Influence of pressure effect on Fermi resonance in binary solution*

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The Fermi resonance behaviours of the two groups of binary solutions — pyridine and methanol, benzene and carbon tetrachloride, under different pressures are investigated according to their Raman spectra. The effect of pressure on Fermi resonance in binary solution differs significantly from that in pure liquid. In a binary solution, with the intermolecular distance shortening, the intermolecular interaction potential increases, the shift rates of the Raman spectral lines increase, the spectral line splitting occurs ahead of that in pure liquid, and the wavenumber separation Δ_0 between the unperturbed harmonic levels shifts more quickly, too. The Fermi resonance parameters, the coupling coefficient W and the intensity ratio R of the two Raman bands, decrease rapidly with pressure increasing, and the pressure at which Fermi resonance phenomenon disappears is much lower than that in pure liquid, especially in the solution whose molecules are of the same polarity. This article is valuable in the identification and the assignment of spectral lines under high pressure, as well as the study of high pressure effect, intermolecular interaction, and solvent effects in different cases, etc.

Keywords: Fermi resonance, binary solution, Raman spectra

PACC: 3330, 3450

1. Introduction

Although the molecular structures, properties, as well as the intra- and inter-molecular interactions have been widely developed by various methods such as spectroscopic methodology,[1,2] etc., the study of pressure-induced matter phase transition and chemical reaction is important in theory and also extensively useful in the investigation of thermodynamics and molecular structures.[3−7] Moreover, the investigation of Fermi resonance (FR) under high pressure is closely concerned by researchers because of its important application in the study of molecular structures, properties and phase transition under high pressure, as well as the determination of internal pressure of inclusions in geology.[8−15] Nevertheless, the previous investigations of FR under high pressure only focus on a few kinds of molecules such as CO_2, CS_2, etc., but little on polyatomic molecules, which were conducted mostly under much lower pressure.[16] To the best of our knowledge, the study of matter phase transition and FR phenomenon under high pressure in binary solution, especially of the comparison of these two counterparts in binary solution and in pure liquid, has not yet been reported before.

Our investigation demonstrates that the FR behaviours in binary solution are quite different from their counterparts in pure liquid. Concretely, the shift rates of the Raman spectral lines as well as the wavenumber separation Δ_0 between the unperturbed harmonic levels involved in FR change much more markedly in each kind of binary solutions under pressure than their counterparts in pure liquid. In addition, the FR parameters, the coupling coefficient W and the intensity ratio R of the unperturbed levels, decrease rapidly with the increase of pressure, and the FR phenomenon disappears at much lower pressure than in pure liquid.

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2. Experiment

In the present work, spectral grade samples, which are all in liquid — pyridine (C_5H_5N), methanol (CH_3OH), benzene (C_6H_6) and carbon tetrachloride (CCl_4), were chosen to probe their FR features according to the Raman spectra both in binary solution and in pure liquid at different pressures using a Mao–Bell-type diamond anvil cell (DAC) as high pressure sample cell. The diameters of the two diamond anvils are both 500 μm. The stainless sheet steel T301 in the DAC that was pressurized ranged from 250 μm to 80 μm in thickness before a hole (200 μm in diameter) was drilled. Before measurement, the samples were divided into two groups: one group includes C_5H_5N and CH_3OH; the other group involves C_6H_6 and CCl_4. The samples of the two groups as well as the pure liquids serving as comparative ones, contained respectively in the DAC together with ruby chips (about 10 μm round in diameter), were placed statically several minutes after being compressed. The pressure inside the DAC was determined according to the laser-induced fluorescence spectra of ruby chips immersed in the liquid. All Raman spectra were measured by a microscope-based Raman spectrometer Renishaw in Via with 514.5 nm for excitation (Spectra-Physics 160 M argon ion laser), backscattered, and collected using its 5× object lenses. The laser power was 10 mW, and the typical integration time was 30 s for one measurement. The Raman spectrometer was calibrated by the Si 520 cm^{-1} Raman line before the experiment. All measurements were taken at room temperature (23±2 °C).

