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**Authors:** Arachchige, G. L. S., Andersen, N. H., Perinu, C., & Jens, K.-J.

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# Equilibria of MEA, DEA and AMP with Bicarbonate and Carbamate: A Raman Study

Gamunu L. Samarakoon P.A.[a], Niels H. Andersen[b], Cristina Perinu[a], Klaus-J.Jens[a]*

[a]*Faculty of Technology, Telemark University College, P.O. Box 203, Porsgrunn N-3901, Norway*
[b] *Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, Oslo N-0372,Norway*

**Abstract**

Species distribution analysis in carbonated alkanolamine solution is import in order to estimate accurate thermodynamic properties. The applicability of Raman spectroscopy as an analytical tool for speciation of carbonated aqueous alkanolamine systems was studied. Alkanolamine solutions loaded with $HCO_3^-$ were measured using $ClO_4^-$ as internal standard. The same solutions were measured with $^{13}$C-NMR spectroscopy. The molar scattering intensity factors for $HCO_3^-$, $CO_3^{2-}$ and MEA- and DEA-carbamate were found to be 0.1973, 0.2901, 0.0632 and 0.0400 respectively. Characteristic bands of these species were identified at 1017, 1067, and 1162 $cm^{-1}$. A lower detection limit for $HCO_3^-$ anions in MEA and DEA solution was observed. Bands for potential quantification of free- and protonated alkanolamine are identified in the region of 2800 - 3800 $cm^{-1}$.


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*Keywords* : CCS; $CO_2$ ; Raman spectroscopy; alkanolalkanolamine solution; carbamate

## 1. Introduction

Aqueous alkanolamine solutions are the current state-of-the-art sorbents in post-combustion $CO_2$ capture (PCC) technology[1]. Chemical absorption of $CO_2$ into an aqueous alkanolamine solution typically comprises several parallel reaction pathways leading to formation of many different species. It is important for prediction purposes to determine reliable thermodynamic vapour-liquid equilibrium models. Hence, analysis of the liquid phase species distribution is mandatory for thermodynamic model optimization. Furthermore, such species analysis provides structure-property information on the

* Corresponding author. Tel.: +47 35 57 51 93; fax: +47 35 57 50 01.
*E-mail address:* Klaus.J.Jens@hit.no.

alkanolamine - $CO_2$ reaction. Despite the importance, detailed liquid phase speciation is difficult due to the lack of easily available analytical methods

Speciation based on spectroscopic methods is receiving increased attention. $^{1}H$- and $^{13}C$-NMR spectroscopy is being used for this purpose [2-4]. $^{13}C$-NMR spectroscopy can be considered to be a successful technique because non-invasive, direct measurements can be performed allowing estimation of all species formed in aqueous alkanolamine solvents with the exception of $H_2O$ and its ions. However, because of low natural isotopic abundance and slow relaxation time of the $^{13}C$ nuclei, long measurement times are required for determination of accurate quantitative data [4].

FT-IR spectroscopy combined with an attenuated total reflectance (ATR) probe head is a recent method for alkanolamine-$CO_2$-$H_2O$ system speciation [5-7]. However, high absorption of water still remains an obstacle in certain spectral ranges. In this regard, Raman spectroscopy is more promising for disclosing speciation in carbonated alkanolamine solution, both because special sample preparation is not necessary and that it shows less sensitivity to water content in the sample as compared to IR spectroscopy. Hence Raman spectroscopy is also a tempting method because of reasonable acquisition times which are considerably shorter than for $^{13}C$-NMR based techniques.

The focus of this work is on the applicability of Raman spectroscopy as an analytical tool to determine the speciation of carbonated aqueous alkanolamine systems. Previously, two such Raman studies [8,9] have been reported, both utilizing a multivariate linear regression analysis approach for spectrum calibration. While such methods work well in practice, a drawback is the large number of calibration samples that has to be prepared and measured. This work constitutes a simple 'short-cut' type approach to semi-quantitative speciation information employing measurement of selected Raman bands in conjunction with an internal standard ($ClO_4^-$), assisted by $^{13}C$-NMR .

