Supplemental Information

Formic and Acetic Acid pKa Values Increase Under Nanoconfinement

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1. Potentiometric titrations for pKa measurements

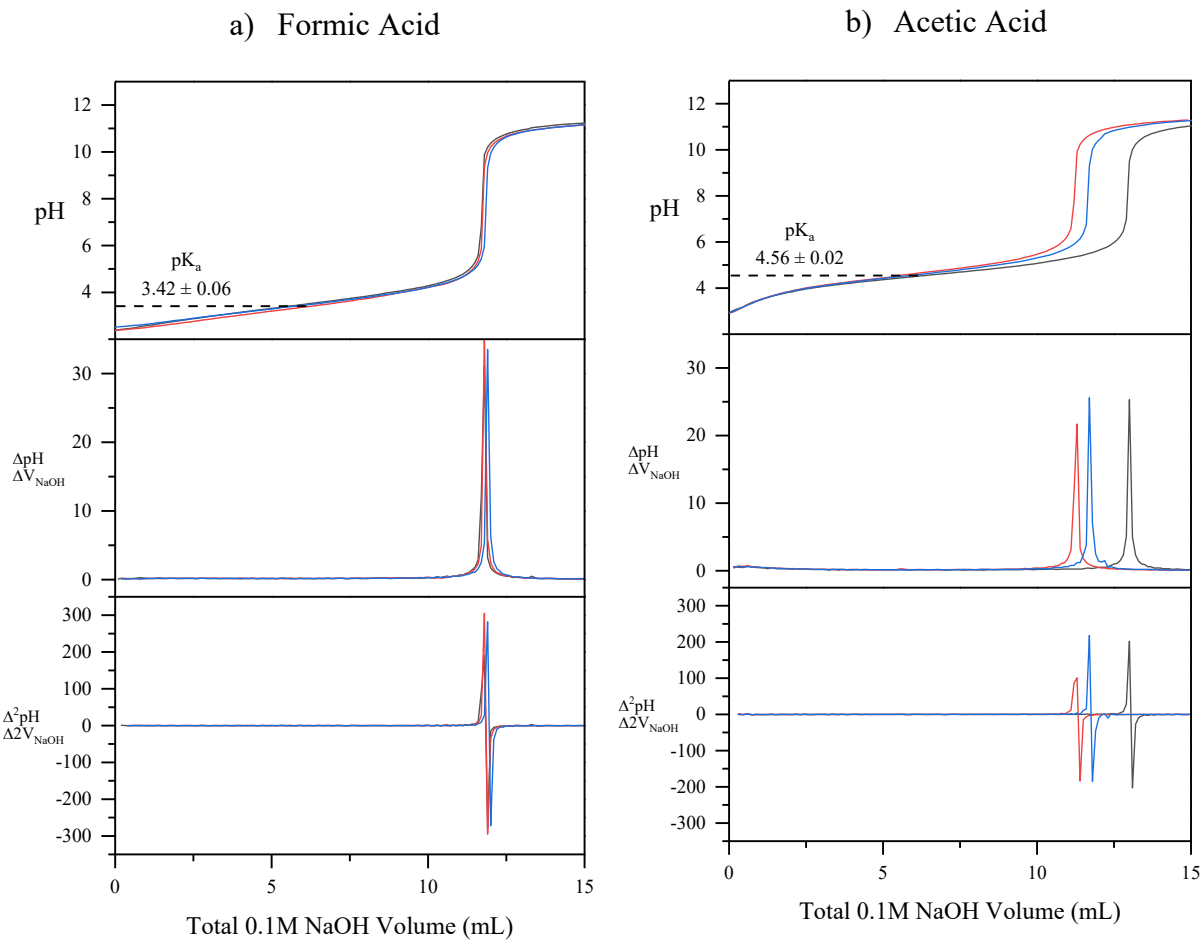

Figure S1: Potentiometric triplicate measurements to determine solution pKa value for a) 25mM formic acid and b) 25mM acetic acid. pH measurements as a function of total NaOH volume added (top), first derivative of pH response (middle), and second derivative of pH response (bottom). pKa was determined at half the volume of the equivalence volume.

