1. Introduction

Raman spectroscopy is extensively used in several branches of engineering and sciences such as: material science, biomedical engineering, chemical, environmental and other industrial fields. It is a powerful non-destructive tool used in stimulation of chemical and physical properties of materials. It provides important information about the molecular structure and chemical composition of a substance. Raman spectrum is a plotting of the energy difference between the Raman-scattered photons and the incident photons versus the intensity of scattered light. High level of elastic scattering has always created problem in Raman spectroscopy. This situation had occurred specially in investigation of the lines at short Raman shift. To take care of such situations, the monochromator is fitted with two or three dispersion stages. Two different forms of noise are observed in Raman spectra caused by low frequency and high frequency. Another is cosmic spike which is observed as very narrow spike.

De-noising of Raman spectra can be categorized in two ways: smoothing and filtering. For smoothing, classical Savitzky-Golay algorithm is used. For filtering: finite impulse response filtration, wavelet transform and its variants, factor analysis methods have been used. Weiner estimation and interval thresholding methods have also been used for de-noising the Raman spectra. Sudha has developed a tool to de-noise Raman spectra. Liao et al. have used total variation de-noising in Raman spectroscopic images. Tripathi and Siddiqi have denoised Raman spectra using total variation with majorization-minimization algorithm. Dixon et al. have used least square weighted regularization method for de-noising.

Signal de-noising is an important aspect of signal analysis. Numerous methods have been proposed in last decades. Total variation de-noising which was introduced by Rudin et al. has been an interesting and powerful technique since its inception. Rodriguez and Wohlberg, Hu and Jacob, Bredies et al. have extended and generalized the idea of total variation. In image processing and sparse signal processing, Couprie et al. applied total variation as a regularizer. TV de-noising is defined as a convex optimization problem consisting of two terms: quadratic data fidelity and convex regularization. For linear inverse problems, Blake and Zimmerman.
Nikolova have proposed the concept of non-convex penalties in formulating a convex optimization problem. Selesnick et al. have applied a non-convex regularizer in place of non-smooth convex regularizer.

In this article, Raman spectra of Sr$^2+$ modified PMN-PZT ceramics has been de-noised using non-convex regularizer in total variation proposed in. SNR and RMSE have also been used to measure the performance of method. It is observed that the method works well for de-noising the Raman spectra.

2. Material and Methodology

2.1 Material
Raman Spectral data of Sr$^2+$ modified PZT-PMN (with Sr = 0.075) collected at about 25°C room temperature by Raman spectrometer of Renishaw RM-1000 spectroscope, which uses 1.19 nm as a unit in the range of 200 – 1000 cm$^{-1}$, have been used here.

2.2 Methodology
Let the measured data $\beta(m)$ be represented as:
\[
\beta(m) = \alpha(m) + \epsilon(m), m = 0, 1, 2, ..., M-1
\]

where, $\alpha(m)$ is a signal which is piecewise constant and is to be estimated, $\epsilon(m)$ is white Gaussian noise.

Let the objective function $G: \mathbb{R}^M \rightarrow \mathbb{R}$ given by
\[
G(x) = \frac{1}{2} \| \beta - \alpha \|_2^2 + \lambda \sum_m \psi(\| D\alpha \|_m)
\]

where, $\lambda > 0$ is a constant called the regularization parameter, penalty function $\psi: \mathbb{R} \rightarrow \mathbb{R}$ is called regularizer which promotes the sparsity, $D$ is the matrix
\[
D = \begin{bmatrix}
-1 & 1 \\
-1 & 1 \\
... & ...
-1 & 1
\end{bmatrix}
\]

and $\| D\alpha \|_m$ is representation of the $m^{th}$ component of vector $D\alpha$. TV de-noising (1-dimensional) is defined as minimizing $G$:
\[
\alpha^* = \arg \min_{\alpha \in \mathbb{R}^M} G(\alpha) \tag{3}
\]

where, $\alpha \in \mathbb{R}^M$, and $\psi$ is taken as $\psi(\alpha) = |\alpha|$. Here, $G$ is strictly convex on $\mathbb{R}^M$. Therefore, minimizer of $G$ is unique. Nikolova has shown that non-convex penalties recover the signals more accurately than the convex penalties. Here, $\psi$ is set in such a way that $G$ remains strictly convex. In this case, minimizer will be unique and de-noising process will be stable and minimizer can be obtained using convex optimization techniques. Selesnick et al. have shown that for logarithmic penalty
\[
\psi(\alpha; \delta) = \frac{1}{\delta} \log(1 + \delta |\alpha|), \quad \delta > 0
\]

and the arctangent penalty
\[
\psi(\alpha; \delta) = \frac{2}{\delta \sqrt{3}} \left( \tan^{-1} \left( \frac{1 + 2\delta |\alpha|}{\sqrt{3}} \right) - \frac{\pi}{6} \right), \quad \delta > 0
\]

using theorem 6.4 of the convexity condition is obtained as
\[
\delta < \frac{1}{4\lambda}
\]

