Influence of Dilution with Methanol on Fermi's Resonance inCCL$_4$Vibrational Spectra

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Abstract: Raman spectra of Carbon Tetrachloride and Methanol solutions were measured. Spectral lines $\nu_3, \nu_{com}(\nu_1+\nu_4)$ of Carbon Tetrachloride Vibrational Spectra were analyzed. The results showed that Fermi resonance coefficients depend on methanol concentration, besides to the existence of clear effect for the polarization of carbon on these coefficients. In addition, cases of splitting in the energy levels of the spectral line ν_3 were observed at specific concentrations of methanol.
Keywords: Raman – Carbon Tetrachloride – Methanol – Fermi resonance.

1.Introduction

Fermi resonance is a very common phenomenon in molecule vibration spectra, especially in polyatomic molecule with complex structure. Fermi resonance appears when a fundamental vibration frequency lies closely to an overtone or combination frequencies. One can observe two peaks coming from Fermi resonance and the energy transfer also occurs between the two peaks. Fermi resonance phenomenon appears in both infrared spectrum and Raman spectrum.

CCl$_4$ is considered to be a non-polar solvent as it doesn't express any permanent molecular dipole 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[1-5], 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[5-8] , 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[9-11].

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 ringed structures in the range of the low concentrations level[12]. 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[9]. Some researches[13,14] suggest that

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

2. Experimental procedure

CCL$_4$ and CH$_3$OH 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 measured as a function of concentration at room temperature with a Nicolet-6700/NXR-Raman, provided with laser source He/Ne at 632.8 nm, with resolution of4 cm^{-1}. The Raman spectra were fitted by using Peak-Fit program by a sum of Gaussian and Lorentzian components.

Fermi resonance parameters were calculated by using the following equations[2,3]:

$$\Delta = (\Delta_0^2 + 4w^2)^{1/2} \qquad (1)$$

$$R_{f/a} = \frac{I_f}{I_a} = \frac{\Delta - (\Delta^2 - 4w^2)^{1/2}}{\Delta + (\Delta^2 - 4w^2)^{1/2}} \qquad (2)$$

where Δ is the wavenumber separation between the perturbed levels in the presence of FR; $\Delta 0$ is the wavenumber separation between the unperturbed harmonic levels in the absence of FR; W is the Fermi coupling coefficient; $R_{f/a}$is the ratio between intensities of FR components; $I_f$is the spectral intensity of the combination (forbidden vibrational transition) involved in FR; $I_a$is the spectral intensity of the fundamental (allowed vibrational transition) involved in FR.

3. Results and Discussion

Figure(1)illustrates the peak position dependency on the methanol concentration for peaks υ_1, and υ_{com}. The peak υ_{com} results from the combination of the two frequencies υ_1 and υ_4. The direction of υ_{com} shift is related to the type of the forces acting on each of the symmetrical stretch vibrations, and asymmetrical deformation vibrations[1]. We notice that the position of the peak υ_3 follows to methanol concentration in a manner similar to those of the spectral line υ_{com},and this is the result of energy exchange between the two lines due to Fermi resonance.
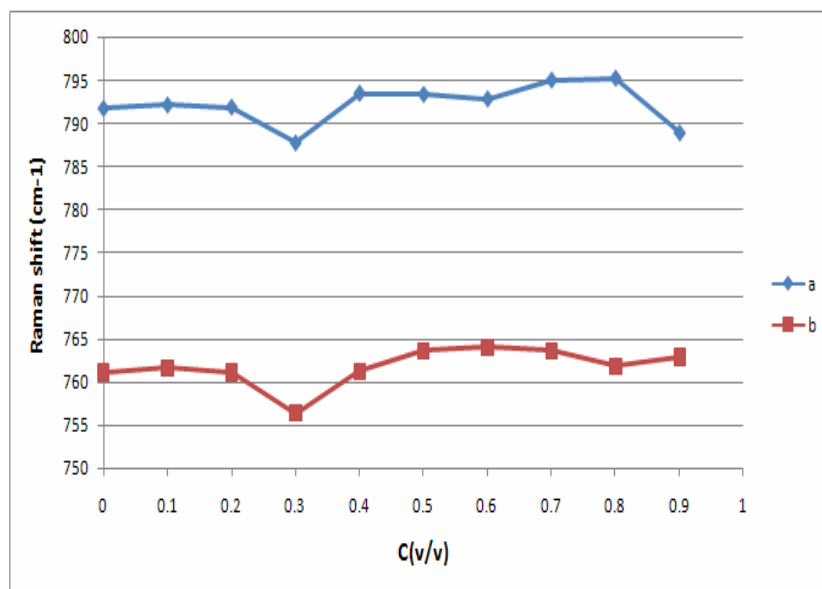

Fig. 1 Variation of Raman shift as a function of concentration
(a) line υ_3 (b) line υ_{com}.

