Open Access Journal of Physics
Volume 3, Issue 3, 2019, PP 10-14
ISSN 2637-5826

Studying the Processes of Intermolecular Interactions in Xylene Solutions by Spectra of Raman Scattering and Ab Initio Calculations

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ABSTRACT

In this study intermolecular interactions in solutions of meta-Xylene and its solutions in a mixture of binary solvents xylene-nitromethane and Xylene-carbon tetrachloride have been investigated by Raman spectroscopy. The structure and the energies of the titled complexes were performed using quantum mechanical calculations with RHF and B3LYP methods and a basis set of 6-31G++(d, p) in order to consider in more detail the possibility of the formation of aggregated intermolecular complexes in the liquid, which are in good agreement with the experimental results. The frequency shift of Xylene 995.2 cm-1 was analyzed in nitro methane solutions. In contrast to conventional H bond concepts, a significant blue shift was detected in these C-H proton-donor complexes. A new type of bond characterized by this blue shift is called an anti-H bond.

Keywords: *Raman spectra of meta-Xylene, Ab initio calculations, □- type interaction, blue shift, dimeric aggregation, anti-H bond*

INTRODUCTION

The study of Raman spectra (RS) shows that the formation of molecular complexes of any type, including through an intermolecular hydrogen bond, leads to a change in the spectral parameters of the interacting molecules. The study of solutions of xylene in proton solvents is important because the formation of complexes changes the proton-acceptor properties of the object under study.

In our papers [1-2], the results of studying the interaction of benzene molecules with each other and the interaction of benzene molecules with chloroform molecules were presented. Calculations and experimental studies of Raman scattering (RS) spectra showed that dimeric aggregation of benzene molecules with a molecule of methyl alcohol and formic acid using the π-electrons of the benzene ring occurs.

Recently, Brutschy et al. [3] reported on other evidence of the formation of this type of H-bond, which revealed a significant red shift of the fundamental O-H stretching frequency in the CH_3OH-benzene complex. The assumption of a similar type of bond, such as the C-H$\cdots\pi$ type, was stimulated by experimental [4] and theoretical [5-6] evidence from the T-shaped equilibrium structure of the benzene dimer. The T-shaped arrangement of the aromatic rings, which is believed to be stabilized by neighboring H-bonds, is quite common in the biological environment (for example, it is believed to be responsible for the structure of phenyl-nine) [7] and as such some interest [8].

Xylene (dimethyl benzene, $(CH_3)_2C_6H_4$) has a central benzene ring with two methyl groups attached as substituents, the relative position of which is distinguished by three isomers ortho-, meta- and para-xylene. In the liquid or vapor form, benzene, xylene are toxic compounds for living organisms, and their detection at low concentrations is important in analytical spectroscopy [9].

For a better description of xylene and for its more effective detection, the qualitative and quantitative vapor-phase infrared spectra of all three isomers in the range 6500-540 cm^{-1} are reported. All fundamental vibrational modes are assigned on the basis of these vapor-phase infrared spectra, liquid-phase infrared and RS spectra, and also the density functional theory [10].

The properties of xylene liquid mixtures were analyzed using computational chemistry, molecular dynamics modeling, and quantum chemistry calculations to derive the main features of intermolecular forces and structural characteristics that can justify the large affinity of molecules for aromatic compounds. Molecular clustering, spatial distribution, energy pattern of the forces involved, the dynamics of mixtures are analyzed depending on the composition of the mixture and temperature, and the results obtained are related to the suitability of xylene for use in the oil and gas industry [11].

This paper presents the results of the study of intermolecular interactions in solutions of meta-xylene and its solutions in a mixture of binary solvents xylene-nitromethane and xylene-carbon tetrachloride. For a more complete and reasoned interpretation of the results obtained, *Ab initio* calculation was performed in order to consider in more detail the possibility of the formation of aggregated intermolecular complexes in the liquid, which are compared with the experimental results.

