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Formation of hydrogen bonding network of methane sulfonic acid at low degree of hydration $(\text{MSA})_m \cdot (\text{H}_2\text{O})_n$ ($m = 1-2$ and $n = 1-5$)

Ahmad Telfah^{1,2,3,✉}, Z. Charifi^{4,5,12}, N. Iatelli^{6,7}, Issam A. Qattan^{8,9}, H. Baaziz^{4,5}, Qais M. Al-Bataineh^{9,10}, A. M. Alsaad^{11,12} & R. F. Sabirianov³

This study employs ab initio calculations based on density functional theory (DFT) to investigate the structural properties, ¹H-NMR spectra, and vibrational spectra of methane sulfonic acid (MSA) at low degree of hydration. The findings reveal that energetically stable structures are formed by small clusters consisting of one or two MSA molecules ($m = 1$ and 2) and one or two water molecules in $(\text{MSA})_m \cdot (\text{H}_2\text{O})_n$ ($m = 1-2$ and $n = 1-5$). These stable structures arise from the formation of strong cyclic hydrogen bonds between the proton of the hydroxyl (OH) group in MSA and the water molecules. However, clusters containing three or more water molecules ($n > 2$) exhibit proton transfer from MSA to water, resulting in the formation of ion-pairs composed of CH_3SO_3^- and H_3O^+ species. The measured ¹H-NMR spectra demonstrate the presence of hydrogen-bonded interactions between MSA and water, with a single MSA molecule interacting with water molecules. This interaction model accurately represents the hydrogen bonding network, as supported by the agreement between the experimental and calculated NMR chemical shift results.

Keywords Density functional theory (DFT), Methane sulfonic acid (MSA), Hydrated clusters, Nuclear magnetic resonance (NMR), IR vibrational bands, Raman vibrational bands, Heat capacity

Water, as a vital solvent for acids and dissociated ions, plays a crucial role in various applications, including fuel cells, condensation reactions, and electrochemical processes^{1,2}. Water contains the H-bonding networks that can rearrange according to the changes in the environmental conditions (such as acidity, temperature etc.)³. In water solutions, H-bonds are randomly distributed with equal probability for four H-bonds, i.e. two H-donors and two H-acceptors⁴. Methane sulfonic acid (MSA) is a strong organic acid with the formula $\text{CH}_3\text{SO}_3\text{H}$ and it is the smallest member of the series of the alkane sulfonic acids. MSA is a main atmospheric oxidation product of ocean-released dimethyl sulfide^{5,6}. The MSA consists of OH acidic group, two S=O shares, and one methyl part, is an appropriate model for H-bonding with H_2O through the sites of OH group and the S=O positions. Investigation of the surface of water structure exposed to adhesions of MSA obviously shows that hydrogen bonding between H_2O molecules becomes stronger in presence of MSA. Consequently, as the MSA concentration increases, the number of free-OH bonds decreases⁷.

Density Functional Theory (DFT) is a powerful tool for studying and interpreting the dissociation and hydrogen bonding, as well as vibrational and NMR spectra⁸⁻¹⁰. DFT description of intra- and intermolecular hydrogen bonding can be tuned by the choice of the specific functional used to approximate the electronic exchange and

¹Nanotechnology Center, The University of Jordan, Amman 11942, Jordan. ²Fachhochschule Dortmund University of Applied Sciences and Arts, Dortmund, Germany. ³Department of Physics, University of Nebraska at Omaha, Omaha, NE 68182, USA. ⁴Department of Physics, Faculty of Science, University of M'sila, 28000 M'sila, Algeria. ⁵Laboratory of Physics and Chemistry of Materials, University of M'sila, M'sila, Algeria. ⁶Department of Chemistry, Faculty of Science, University of M'sila, 28000 M'sila, Algeria. ⁷Laboratoire Chimie des Matériaux et des Vivants: Activité, Réactivité, Université Batna1, 05001 Batna, Algeria. ⁸Department of Physics, Khalifa University of Science and Technology, P.O. Box 127788, 127788 Abu Dhabi, United Arab Emirates. ⁹Leibniz Institut für Analytische Wissenschaften-ISA-e.V., 44139 Dortmund, Germany. ¹⁰Experimental Physics, TU Dortmund University, 44227 Dortmund, Germany. ¹¹Department of Physical Sciences, Jordan University of Science and Technology, Irbid 22110, Jordan. ¹²These authors contributed equally: Z. Charifi and AM Alsaad. ✉email: ahmad.telfah@fh-dortmund.de; issam.qattan@ku.ac.ae