2.3 Algorithm
The algorithm proposed by Selesnick et al. based on the procedure is used here. Iterations are given by
\[
\alpha^{(i+1)} = \beta - D^T \left( \frac{1}{\lambda} \left[ \left( ZD\alpha^{(i)} \right)^T \right]^2 + DD^T \right) D\beta \tag{6}
\]

where, $Z$ is a diagonal matrix given by
\[
[Z(Dv)]_{m,m} = \frac{\psi'(\| Dv \|_m)}{[Dv]_m}.
\]

The iteration is initialized with $\alpha^{(0)} = \beta$.

2.4 Numerical Implementation and Performance Analysis
The format of obtained data is .txt. Data has two kinds of 876x2 data representing the intensity-Raman shift and the intensity-pixel. Only 876 x 1 Intensity values have been exported and chosen as 1 – dimensional signal. MATLAB program described in has been applied for total variation de-noising with non-convex penalty based on (6). Two non-convex penalties namely log and arctangent have been used to de-noise the signal and is compared with de-noising using a convex penalty. Value of regularization parameter $\lambda$ has been taken as 2 and number of iterations is kept fixed at 20 in the algorithm.
To evaluate the performance of the proposed methodology, SNR and RMSE have been taken in account for convex, log and arctangent penalties in Table 1.

Table 1. SNR and RMSE for different penalties

| Penalty  | SNR   | RMSE  |
|----------|-------|-------|
| Convex   | 65.6806 | 1.2648 |
| Log      | 67.3118 | 1.0482 |
| Arctangent | 69.5047 | 0.8143 |

Figure 1 shows the original signal while Figures 2, 3 and 4 show the denoised signals.

Figure 1. Original Raman Spectra.

Figure 2. De-noised signal using convex penalty.

Figure 3. De-noised signal using log penalty.

Figure 4. De-noised signal using arctangent penalty.

3. Discussion

In this article, de-noising Raman spectra is modeled as a convex optimization problem with total variation in which non-convex penalty has been chosen. Generally, convex penalties are used in solving such problems. Convex penalties always result in a convex optimization problem. Several methods are proposed for solving such problems. Here, two non-convex penalties namely log penalty and arctangent penalties have been used to solve the de-noising problem. Non-convex penalties result in a non-convex optimization problem. Solution of non-convex problems is very complicated. Hence, the problem is constrained in such a way that it remains convex and hence its solution is obtained easily. Condition of optimality for such penalties is that the value of constant $\delta$ in penalties must be less than $1/4\lambda$. To measure the performance of the method, two parameters: SNR and RMSE have been evaluated. Higher the SNR values and lower the RMSE values imply better de-noising of the spectra. De-noising based on convex and non-convex penalties has been compared. Value of $\lambda$ has been fixed to 2. We observe from Table 1 that for convex penalty, value of SNR is 65.6806 (Figure 2); for non-convex (log) penalty, value of SNR is 67.3118 (Figure 3) and for non-convex (arctangent) penalty, value of SNR is 69.5047 (Figure 4). Thus, the values of SNR for non-convex penalties are higher than the values of SNR for convex penalty. This shows that spectra are de-noised efficiently. Similarly, we see that for convex penalty, value of RMSE is 1.2648 (Figure 2); for non-convex (log) penalty, value of RMSE is 1.0482 (Figure 3) and for non-convex (arctangent) penalty, value of RMSE is 0.8143 (Figure 4). Thus, the values of RMSE for non-convex penalties are lower than the values of RMSE for convex penalty. Again,
this shows that spectra are de-noised efficiently. Also, we observe that the arctangent penalty works better than the log penalty. Thus, overall observation is that non-convex penalties work well in de-noising Raman spectra provided the optimization problem is maintained to be convex.

4. Conclusion

Convex penalties (regularizers) are very popular in TV de-noising. Here we have used non-convex penalties (regularizers) and observe that TV de-noising using a non-convex regularizer where the problem is constrained in such a way that the objective function remains convex, works very well in de-noising of Raman spectra of PMN-PZT Sr2+ ceramics. This is reflected from Table1. The most important part of this approach is to maintain the convexity of the problem.

Further studies can be done using other non-convex penalties. When using the non-convex penalty, the problem of de-noising is converted to an optimization problem of non-convex type, its solution may be tried to find out and the performance of de-noising may be studied.

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