CALCULATIONS AND EXPERIMENTAL TECHNIQUE

The Raman spectra of liquid xylene and its solutions with nitromethane and carbon tetrachloride were studied using DFS–52 spectrometer and part of the spectra were taken with Thermo Nicolet 6700 FTIR/FT-Raman spectrophotometer. Non-empirical calculations were performed using RHF and B3LYP methods with a set of 6-31G++(d, p) Gaussian functions [12] for the monomer and dimer of isolated xylene molecules.

When interpreting the experimental results obtained, theoretical non-empirical calculations were carried out, to determine which at present there are great opportunities. Such calculations can significantly clarify the changes in molecules that accompany the formation of intermolecular bonds, determine the structure of aggregates and the energy of formation of aggregates test the correct interpretation of spectroscopic data.

RESULTS OF CALCULATIONS, EXPERIMENTAL STUDIES AND DISCUSSION

To study molecular relaxation in experimental measurements, the polarized isotropic and anisotropic components of the Raman scattered light emitted were distinguished, associated with various factors of broadening of the vibrational bands in liquid xylene. The shape of the bands was determined by the processes of vibrational and orientational relaxation. For liquid xylene, the effect of intermolecular interactions on the molecular relaxation process has been studied. The isolation of molecules in liquid xylene makes it possible to qualitatively study of the influence of the intermolecular interactions on the contour of the band under study with a frequency of 995.2 cm-1 in the Raman spectrum and various types of relaxation of vibrational excitation.

The intermolecular interactions in the Raman spectra manifest itself in the frequency shift and broadening of the vibrational bands. In this case, the isotropic and anisotropic components of the Raman band may have different sensitivity to the processes of intermolecular interaction [13–15].

The studies have shown that in pure xylene, the parallel and perpendicular components of the 995.2 cm-1 band are slightly shifted relative to each other by 0.9 cm-1 (the anisotropic component is shifted toward higher frequencies, Figure.1). In case 1, pure xylene is considered, the maximum of the spectrum of which is traceable to 995.2 cm-1. This line is asymmetric and shifted towards high frequencies, the half-width of this line is 1.8 cm-1. It is appropriate to say here that the maxima of the parallel and perpendicular components do not coincide.

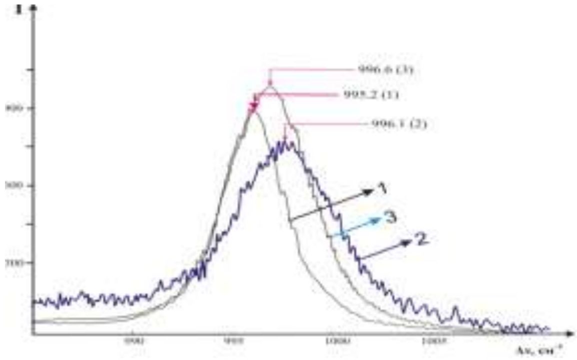

Figure1. *Raman spectra of 995.2 cm^{-1} xylene: 1) parallel and 2) perpendicular components; 3) xylene+nitrome-thane (0.5-0.5 m.f.); intensity is not reduced to a single scale.*

In Figure.1 curve 2 correspond to the perpendicular component of the Raman spectra in the solution of xylene with nitromethane. If we assume that the spectral line of 995.2 cm^{-1} is complex and the half-width of the perpendicular component is 2.9 cm-1, than this complexity of the component can be explained using the secondary orientation of the molecules. Calculations show that the relaxation time of oriented molecules is 3.1 ps. This value is for a molecule that is secondary oriented around the main axis and having an energy values are 1.47 kcal·mole-1 and 0.19 kcal·mole-1 performed RHF and B3LYP methods, respectively.

To achieve this goal, the behavior of the spectral line of 995.2 cm-1 of xylene in solutions with nitromethane was studied. From Fig.1 one can see that for the solution of xylene with nitromethane at a concentration of 0.5 m.f., the maximum of the spectrum relative to pure xylene is shifted by 1.4 cm-1 in the high-frequency side and the half-width of the line increases. The half-width of this band is 2.5 cm^{-1}[16].

