Study of molecular interactions in aniline and its aqueous solutions: experiment and calculations

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В данной работе жидкий анилин изучали в чистом виде и водном растворе с использованием экспериментальных и теоретических расчетов. С помощью спектров КР анализировали область 100–3200 см$^{-1}$. В этой области наблюдалось синее и красное смещение. Впервые установлено, что причины этого сдвига связаны с неклассической водородной связью C–H···O в комплексообразовании и подтверждены результатами расчетов с использованием теоретического DFT//BL3YP/6-311+G(2d,p) метода. Механизмы образования агрегатов с молекулами анилин+$(H_2O)_7$ также были проанализированы с помощью теоретических расчетов. Расчеты показывают, что полная энергия увеличивается с увеличением числа молекул воды при образовании агрегатов.

Ключевые слова: анилин, ароматическое кольцо, водородная связь, красное смещение, синее смещение, расчеты DFT.

In this work, a liquid aniline was studied in a pure and aqueous solution using experimental and theoretical calculations. Using Raman spectra, the region of 100–3200 cm^{-1} was analyzed, and blue shift and red shift were observed in this region. For the first time, the reasons for this shift were found to be due to the C–H···O nonclassical hydrogen bonding in the complex formation and were confirmed in the results calculated using the theoretical DFT//BL3YP/6-311+G(2d,p) method. Mechanisms of aggregate formation with aniline+$(H_2O)_7$ molecules were also analyzed using theoretical calculations. Calculations show that the total energy increases with the increase in the number of water molecules in the formation of aggregates.

Keywords: aniline, aromatic ring, hydrogen bond, red shift, blue shift, DFT calculations.

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I. Introduction

The study of the nature of weak intermolecular interactions has been of great interest in recent years because they play a key role in determining the physical-chemical properties of molecular structures in a condensed medium [1-6]. It is also important to study the weak nonclassical interactions (NH-π, OH-π, CH-π, and cation-π) in addition to normal hydrogen bonding [7]. Aniline is a simple amine representative of aromatic ring substances, and N-H vibration gives good results in the study of hydrogen bonding [8-9]. Water is the most important inorganic solvent in solution acts as a proton-donor or proton-acceptor [10-11]. In [12-13] are studied clusters of water formed with phenol and benzene. The aniline and water molecule are bound to the aniline by the NH cation and the oxygen of the water by H bonding [14]. The NH stretching vibration band is observed around 3250 cm^{-1}, and this band shifts toward the low frequency of 200 cm^{-1} [15]. Israel Wolf et al. [16] studied the mechanism of proton transfer from the water molecule to the anion in the aniline molecule and up to 6 water molecules. In this work, the energy value of water decreases with increasing number of molecules. The values of the calculations and experimental results were found to differ significantly when the number of water molecules was 3 [16]. In [17] are studied the interactions of

aniline and water molecules, suggesting that an N atom in the NH group of aniline had a strong hydrogen bond between the unbound O-atom of the water molecule. In [17-18] is reported that in an aqueous medium of aniline the spectral bands shift in a low frequency side. In the study [19], in contrast, it was found that at high pressures these bands shift towards a higher frequency. Hobza et al. [20] observed a red shift due to hydrogen bonding and a blue shift when the H-bond was C–H···O or C–H···N in aromatic ring substances. This phenomenon was called anti-hydrogen bonding.

In [21] is analyzed the work of Hobza and several scientists and confirmed the phenomenon of blue shift, which, unlike Hobza, was called a nonclassical hydrogen bonding phenomenon. It is clear from the above literature review that the change in spectral band shape in aqueous solutions of aniline has not yet been completed, which in turn requires scientific research in this area. In this paper, an attempt has been made to explain in more detail the mechanisms of formation of molecular clusters in the aniline-water system. To this end, we have studied in this work the interaction of aniline with water molecules and its manifestation in the vibration spectrum.

II. Experimental and calculation methods

The experiments were taken on a 1200 line/mm diffraction grating in ViaRaman spectrometer, using a Spectrum Stabilized Laser Module with a wavelength of 785 nm and a power of 100 mW as the excitation source. The Renishaw CCD was recorded using a camera detector. The calculations were performed in the Gaussian 09 program, based on the DFT method and a set of BL3YP/6-311+G(2d,p) bases [22].