## 2. Experimental Methods

### *2.1. Sample preparation*

All chemicals were of analytical grade or better quality and used as received. AMP was purchased from Acros Organic, $NaClO_4$ from Sigma Aladrich while the others were purchased from Merck. Carbonated alkanolamine samples were prepared according to literature [10,11]. Deionised (Milli-Q) water was used to prepare the aqueous alkanolamine solution (20 % w/w: 3.28 mol/l of MEA, 1.97 mol/l of DEA 1.78 mol/l of MDEA and 2.22 mol/l of AMP) which was degassed before use. In a typical sample preparation run, the carbonated aqueous alkanolamine solution was prepared by dissolution of a predetermined $NaHCO_3$ amount into an aqueous alkanolamine (MEA, DEA, MDEA or AMP) solution. The system was allowed to react and equilibrate for 24 hours in a thermostated closed cell (Grant LTD 6G) at 23 ± 2 $^{o}$C. After equilibration, the samples were transferred to a NMR tube (Wilmad LabGlas, 500MHz quality) after addition of a known amount of the internal standard $NaClO_4$.

### *2.2. Raman measurement*

The Raman scans were performed with a Jobyn Yvon Horiba T64000 instrument working in backscattering single grating mode. The light was collected through a confocal microscope with a Olympus 10x objective while the samples were kept in rotating 13C-NMR -tubes. The 400mW 532nm illumination was generated by a frequency doubled Millennia Pro 12sJS Nd:$YVO_4$ laser. To keep the signal to noise level low, 3 scans of 120 seconds were collected for each Raman spectral range. An extended range protocol was employed to cover the ranges from 700 to 1700 $cm^{-1}$ (three overlapping spectra) and from 2600 to 3700 $cm^{-1}$ (five overlapping spectra). A grating with 1800 rules pr. mm and a

slit width of 100 microns ensured a spectral resolution ranging from 2 $cm^{-1}$ at 1000 $cm^{-1}$ to 1.6 $cm^{-1}$ in the neighborhood of 3000 $cm^{-1}$. After removal of spikes and spectrograph artifacts, the overlapping spectra were merged. Fluorescence effects were subtracted by fitting with moderate degree polynomial functions. The wavenumber scale was calibrated against the Raman spectrum of a 50/50% (v/v) mixture of toluene and acetonitrile. No attempts were made to control polarization. However, the optical setup between each experiment was kept unchanged, to prevent such effects to interfere. All the scans were done at room temperature (20 ± 1 $^{o}$C).

For a given Raman band *j*, of a given species *i*, the relative scattering intensity $I_{ij}$ is directly related to the concentration of the determined substance through the formula.

$$I_{ij} = J_{ij} c_i \tag{1}$$

$I_{ij}$ is the relative scattering intensity. $J_{ij}$ is the Molar scattering intensity factor for each Raman band of each substance and is characteristic of the designated band at given measurement conditions and medium. $c_i$ is the concentration of the species. According to the formula (1), once the relative scattering intensity is known, the concentration of the substance can be calculated. Since many instrument and sample factors influence this linear relationship an internal standard is added to each sample assuming its Raman band to be independent of the other molecules in the solution.

Raman active bands for the carbonated aqueous alkanolamine solutions (alkanolamine/ $HCO_3^-$) were identified based on previous work [8,9,12] in addition to this work. $ClO_4^-$ has a Raman shift at 935 $cm^{-1}$. Having identified the relevant Raman active band, the spectral envelops was fitted to an area-normalized Gauss-Lorentzian peak function along with a polynomial baseline. Numeric evaluation of the corresponding parameters was performed using the Gnuplot program. The accuracy of this method is dependent on sufficient resolution to clearly distinguish the bands to be analyzed.

The molar scattering intensity factors ($J$ ) were calculated relative to the internal $ClO_4^-$ standard according to equation 2. The integrated area ($A$) under the relevant band was calculated since it is proportional to the band intensity. The concentration $c$ is given in mol/l.

$$\frac{A_i}{A_{ClO_4^-}} = J \frac{c_i}{c_{ClO_4^-}} \tag{2}$$

For determination of the molar scattering intensity factor of $HCO_3^-$, $CO_3^{2-}$ and the alkanolamines, pure solutions of each substance in different concentration were prepared containing $NaClO_4$ as internal standard. Since $HCO_3^-$ is in equilibrium with $CO_3^{2-}$, the $CO_3^{2-}$ concentration was calculated first according to equation 2 followed by the $HCO_3^-$ concentration calculation taking into account carbon mass conservation. The solutions of MEA and DEA were standardized by titration.