This phenomenon is due to a partial change in the interactivity of the spectral lines of aggregates of various molecules, which leads to a shift in the maximum of the main line in the spectrum. From this it follows that for pure xylene and its solution with nitromethane, the lines relating to the monomer and dimer lines are preserved. If the low frequency lines correspond to the monomeric xylene molecule, the high frequency lines correspond to the dimers of various molecules.

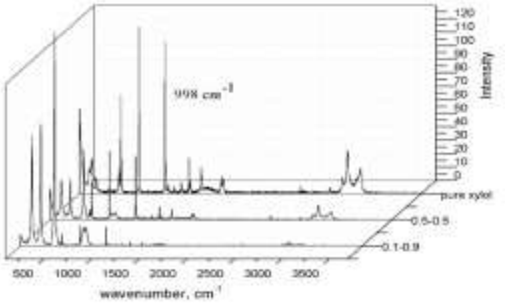

Figure2. *Raman spectra of 995.2 cm-1 m-xylene in CCl4 solutions: (pure m-xylene, 0.5-0.5 m.f., 0.1-0.9 m.f.)*

Fig.2 shows the Raman spectra of xylene solutions with CCl4 solutions. In solutions with CCl4 a different picture is observed in Raman spectra; at low xylene concentrations in solution, a strong reduced band of 995.2 cm-1 is observed. This means that when xylene is diluted in CCl4, the number of aggregates consisting of two or three molecules decreases [17].

The results of the experiments were explained in detail in non-empirical calculations. The non-empirical calculations were performed in RHF and B3LYP approximation with a set of Gaussian functions of 6-31G++(d, p) for the monomer and dimer of isolated xylene molecules. The orientation of the molecules, the relationship between the length and frequency of oscillations, and the energy of dimer formation were determined. As a result of the calculation, it was found that for xylene monomers the dipole moment is 0.45, for xylene dimers the dipole moment is 0.70 D.

From the obtained results, it follows that two xylene molecules, interacting with each other due to electrostatic forces, form monomeric and dimeric aggregates.

On the basis of non-empirical calculations, it was revealed that the monomeric molecule band 995.2 cm-1 is complex, and for the dimeric molecule two lines of 1072.8 cm-1 and 1103.3 cm-1 were traced. If we use the scaling factor given in [18], then these calculations coincide with the results of the experiments performed.

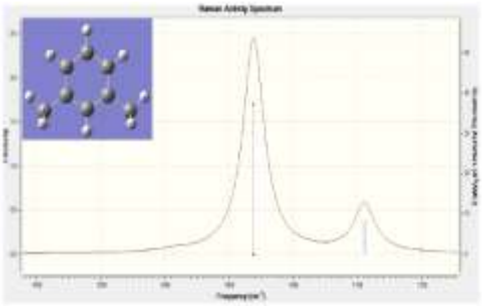

Figure3. *Calculated spectra of m-xylene for monomers*

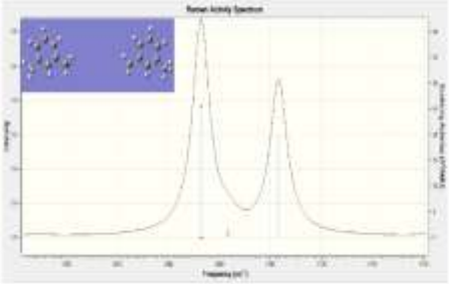

Figure4. *Calculated spectra of m-xylene for dimers*

More detailed results of non-empirical calculations are given in table.

