

# Infrared depletion spectroscopy of the doubly hydrogen-bonded aniline–(tetrahydrofuran)<sub>2</sub> complex produced in supersonic jet

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## Abstract

The vibrational frequencies of the N–H stretching modes of aniline after forming a strong doubly H-bonded complex with tetrahydrofuran (THF) are measured with infrared depletion spectroscopy that uses cluster-size-selective resonance-enhanced multiphoton ionization (REMPI) time-of-flight mass spectrometry. Two strong infrared absorption features observed at 3355 and 3488 cm<sup>-1</sup> are assigned to the symmetric and antisymmetric N–H stretching vibrations of the 1:2 aniline–THF complex, respectively. The red-shifts of the N–H stretching vibrations of aniline agree with the ab initio calculated (MP2/6-31G\*\*) aniline–(THF)<sub>2</sub> structure in which both aniline N–H bonds interact with the oxygen atom of THF through two hydrogen bonds. The calculated binding energy is found to be 29.6 kJ mol<sup>-1</sup> after corrections for basis set superposition error (BSSE) and zero-point energy. The calculated structure revealed that the angle between the N–H bonds in the NH<sub>2</sub> group increased to 112.5° in the aniline–(THF)<sub>2</sub> complex from that of 109.8° in the aniline. The electronic 0–0 band origin for the S<sub>1</sub> ← S<sub>0</sub> transition is observed at 32,900 cm<sup>-1</sup> in the aniline–(THF)<sub>2</sub> complex, giving a red-shift of 1129 cm<sup>-1</sup> from that of the aniline molecule.

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## 1. Introduction

Hydrogen bonds formed between a proton donor molecule and a base (e.g., containing nitrogen or oxygen lone pair donors) are responsible for the existence of various stable H-bonded complexes in biological systems [1]. The partial charge-transfer nature of such bonds makes them exceptionally stable among neutral clusters, with binding energies of 8–24 kJ/mol [1]. When a molecule is involved in a hydrogen bond, its vibrational frequencies are red-shifted (or sometimes blue-shifted) from the isolated molecular values [2,3]. It is

possible to study the nature of the hydrogen bond by observing the infrared spectrum of the complex in a supersonic jet in which the number of interacting molecules is well-defined [4–8]. Among the new spectroscopic methods available, infrared depletion spectroscopy that utilizes the IR–UV double resonance and REMPI-TOF mass spectrometry enables one to measure the infrared spectrum of the hydrogen-bonded complexes with relatively high sensitivity and mass selectivity [9,10]. We have recently reported [11] the resonant two-photon ionization (R2PI) spectrum of 1:1 aniline–tetrahydrofuran (THF) complex at a mass number of 165. The R2PI spectrum has revealed an absorption band at 33,255 cm<sup>-1</sup>, which is red-shifted by 774 cm<sup>-1</sup> from the 0–0 band of free aniline, has been assigned to the S<sub>1</sub> ← S<sub>0</sub> 0–0 transition of the aniline–THF complex. By measuring the depletion of the R2PI signal as a

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function of infrared laser frequency, two strong features observed at 3370 and 3479.3  $\text{cm}^{-1}$  have been assigned to the H-bonded and free N–H stretching vibrations respectively of the 1:1 aniline–THF complex. An intermolecular bending mode with a long progression at 15.5  $\text{cm}^{-1}$  has been found to associate with the lower wavelength region of the R2PI spectrum. It has been speculated [11] that two bands observed at longer wavelengths than the 0–0 band, might be carried by the 1:2 aniline–THF complex. To test this hypothesis we have investigated the 1:2 aniline–THF complex. When the recording of the R2PI spectrum of aniline–THF at mass number 165 was extended further to a significantly higher wavelength region, a rich spectrum was observed until an intense feature appeared at 32,900  $\text{cm}^{-1}$ . The feature at 32,900  $\text{cm}^{-1}$  was tentatively assigned to the  $S_1 \leftarrow S_0$  0–0 transition of the 1:2 aniline–THF complex, which is followed by the elimination of a THF molecule. The 1-color two photon method injects a large amount of energy into the molecule, which apparently is sufficient to dissociate the ionized aniline–(THF)<sub>2</sub> complex.

