



Vibrational predissociation of aniline(pyrrole)(water)₂⁺ and aniline(pyrrole)(water)₃⁺: Structures and dissociation dynamics



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ABSTRACT

Vibrational predissociation spectra of aniline(pyrrole)(water)₂⁺ and aniline(pyrrole)(water)₃⁺ clusters were taken at 2700–4000 cm⁻¹ to verify their most stable structures. One N–H of aniline was bonded to the π electron of pyrrole while the other N–H was bonded to water. Pyrrole molecule was arranged in such a way that N–H of pyrrole formed another hydrogen bond with a water molecule nearby. Water molecule was more easily ejected than pyrrole for both AnPyW₂⁺ and AnPyW₃⁺ although pyrrole had smaller binding energy than water.

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1. Introduction

Vibrational spectroscopy presents both static and dynamical pictures of molecules whereas ordinary X-ray diffraction (XRD) method gives their structural information [1]. While vibrational spectroscopy is less powerful for the purpose of structural analysis than XRD, it certainly manifests its unique advantages and provides essential information on intramolecular forces which act between atoms in molecules, intermolecular forces in clusters and condensed phase, and nature of chemical bonding. Besides, vibrational spectroscopy can be employed for any types of samples such as solids or powders, liquids, gases, films, and adsorbed species.

Recently, vibrational spectroscopy proved to be extremely powerful to elucidate structures of various gas-phase clusters [2–4] produced by molecular beam expansion. Among many, molecular clusters formed *via* hydrogen bonds are of particular interest as they can be regarded as a model system to mimic solvated biological molecules *in vivo*, providing their intrinsic characteristics of fundamental processes without the presence of external biological environment [5]. Furthermore, determination of the structures for complicated clusters [2,6] is now feasible through comparison of theoretical calculations with spectroscopic data.

Aniline is one of the simplest prototype molecules to be adopted to investigate the solvated structures of so called “bio-building blocks” such as DNA bases as it has two N–H bonds which can make

hydrogen bonds with solvent molecules [7]. Many researchers reported experimental results on various solvated aniline systems employing infrared (IR) spectroscopy as well as bare aniline [8], taking advantage of its unsurpassed sensitivity to the presence of hydrogen bonding: dynamics [9], homo and hetero dimers [10–13], ternary clusters [14,15], and solvated aniline clusters with inert gas [16], water [17–19], methanol [17,20,21], N₂, CH₄, CHF₃, and CO as solvents [22].

Here, we have chosen water and pyrrole as solvent molecules around aniline cation to investigate large cluster ions with more than two solvent molecules such as aniline(pyrrole)(water)₂⁺ (AnPyW₂⁺) and aniline(pyrrole)(water)₃⁺ (AnPyW₃⁺). Most of the spectroscopic works on hydrogen-bonded clusters of aromatic ions were carried out for ternary clusters and experimental results on larger systems are quite limited [4,6,23–25]. In this respect, we attempt to verify the detailed structures of AnPyW₂⁺ and AnPyW₃⁺ by employing IR predissociation spectroscopy together with density functional theory (DFT) calculation. Interestingly, we observed that ejection of one water molecule was the dominant channel in IR dissociation.

2. Experimental

Details of the experimental setup were given previously [15,20,26]. Briefly, a linear tandem type mass spectrometer was employed to detect mass-selected cluster ions. Neutral clusters were generated by supersonic expansion of a gas mixture consisting of aniline, pyrrole, and deionized water with a ratio of 1:1:10, respectively. They were ionized at the first stage of the tandem mass

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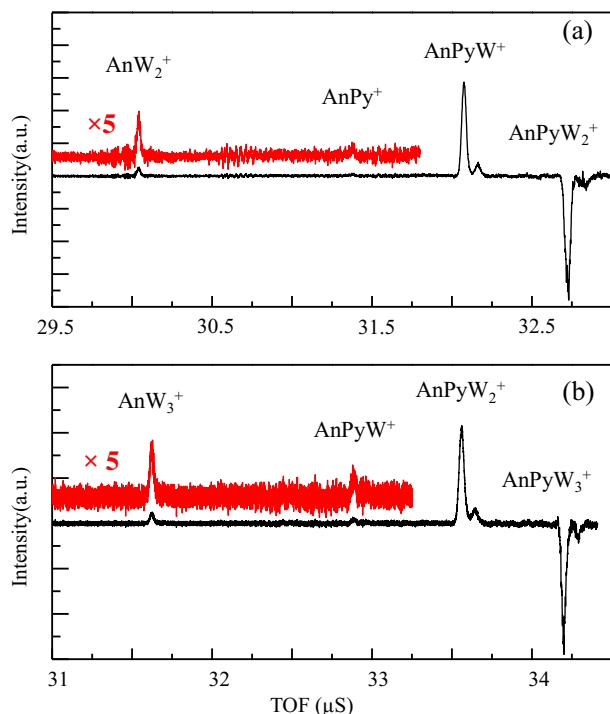


Fig. 1. Infrared photodissociation spectra of (a) AnPyW_2^+ and (b) AnPyW_3^+ exciting symmetric N–H mode of aniline 3000 cm^{-1} and 2990 cm^{-1} , respectively.

spectrometer by two photon absorption at 266 nm, the fourth harmonic output of an Nd^{3+} -YAG laser (GCR 150-10, Spectra Physics). Cluster ions were mass selected by a deflector mounted between the first and the second stage. Mass-selected ions were photodissociated in the second stage upon absorption of an IR photon from a lithium niobate optical parametric oscillator pumped by an injection-seeded Nd^{3+} -YAG laser (1064 nm, SL III-10, Continuum). Photofragmentation was carried out under an electric field so that the fragment ions were separated from the parents. Both fragment and parent ions were detected using a micro channel plate (MCP), whose signals were accumulated by a digital storage oscilloscope (500 MHz, Wave Surfer, LeCroy). The structures of cluster ions were calculated by DFT at the level of B3LYP/cc-pVDZ using GAUSSIAN 09. Besides, the theoretical absorption spectra of the optimized structural isomers were obtained and they were compared with the experimental IR predissociation spectra. Relative energies of the isomers were calculated after zero point energy correction from frequency calculation. For the binding energies, basis set superposition error (BSSE) correction was performed. Multiplying factors of 0.96 and 0.975 for AnPyW_2^+ and AnPyW_3^+ , respectively, were applied to match the theoretical and experimental spectra.