*2.3. 13C-NMR measurement*

The $^{13}$C-NMR experiments were performed at 9.4 T on a Bruker Avance III 400 MHz spectrometer using a BBFO Plus double resonance probehead at room temperature and the spectra were using MestreNova software v 7.1.1. A capillary containing a solution of $CH_3CN$ / $D_2O$ was inserted in the $^{13}$C-NMR tube as a reference standard and 'lock' solvent respectively. After the measurements of the longitudinal relaxation time $T_1$ of the $^{13}$C nuclei of all the species in solution, including the standard in the

capillary, the following $^{13}$C-NMR parameters were adjusted: recycle delay was 120 s, pulse angle=90° and number of scans was 480.

To obtain quantitative results, the area under the spectral peaks were integrated and scaled to the area of the reference standard peak. The effective concentration of the reference standard in the capillary was calibrated as a function of the solutions under study. Since the fast exchanging protons species are represented by a common signal in the $^{13}$C-NMR spectra, calibration experiments to distinguish between $HCO_3^-$ and $CO_3^{2-}$ and between alkanolamine and its protonated form were performed. Solutions of $HCO_3^-$ and $CO_3^{2-}$ and of alkanolamine and its protonated form were prepared and mixed in appropriate ratios. The pH of each sample was measured (using a 718 STAT Tritino produced by Metrohm) and $^{13}$C-NMR spectra were acquired. Since the chemical shift of the common peak depends on the relative amount of the two species, the variations of chemical shift were recorded and reported as a function of the species ratios and pH [3].

## 3. Results and discussion

After identification of the relevant characteristic Raman active bands for each substance by use of reference spectra, the molar scattering intensity factors ($J$ ) were calculated. Finally spectra of aqueous alkanolamine solutions loaded with $HCO_3^-$ were acquired and analyzed.

### *3.1. Band identification*

The most characteristic Raman active band of $CO_3^{2-}$ suitable for quantitative measurement [13] is reported [8,12] to be 1065 cm$^{-1}$ while the most characteristic bands of $HCO_3^-$ are reported [13] at 1017, 1302, 1360 and 1630 cm$^{-1}$. Figure 1 shows our reference spectra for $CO_3^{2-}$ and $HCO_3^-$ including the internal $ClO_4^-$ standard (935 cm$^{-1}$). We observed the characteristic $CO_3^{2-}$ band at 1067 cm$^{-1}$ and the characteristic $HCO_3^-$ bands at 1017 and 1360 cm$^{-1}$.

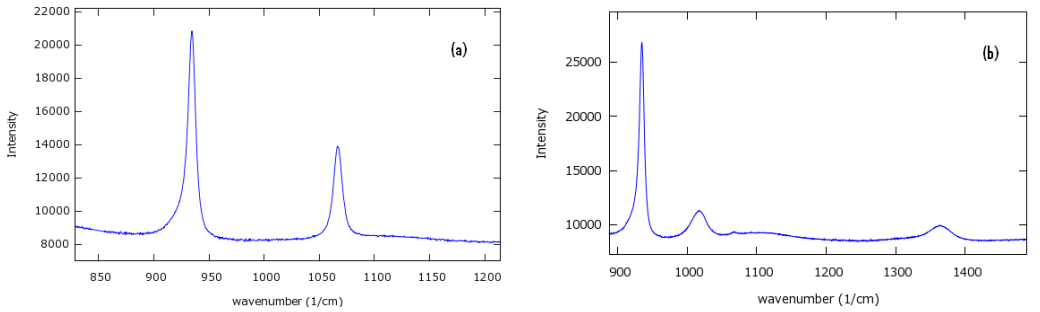


Figure 1: Reference Raman spectra for $CO_3^{2-}$ (a) and $HCO_3^-$ (b). $CO_3^{2-}$ concentration is 0.185 mol/l and $HCO_3^-$ concentration is 0.216 mol/l

Ammonium carbamate shows 5 characteristic Raman active bands[13]. Only the band at 1034 cm$^{-1}$ is suitable for quantitative measurement. For MEA and DEA solutions loaded with $CO_2$, the carbamate band was clearly identified at 1162 cm$^{-1}$ [8].

