The Combination of the Frequencies ϵ_1 and ϵ_4 in Raman Spectra of CCl$_4$

Kamal Kayed*, Iman Alawa, Fawaz Saiof

Higher Institute for Laser Research and Application (HILRA), Damascus University, Damascus, Syria

*Corres.authro : khmk2000@gmail.com

Abstract: Raman spectra of Carbon Tetrachloride and Methanol solutions were measured. Spectral lines ν1, ν4, ν1+ν4 of Carbon Tetrachloride were analyzed. Results indicate that, by comparing the spectral data for these lines, it is possible to get some information about the relative intensities of the various forces acting on the C-Cl bond in the mixture. In addition, preliminary indications were monitored on the possibility of forming some kind of bounding between Methanol and Carbon Tetrachloride molecules at the high levels of Methanol concentrations.

Keywords: Raman – Carbon Tetrachloride – Methanol – Combination.

1. Introduction

CCl$_4$ is considered to be a non-polar solvent as it doesn't express any permanent moleculardipole moment. This feature is very important in the spectral studies in the cases of using Carbon Tetrachloride as a dilute for some polar substances such as Methanol and Acetone [1-3], because it is possible to study the interactions between the molecules of the dissolved substances without having a strong influence of the Carbon Tetrachloride molecules.

Methanol/Carbon Tetrachloride mixture gained the attention of many research groups[2-6], where the attention was focused on developing an ideation for the microscopic structure of the mixture, and the changes that happen as a result of concentration alteration. Some of these studies relied on the use of Raman spectroscopy, which is the appropriate way to study the structure as a function of concentration, because in liquid mixtures, the band shape of a reference vibrational mode of the molecule is influenced by the concentration fluctuations of the environment [7–9].

The dependence of the bandwidth and frequency of Raman bands on the environment provides useful information regarding the solute–solvent interactions and intermolecular forces[7].

In Methanol/Carbon Tetrachloride mixture, the Methanol molecules are linked together in hydrogen bonds forming winding chains in the range of the high concentrations level, and cyclic structuresin the range of the low concentrations level[10]. The mutual influence between Methanol molecules and CCL$_4$ molecules increased up to the solvent cage effect at the high concentrations of Methanol, where the molecules of Carbon Tetrachloride are confined in a potential well created by Methanol molecules[7]. Some researches[11,12]

suggest that solvent cage effect may be accompanied with forming HO..Cl bonds, although there is no structural evidence to support this prediction.

In our present study, we are trying to lay a new ideation based on taking advantage of the characteristics of Raman spectrum of Carbon Tetrachloride in order to obtain information about the nature of the interaction between molecules of Methanol/Carbon Tetrachloride. We compared the spectral characteristics of $\nu_{com}=\nu1+\nu4$ band in Raman spectroscopy of Carbon Tetrachloride with the spectral characteristics of its components; $\nu1$ and $\nu4$.Such comparison is very useful because the changes that arise upon longitudinal optical vibrations ($\nu1$) and transverse optical vibrations ($\nu4$) due to the alteration of Methanol concentration will be combined in the bond spectrum$\nu1+\nu4$ resulting from combining $\nu1$ with $\nu4$.

2. Experimental procedure

CCL_4 and CH_3OH solutions were prepared in different concentrations of Methanol ranged from 0 to 1 (v/v).The compounds (Aldrich) are commercial products which were used without further purification.The FT-IR and Raman spectra were measuredas a function of concentrationat room temperature with a Nicolet-6700/NXR-Raman, provided with laser source He/Ne at 632.8 nm, with resolution of 4 cm^{-1}. The Raman spectra were fitted by using Peak-Fit programby a sum of Gaussian and Lorentzian components.

3. Results and Discussion

3.1.The relation between the ϵ_{com} peak intensity and the intensities of its components:

Figure (1)shows the peaks' intensities of$\nu1$, $\nu4$, and ν_{com}lines as a function of the concentration of Methanol in the mixture. The similarity in the behavior of the three curves, where intensity tends to decrease as the Methanol concentration increased, is noticeable.

