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Absorption Spectra of Benzoic Acid in Water at Different pH and in the Presence of Salts: Insights from the Integration of Experimental Data and Theoretical Cluster Models

Natalia V. Karimova[1], Man Luo[2], Vicki H. Grassian[2,3], R. Benny Gerber[1,4]

[1]Department of Chemistry, University of California, Irvine, CA 92697, USA

[2]Department of Chemistry and Biochemistry, University of California, San Diego, CA 92093, USA

[3]Department of Nanoengineering and Scripps Institution of Oceanography, University of California, San Diego, CA 92093, USA

[3]Institute of Chemistry and Fritz Haber Research Center, Hebrew University of Jerusalem, Jerusalem 91904, Israel

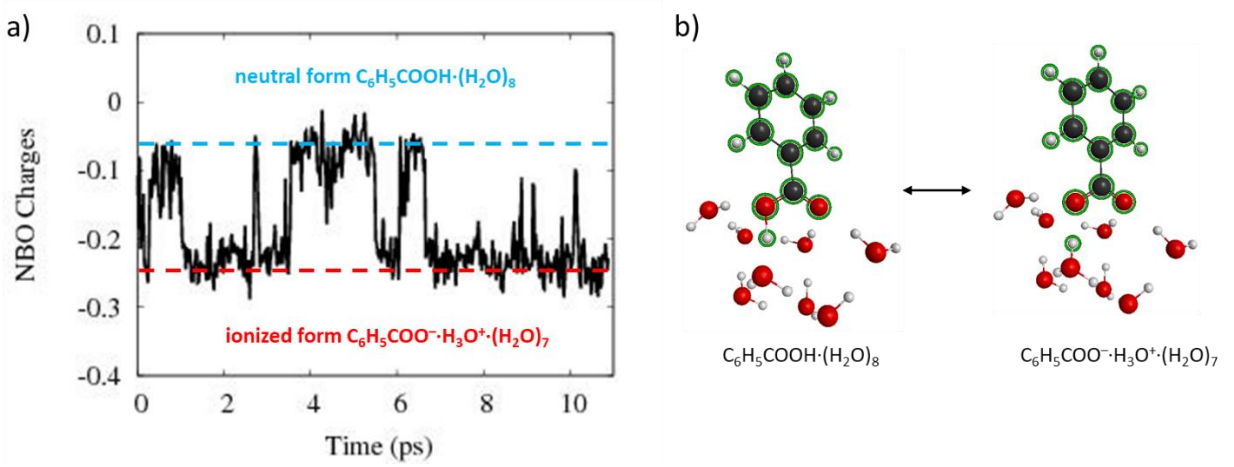

Figure S1. Proton transfer process between benzoic acid and water molecules $C_6H_5COOH\cdot(H_2O)_8 \leftrightarrow C_6H_5COO^-\cdot H_3O^+\cdot(H_2O)_7$. (a) NBO charges of the fragments $C_6H_5COOH/(C_6H_5COO\cdots H)$ stabilized by 8 water molecules; and (b) structures of $C_6H_5COOH\cdot(H_2O)_8 \leftrightarrow C_6H_5COO^-\cdot H_3O^+\cdot(H_2O)_7$.

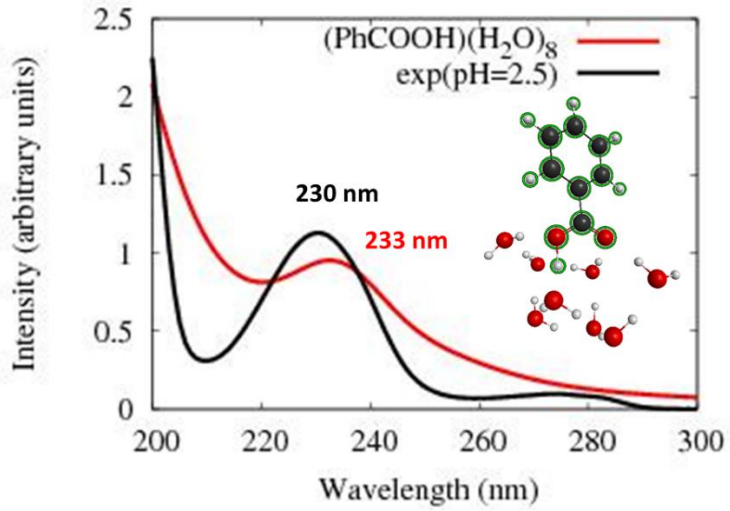

Figure S2. Comparison of the theoretical and experimental spectral data. Theoretical spectrum presented here is an average spectrum of all structures along AIMD trajectories. Optical absorption spectra of $C_6H_5COOH \cdot (H_2O)_8$ versus the experimental data at pH 2.5. Method B3LYP/6-31+G*. Theory – red curve, experiment – black.

Table S1. Experimental (in water at pH 2.5) and theoretical optical absorption spectral data for benzoic acid (where the $\Delta(E_B\text{-}E_C)$ is the energy gap between the maximums of C- and B-bands).

Basis Set	Peak Maximum		$\Delta(E_B\text{-}E_C)$
	C-band	B-band	
ADC(3)			
6-31+G*	4.71 eV	5.73 eV	1.02 eV
6-311+G*	4.71 eV	5.69 eV	0.98 eV
6-311++G**	4.70 eV	5.69 eV	0.99 eV
ADC(2)			
6-31+G*	4.98 eV	5.91 eV	0.93 eV
6-311+G*	4.96 eV	5.85 eV	0.89 eV
6-311++G**	4.95 eV	5.84 eV	0.89 eV
B3LYP			
6-31+G*	4.87 eV	5.38 eV	0.51 eV
6-311+G*	4.85 eV	5.37 eV	0.52 eV
6-311++G**	4.85 eV	5.36 eV	0.51 eV
aug-cc-pVTZ	4.85 eV	5.36 eV	0.51 eV
aug-cc-pVQZ	4.85 eV	5.35 eV	0.50 eV
Experiment	4.35 – 4.50 eV	5.40 eV	0.9 ÷ 1.05 eV