3. Results and discussion

3.1. The $\upsilon_1 \sim \upsilon_{12}$ FR of C_5H_5N in CH_3OH and in pure liquid

As the totally symmetric ring breathing vibration mode υ_1 (992 cm^{-1}) and the formation vibration mode υ_{12} (1030 cm^{-1}) of C_5H_5N are of the identical symmetry α_1, the FR between the υ_1 band and the υ_{12} band occurred. Detailed experiments were conducted in the present work in order to develop the FR features occurring over a pressure range up to 13.15 GPa in pure liquid and 6.31 GPa in the solution of CH_3OH. When measuring the Raman spectra of pure liquid C_5H_5N and its mixture with CH_3OH at different pressures respectively (shown in Fig. 1), we analysed the influence of pressure effect on FR in binary solution based on the equations given in Ref. [17] as follows:

$$\Delta = \left(\Delta_0^2 + 4W^2\right)^{1/2}, \tag{1}$$

$$R_{\mathrm{f/a}} = \frac{I_{\mathrm{f}}}{I_{\mathrm{a}}} = \frac{\Delta - \left(\Delta^2 - 4W^2\right)^{1/2}}{\Delta + \left(\Delta^2 - 4W^2\right)^{1/2}}, \tag{2}$$

where Δ denotes the wavenumber separation between the perturbed levels in the presence of FR; Δ_0 denotes the wavenumber separation between the unperturbed harmonic levels in the absence of FR; W denotes the Fermi coupling coefficient; $R_{\mathrm{f/a}}$ denotes the ratio between intensities of FR components; I_{f} denotes the spectral intensity of the combination (forbidden vibrational transition) involved in FR, obtained using the OriginPro software (so is I_{a}); I_{a} denotes the spectral intensity of the fundamental (allowed vibrational transition) involved in FR.

3.1.1. Comparison of shift rate of Δ_0 between the unperturbed levels of C_5H_5N in pure liquid and in its mixture with CH_3OH

The shift rate of Δ_0 between the unperturbed levels involved in the $\upsilon_1 \sim \upsilon_{12}$ FR of C_5H_5N in pure liquid and in the mixture of C_5H_5N and CH_3OH with increasing pressure were obtained based on Eqs. (1) and (2) according to the observed Raman spectra, and they are shown in Figs. 1(a) and 1(b). Figure 2 shows clearly the variations of the totally symmetric ring breathing mode υ_1 of C_5H_5N in CH_3OH and in pure liquid with pressure, and figure 3 shows the variations of the shift rate of Δ_0 with pressure. It is obviously found in Fig. 3 that Δ_0 in binary solution decreases more rapidly with pressure increasing than in pure liquid. The interpretation for the results above embodies mainly two causes discussed below. Firstly, compared with the υ_{12} band, the υ_1 band is low, i.e., the corresponding bond force constant is relatively small, which commonly means that the corresponding bond length is easily compressed. On the contrary, the bond length of the υ_{12} band is hard to compress. In consequence, the υ_1 band changes more rapidly towards higher wavenumbers than the υ_{12} band when the sample is compressed in the same range of pressure. Δ_0 between the bands of

υ_1 and υ_{12}, therefore, decreases with pressure increasing. Secondly, with the solution density increasing when the two liquids of C_5H_5N and CH_3OH are mixed together, the intermolecular distance is shortened, the intermolecular interaction potential increased, which induces the shift in molecular vibrational frequency towards higher wavenumbers because of the effect of solvents.[18] Consequently, when the sample is compressed, the vibrational frequency having shifted towards higher wavenumbers under the effect of solvents shifts further towards the same direction. Further, due to the difference in density between the two liquids of C_5H_5N and CH_3OH, i.e., the difference in compressibility coefficient between these two matters, the extending space for molecules in mixed solution is more enlarged than in pure liquid, the compressibility of the binary solution is increased, which induces more dramatic change of the FR in binary solution than in pure liquid. Thus, compared with in pure liquid, the Raman bands in binary solution shift more significantly, that is, Δ_0 between the unperturbed levels involved in FR changes more dramatically.

