Chemical Physics 419 (2013) 184–192

Contents lists available at SciVerse ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Solvated structures of pyrrole–acetonitrile binary clusters studied by infrared cavity ringdown spectroscopy

Jun-ichi Iwamoto, Yoshiteru Matsumoto *, Kenji Honma

Graduate School of Material Science, University of Hyogo, 3-2-1 Kohto, Kamigori, Hyogo 678-1297, Japan

ARTICLE INFO

Article history:
Available online 31 January 2013

Keywords:
Pyrrole
NH stretching vibration
Jet-cooled cluster
IR cavity ringdown spectroscopy
Solvated structure
DFT calculation
Natural bond orbital analysis
Cooperative effect

ABSTRACT

We studied solvated structures of jet-cooled pyrrole–acetonitrile (Py–AcN) binary clusters by infrared cavity ringdown spectroscopy. The observed NH stretching vibrations were analyzed by density functional theory of the M06-2X/6-311++G(d, p) level, in which the energetically optimized structures, harmonic frequencies, and binding energies were calculated for various sizes of binary clusters. We found that the Py_1–$(AcN)_1$ cluster has two structural isomers; one is a hydrogen-bonded structure having a linear N–H···N≡C H-bond, and the other is a dipole-interacted structure, in which the AcN molecule is above the Py plane. The Py_1–$(AcN)_2$ cluster was found to have a cyclic structure formed by a single N–H···N≡C H-bond and dipole–dipole interactions among Py and two AcN molecules. A natural bond orbital analysis was performed to reveal the large NH stretching red-shift of the Py_1–$(AcN)_2$ cluster, which can be explained by a cooperative effect on the solvation of the dipole interaction and the CH H-bonds.

1. Introduction

Supersonically jet-cooled solvated clusters are recognized as a microscopic model of the intermolecular interactions between solute and solvent molecules in a solution phase. Such clusters have been studied by experiments and theories to understand the intermolecular structures. Among various solvated clusters, the hydrogen-bonded (H-bonded) clusters constructed by an aromatic molecule with protic solvent molecules, such as water and alcohol, have been investigated by laser spectroscopy very often, because of their fundamental importance in many chemical aspects [1–4]. However, the H-bonded clusters with protic solvents cannot be considered as real "solvated clusters", as described below. An aromatic molecule has a hydrophobic π cloud, whose interaction with the protic moiety of the solvent molecules is usually weak. In addition, if an aromatic molecule also has a protic moiety, such as an OH group, solvent molecules are expected to form H-bonds with the OH group of the solute molecule prior to the hydrophobic π cloud. Thus, the hydrophobic moiety of the solute molecule is isolated from a self-aggregate cluster by solvent molecules. That is, the solute molecule is not surrounded by solvent molecules. If we want to obtain such a solvated structure in a jet-cooled cluster, it is appropriate to apply aprotic solvent molecules. An aprotic molecule is expected to interact easily with the hydrophobic moiety of the solute molecule by weak van der Waals interaction.

Acetonitrile (C_2H_3N, AcN) is one of the most fundamental polar-aprotic molecules. The AcN molecule has several H-bonding sites, such as lone-pair electrons on the N atom of the C≡N group and the C–H bond of the methyl group. In addition, the most characteristic property of AcN is a large permanent dipole moment (3.44 Debye), which makes dipole–dipole or dipole-induced dipole interactions with a hydrophobic solute molecule. Even if the solute molecule has a small permanent dipole moment, AcN can easily induce a large dipole moment to the hydrophobic aromatic π cloud. Therefore, the AcN molecule is appropriate to understand the intermolecular structures of solvated clusters, whose aromatic π cloud is surrounded by solvent molecules. However, there have been a few spectroscopic and theoretical studies of solvated clusters containing AcN molecules until now. Sammy El-Shall et al. presented the well-resolved $B_{2u} \leftarrow A_{1g}$ transition of benzene–AcN binary clusters based on the resonant two-photon ionization technique [5]. By combining with a Monte-Carlo simulation, they revealed that the benzene–$(AcN)_{1-4}$ clusters are dominated by the anti-parallel AcN dimer, or the cyclic AcN trimer. Kryachko et al. [6] and Cabaleiro-Lago et al. [7] presented *ab initio* and density functional theory calculations of phenol–$(AcN)_{1,2}$ clusters to reveal the intermolecular structures, energies and vibrational frequencies.