2. Spectral assignments

Table S1. Vibrational band assignments for formic and acetic acids.

Band (cm^{-1})	Assignment	Reference
1711-1718	C=O	Ito, K., & Bernstein, H. J. (1956)
1400-1418	C—O stretching[a,b]	Ito, K., & Bernstein, H. J. (1956), Olbert-Majkut et al. (2011)
1344-1352	C—O stretching[a]	Ito, K., & Bernstein, H. J. (1956)
892	C—O and O-H stretching[a,c]	Ito, K., & Bernstein, H. J. (1956), Wan et al. (2017)
652	COO deformation[a]	Ito, K., & Bernstein, H. J. (1956)

3. ATR-FTIR measurements on acetic acid in alumina nanopores

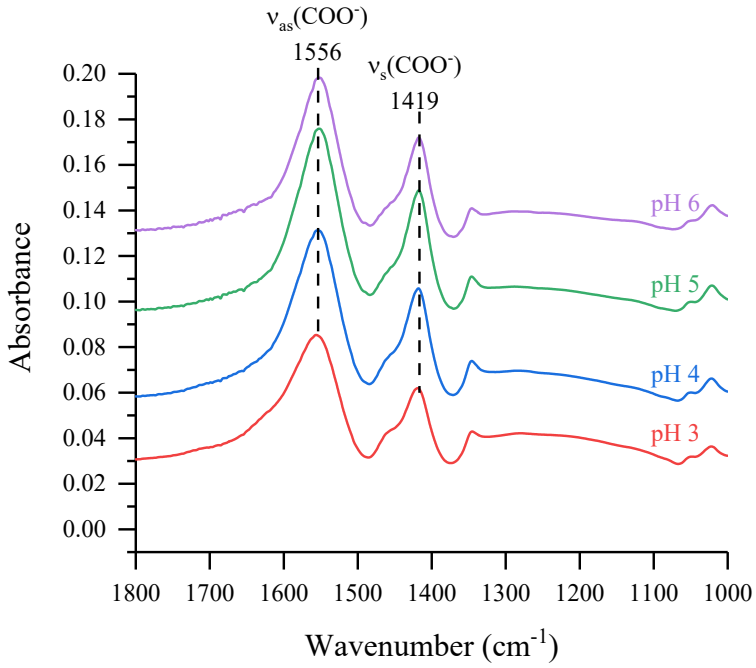

Figure S2. 10mM acetic acid adsorbed on nanoporous alumina as a function of pH. Spectra does not change as pH increases, suggesting that acetate is strongly complexed with the surface.

4. ATR-FTIR and Raman measurements on acetic acid in alumina nanopores

Figure S3 shows ATR-FTIR and Raman spectral intensities for characteristic protonated and deprotonated peaks of formic and acetic acid solutions. For both organic acids, the highest intensity for the protonated form is observed at pH 2, whereas the highest intensity for the deprotonated form is observed at pH 6 or pH 7. Since these bands are considered characteristic, as the (de)protonated forms become the dominant species in the solution, peak intensities would also be dominant for their representative forms. However, since infrared absorption coefficients and Raman scattering cross-sections depend on specific vibrational modes, the data are normalized to reflect these differences.