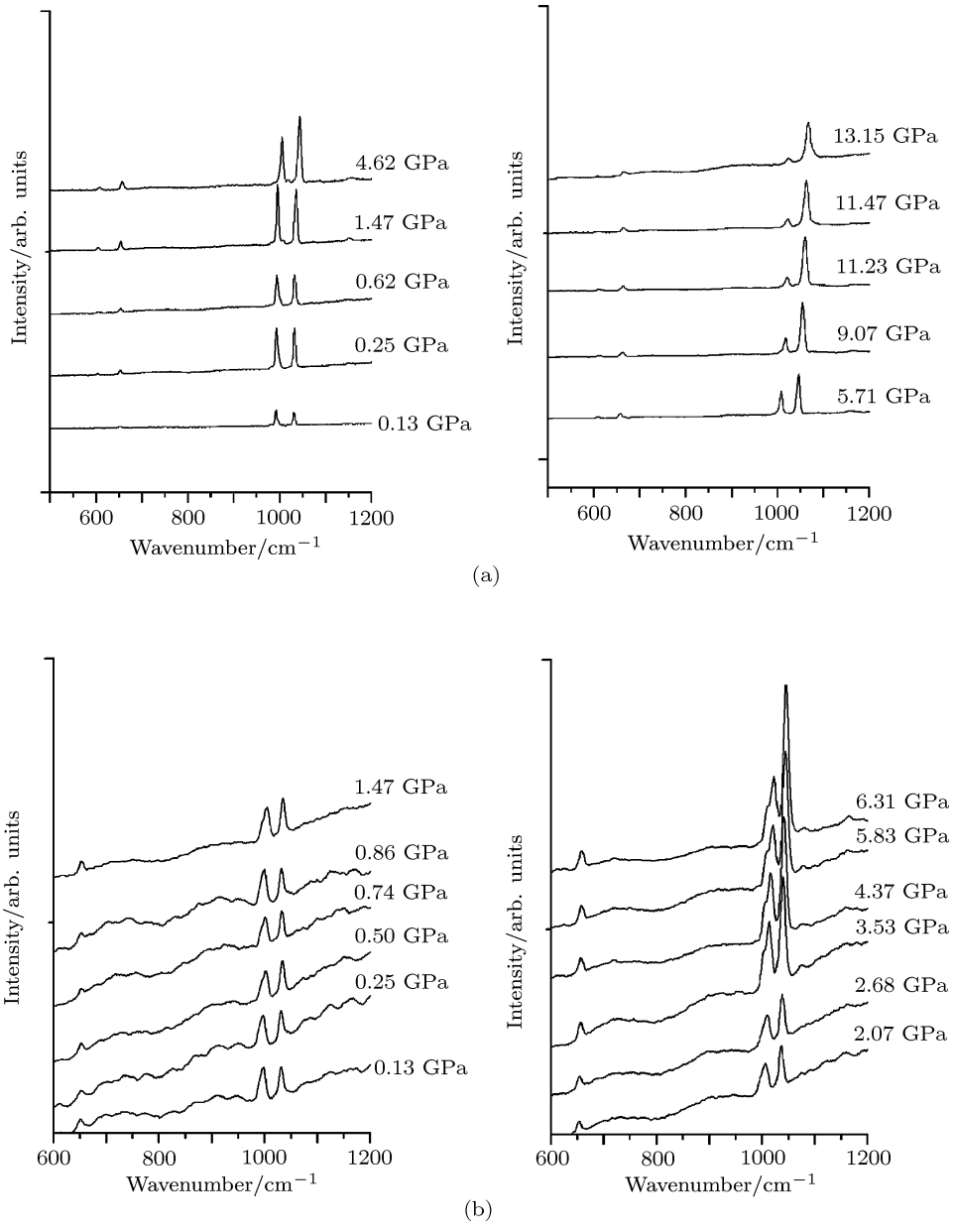


Fig. 1. Raman spectra of pure liquid C_5H_5N (a) and C_5H_5N in CH_3OH (b) at different pressures.

