report while those in Figure 2c and 2d are newly found in this work. All the bands appearing in the REMPI spectra were observed in the four HB spectra. It means that four conformers of adrenaline co-exist in the jet.

In order to assign the structures of observed conformers, IR dip spectra were also measured and presented in Figure 2a-d. Here, the IR dip spectra correspond to the conformer-selected IR spectra which can be measured by replacing the UV burn laser to the tunable IR laser in the HB spectroscopy. Four conformers of adrenaline show vibrational bands at ~3680 cm^{-1} and ~3610 cm^{-1} commonly. From the analogy to catechol,[3] the vibrational bands are assigned to the free and hydrogen-bonded OH stretching vibrations, respectively. The positions of the vibrational bands at around 3500 cm^{-1} strongly depend on the conformers and are assigned to the stretching vibration of the OH group in the chain. It suggests that the major difference among the conformers is the conformation of the chain. These vibrational frequencies are very close to the corresponding OH stretching vibrations in synephrine.[4] Synephrine is the molecule which has the same chain as that in adrenaline with phenolic ring instead of the catechol ring (see Figure 2). For example, the band locations of PS-AG-OHN (for the notations, see reference 4) of synephrine at 3526 cm^{-1} and 3528 cm^{-1} are very similar with those of spectra a and c of adrenaline (3523 cm^{-1} and 3528 cm^{-1}, respectively). Similarly, the band of S-AG-OHN at 3498 cm^{-1} corresponds to that of spectrum b (3494 cm^{-1}) and the band of S-GG-OHN at 3515 cm^{-1} corresponds to that in the spectrum d (3513 cm^{-1}). Thus, we tentatively assign the conformation of the chain in adrenaline from the analogy to synephrine. The detail assignments including catechol OHs will be discussed in the presentation together with theoretical IR spectra.

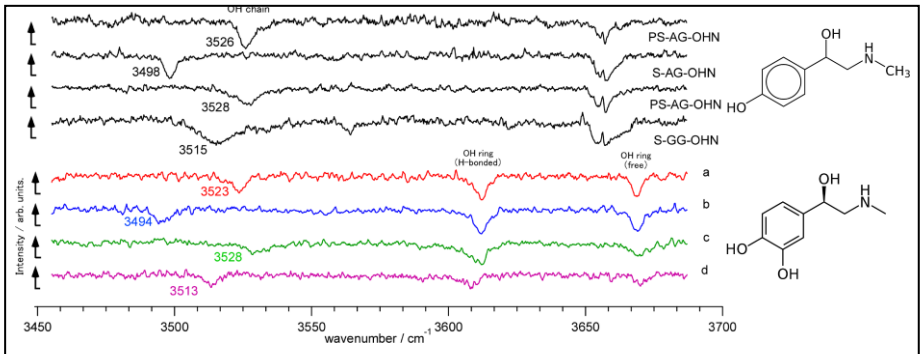

Figure 2. IR dip spectra of adrenaline (lower) and synephrine (upper)

The hydrated adrenaline (1:1) was also investigated by the REMPI and HB spectroscopy to understand the role of the water for the conformation. It will be discussed in the presentation.

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(4) Ishiuchi, S.; Asakawa, T.; Mitsuda, H.; Miyazaki, M.; Chakraborty, S.; Fujii, M. *J. Phys. Chem. A* **2011**, *115*, 10363.