

# Report on spectroscopic research of tryptamine-(N<sub>2</sub>)<sub>n</sub> (n = 1 - 6) cluster cations through a visit to Technische Universität Berlin in Germany

(JSPS Core to Core program)

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I visited the laboratory of Prof. Otto Dopfer in Technische Universität Berlin and studied there with his students for two weeks from November 12<sup>th</sup> to 25<sup>th</sup> as a part of the JSPS Core to Core program. Infrared photodissociation (IRPD) spectra of the Tryptamine-nitrogen cluster (TRA<sup>+</sup>)-(N<sub>2</sub>)<sub>n</sub> (n = 1 - 6) cations were obtained. The following paragraphs discuss the experimental results of IRPD spectra of (TRA<sup>+</sup>)-(N<sub>2</sub>)<sub>n</sub> (n = 1 - 6).

## 1. Introduction

The conventional H-bonding interactions between an electropositive hydrogen atom and an electronegative atom, such as O-H...O and N-H...N, have been investigated intensely using various spectroscopic techniques. Although each of “weak” H-bonds, such as C-H...O and C-H...π, has much smaller interaction energy than the conventional H-bonds, the sum of such a weak H-bond cannot be ignored, and it may in part regulate the shapes and reactivity of biological macromolecules.<sup>1</sup> Tryptamine (TRA) is an analogue of tryptophan and serotonin, and TRA<sup>+</sup> is expected to form the weak H-bond with non-polar nitrogen molecules. To the best of our knowledge, however, no report on TRA<sup>+</sup>-(N<sub>2</sub>)<sub>n</sub> has been reported so far. Therefore, we investigate the structural motifs of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>n</sub> (n = 1 - 6) by IRPD spectroscopy and quantum chemical calculations due to obtain the knowledge of weak H-bonds.

## 2. Result and Discussion

Fig. 1(a) shows the IRPD spectrum of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>1</sub> in the NH stretch fundamental region of the indole moiety. In Fig. 1(a), a strong vibrational transition is observed at 3398 cm<sup>-1</sup>, which has a tail to the higher wavenumber region. In addition, a weak vibrational transition is observed at 3449 cm<sup>-1</sup> in Fig. 1(b), which is the IRPD spectrum of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>1</sub> with higher sensitivity. In In<sup>+</sup>-(N<sub>2</sub>)<sub>1</sub>, H-bound (1H) and π-bound (1π) isomers have been identified.<sup>2</sup> The 1H and 1π isomers of In<sup>+</sup>-(N<sub>2</sub>)<sub>1</sub> show the NH stretching vibration at 3379 and 3450 cm<sup>-1</sup> with the strong and weak intensities, respectively. The spectral features of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>1</sub> in Fig. 1 are very similar to those of In<sup>+</sup>-(N<sub>2</sub>)<sub>1</sub>. Thus, the intense and weak vibrational bands at 3398 and 3449 cm<sup>-1</sup> in Fig. 1 can be assigned to the NH stretching vibrations of 1H and 1π isomers of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>1</sub>, respectively.

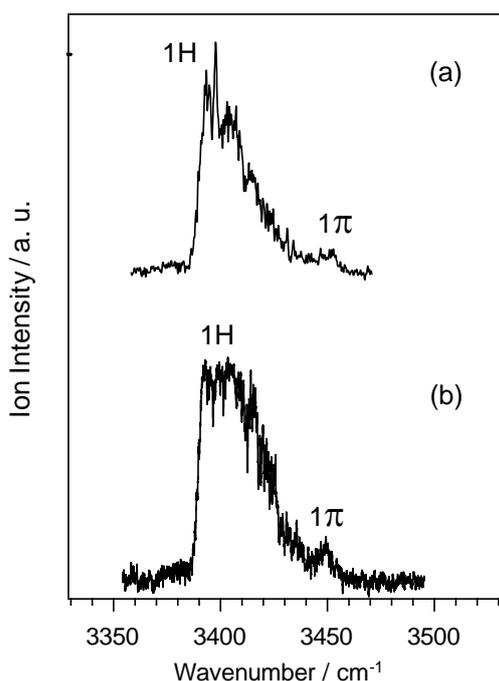


Fig. 1. (a) IRPD spectrum of  $\text{TRA}^+(\text{N}_2)_1$  in the vicinity of the NH stretch fundamental of the indole moiety. (b) IRPD spectrum of  $\text{TRA}^+(\text{N}_2)_1$  with higher sensitivity. Both of the IRPD spectra were obtained by monitoring the  $\text{TRA}^+$  fragment mass channel.