Figure (2) illustrates Δ_0 as a function of methanol concentration. We notice difference in the shape of the curve, compared with the curves in the figure (1), which indicates that the amount Δ_0 does not only related to the relative positions of the two spectral lines υ_3 and υ_{com}, but rather to other factors, such as the polarization of carbon tetrachloride particles that are caused due to Mutual influence with the particles of methanol.
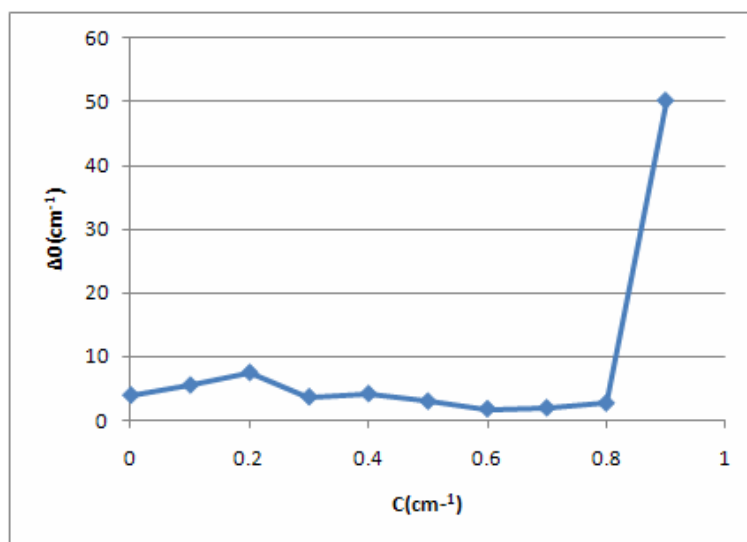

Fig. 2 Theplots of Δ_0 as a function of concentration.

This polarization has low values for low concentrations of methanol, and also for the concentration 0.9v/v. The polarization is reduced at the concentration 0.9v/v due to the formation of a electrostatic link between the O atom of oneCH_3OH molecule and the Cl atom of the CCl_4 molecule. This electrostatic ink obviously with draws some electronic charge density from the Cl region. We notice that increasing$\Delta0$ with increasing methanol concentration, for the points which have low polarization rate of the carbon tetrachloride molecules.

The low polarization leads to weakening the forces of attraction between molecules of methanol and carbon tetrachloride, and consequently it leads to increase in the centrifugal forces, which leads to shift in the positions of the spectral lines towards the high wave numbers with varying values depending upon the constant power for each bond, and consequently increasing the $\Delta0$ value.
The diagram of the coupling coefficient W as a function of concentration is plotted in figure (3).In this figure, we note a pattern of behavior which is different from what has been observed in experiments focused on studying the effects of developments on Fermi response due to exposing pure Carbon tetrachloride to high pressures[1] which showed a consistent changing trend in W amount with an the pressure increased (always decreasing). The reason behind not achieving this in our case is a link between the type of forces acting on the vibrations υ_{com} and the numerical value of the concentration. In addition to that, a split in the peak υ_3 is noted for the values of W bigger than 15. Such divisions have not been observed in experiments which relied on diversifying pressure instead of diversifying the concentration[2].
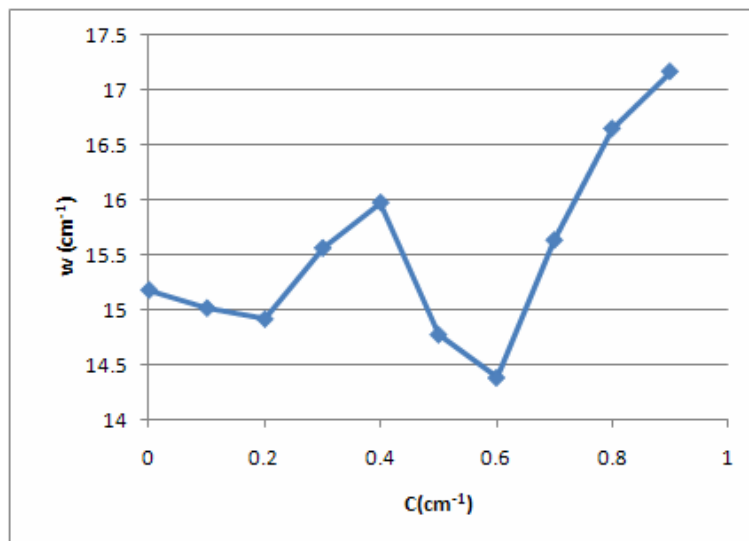
Fig. 3 The variation coefficient W as a function of concentration.