Among many experimental techniques of laser spectroscopy, IR spectroscopy in the OH or NH stretching regions is a powerful method to probe intermolecular interactions like H-bonds and van der Waals interactions. Recently, we reported on the IR cavity ringdown spectroscopy (IR-CRDS) of the pyrrole (C_4H_5N, Py) clusters in the NH stretching region [8,9]. In this study, we revealed that the H-bond formations between the NH group and the

---

* Corresponding author. Tel./fax: +81 791 58 0166.
E-mail address: matsu@sci.u-hyogo.ac.jp (Y. Matsumoto).

0301-0104/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemphys.2013.01.032

aromatic π electron cloud assemble the Py self-aggregate clusters of the T-shaped dimer, the cyclic trimer and tetramer. The Py molecule has not only the above-mentioned H-bond sites (NH group and aromatic π cloud), but also a relatively large permanent dipole moment (∼2 Debye). This suggests that the polar-aprotic solvent molecules, such as AcN, are expected to cause dipole–dipole and dipole-induced dipole interactions with the Py molecule. Therefore, the Py–AcN binary clusters can be a good model to understand solvated structures in a solution phase. In fact, most recently, we have presented the IR spectroscopy of the Py–acetone binary clusters [10]. In this study, we revealed that the Py–(acetone)$_2$ binary cluster has a cyclic structure, which is formed by the N–H⋯O=C H-bond between Py and acetone, the dipole–dipole interaction between two acetone molecules, and a weak C–H⋯π H-bond between Py and acetone. This previous study will be a good reference to analyze the structures and vibrations of Py–AcN binary clusters.

In this paper, we consider the NH stretching vibrations of the Py–AcN binary clusters measured by IR-CRDS. The intermolecular structures were determined by combining the observed IR spectra and the vibrational analysis by DFT calculations. First, we show the IR spectra of the binary clusters measured under the various jet conditions in order to assign the observed bands. Then, we discuss the intermolecular interactions, such as H-bonds and dipole interactions, and their harmonic frequencies of the NH stretching vibrations by applying the DFT calculation to the observed results. Second, we apply the natural bond orbital (NBO) analysis to the Py$_1$–(AcN)$_1$ and Py$_1$–(AcN)$_2$ binary clusters, and discuss the donor–acceptor interactions and the associated stabilization energies due to various H-bonds of N–H⋯N≡C, C–H⋯N, and C–H⋯π. Then, we reveal that the difference of the NH stretching red-shift between Py$_1$–(AcN)$_1$ and Py$_1$–(AcN)$_2$ clusters is caused by a cooperative effect for the Py$_1$–(AcN)$_2$ cluster due to dipole interactions and CH H-bond formations.

2. Experimental and theoretical section

The IR cavity ringdown spectrometer used in this study has been described in detail elsewhere [8,9]. Briefly, we produced Py–AcN binary clusters in a supersonic expansion. Py and AcN vapors were diluted by the helium (He) carrier gas through liquid AcN and Py sequentially. The vapor pressure of Py was fixed to 4 Torr by cooling a liquid sample at 273 K, while that of AcN was changed to 1.3–23 Torr at 233–273 K. The stagnation pressure was fixed to 2 atm. The gas mixture of Py/AcN/He was expanded into a vacuum chamber through a pulsed nozzle. In this work, we used two kinds of nozzle shapes: one was a circular orifice with a 2 mm diameter; the other was a thin slit ($0.1 \times 10\ \mathrm{mm}^2$), which was directly mounted on the above-mentioned circular shape nozzle [8,9]. The vacuum chamber was pumped by a 10 inch diffusion pump backed by a rotary pump, and the typical background pressures without and during a pulsed nozzle operation were 3×10^{-6} and 6×10^{-5} Torr, respectively.