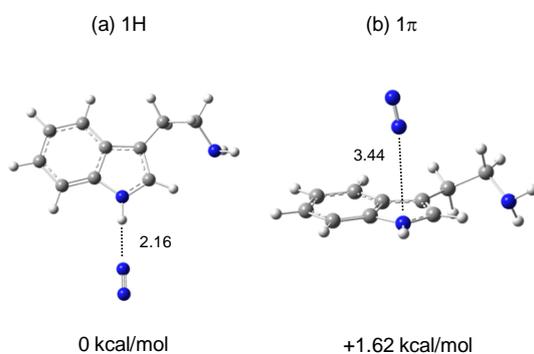


Fig. 2. Stable structures of (a) the 1H isomer and (b) the 1 $\pi$  isomer, which are obtained by the CAM-B3LYP/ aug-cc-pVDZ level of theory. The relative stabilization energies are shown in units of kcal/mol, for which BSSE and zero point vibrational energies are corrected. The intermolecular distances of (a)  $\text{NH}\cdots\text{N}_2$  and (b)  $\text{N}\cdots\text{N}_2$  are also shown in units of Å.

The stable structures of  $\text{TRA}^+(\text{N}_2)_1$  are illustrated in Fig. 2. In the 1H isomer, a nitrogen molecule is linearly H-bonded to the NH group, while it is attached to the  $\pi$ -cloud of the five-membered ring of  $\text{TRA}^+$  in the 1 $\pi$

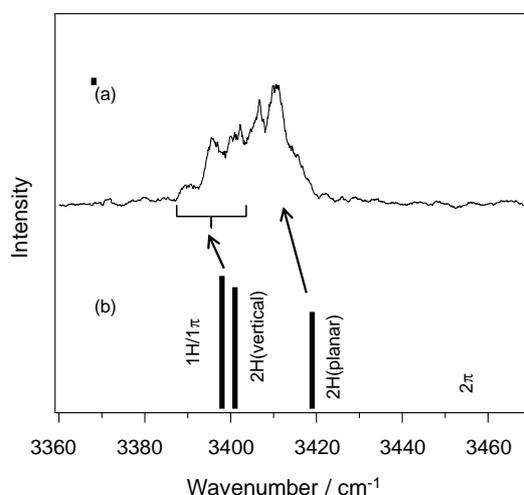


Fig. 3. (a) IRPD spectrum of  $\text{TRA}^+(\text{N}_2)_2$  in the vicinity of the NH stretch fundamental of the indole moiety by monitoring the  $\text{TRA}^+$  fragment mass channel. (b) NH stretching vibrations of the 1H/1 $\pi$ , 2H(vertical), 2H(planar), and 2 $\pi$  isomers predicted by the CAM-B3LYP/ aug-cc-pVDZ level of theory. Vibrational wavenumbers in (b) is scaled by a factor of 0.9539.

isomer. The binding energy of the 1H isomer is stronger by 1.62 kcal/mol than that of the 1 $\pi$  isomer, and an intermolecular distance is also shorter in the 1H isomer than in the 1 $\pi$  isomer. This is consistent with the experimental result that the band intensity of the 1H isomer is much stronger than that of the 1 $\pi$  isomer in Fig. 2.

Fig. 3(a) shows the IRPD spectrum of  $\text{TRA}^+(\text{N}_2)_2$  in the NH stretch fundamental region of the indole moiety. The dissociation channel,  $\text{TRA}^+(\text{N}_2)_2 + h\nu_{\text{IR}} \rightarrow \text{TRA}^+ + 2\text{N}_2$ , is monitored in Fig. 3(a). Fig. 3(b) shows the theoretically predicted NH stretching vibrations of the 1H/1 $\pi$ , 2H(vertical), 2H(planar), and 2 $\pi$  isomers, respectively, where the notation  $x\text{H}/y\pi$  designates  $\text{TRA}^+(\text{N}_2)_2$  with  $x$  H-bound and  $y$   $\pi$ -bound ligands ( $x + y = 2$ ). Each of stable structures is illustrated in Fig. 4. The theoretical IR spectra in Fig. 3(b) predict that three stable isomers, 1H/1 $\pi$ , 2H(vertical), and 2H(planar),