Fig. 1 The variation of Raman intensity as a function of concentration
(a) line $_1$ (b) line $_4$ (c)   line $_{com}$.
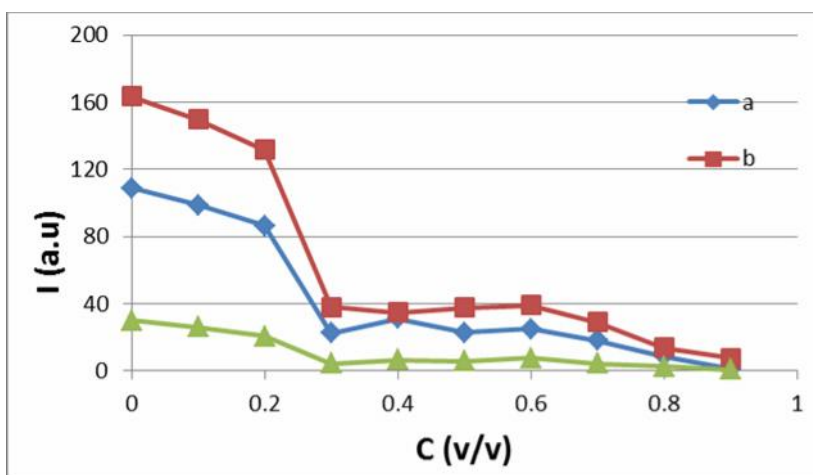
Keeping away from linearity between intensity and concentration is caused by the effects of adding Methanol. We can also notice a reduction of intensity at high rates in the range of low concentrations levels. This rate is decreased soon as moving to the range of high concentrations levels.

Figure(2)illustratesν_{com} peak intensity as a function of$\nu1$(curve a),and $\nu2$(curve b) lines intensity.In both cases, we observe a high degree of linearity,which suggests that the linear relation between these components doesn't get changed by the existence of Methanol molecules.

Fig. 2 Theplots of I_{com} as a function of (a) I_1 (b) I_4
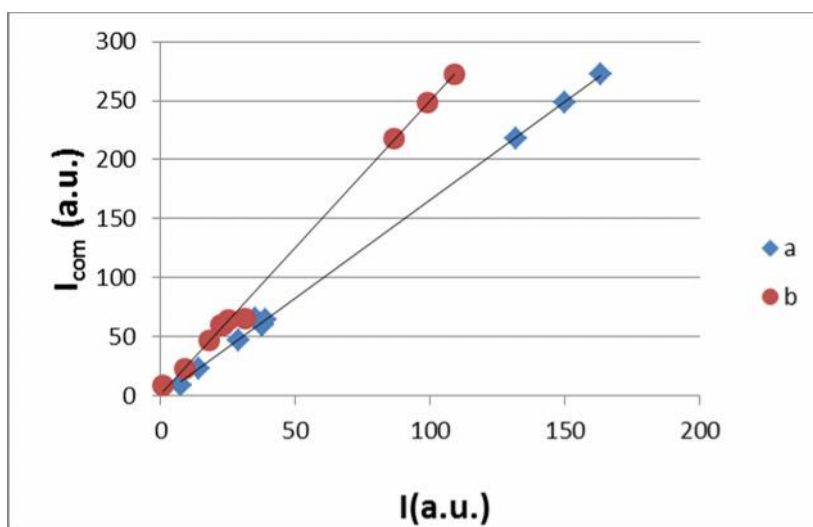
## 3.2. The Relation between Peaks Positions Shifts:

Figure(3)illustrates the peak position dependency on the concentration for peaks $\nu 1$, $\nu 4$, and ν_{com}. We notice thatas concentration increases, peak $\nu 1$ shifts toward low wavenumbers, indicating the influence of attractant forces on longitudinal optical vibrations, which increase with the increment of Methanol molecules concentration in the solution. These forces arise from Carbon Tetrachloride molecules depolarization and its mutual influence with Methanol molecules, which are permanent dipoles.