Table1. *The results of non-empirical calculations carried out in RHF and B3LYP approximation with a set of Gaussian functions 6-31G ++ (d, p) for the monomer and dimer of isolated m-xylene molecules*

Parameter	**Monomer (RHF)**	**Monomer (B3LYP)**	**Dimer (RHF)**	**Dimer (B3LYP)**
Total energy (Hartree)	-308.635151	-310.755206	-617.272646 1.47 kcal/mole	-621.510098 0.19 kcal/mole
Dipole moment (D)	0.4303	0.4503	0.6852	0.7054

Vibration frequency (cm^{-1})	1067.6 1102.2		1072.8 1103.3	
Raman activity (A^4/AMU)	36.9 8.4		25.4 16.1	
Atom charges	1 C -1.196604 2C 0.409988 3C -1.196593 4C 1.215558 5C -0.907352 6C 1.215555 7C -0.360359 8C -0.360358 9H 0.093852 10H 0.150157 11H 0.093852 12H 0.104230 13H 0.119646 14H 0.129731 15H 0.119660 16H 0.129730 17H 0.119658 18H 0.119649	1C -1.351041 2C 0.570525 3C -1.351025 4C 1.175704 5C -0.639380 6C 1.175700 7C -0.448401 8C -0.448400 9H 0.058334 10H 0.127123 11H 0.058334 12H 0.062509 13H 0.168192 14H 0.168412 15H 0.168405 16H 0.168412 17H 0.168423 18H 0.168174	1 C -0.683601 2C 0.380494 3C -1.191316 4 C 1.176673 5C -1.391123 6C 1.278635 7C -0.392909 8C -0.351449 9H 0.115575 10H 0.148131 11H 0.095327 12H 0.079153 13H 0.134833 14H 0.114361 15H 0.117497 16H 0.129705 17H 0.119928 18H 0.120063 19C - 0.681881 20C 0.382105 21C -1.189370 22C 1.170205 23C -1.395894 24C 1.294327 25C -0.402442 26C -0.352064 27H 0.115166 28H 0.148134 29H 0.095355 30H 0.079151 31H 0.134859 32H 0.117768 33H 0.117706 34H 0.126774 35H 0.119993 36H 0.120130	1C -0.869232 2C 0.604014 3C -1.038247 4C 1.200771 5C -1.509069 6C 1.209275 7C -0.461761 8C -0.443924 9H 0.071115 10H 0.124280 11H 0.067883 12H 0.040680 13H 0.166124 14H 0.161905 15H 0.175294 16H 0.160864 17H 0.176861 18H 0.163161 19C -0.659884 20C 0.569615 21C -1.253984 22C 1.139846 23C -1.427128 24C 1.232715 25C -0.467956 26C -0.442857 27H 0.072999 28H 0.123275 29H 0.063075 30H 0.038594 31H 0.173748 32H 0.167288 33H 0.166688 34H 0.165742 35H 0.173904 36H 0.164323

From the experimental data and the corresponding results of non-empirical calculations, it follows that the xylene band at 995.2 cm-1 has a complex structure: there are lines of monomer molecules and aggregates.

CONCLUSION

Not excluding the role of resonant interaction of molecules with the transfer of vibrational energy, it can be said that the aggregation of molecules and the changes in the Raman spectra associated with this aggregation can play an important role in the effect of charge transfer.

The behavior of the band 995.2 cm^{-1} shows that the band is complex; molecular complexes are formed in the liquid due to electrostatic interaction with an energy gain of 0.19 kcal/mole. The study of xylene solutions in proton solvents showed that the formed complexes change the associative state of xylene and its proton acceptor properties.

Literature data [8] and our studies show that organic compounds with benzene rings do not form a standard H-bond with the benzene π-system, which would be characterized by a red shift of the frequency of stretching C-H vibrations of the proton donor. In contrast, a significant blue shift was detected in these C-H proton-donor complexes. A new type of bond characterized by this blue shift is called an anti-H bond.

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Citation: *G. Sharifov, A. Jumabaev, H. Hushvaktov, et al, "Studying the Processes of Intermolecular Interactions in Xylene Solutions by Spectra of Raman Scattering and Ab Initio Calculations", Open Access Journal of Physics, 3(3), 2019, pp. 10-14.*