We report here experimental results, from an infrared depletion spectroscopic technique [12], on the vibrational frequencies of the N–H stretching modes of the aniline–(THF)<sub>2</sub> complex. The one-color-resonant two-photon ionization (R2PI) spectrum of aniline–(THF)<sub>2</sub> complex was recorded at mass number 237. The strong band at 32,900  $\text{cm}^{-1}$ , which appears as the last feature in the spectrum, has been assigned to the 0–0 band of the  $S_1 \leftarrow S_0$  electronic transition. The depletion of the two-photon ionization signal at 32,900  $\text{cm}^{-1}$  was measured as a function of infrared laser frequency. In the infrared depletion spectrum two strong features observed at 3355 and 3488  $\text{cm}^{-1}$  are assigned to the symmetric and anti-symmetric H-bonded N–H stretching vibrations of the aniline–(THF)<sub>2</sub> complex. The red-shift of the N–H stretching vibrations of aniline is used as a reference for the ab initio calculated aniline–(THF)<sub>2</sub> structure, where both the N–H bonds of aniline interacts with the lone pair of the oxygen atom of two THF molecules through hydrogen bonds. The calculated (MP2/6-31G\*\*) aniline–(THF)<sub>2</sub> structure gives a binding energy of 29.6  $\text{kJ mol}^{-1}$  after corrections for basis set superposition error (BSSE) and zero-point energy. Interestingly the structure reveals that the angle between the N–H bonds in the NH<sub>2</sub> group increases from 109.8° in aniline monomer to 112.5° in the aniline–(THF)<sub>2</sub> complex.

## 2. Experimental

The experimental apparatus used for the study of infrared depletion spectroscopy of aniline–(THF)<sub>2</sub> complex is shown in Fig. 1. Details of the apparatus and of the measurement procedures have been previously reported [13–16]. Only salient features are given here.

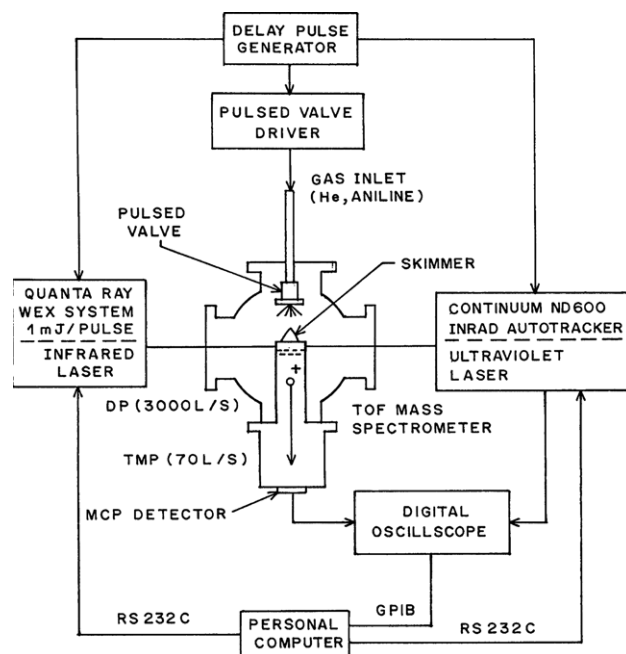


Fig. 1. A schematic diagram of the apparatus used for REMPI and IR depletion spectrum.

Aniline complexes were formed in the supersonic expansion of a mixture of aniline and tetrahydrofuran (THF) vapors by helium carrier gas at room temperature, with a stagnation pressure of 2.0 bar. The vapors of aniline and THF were obtained by bubbling helium gas in their liquid mixture. Only a small amount (about 0.1%) of THF was dissolved in liquid aniline. Finally, the gas mixture was injected into a vacuum chamber through a pulsed valve (general valve, 0.8 mm diameter), which was operated at 10 Hz with a pulse duration time of 250  $\mu\text{s}$ , and then introduced into the ionization region of a time of flight mass spectrometer (TOF/MS) through a skimmer of 1 mm diameter. The skimmed beam intersected the frequency doubled dye-laser beam in the ion acceleration region of the TOF/MS. A high-voltage extraction pulse sampled the positive ionized complexes. A 12-inch oil diffusion pump and a turbo-molecular pump differentially pumped the source chamber and the flight tube, respectively. Under normal operating conditions, the pressure in the source chamber was  $1 \times 10^{-5}$  Torr.

The aniline–(THF)<sub>2</sub> complex was detected by the TOF/MS after one-color resonant two photon ionization (R2PI) via the  $S_1$  state, with a UV laser around 300 nm, generated by the frequency doubling of the output of a dye laser (Continuum, ND6000). The pulse and bandwidths of the laser were 5 ns and 0.1  $\text{cm}^{-1}$ , respectively. The energy of the UV laser beam was reduced to a few hundreds  $\mu\text{J/pulse}$  in order to minimize the fragmentation of the aniline–(THF)<sub>2</sub> complexes by UV multiphoton absorption.

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