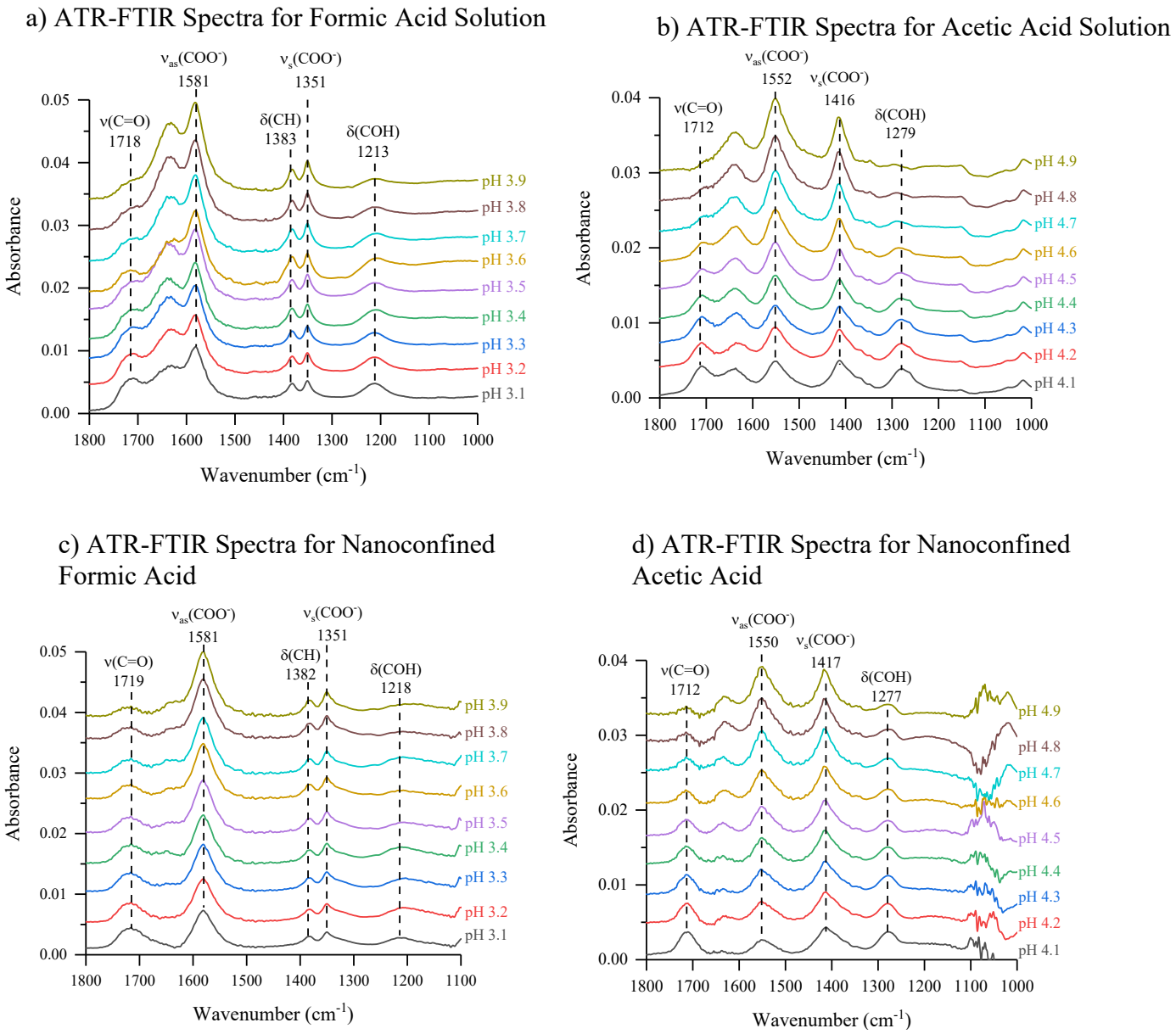

Figure S3. Solution spectra of a) ATR-FTIR formic acid, b) ATR-FTIR acetic acid; Nanoconfined spectra c) ATR-FTIR formic acid, and d) ATR-FTIR acetic acid.

References

Ito, K., & Bernstein, H. J. (1956). The vibrational spectra of the formate, acetate, and oxalate ions. *Canadian Journal of Chemistry*, *34*(2), 170-178.

Olbert-Majkut, A., Ahokas, J., Lundell, J., & Pettersson, M. (2011). Raman spectroscopy of acetic acid monomer and dimers isolated in solid argon. *Journal of Raman Spectroscopy*, *42*(8), 1670-1681.

Wan, F., Du, L., Chen, W., Wang, P., Wang, J., & Shi, H. (2017). A novel method to directly analyze dissolved acetic acid in transformer oil without extraction using Raman spectroscopy. *Energies*, *10*(7), 967.