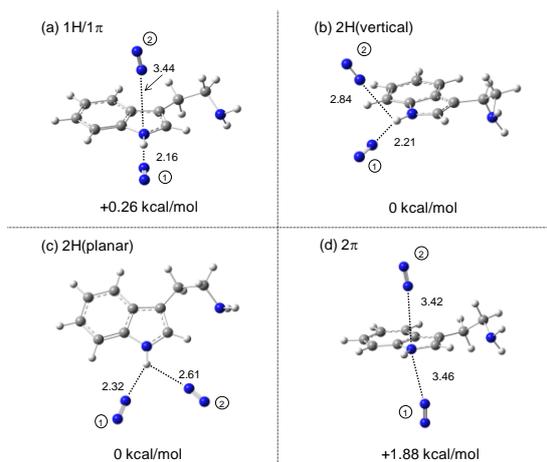


Fig. 4. Stable structures of (a) 1H/1 $\pi$ , (b) 2H(vertical), (c) 2H(planar), and (d) 2 $\pi$  isomers, which are obtained by the CAM-B3LYP/aug-cc-pVDZ level of theory. The relative stabilization energies are shown in units of kcal/mol, for which BSSE and zero point vibrational energies are corrected. The intermolecular distances are shown in units of Å.

have the NH stretching vibrations in the vicinity of the vibrational band in Fig. 3(a). In the 1H/1 $\pi$  isomer, a nitrogen molecule is H-bonded to the NH group linearly, and the other nitrogen molecule is attached to the  $\pi$ -cloud of TRA<sup>+</sup>. In the 2H(vertical) isomer, two H-bonds are formed between the NH group and two nitrogen molecules. In the 2H(planar) isomer, on the other hand, two nitrogen molecules are H-bonded to the NH group on the same plane of the indole ring.

It should be noted that five (or six) peaks are observed in Fig. 3(a), while they are ascribed to three isomers. This may be due to the contributions of the rotational band contours of each isomer, although we cannot rule out the possibility that more than three isomers contribute to the experimental spectrum.

Fig. 5 shows the IRPD spectra of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>n</sub> ( $n = 1 - 6$ ) in the NH stretch fundamental region of the indole moiety. The

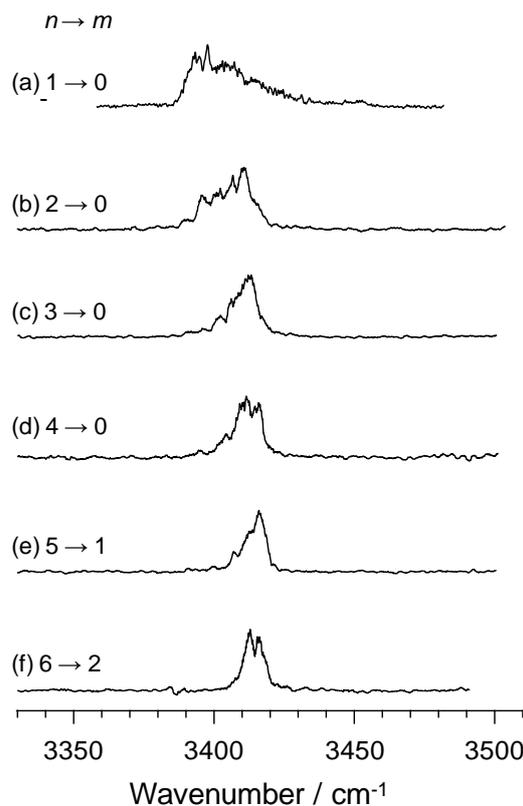


Fig. 5. IRPD spectra of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>n</sub> ( $n = 1 - 6$ ) obtained by monitoring the TRA<sup>+</sup>-(N<sub>2</sub>)<sub>m</sub> fragment channels (denoted as  $n \rightarrow m$ ).

dissociation channels, TRA<sup>+</sup>-(N<sub>2</sub>)<sub>n</sub> +  $h\nu_{\text{IR}} \rightarrow$  TRA<sup>+</sup>-(N<sub>2</sub>)<sub>m</sub> +  $(n-m)$ N<sub>2</sub>, are monitored, denoted as  $n \rightarrow m$  in the figure. In Fig. 6, the wavenumbers of the NH stretching vibration of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>n</sub> ( $n = 1 - 6$ ) at the maximum intensity are plotted as a function of the cluster size. In Fig. 5(c)–(f), the band profiles of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>n</sub> ( $n = 3 - 6$ ) are symmetric as compared to that of TRA<sup>+</sup>-(N<sub>2</sub>)<sub>2</sub> due to drastic decrease in the band intensities on the red side of the bands in Fig. 5(c)–(f). As is shown in Fig. 6, the wavenumbers of the maximum intensity for TRA<sup>+</sup>-(N<sub>2</sub>)<sub>n</sub> ( $n = 3 - 6$ ) show no further large spectral shifts from that of the 2H(planar) isomer. This observation implies that the microsolvation of more than two nitrogen

