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Low-Cost Raman System for Continuous Measurement of Aqueous Ammonium Bicarbonate in Carbon Capture Processes

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Summary:
Raman spectroscopy is demonstrated as a direct and non-invasive method for quantifying dissolved inorganic carbon and ammonium species in aqueous solution. This paper presents a cost-effective setup that utilizes the strong concentration dependence of the bicarbonate band at 1022 cm^{-1} as the primary measurement feature. Ongoing work targets system optimization, advanced spectral analysis, equilibrium-based species modeling, and further cost reduction through simplified detector configurations.

Keywords: Raman sensor, spectroscopy, ammonium bicarbonate, low-cost, carbon capture.

Introduction

Aqueous ammonia is a promising solvent for carbon capture due to its high absorption capacity, low regeneration energy, and compatibility with circular utilization pathways [1,2]. However, practical implementation is limited by operational challenges, including ammonia slip, incomplete conversion, and limited real-time process monitoring [3]. These limitations are particularly critical due to the formation of high concentrations of ammonium bicarbonate ($H_2O + NH_3 + CO_2 \rightarrow NH_4HCO_3$), for which no reliable and cost-effective online sensors currently exist [4].

Raman spectroscopy has been used for speciation and quantification in CO_2-NH_3-H_2O systems, enabling the resolution of carbonate, bicarbonate, and carbamate species and the development of multivariate calibration models [4,5]. However, most studies employ excitation wavelengths in the visible range, which are more susceptible to fluorescence interference in complex aqueous systems [6]. In addition, conventional Raman instrumentation remains expensive, restricting broader implementation [7].

This paper describes the development of a Raman sensor based on a 785 nm excitation laser for the quantification of ammonium bicarbonate in aqueous solutions. The choice of excitation wavelength reduces susceptibility to fluorescence interference, while the system design follows a low-cost approach (<20 k€), addressing key practical limitations of existing Raman-based methods.

Methodology

Solutions with concentrations of 0.1 - 1.0 mol/L were prepared by dissolving solid ammonium bicarbonate (99%) in deionized water. The excitation source was a multimode diode laser (Thorlabs FPV785M) emitting at 785 nm with 600 mW. Samples were placed in a cuvette holder and measured using a non-contact probe with back-scattering collection geometry. The collected signal was filtered to remove Rayleigh-scattered light and analyzed with a Raman spectrometer (Ocean Optics QE Pro). Prior to analysis, dark spectra were subtracted to account for detector bias and non-laser-induced background signals, followed by subtraction of a deionized water reference spectrum to isolate solute-specific contributions. Characteristic spectral peaks were identified and assigned to corresponding ionic species based on literature data. Peak intensities were quantified based on peak height as a function of bicarbonate concentration.

Results

Figure 1 shows the measured Raman spectrum of a 1.0 mol/L ammonium bicarbonate solution.

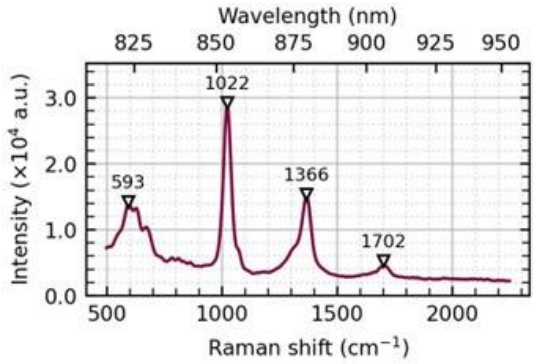


Fig. 1: Raman spectrum of an aqueous 1.0 mol/L ammonium bicarbonate solution with indicated peak positions.

The Raman spectrum is dominated by prominent peaks at 1022 and 1366 cm^{-1}, both attributed to bicarbonate [5,8]. Additional bands at 593 and 1702 cm^{-1} could be associated with ammonium but need further investigation [8].

Figure 2 presents the intensity of selected Raman peaks as a function of ammonium bicarbonate concentration. The data illustrates the relationship between the spectral signal and concentration for the investigated range.

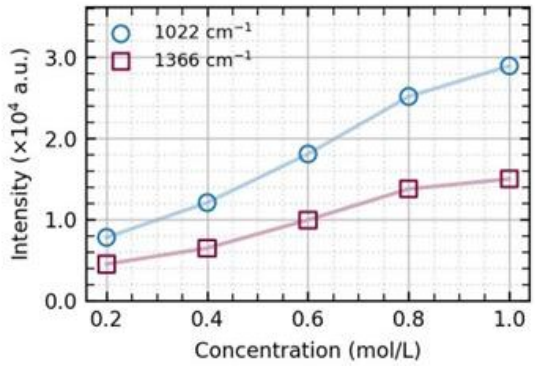


Fig. 2 Intensity of selected Raman peaks as a function of ammonium bicarbonate concentration in the range of 0.2 – 1.0 mol/L.

Both the 1022 cm^{-1} and the 1366 cm^{-1} bands show a slightly non-linear response with a possible saturation effect at higher concentrations, which requires further investigation. Nevertheless, the 1022 cm^{-1} band exhibits significantly higher overall sensitivity, making it the most suitable candidate for quantitative analysis and calibration.

Discussion

The strong and well-defined bicarbonate signal demonstrates the suitability of Raman spectroscopy for direct quantification of dissolved inorganic carbon species in ammonium-based systems. Ongoing work will extend these preliminary results through: (1) sensor optimization and limit of detection analysis, (2) extraction of ammonium signals using advanced spectral analysis algorithms, (3) development of a comprehensive model for complete quantification of NH_4^+ and HCO_3^- species incorporating pH measurements, and (4) replacement of the spectrometer with a filter-and-detector configuration to reduce sensor costs while maintaining analytical performance.

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