In a previous study[9] characteristic Raman bands for free alkanolamine have been observed at 400, 1200, 1350 and 1600 cm$^{-1}$. Two of these were detected at 1350 and 1600 cm$^{-1}$ in our spectra for MEA (Figure 2). Figure 5 shows corresponding bands in the DEA Raman spectrum at 1200 cm$^{-1}$. These two bands have the potential for quantification of free MEA (1350 cm$^{-1}$) and DEA (1200 cm$^{-1}$). However, these bands become weak at lower concentration leading to an under estimation of the quantification. As

similarly for ammonia (3310 $cm^{-1}$) [13], we can observe a band at 3313 $cm^{-1}$ in the MEA spectrum (figure 2) which is not visible in the spectrum of the protonated form (figure 3). Therefore the 3313 $cm^{-1}$ band is characteristic for the free alkanolamine; however the band is overlapping somewhat with a water band. A proper curve model in this spectral range is expected to enable quantification of free alkanolamine. In addition to the band at 3313 $cm^{-1}$, further bands be observed at 2890, 2930-2960 and 3381 $cm^{-1}$. Previous work[14] on protonated alkanolamines has reported that characteristic bands at 2952, 2940 and 2884 $cm^{-1}$ for MEA were shifted to 3005 , 2971 and 2898 $cm^{-1}$ on protonation. A similar result is demonstrated in Figure 3 showing that protonated MEA leads to a Raman shift at 2900 and 2980 $cm^{-1}$ with a shoulder.

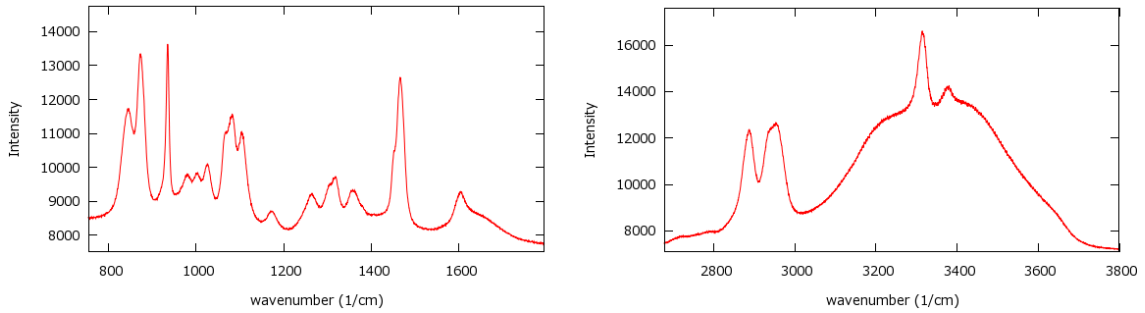


Figure 2: Reference Raman spectra for MEA

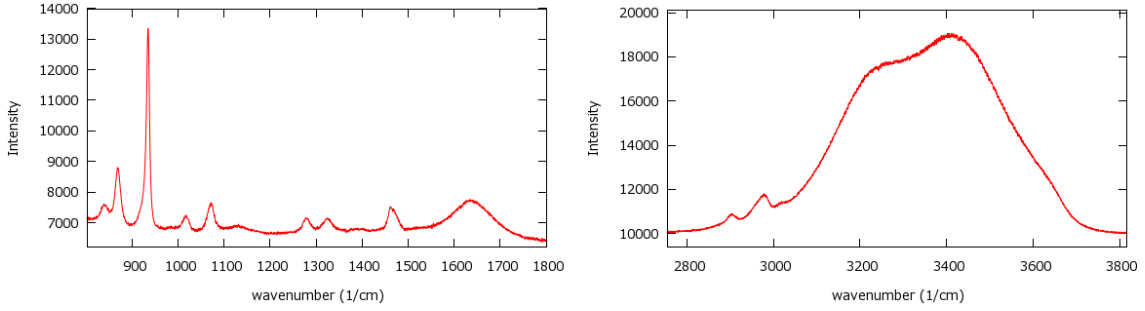


Figure 3: Reference Raman spectra for protonated MEA

### *3.2. Molar scattering intensity factor*

The determined molar scattering intensity factors are presented in Table 1.The value for $HCO_3^-$ and $CO_3^{2-}$ were calculated to be 0.1973 and 0.2901 respectively. These values are consistent with a previous study [12] which reported 0.188 and 0.302 respectively. Our calculations are based on the 1350 and 1200 $cm^{-1}$ band for MEA and DEA respectively. However these bands were weak in the scattering envelop which increases the error margin; it was found that the bands were not visible in samples with low alkanolamine concentration. More work is needed to reduce the error margin.