3. Results and discussion

3.1. Infrared predissociation of AnPyW_2^+

Fig. 1(a) shows the IR photodissociation mass spectrum for AnPyW_2^+ at 3000 cm^{-1} . As it is a difference (IR photodissociation laser on-off) spectrum, the negative signal for the parent ion corresponds to the reduced intensity of the parent ions due to the photofragmentation by absorbing an IR photon. Positive daughter ion signals at $\sim 32.07\text{ }\mu\text{s}$ and $\sim 30.03\text{ }\mu\text{s}$ represent the removal of one water and one pyrrole molecule from the parent, respectively. The daughter ion signal for AnPy^+ was barely visible at $\sim 31.38\text{ }\mu\text{s}$ implying that the dissociation channel for the ejection of two water molecules is nearly blocked.

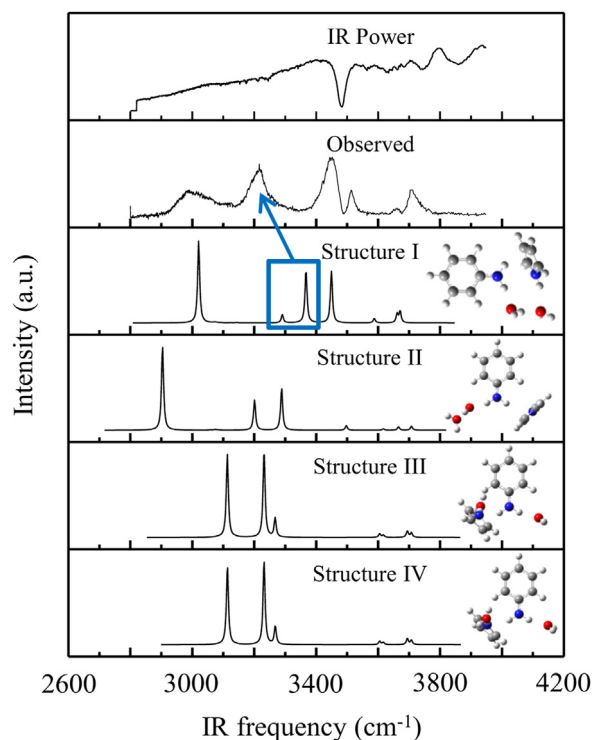


Fig. 2. Observed and calculated infrared spectra with possible structures of AnPyW_2^+ with IR laser fluence. The wave number in the calculated result was multiplied by 0.96. Calculated structures by the density functional theory at a level of B3LYP/cc-pVDZ using GAUSSIAN 09 are also shown.

The IR predissociation spectrum of AnPyW_2^+ was obtained in the range of $2700\text{--}4000\text{ cm}^{-1}$ as shown in Fig. 2 by monitoring AnPyW^+ daughter ion intensity. The signal-to-noise ratio of the IR predissociation spectra for the minor channels was not satisfactory but the overall features were nearly the same as the major channel. Also, the mode-dependence in the branching ratio was not significant; the changes in the branching ratio for different modes were less than 7%. All the observed vibrational peaks were assigned and compared with the calculated spectra for four different optimized structures (shown in Figs. 2 and S2 for clear view) obtained by DFT calculation. The zero point corrected energies (ZPCE) of the possible isomers are listed in Tables 1 and S1 [27]. The structure I is considered to be the most probable isomer for AnPyW_2^+ through comparison of the experimental and theoretical spectra. The ZPCE for each optimized structure indicates that the structure I is more stabilized by 905 , 1461 , and 1462 cm^{-1} than the structures II, III, and IV, respectively. Table S2 [27] displays the assignment of different vibrational modes for the observed and calculated possible structures. The broad absorption signal at $\sim 3000\text{ cm}^{-1}$ is assigned as N–H of aniline bonded to water or symmetric stretching mode of NH_2 of aniline, which is in good agreement with the calculated spectrum at 3020 cm^{-1} . For ordinary intermolecular vibrational mode with no broadening due to hydrogen bonding such as aniline–Ne, the bandwidth as measured using the same instrument was $\sim 13\text{ cm}^{-1}$.

According to Inokuchi et al. [18], the symmetric NH_2 stretching mode of aniline was observed at $\sim 3105\text{ cm}^{-1}$ when one water molecule was bound to the N–H of aniline via hydrogen bonding as they analyzed the structure of AnW_n^+ ($n=1\text{--}8$) cluster ions. On the other hand, it shifted to red when either two or more hydrogen bonded water molecules were associated with N–H of aniline in AnW_3^+ or larger clusters; the symmetric NH_2 modes of AnW_3^+ and AnW_4^+ were observed at 3070 and 2960 cm^{-1} , respectively [18]. In case of AnPyW_2^+ , the symmetric NH_2 stretching mode also showed

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