Fig. 3 Variation of Raman shift as a function of concentration
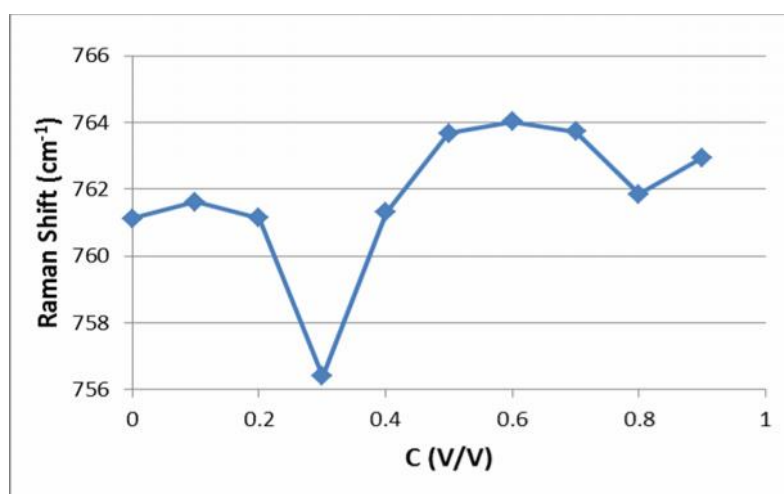(a) line $_1$ (b) line $_4$ (c) line $_{com}$.

(a)
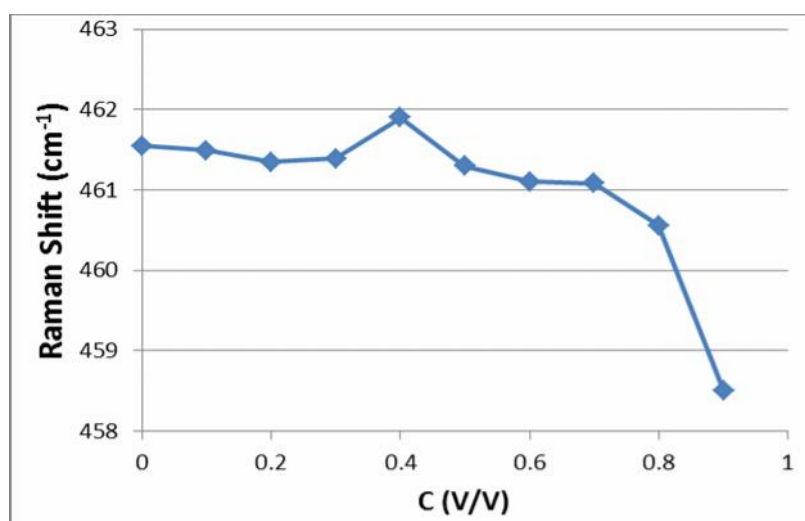
(b)
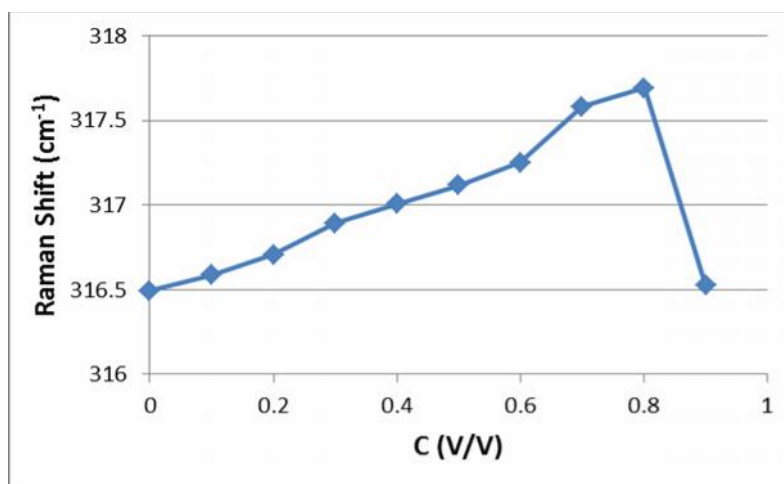
(c)

On the contrary, we can observe that peak position $\nu 1$ shifts towards high wavenumbers. These shifts can be interpreted as Methanol molecule exposed to internal centrifugal forces that arose between two charged Chloride atoms. Moreover, the attractant forces contribute in these shifts by affecting Chloride atoms existing in Cl-C-Cl structure. Consequently, the attractant forces have different impact on the twovibration patterns. In both cases, an acute shift toward high wavenumbers occurs when moving to high concentrations. This indicates an alteration in the bonding characteristics between Carbon and Chloride atoms, and an onset of new formations, possibly from OH…CL type.