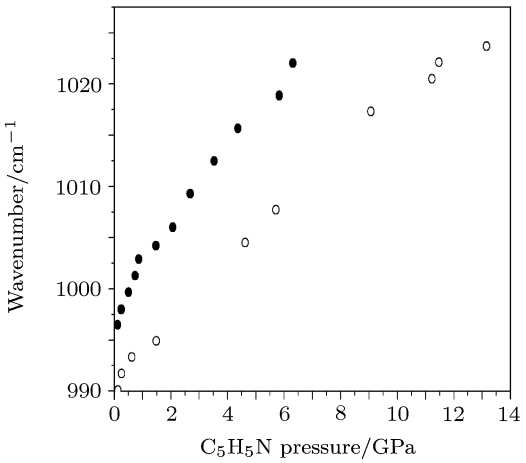


Fig. 2. Values of the υ_1 band of C_5H_5N in CH_3OH (•) and in pure liquid (○) at different pressures.

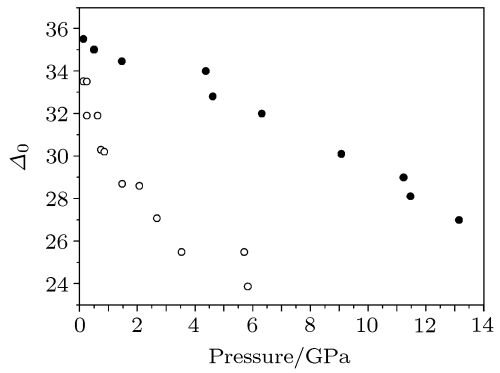


Fig. 3. Values of Δ_0 of υ_1–υ_{12} FR of C_5H_5N in CH_3OH (○) and in pure liquid (•).

3.1.2. Intensity ratio R and coupling coefficient W of $\upsilon_1 \sim \upsilon_{12}$ FR of C_5H_5N in CH_3OH decreasing significantly with pressure increasing

The changes of the intensity ratio R and coupling coefficient W of pure liquid and binary solution with pressure (shown in Figs. 4 and 5) were obtained based on Eqs. (1), (2) and the observed spectra shown in Fig. 1. Figures 4 and 5 clearly display that the parameters, R and W of $\upsilon_1 \sim \upsilon_{12}$ FR of C_5H_5N in CH_3OH solution, decrease with pressure increasing, and their decreasing rates change more markedly than their counterparts in pure C_5H_5N.[19] Apparently, because C_5H_5N and CH_3OH are both polar, the interactions — electrostatic, hydrogen bond, dispersion, etc., are the principal interactions between a single molecule and neighbouring molecules in the mixture of C_5H_5N and CH_3OH. These interactions are closely correlated to intermolecular distance R_i. Specifically, electrostatic is in inverse proportion to R_i^3, and dispersion is in inverse proportion to R_i^6. With density increasing and intermolecular distance shortening when the two liquids are mixed together, the intermolecular interaction increases under pressure. Consequently, the molecular vibrational symmetry worsens and the spectral line splitting appears (see Table 1(a)), which implies that even matter phase transition occurs (more details need to be developed further), and W of FR decreases.

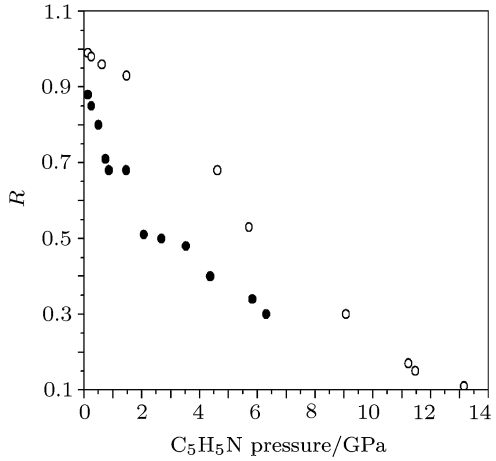


Fig. 4. Changing tendencies of R of C_5H_5N in CH_3OH (•) and in pure C_5H_5N (○) with pressure.