Figure 4 and 5 show a clearly distinguishable band at 1160 $cm^{-1}$. The band was not visible in the MDEA Raman spectrum with 0.5 loading. Since MDEA is a tertiary alkanolamine, no carbamate can be formed. Our molar scattering intensity factors for carbamate are relevant for this band. The reference

concentrations for the calculations were taken from $^{13}$C-NMR measurements on the carbonated solutions analyzed by Raman at different concentration levels. The calculated value for the MEA- and DEA-carbamate is 0.0632 and 0.04 respectively.

Table 1: Molar scattering intensity factors.

| Component | J | Standard deviation |
|---|---|---|
| $CO_3^{2-}$ | 0.2901 | 0.0062 |
| $HCO_3^{2-}$ | 0.1973 | 0.0250 |
| $OHC_2H_4$ $NHCOO^-$ | 0.0632 | 0.0070 |
| $(HOC_2H_4)_2NHCOO^-$ | 0.0400 | 0.0060 |
| $HOC_2H_4NH_2$ at 1350 $cm^{-1}$ | 0.0040 | 0.0012 |
| $(HOC_2H_4)_2NH$ at 1200 $cm^{-1}$ | 0.0130 | 0.0014 |

### *3.3. $HCO_3^-$ loaded alkanolamine solutions*

Three different concentration levels ($HCO_3^-$ to alkanolamine loading ratio: 0.5, 0.75, 1) of carbonated aqueous systems were analyzed for MEA and DEA. MDEA and AMP were analyzed only at 0.5 loading. The spectra of MEA solution with/without 0.5 loading are given in Figure 5. The characteristic bands of $CO_3^{2-}$ and MEA-carbamate are clearly visible at 1067 $cm^{-1}$ and 1162 $cm^{-1}$ respectively. A similar result was observed for the other two loadings.

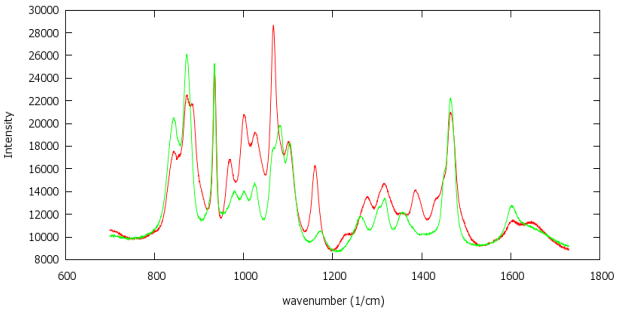


Figure 4: Raman spectra of MEA 20 % w/w aqueous solution without loading (green) and with 0.5 loading (red).

The $CO_3^{2-}$ concentration was calculated using equation 2 and the bicarbonate loaded MEA Raman spectra. The calculated concentrations were 0.285, 0.382 and 0.536 mol/l at 0.5, 0.75 and 1.00 loadings respectively. $^{13}$C-NMR measurements ware run for each of the prepared samples. The results are summerized in Table 2. The $CO_3^{2-}$ quantification based on Raman measurements are in the same order of magnitude as the $^{13}$C-NMR quantification. The $CO_3^{2-}$ Raman band is particularly strong. It might be a reason for over estimated values. We speculate that this effect may be due to molecular species interaction effect as concentration increases. However, the correspondence between Raman and $^{13}$C-NMR

determined concentration varies. This could be due to overlapping bands in combination with our method of data deconvolution.

Furthermore, neither the characteristic $HCO_3^-$ band (1017 $cm^{-1}$) nor the 1350 $cm^{-1}$ alkanolamine band was truly visible at all three loadings. The reason may be that the $HCO_3^-$ band is masked by the alkanolamine spectrum due to low concentration of the former. According to $^{13}$C-NMR results, the $HCO_3^-$ concentration is rather low. However, even though the alkanolamine concentration is quite high, the band at 1350 $cm^{-1}$ is very weak and below the detection level. Thus the 1.521 mole/l of free MEA was under estimated by more than 50 %. Hence, we suggest use of the stronger bands in the high frequency range (2800-4000 $cm^{-1}$) for quantification of free- and protonated alkanolamine.