The changes of the intensity ratio R with concentration is shown in Fig (4). We can observe a linear relationship between them for the points that correspond to low polarization ratios of CCl4. In this figure, we note also that increased concentration in the range(0.2 _ 0.8v//v) is associated with a gradual increase in the R amount. The drift away from linearity in other points is Associated with the increasing in polarization in Carbon tetrachloride molecules.
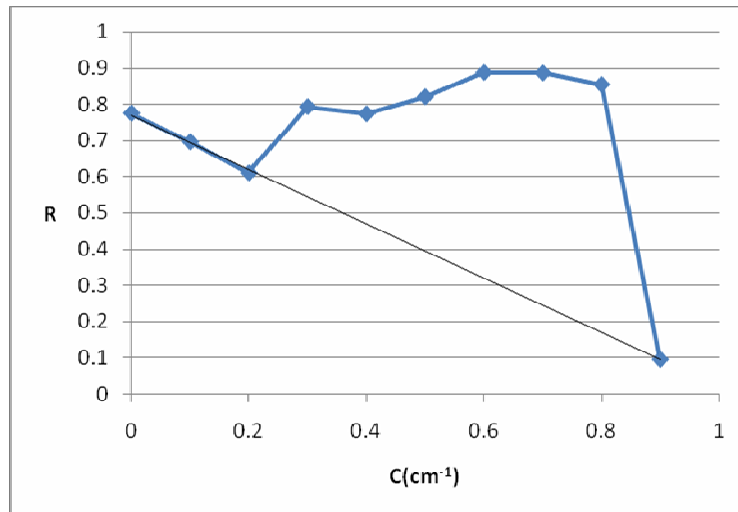

Fig. 4 The variation of intensity ratio R as a function of concentration.

We conducted a similar study on the FI-IR spectra for the same samples, and we conclude that increased concentration does not have any effect on the value of Δ_0 and R where the value of Δ_0 was set at $\Delta_0 = 1$ and R as well was set at the value of $R = 0$. In addition, we did not notice any occurrence of splits in the spectrums. Figure (5) contains the diagram of the coupling coefficient W as a function of concentration. In this figure, we note that the value of W reaches the highest value at $C = 0.2$v/v and then decreases to Stabilize at the value $W = 14$ approx. In addition, we note that Fermi response disappears at the concentration (0.9v/v).
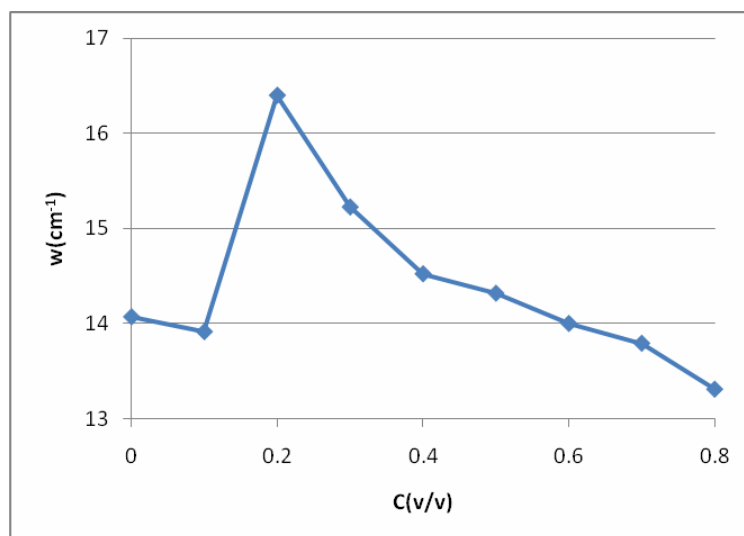
Fig. 5 The Variation coefficient W as a function of concentration.

These results indicate that the energy exchange in Fermi response in the FT-IR spectra will occur only as a slight shift in the relative positions of the peaks υ_3 and υ_{com}. It also is influenced by the concentration of methanol only when the ringed structures of methanol are dominant.

4. Conclusion

In this research, Fermi resonance in Raman and infrared spectra for Carbon tetrachloride in Methanol and Carbon Tetrachloride solutions was studied. The study focused on Fermi response happening between $\upsilon3$ and υ_{com} vibrations because of peak $\upsilon4$ was not affected by the emergence of peaks resulting from the adding methanol. Results showed a special type of behavior for the coefficients of Fermi resonance when studying them as a subordinate to methanol concentration. We found that these coefficients are largely affected by the spatial distribution of methanol molecules in the mixture, as well as the rates polarization of carbon tetrachloride particles, as the relation between the coefficient R and the concentration of methanol is a linear relationship for the cases in which the particles of carbon tetrachloride possess low polarization rates. In addition to that, occurrence of splits in the spectral line υ_3 has been observed at certain concentrations.
For infrared spectra, no significant effects to the change in methanol concentration were observed, except for W amount. It was observed that Fermi response disappears at the concentration (0.9v/v).

Acknowledgments

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