III. Results and discussion

Figure 1 shows the experimental results obtained in liquid aniline and its solutions with water. As can be seen from the figure, the Raman scattering spectra of pure aniline are complex and have multiple vibration maxima. Aniline in pure form corresponds to the C-H stretching vibration band 3056 cm^{-1}, and in solution with water this line shifts to a high frequency of 10 cm^{-1}. Similarly, the 1604 cm^{-1} spectral band corresponding to the stretching vibration CC of the ring shifts in the direction of the high frequency of 2 cm^{-1} in solution with water. The spectral bands 1155 cm^{-1} and 998 cm^{-1} correspond to the HCC and CCC bending vibrations of the ring and shifted in the direction of high frequency by 4 cm^{-1} and 2 cm^{-1}, respectively, in the solution with water.

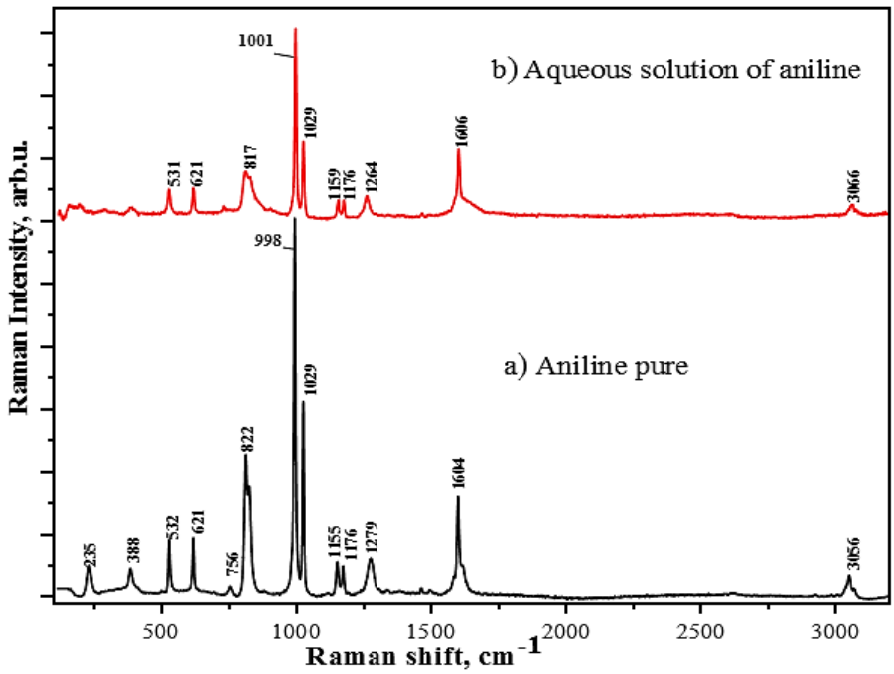


Figure 1. Raman spectra of aniline molecule: a) pure and b) aqueous solution.

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This corresponds to the blue shift phenomenon observed in aromatic ring substances in [20-21] studies, and concludes that the C-H groups of aniline are formed due to the nonclassical hydrogen bond formed by the O atom of water. The spectral bands 1279 cm^{-1} corresponding to the N-C stretching vibration and 822 cm^{-1} corresponding to the bending vibration NH_2 shifted to the lower frequency side by 15 cm^{-1} and 5 cm^{-1}, respectively. This may be due to a red shift in the N–H···O classical hydrogen bond. No shifts are observed in the 532 cm^{-1}, 621 cm^{-1}, 1029 cm^{-1}, and 1176 cm^{-1} bands, suggesting that the atoms that generate the vibrations were not involved in the H-bond. Theoretical calculations were performed to fully explain this process.

Figure 2 shows the orientation of aniline+$(H_2O)_7$ with water molecules. Figure 2a shows the optimization state with the aniline+(H_2O) molecule. As can be seen from the figure, the H14 atom of aniline forms H-bond with the O15 atom of the water molecule, and the bond length is 2.11 Å. Figure 2b shows an aniline+$(H_2O)_2$ aggregate bonded by 3 hydrogen bonds. One of these bonds is a C-H···O shaped nonclassical H-bond between O18 atom of water with aniline H10 atom and bond length of 2.66 Å, and the other is a hydrogen bond with a bond length of 1.91 Å between two water molecules. Also, the H16 atom of water is bonded to the center of the aniline ring by an OH-π type of H-bond with a bond length of ~ 2.8 Å

The energy of formation of this aggregate is 11.0 kcal/mol and the dipole moment is 2.72 D. These bonds are formed by the N12, H14 atoms of aniline and the oxygen, hydrogen atoms of water. The bond length ranged from 1.77 up to 1.98 Å, and the aggregate formation energy and dipole moment had a minimum value of 24.0 kcal/mol and 0.26 D, respectively, it is dependend on the orientation of the molecule.

