Utilization of Raman Spectroscopy for Gas Adsorption Investigations on Opaque Samples

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Constantly increasing demands in technological processes regarding complexity, functionality, and efficiency directly lead to a great need for accurate models and equations to predict the thermophysical behavior of pure fluids or systems with fluid interactions. However, such theoretical approaches substantially depend on high-quality experimental data for their development, improvement, and validation. Reliable gas adsorption data is mandatory, especially for models used to describe gas separation and storage processes and hydrogen applications. Raman spectroscopy, as an optical, non-invasive measuring technique, has shown great potential to provide such data using rapid measurements on various samples simultaneously with minimal sample quantities required. Our groups previously presented a method to investigate the gas adsorption for translucent, porous materials. However, this work focuses on modifying and adapting this approach to make it suitable for application with opaque materials, such as metal-organic frameworks (MOFs) and catalyst materials. The presented investigations were conducted in a custom-built view cell within a commercially available confocal Raman microscope. Here, we provide an overview of the experimental setup, the utilized components, and the optical equipment and outline the applied measuring procedure. Subsequently, the post-processing and correction of the acquired spectral data are discussed, and finally, an approach for calculating the adsorption loading from the optical measurements is presented. The presented experimental and mathematical framework was validated using measurements of carbon dioxide on two MOFs (ZIF-8 and aluminum fumarate). The results were compared to literature data mainly obtained from gravimetric measurements. Additional investigations with fluid mixtures indicate that Raman spectroscopy can be utilized to observe selective sorption effects, which gravimetric or volumetric systems cannot resolve. Ultimately, we summarize the potential of Raman spectroscopy for gas adsorption investigations and discuss future improvements for the presented technique and evaluation method.