Table 2: Concentration determined by $^{13}$C-NMR measurement for MEA/$HCO_3^-$ and DEA/$HCO_3^-$ systems

| **$HCO_3^-$ loading** | **Alkanolamine** | **$CO_3^{2-}$ mole/l** | **$HCO_3^{2-}$ mole/l** | **$RNHCOO^-$ mole/l** | **Free alkanolamine mole/l** |
|---|---|---|---|---|---|
| 0.50 | MEA | 0.243 | 0.018 | 1.340 | 1.521 |
| | DEA | 0.219 | 0.108 | 0.595 | 0.953 |
| 0.75 | MEA | 0.360 | 0.044 | 1.880 | 0.793 |
| | DEA | 0.312 | 0.208 | 0.787 | 0.602 |
| 1.00 | MEA | 0.520 | 0.234 | 2.475 | 0.187 |
| | DEA | 0.396 | 0.412 | 0.911 | 0.344 |

Similar results as for MEA were observed for the DEA solutions at the three different loadings. Again, clearly visible characteristic bands for $CO_3^{2-}$ and carbamate were noticed. The Raman and $^{13}$C-NMR results are quite compatible in respect to $CO_3^{2-}$ concentration. The calculated 'Raman' concentrations were 0.273, 0.372 and 0.306 mol/l for the respective loadings at 0.5, 0.75 and 1.00. Figure 5 shows the Raman spectra of the DEA sample with/without 0.5 loading. The characteristic $HCO_3^-$ Raman band at 1017 $cm^{-1}$ is probably masked by other bands near 1017 $cm^{-1}$ which is seen in the unloaded DEA solution spectra. Interestingly, a 0.412 mol/l of $HCO_3^-$ concentration was not detected in loaded DEA solution, while a 0.216 mol/l of $HCO_3^-$was clearly visible in the pure solution (Figure 1). This demonstrates clearly the masking of the 1017 $cm^{-1}$ band.

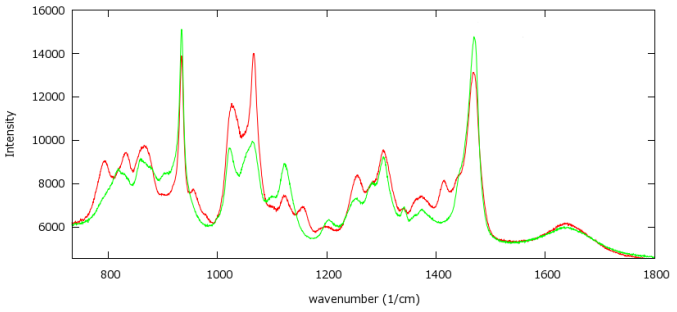


Figure 5: Raman spectra of DEA 20 % w/w aqueous solution without loading (green) and with 0.5 loading (red).

In comparison with MEA, a quite distinct band at 1200 $cm^{-1}$ is visible for free DEA. However, it is barely visible at 0.75 and 1.00 loading and gave 0.584 mol/l of DEA concentration at 0.5 loading.

Figure 6 shows the AMP Raman spectra with/without 0.5 loading. AMP is a sterically hindered alkanolamine which is believed not to form carbamate. Hence no corresponding band at 1067 $cm^{-1}$ is detected. The characteristic bands for $CO_3^{2-}$ and free alkanolamine are visible. However the band of $ClO_4^-$ internal standard is overlapping with the AMP spectrum precluding use of the internal standard for quantification.

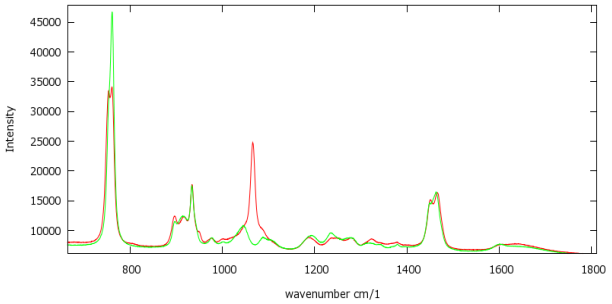


Figure 6: Raman spectra of AMP 20 % w/w aqueous solution without loading (green) and with 0.5 loading (red).

## 4. Conclusion

This demonstrated Raman spectroscopic method is able to pick out selected characteristic Raman bands which can be used as part of a simple model allowing quick, semi-quantitative insight into carbonated alkanolalkanolamine solutions.

The molar scattering intensity factors for $HCO_3^-$, $CO_3^{2-}$ and MEA- and DEA-carbamate were found to be 0.1973, 0.2901, 0.0632 and 0.0400 respectively.

For alkanolalkanolamine samples, a lower detection limit was observed for the $HCO_3^-$ concentration

Potential bands for quantification of free- and protonated alkanolamine are identified in the spectral region of 2800 - 3800 $cm^{-1}$

The well known internal $ClO_4^-$ standard (935$cm^{-1}$) cannot be used for AMP.

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