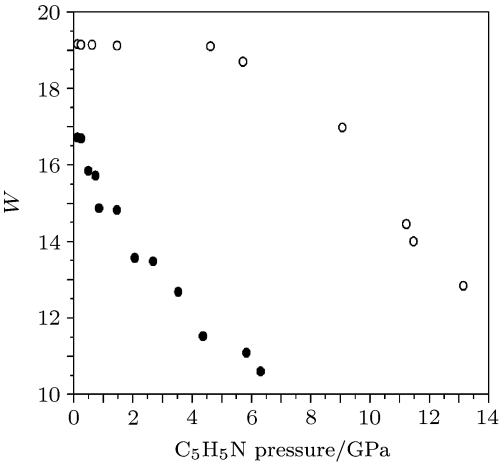


Fig. 5. Changing tendencies of W of C_5H_5N in CH_3OH (•) and in pure C_5H_5N (○) with pressure.

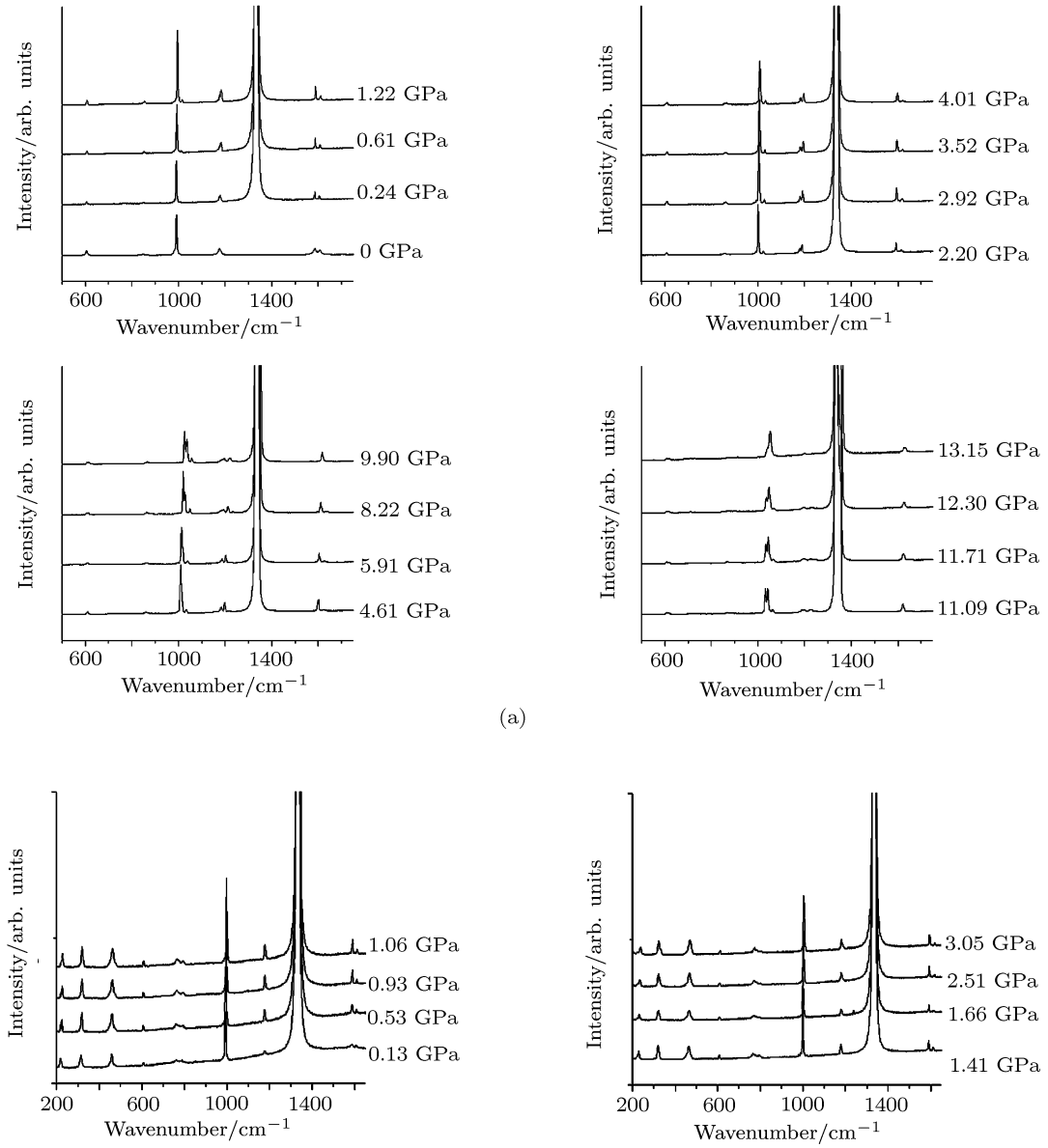
3.2. FR in binary solution of C_6H_6 and CCl_4