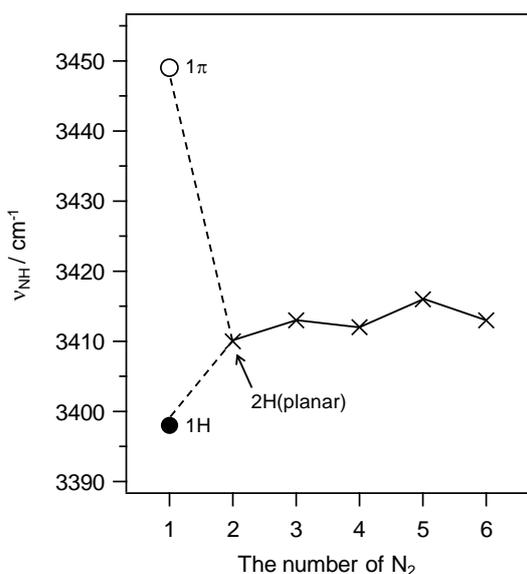


Fig. 6. Plot of the maxima of the NH stretching vibration in the IRPD spectra of  $\text{TRA}^+(\text{N}_2)_n$  ( $n = 1 - 6$ ) as a function of the cluster size. The two isomers, 1H and 1 $\pi$ , are indicated by the open and filled circles. In  $\text{TRA}^+(\text{N}_2)_2$ , three structural isomers are identified in the IRPD spectrum, but the wavenumber of the 2H(planar) isomer is shown in the figure. Further large spectral shifts are not observed for  $\text{TRA}^+(\text{N}_2)_n$  ( $n = 3 - 6$ ) as compared with that of the 2H(planar) isomer.

molecules to  $\text{TRA}^+$  proceeds with the core H-bond structure where two nitrogen molecules are H-bonded to the NH group on the same plane of the indole ring, and the other nitrogen molecules are attached to the  $\pi$ -cloud of  $\text{TRA}^+(\text{N}_2)_n$  ( $n \geq 3$ ).

### 3. Conclusion

IR photodissociation spectra of  $\text{TRA}^+(\text{N}_2)_n$  ( $n = 1 - 6$ ) have been measured in the vicinity of the NH stretch fundamental of the indole moiety to investigate the weak H-bonding interaction of  $\text{TRA}^+$  with non-polar nitrogen molecules. In the IRPD spectrum of  $\text{TRA}^+(\text{N}_2)_1$ , two structural isomers were identified, in which a nitrogen molecule is H-bonded to the NH group of the indole moiety of  $\text{TRA}^+$ , or it is attached to the  $\pi$ -cloud of

$\text{TRA}^+$ . In the IRPD spectrum of  $\text{TRA}^+(\text{H}_2\text{O})_2$ , three stable isomers contribute to the red-shaded asymmetric band profile. The red side of the band is assigned to the NH stretching vibrations of the 1H/1 $\pi$  and 2H(vertical) isomers, whereas the blue side at the maximum intensity is assigned to that of the 2H(planar) isomer.  $\text{TRA}^+(\text{N}_2)_n$  ( $n = 3 - 6$ ) show no further large spectral shifts from that of the 2H(planar) isomer, indicating that the microsolvation of  $\text{TRA}^+(\text{N}_2)_n$  ( $n = 3 - 6$ ) proceeds with the H-bond core where two nitrogen molecules are doubly H-bonded to the NH group. Thus, the core structures of  $\text{TRA}^+(\text{N}_2)_n$  ( $n = 3 - 6$ ) change from the mono to doubly H-bonded structures, and  $\text{TRA}^+(\text{H}_2\text{O})_2$  is on the borderline of the structural switching, because three structural isomers having different H-bond motifs are identified in  $\text{TRA}^+(\text{N}_2)_2$ .

### 4. Acknowledgement

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### 5. References

- 1 G. R. Desiraju and T. Steiner, *The weak hydrogen bond in structural chemistry and biology*, Oxford University Press, 2001.
- 2 N. Solca and O. Dopfer, *Phys. Chem. Chem. Phys.* 2004, **6**, 2732.