Figure 2c shows an aniline+$(H_2O)_3$ aggregate bonded by four H-bonds. These bonds are formed by the N_{12} and H_{14} atoms of aniline and the oxygen and hydrogen atoms of water, and the bond length is in the range of 1.77–1.98 Å. The aggregate formation energy and dipole moment had a minimum value of 24.0 kcal/mol and 0.26 D, respectively, which is related to the orientation of the molecule.

Figure 2d shows an aniline+$(H_2O)_4$ aggregate with an aggregate formation energy of 16.25 kcal/mol. This is small compared to the energy of aniline+$(H_2O)_3$, which may be due to the fact that this aggregate is mainly formed by weak bonds. The bonds are bonded by a total of 5 H-bonds, two of which are C-H···O with a bond length of 2.86 Å type nonclassical, OH-π type H-bond with a bond length of ~2.61 Å, N_{12}-H_{26} (H-bond length 1.95 Å) and H_{22}-O_{24} (H-bond length 1.94 Å). The dipole moment had a maximum value of 7.19 D.

Figures 2e and 2f show the aniline+$(H_2O)_5$ and aniline+$(H_2O)_6$ aggregates. In this case, the bond lengths were bonded by 8 H-bonds in the range of 1.79–1.98 Å and bonded by OH-π shaped H-bonds with lengths of 2.61 Å and ~2.69 Å, respectively.

The energy of formation of this aggregate are 35.0 kcal/mol and 39.0 kcal/mol. The dipole moments are 1.09 and 3.93 D, respectively.

Figure 2g shows the aniline+$(H_2O)_7$ aggregate, which is bonded by 11 H bonds. These bonds are bonded by H-bonds with lengths of 1.74–2.42 Å, 3 of which are bonded by the NH_2 atomic group of aniline and the rest by water molecules, the aggregate formation energy is 46.8 kcal/mol, and the dipole moment is 2.48 D.

Table 1. The results of calculations for molecular clusters of aniline+$(H_2O)_n$ molecules.

Structure	Dipole moment, D	Energy of vibration, kcal/mol
Aniline	1.24	
Aniline+1W	4.00	8.0
Aniline+2W	2.72	11.0
Aniline+3W	0.26	24.0
Aniline+4W	7.19	16.25
Aniline+5W	1.09	35.0
Aniline+6W	3.93	39.0
Aniline+7W	2.84	46.8

Table 1 also shows the theoretically calculated dipole moments and interaction energies for aniline+$(H_2O)_n$. The mechanics of aggregation formation with aniline+$(H_2O)_7$ molecules were studied using theoretical calculations.The dipole moment for the aniline monomer was 1.24 D, and this value increased to 4.0 D when one $(H_2O)_1$ was added. Calculations demonstrate that the overall energy increases as the number of water molecules in aggregate formation grows.