A tunable IR laser was generated by difference frequency mixing between the second harmonic of a Nd:YAG laser and a dye laser pumped by the same YAG laser. A LiNbO$_3$ nonlinear crystal was used for mixing. The output pulse energy and the linewidth were ∼1.0 mJ/pulse and ∼1 cm^{-1}, respectively. The ringdown cavity was constructed by two highly reflective concave mirrors (R = 99.97% at 2.9 μm, f = −3000 mm). The cavity length was 600 mm, and its axis was set to 10 mm downstream from the pulsed nozzle for a supersonic expansion. An IR laser was introduced from one side of the cavity, and the transmitted laser light from the other side of the cavity was detected by a thermoelectrically cooled InAs detector through a CaF$_2$ lens (f = 25 mm). The detected signal was digitized in a digital oscilloscope. The decay curve, usually called the ringdown waveform, for each laser shot was sent to a personal computer, in which the waveforms were averaged over every 10 shots. Then, the decay time (τ) was obtained by a least-squares fitting of a first-order exponential function. The total round-trip loss (Γ) of light in the cavity was calculated from τ using

$$\Gamma = 1 - \exp(-2L/c\tau),$$

where L is the cavity length and c is the speed of light. The absorption loss per round-trip could be obtained by subtracting the Γ measured in an empty cavity from that with the jet-cooled clusters. As can be seen in the IR spectra of this paper, the signal-to-noise ratio in the range of 3460–3500 cm^{-1} is poor. Since the nonlinear crystal (LiNbO$_3$) used in this study contained a small amount of water, the IR laser output became very low in this region. Then, the ringdown waveform digitized in an oscilloscope was substantially distorted in this region. As a result, the exponential curve fitting is inaccurate.

The GAUSSIAN 09 program [11] was used to calculate the optimized structures, the intermolecular binding energies, and the vibrational frequencies of the Py–AcN binary clusters. The calculations were carried out by DFT of M06-2X/6-311++G(d, p). For all of the optimized structures, the calculated vibrational frequencies were scaled down by a factor of 0.9507 to correct for any anharmonic effects. The intermolecular binding energies were corrected by the zero-point energy (ZPE) and the basis set superposition error (BSSE). The ZPE was also scaled by the above-mentioned factors. The BSSE was obtained by the full counterpoise procedure [12,13]. We also performed the natural bond orbital (NBO) analysis for the optimized structures of the Py$_1$–(AcN)$_1$ and Py$_1$–(AcN)$_2$ clusters to obtain the second-order stabilization energies in donor–acceptor perturbative interactions [14,15]. We used the GaussView 5.0 program to analyze and visualize the calculated structures and vibrations [16]

3. Result and discussion

3.1. Vibrations and structures of pyrrole–acetonitrile binary clusters

The IR spectra of the Py self-aggregate and the Py–AcN binary clusters are shown in Fig. 1. These spectra were measured at various AcN vapor pressures (1.3, 6.4, and 23 Torr) with a constant Py vapor pressure of 4 Torr and a total stagnation pressure of 2 atm. Fig. 1(a) shows the IR spectrum measured without any AcN vapor. This spectrum is equivalent to those reported in our previous study [8,9]. The band at 3531 cm^{-1} has been assigned to the NH stretching vibration of the Py monomer. In addition, the bands at 3444, 3392, and 3382 cm^{-1} have been assigned to the H-bonded NH stretches of the T-shaped dimer, the cyclic trimer, and the cyclic tetramer, respectively. These assignments and associated structures were consistent with those determined by previous FT-IR spectroscopic studies [17,18].

Fig. 1(b)–(d) show the IR spectra obtained from a mixture gas of Py/AcN/He. The IR spectrum measured under the condition of the AcN vapor pressure of 6.4 Torr is shown in Fig. 1(c). We observed nine bands in the region of 3350–3540 cm^{-1}. Among them, four bands were already assigned to the NH stretches of the Py monomer and its self-aggregate clusters, as shown in Fig. 1(a). On the other hand, the bands at 3501, 3437, 3413, 3376, and 3357 cm^{-1} were only observed under the condition of the Py and AcN vapor mixtures. Thus, we assigned these bands to the NH stretches ascribed to Py–AcN binary clusters. Fig. 1(b) and (d) show the IR spectra measured under the conditions of the AcN vapor pressures of 1.3 and 23 Torr, respectively. Among five NH stretches ascribed