Vibronic spectroscopy of the H-bonded aminophenol–water complex

P. S. Meenakshi, N. Biswas, and S. Wategaonkar

Department of Chemical Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai, 400005, India

(Received 23 January 2002; accepted 30 September 2002)

In this work, the vibronic spectroscopy of the p-aminophenol–water 1:1 complex is presented. The \( S_1 \) vibrational energy levels of the complex were characterized by REMPI spectroscopy up to 2500 cm\(^{-1} \) above the band origin. The dispersed fluorescence spectra were recorded for the B.O., \( \alpha_{S_1} \) and \( \beta_{S_1} \) excitations to characterize the vibrational levels in the \( S_0 \) state of the complex. Stimulated ion depletion spectroscopy was carried out to determine the higher vibrational levels of the ground state all the way up to \( \sim 3075 \) cm\(^{-1} \). The structure and the vibrational levels of the AP–W\(_1\) complex were calculated \( \text{ab initio} \) at the HF level and DFT with B3LYP functional for \( S_0 \), and CIS level for \( S_1 \) using 6-31G** basis set. The structure of the AP–W\(_1\) complex compared well with the earlier calculations for this case as well as the other ROH–water (R=aromatic group) complexes reported in the literature. However, the redshift in the electronic band origin was almost half of that observed in other cases. A good correlation was shown to exist between the electronic red shifts and the respective \( pK_a \) values (the \( pK_a \) in the excited state). © 2002 American Institute of Physics.

[DOI: 10.1063/1.1525059]

INTRODUCTION

Water, a universal protic solvent with fascinating properties has kept researchers constantly intrigued. The strength of water as a solvent lies in its ability to form H-bonding networks that strongly influence the properties of the solutes. In the last couple of decades there has been a surge in the activity of studying the H-bonding interaction of water molecules in the gas phase at a microscopic level. Small clusters of water molecules are formed using supersonic jet expansion method and are probed using various spectroscopic techniques in a size-controlled manner. Some of the molecules whose complexes with water molecules are extensively studied in the H-bonding context are benzene,\(^1\) anthracene,\(^2\) phenol,\(^3\) cresol,\(^4\) \( \beta \)-naphthol,\(^5\) and tropolone.\(^6\)

We present here a comprehensive spectroscopic study of the H-bonded aminophenol–water (AP–W\(_1\)) complex in the \( S_0 \) and \( S_1 \) states. Hydrogen bonding interaction of water molecule with p-aminophenol (AP) presents an interesting case since AP has an amino and a hydroxyl group in para position to each other. Out of four different configurations that are possible only one conformer has been reported\(^7\) in the gas phase. AP also turns out to be a compound that has drug-receptor interactions.

In the recent report\(^8\) on the AP–W\(_1\) complex IR–UV double resonance experiments as well as \( \text{ab initio} \) calculations were carried out on the \( S_0 \) and \( D_0 \) electronic levels. From the IR/R2PI spectrum only one conformer was inferred and based on the observed redshift of 121 cm\(^{-1} \) in the phenolic OH stretching frequency, it was attributed to a structure in which the water molecule attaches to the OH end as a H-bond acceptor. In the \( D_0 \) state, spectral signatures of a second structure that contains the N–H⋯O hydrogen bond were observed. Calculations were carried out at the HF and DFT level and only two stable structures were reported for the ground state. In this work the REMPI studies were carried out up to 2500 cm\(^{-1} \) above the band origin to characterize the vibronic levels of the \( S_1 \) state.

The dispersed fluorescence (DF) measurements and stimulated ion depletion (SID) experiments were also carried out. The ground state vibrational levels were characterized all the way up to 3075 cm\(^{-1} \) with the help of the DF and SID data. The REMPI spectrum of the AP–W\(_1\) indicated the presence of only one conformer that was characterized using \( \text{ab initio} \) calculations at the HF, DFT (B3LYP), and CIS levels with 6-31G** basis set. Our results are in good agreement with and complementary to the results that have been reported.

In the past, our laboratory has reported the spectroscopy of AP (Ref. 8) and the basic spectroscopic data for the monomer is available. Individually, the phenol–water and aniline–water complexes have been studied by several groups in the past and these data are also available for comparison. The phenol–water complex has been extensively studied in \( S_0 \), \( S_1 \),\(^9\)–\(^13\) and \( D_0 \) (Refs. 14–17) states. In all the three states, phenol acts as the proton donor and water as the acceptor. In a report\(^18\) on the aniline–water cation spectroscopy it was suggested that the most stable structure in the ground state is the one in which the NH\(_2\) group acts as the hydrogen bond acceptor and water as the donor. For the \( S_1 \) state an exactly opposite structure was inferred based on the lack of a structured REMPI spectrum. The spectroscopic data presented below characterizes the vibronic structure of the AP–W\(_1\) comple-

\footnote{Electronic mail: sanwat@tifr.res.in}