Because C_6H_6 and CCl_4 are both nonpolar, the intermolecular interaction existing in binary solution acts mainly as a dispersive force when the two liquids are mixed together. With density increasing and intermolecular distance shortening simultaneously, the intermolecular interaction potential increases and the vibrational frequency shifts towards higher wavenumbers under pressure, namely, the molecular frequency

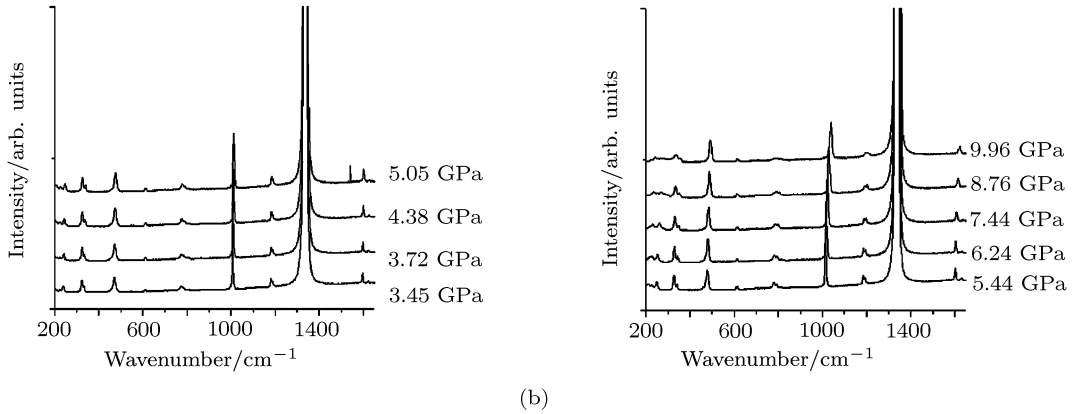
in binary solution is higher than that of the counterpart in pure liquid in the same circumstances. Further discussion shows that the intermolecular interaction potential is increasing, i.e. the perturbed energy is increasing, induced by the change in molecular behaviour at much a lower pressure. Specifically, it induces the changes in molecular symmetry, as well as in spectral line splitting, and even in matter phase transition. As is well known, molecular symmetry and the wavenumber separation between the two vibrational levels, which influence FR, are the principal factors determining the intensity of FR. The changes of these two factors can quicken more markedly in binary solution than in pure liquid under the effect of pressure. The FR features of Raman spectra in binary solution, therefore, are quite different from their counterparts in pure liquid.

3.2.1. $\upsilon_1 + \upsilon_6 \sim \upsilon_8$ FR of C_6H_6 in CCl_4

In C_6H_6, the combination of the totally symmetric ring breathing mode υ_1 (A_1g) and symmetric ring formation vibration mode υ_6 (E_2g) coupled with symmetric stretching vibration fundamental mode υ_8 (E_2g) causes the $\upsilon_1 + \upsilon_6 \sim \upsilon_8$ FR to occur. The observed Raman spectra of pure C_6H_6 and its solution in CCl_4 are shown in Fig. 6, which were measured separately over a pressure range up to 13.15 GPa in pure liquid and 9.96 GPa in CCl_4.



