

## Communications

## Gas-Phase Spectroscopy of Laser-Desorbed Acedan and Proline-Acedan

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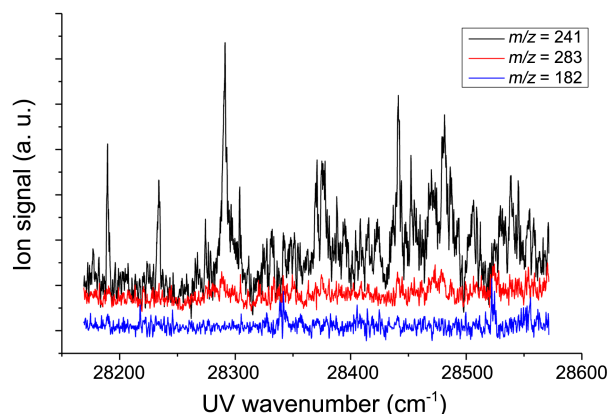
**Key Words :** Two-photon fluorescent probe, Laser-desorption, UV-UV, IR-UV, Conformer

Acedan (2-acetyl-6-dialkylaminonaphthalene) and proline-acedan (**A** and **B** in Scheme 1, respectively) are precursors for two-photon fluorescent probes such as ANO1, which turns on its fluorescence when bound to nitric oxide (NO).<sup>1-3</sup> In spite of their similar molecular structures, **A** and **B** have different photophysical properties including absorption coefficient and fluorescence quantum yield. In order to prove the hypothesis that their different fluorescence properties stem from their different conformational structures, we tried to measure their conformation-specific UV and IR spectra in gas phase.

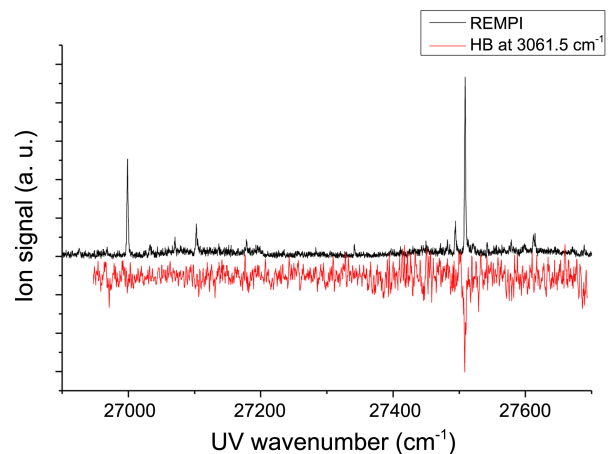
The experimental setup has been described in previous publications.<sup>4-6</sup> In-house synthesized<sup>3</sup> powder sample of **A** or **B** was mixed with carbon black powder and the mixture was deposited on the lateral face of a graphite disk. The sample was desorbed by 1064 nm radiation of a pulsed Nd:YAG laser in vacuum, and the desorbed molecules were subsequently cooled down by pulsed supersonic expansion of Ar gas at 40 bar. UV spectra were measured by two-color resonance-enhanced multiphoton ionization (REMPI) with frequency-doubled output of Nd:YAG pumped dye lasers and a time-of-flight mass spectrometer. IR laser was provided by difference frequency generation of a dye laser and an Nd:YAG laser. IR-UV spectroscopy was used to record conformer-specific IR spectrum while the IR was scanned, and conformer-specific UV spectrum while the UV was scanned.

Figure 1 shows 1+1' REMPI spectra of **B** ( $m/z = 283$ ) and its fragments ( $m/z = 182, 241$ ) with the second UV at 266 nm. Even though laser-desorption was employed to vaporize the sample, significant fragmentation was observed in the photoionization mass spectrum. The fragment of **B** at  $m/z =$

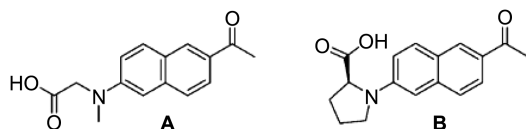
241 (**241**) shows much stronger ion signal than the molecular ion (**B**,  $m/z = 283$ ). As **B** and **241** showed similar vibronic bands in this region, it was assumed that **241** is issued from dissociative ionization of **B**, and the strong REMPI spectrum of **241** was presumed to reflect that of **B**. Figure 2 shows the 1+1' REMPI spectrum of **241** at lower



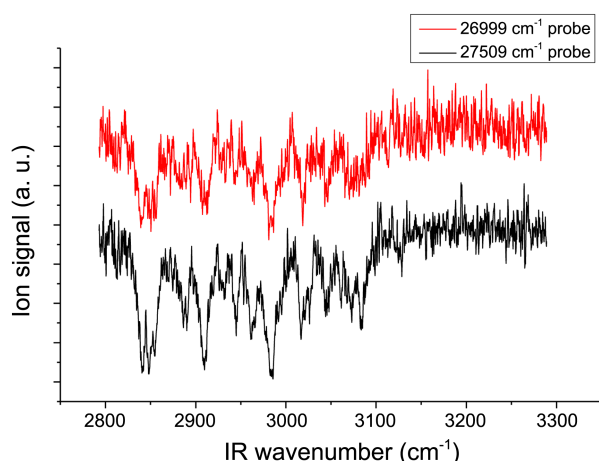
**Figure 1.** 1+1' REMPI spectra of proline-acedan (**B**,  $m/z = 283$ ) and its fragments ( $m/z = 182, 241$ ).