As seen from the curve (C) in figure (3), we can note that for peak ν_{com}, there is no kind of linearity in the relation between position and concentration. This curve is divided into three areas: low concentrations area, extending from (0 to 0.3 v/v). A shift in the peak toward the low wavenumber occurs. Hence, the prevalent forces in this area are the attractant ones.

Medium concentrations area extends from (0.3 to 0.6 v/v). In this area, we can notice a shift in the peak towards high wavenumbers as the concentration increases. The prevalent forces here are the centrifugal ones. High concentrations area extends from (0.6 to 0.9 v/v). Shifts are headed again toward low wavenumbers. However, this time it is as a result of the formation of new chemical structures, not because of traditional attractant forces.

Since $\nu 1$ frequency is related to attractant forces, while $\nu 4$ frequency is related to centrifugal ones, the forces that influence the vibrating bond can be considered as a result of the combination of attractant forces, which have an obvious impact upon longitudinal optical vibrations through curve (a), and repulsive forces, which have an obvious impact upon transverse optical vibrations through curve (b).

Based on the foregoing, we can conclude that in the low concentrations area, the attractant forces are stronger than the centrifugal ones. However, when the concentration increases (medium concentrations area), it becomes reverse. Consequently, the centrifugal forces are the dominant. In the high concentrations area, a new kind of bonding arises.

Another proof of the emergence of such links we got from the infrared spectra where it was noted the disappearance of ν_{com} and ν_3 lines at the concentration 0.9, which means a change in the spectral characteristics related to the emergence of new links.

3.3. The Relation between Spectral Width and Concentration:

The diagram of the spectral width for the three peaks as a function of concentration are plotted in figure (4).For the peak $\nu1$ (curve a), we can see that there is no significant change in low and medium concentrations areas. However, an obvious change in spectral width takes place, and tends to increase when moving to the high concentrations, indicating the interaction intensity between the components of the mixture. As for the peak $\nu4$ (curve b), the spectral width increases in general with some fluctuations in medium concentrations area.

Fig. 4 The variation of Raman bandwidth as a function of concentration
(a) line $_1$ (b) line $_4$ (c) line $_{com}$.