(a)



(b)

Fig. 6. Raman spectra of pure liquid C_6H_6 (a) and C_6H_6 in CCl_4 (b) at different pressures.

The observed spectra are shown in Fig. 6, and the calculated results based on Eqs. (1) and (2) are shown in Figs. 7–9.

Figure 7 indicates that the values of all Raman bands of C_6H_6 in CCl_4 are bigger than their counterparts in pure C_6H_6 under the same pressure, i.e., the shift rates of these Raman bands are more rapid than the counterparts in pure C_6H_6. In particular, it also indicates strongly that the frequency splitting occurs in pure liquid and at a much lower pressure of roughly 4.5 GPa, while the same behaviour is not found yet in binary solution under the pressure up to 10.5 GPa at least in the present work.

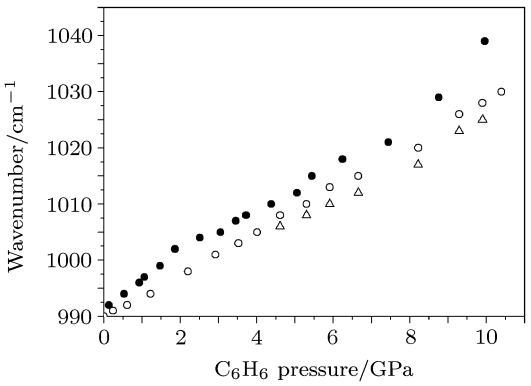


Fig. 7. Changing tendencies of υ_1 band of C_6H_6 in binary solution (•) and in pure liquid (○) with pressure.

Further discussion shows that when the shift rates of all vibrational bands of C_6H_6 in CCl_4 are more rapidly than their counterparts in pure C_6H_6 with pressure increasing, the shift rate of the combination of $\upsilon_1 + \upsilon_6$ (992 cm^{-1}+606 cm^{-1}) FR of C_6H_6 is quicker than its counterpart of the fundamental υ_8 (1585 cm^{-1}) in $\upsilon_1 + \upsilon_6 \sim \upsilon_8$ FR of C_6H_6. In consequence, Δ_0 between the unperturbed harmonic levels involved in FR, therefore, increases with pressure increasing. Furthermore, its shift rate in CCl_4 is more rapid than the counterpart in pure liquid. Together with the higher shift rate, the spectral line in CCl_4 solution splits with pressure increasing, i.e., the vibrational symmetry is worsened. Apparently, these two factors lead the coupling coefficient W of $\upsilon_1+\upsilon_6 \sim \upsilon_8$ FR to decrease rapidly and even induce the disappearance of the FR phenomenon at a much lower pressure than in pure liquid.

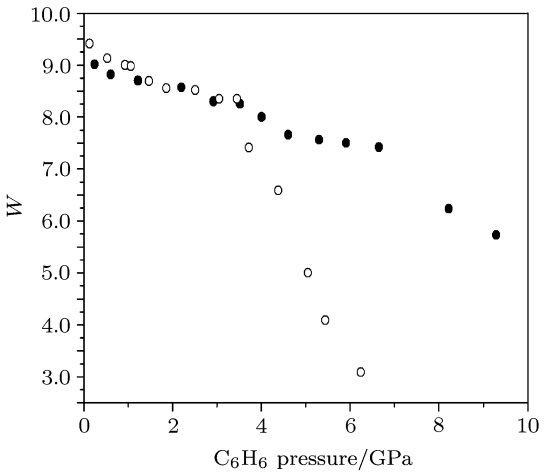


Fig. 8. Changing tendencies of W of C_6H_6 in binary solution (○) and in pure liquid (•) with pressure.

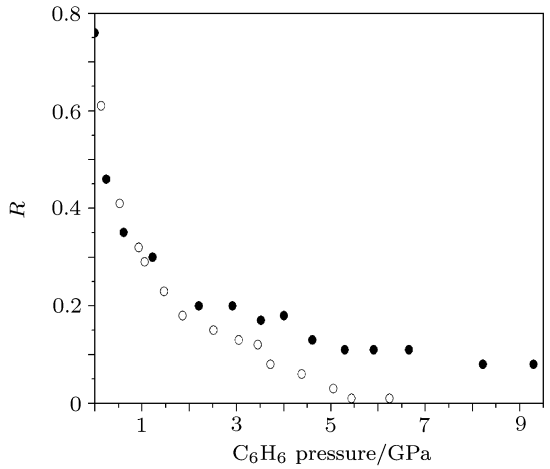


Fig. 9. Changing tendencies of R of C_6H_6 in binary solution (○) and in pure liquid (●) with pressure.