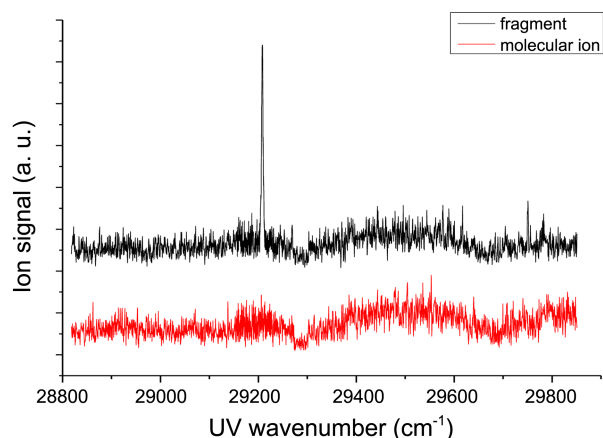
**Figure 2.** IR-UV hole-burning (HB) and REMPI spectra of **241**.



**Scheme 1.** **A**: Acedan, **B**: Proline-acedan.



**Figure 3.** Conformer-specific IR spectra of **241** by observing depletion of UV transition at 26999  $\text{cm}^{-1}$  and 27509  $\text{cm}^{-1}$ , respectively.



**Figure 4.** 1+1' REMPI spectra of acedan (**A**,  $m/z = 257$ ) and its fragment ( $m/z = 213$ ).

wavenumber, together with its IR-depleted UV spectrum, which is explained later. As no ion signal was observed below this region, the two strong peaks at 26999  $\text{cm}^{-1}$  and 27509  $\text{cm}^{-1}$  were tentatively assigned to 0-0 transitions of two possible conformers of **241**, which can reflect those of **B**.

In order to assign the tentative 0-0 transitions to respective conformers, conformer-specific IR spectrum was obtained by observing depletion of **241** ion signal while first UV wavenumber was fixed at each tentative origin band. Figure 3 shows thus obtained two IR spectra of **241**. They are slightly different around the C-H stretching region. However, no O-H stretching IR transition around 3600  $\text{cm}^{-1}$  could be found, which means **241** does not have a free OH group in

the ground state. Therefore **241** seems to be produced by thermal fragmentation of **B** in the ground state before and/or during laser desorption, presumably by ejection of a stable  $\text{CO}_2$  molecule from the carboxylic group and uptake of two hydrogen atoms from nearby molecules. Nevertheless, **241** retains the framework of the fluorophore, and can still serve to probe the conformational landscape of the fluorophore.

UV-UV hole-burning (HB) spectrum was difficult to obtain because it required two-color burn and two-color probe, in total 4-colors. Instead, IR-depleted UV spectrum was obtained for **241**. Its HB spectrum in Figure 2 suggests that the framework of the fluorophore has only two conformers in the cold isolated phase.

The UV spectrum of acedan (**A**) showed an unexpected behavior. Again, thermal fragmentation was observed in the photoionization mass spectrum of **A**, and sharp vibronic transition was observed only in the fragment mass channel. Strikingly, the 1+1' REMPI spectrum of the fragment in Figure 4 shows only one sharp vibronic band at 29208  $\text{cm}^{-1}$ , which suggest that the seemingly more flexible structure of **A** has less number of conformers when it is laser-desorbed, cooled down, and isolated in gas phase.

In summary, conformer-specific IR and UV spectroscopy was attempted for precursors of two-photon fluorescent probes, acedan and proline-acedan. They showed thermal fragmentation even with the soft vaporization method of laser desorption. Though detected on the fragment mass channel, the framework of two-photon fluorescent probes exhibits a highly rigid structure with small number of conformations in the gas phase. Further works are underway to obtain detailed information on conformational landscapes of the fluorescent probes.

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## References

- Kim, H. M.; Cho, B. R. *Chem. Commun.* **2009**, 2, 153-164.
- Kim, H. M.; Cho, B. R. *Acc. Chem. Res.* **2009**, 42(7), 863-872.
- Seo, E. W.; Han, J. H.; Heo, C. H.; Shin, J. H.; Kim, H. M.; Cho, B. R. *Chem. Eur. J.* **2012**, 18(39), 12388-12394.
- Ishiuchi, S.-i.; Mitsuda, H.; Asakawa, T.; Miyazaki, M.; Fujii, M. *Phys. Chem. Chem. Phys.* **2011**, 13(17), 7812-7820.
- Ishiuchi, S.-i.; Asakawa, T.; Mitsuda, H.; Miyazaki, M.; Chakraborty, S.; Fujii, M. *J. Phys. Chem. A* **2011**, 115(37), 10363-10369.
- Mitsuda, H.; Miyazaki, M.; Nielsen, I. B.; Çarçabal, P.; Dedonder, C.; Juvet, C.; Ishiuchi, S.-i.; Fujii, M. *J. Phys. Chem. Lett.* **2010**, 1(7), 1130-1133.