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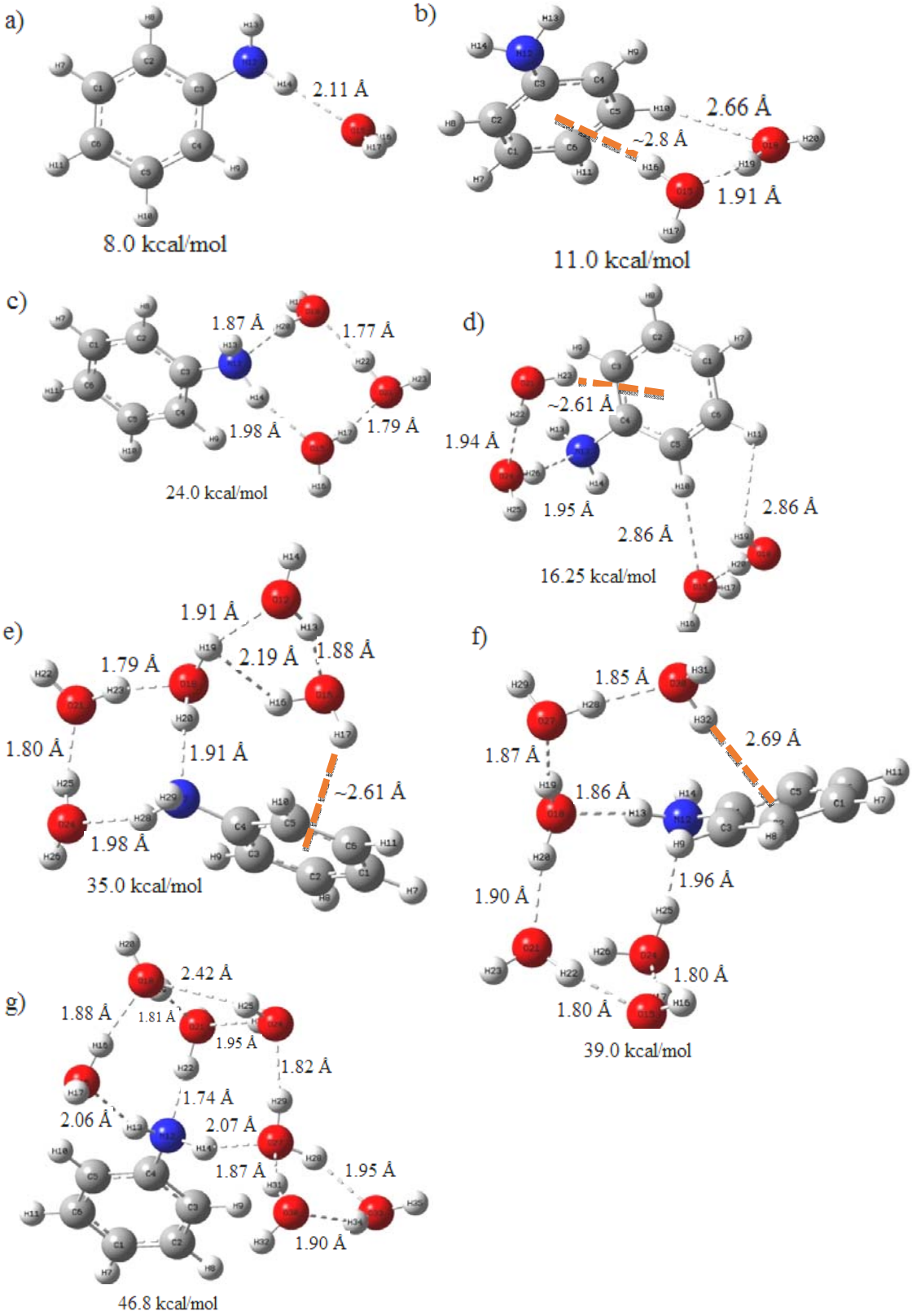


Figure 2. Calculated optimization of aniline+H_2O. Here atoms of different colors are denoted as follows: red – oxygen, gray – carbon, white – hydrogen, and blue – nitrogen.

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IV. Conclusion

In this work, liquid aniline was studied in a pure and aqueous medium using experimental and theoretical calculations. Experimental results show that in aniline aqueous solutions 3056 cm^{-1} band for C-H stretching vibration, 1604 cm^{-1} spectral band for stretching vibration CC, and 1155 cm^{-1} and 998 cm^{-1} spectral bands for NCC, and CCC bending vibrations of the ring are shifted to the high frequency side. The spectral bands 1279 cm^{-1} for the N-C stretching vibration and 822 cm^{-1} for the NH_2 bending vibrations shifted to the low frequency side. Using theoretical calculations, the mechanisms of aggregate formation with aniline+$(H_2O)_7$ molecules were analyzed. Calculations show that the total energy increases with the increase in the number of water molecules in the formation of aggregates. For the first time, blue shifts were observed in the aniline water system along with red shifts, which were assumed to be due to C-H···O H-bonds, and were confirmed by experimental results.

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Анилиннинг сувли муҳитида молекулалараро таъсир кучларини тебраниш спектрлари ҳамда DFT усулида ўрганиш

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Ушбу ишда суюқ анилин тоза ҳамда сувли муҳитда тажриба ва назарий ҳисоблашлар ёрдамида ўрганилди.Раман спектрлари ёрдамида100–3200 $см^{-1}$ оралиқда таҳлил қилинди ва бу оралиқда кўк силжиш ва қизил силжишлар кузатилди. Биринчи марта бу силжиш сабаблари комплекс ҳосил бўлишдаги C–H···O ноклассик водород боғланиш туфайли эканлиги аниқланди ва назарий DFT//BL3YP/6-311+G(2d,p) методи ёрдамида ҳисобланган натижаларда тасдиқланди. Шунингдек назарий ҳисоблашлар ёрдамида анилин+$(H_2O)_7$ гача молекулалари билан агрегатлар шаклланиш механизмлари таҳлил қилинди. Ҳисоблашлар кўрсатадики, агрегатлар ҳосил бўлишида сув молекуласи сони ортиши билан умумий энергия ортар экан.

Калит сўзлар: Анилин, ароматик ҳалқа, водород боғланиш, қизил силжиш, кўк силжиш, стикинг ўзаро таъсир, DFT ҳисоблашлар.

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