(c)
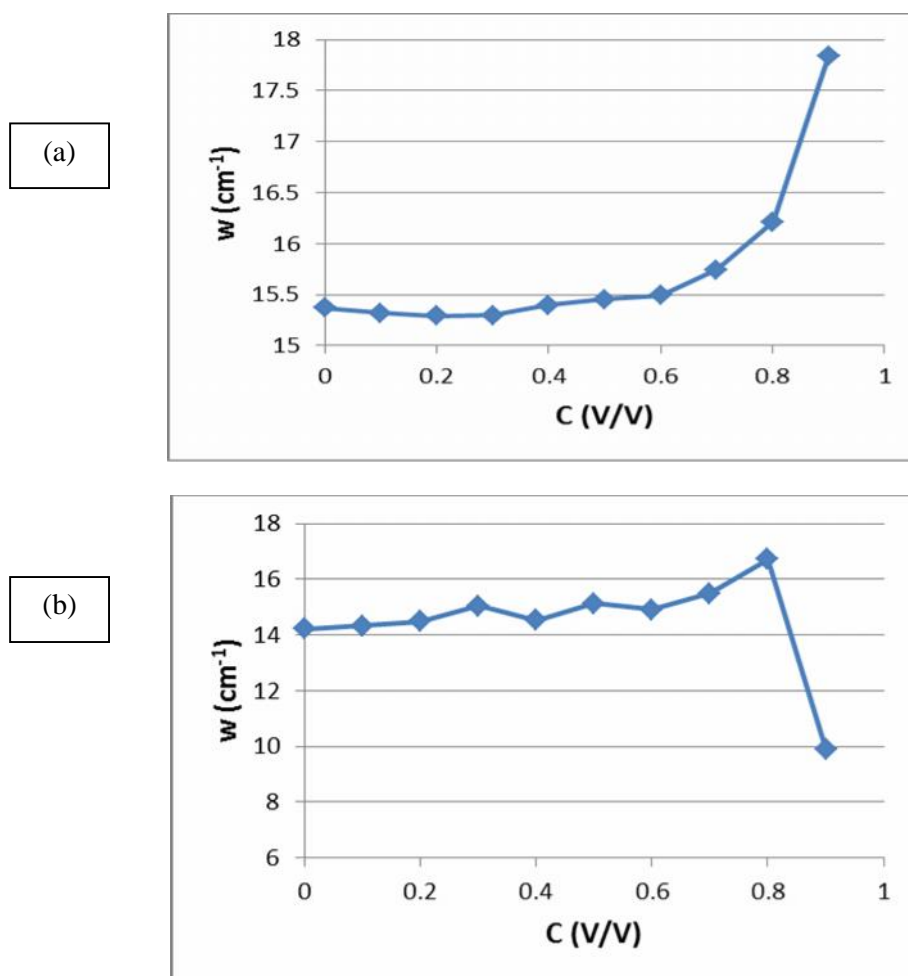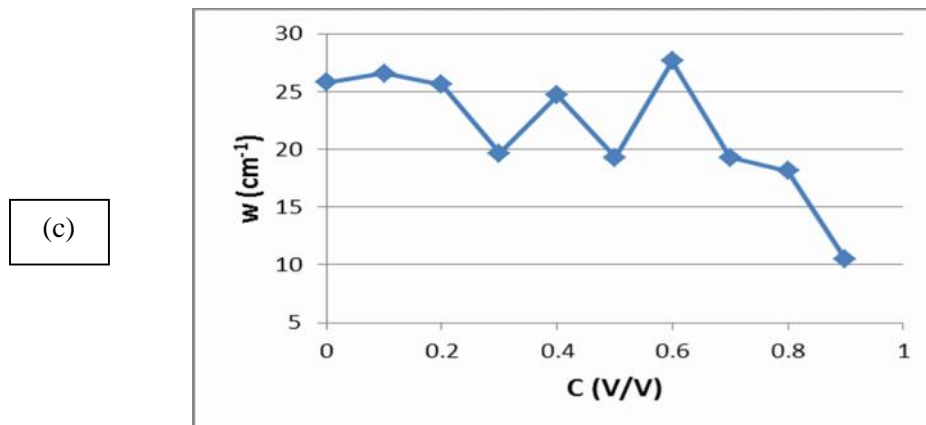
For the peak ν_{com}, the value of spectral width elevated in relation to all concentrations when comparedwith thespectral width of peaks $\nu 1$ and $\nu 2$. The reason of this is the converging of widening mechanisms in each case of longitudinal and transverse vibrations. Reduction of spectral width at high concentrations can be attributed to the decline of repulsive forces intensity in these concentrations [9].

4. Conclusion

In this study, Methanol and Carbon Tetrachloride solutions were prepared, where Methanol concentrations ranged between 0 to 1 (v/v). Raman spectra for the prepared solutions were measured, and $\nu 1$, $\nu 4$, and $\nu 1+\nu 4$ lines of Carbon Tetrachloride were analyzed. Results indicated an occurrence of similar intensity behavior in significance of three lines. Comparison between spectral features of these lines indicated that the relative intensity of the forces influencing on the longitudinal optical vibrations and transverse optical vibrations are related to the concentration. The attractant forces are prevalent on low concentrations, while the centrifugal forces become dominant when we increase the concentration above a certain limit. In addition, a shift in peak $\nu 1+\nu 4$ towards low wavenumbers occurs in the high concentrations, emphasizing the occurrence of the bond between Methanol and Carbon Tetrachloride molecules.

Acknowledgments

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