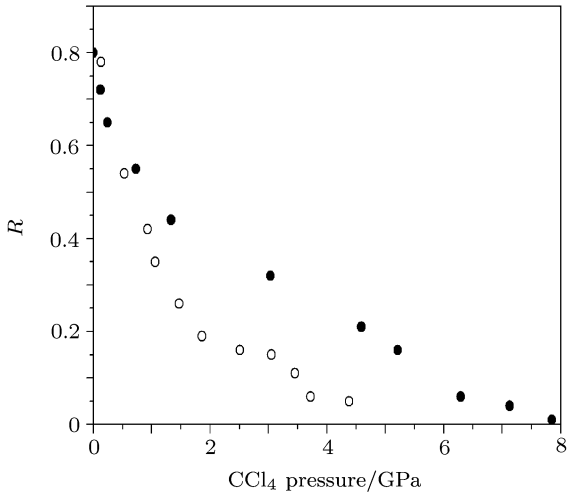


Fig. 10. Changing tendencies of R of CCl_4 in binary solution (○) and in pure liquid (●) with pressure.

3.2.2. $\upsilon_4 + \upsilon_1 \sim \upsilon_3$ FR of CCl_4 in C_6H_6

The modes, i.e., the υ_4 (314 cm^{-1}) band that is the bending vibration mode E, the υ_1 (459 cm^{-1}) band that is the totally symmetric stretching vibration mode A_1, and the υ_3 band that is the stretching vibration mode T_2, are of the C–Cl bond of CCl_4 in its $\upsilon_4 + \upsilon_1 \sim \upsilon_3$ FR, which are similar to those of $\upsilon_1 + \upsilon_6 \sim \upsilon_8$ FR of C_6H_6. In this circumstance, the shift rate of Δ_0 between the unperturbed levels in binary solution is also quicker than that in pure liquid CCl_4. And that the spectral line splitting occurs ahead of that in pure CCl_4 induces the decrease in values of R and W with pressure increasing, as well as the disappearance of FR phenomenon at a much low pressure compared with those in pure liquid. The detailed results are shown in Figs. 10 and 11.

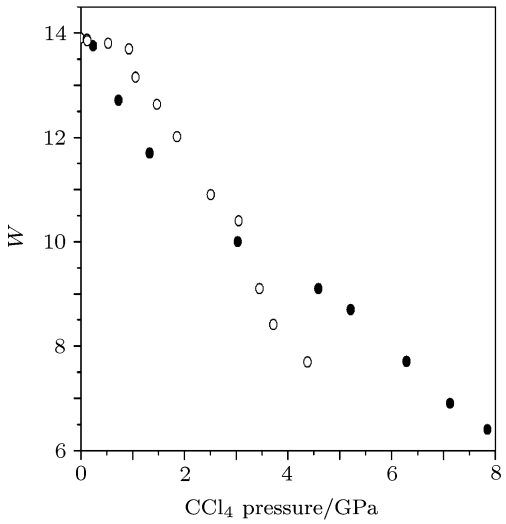


Fig. 11. Changing tendencies of W of CCl_4 in binary solution (○) and in pure liquid (●) with pressure.

Table 1 shows the pressures on CCl_4 and C_6H_6 in binary solution and in pure liquid in which Raman spectral line splits.

Table 1(a). Pressures on CCl_4 in binary solution and in pure liquid at Raman spectral line splitting (P/GPa).

liquid name	wavenumber/cm^{-1}	first splitting	second splitting	third splitting
mixed CCl_4	218	1.86	2.5	5.4
	314	1.86		
	459			
pure CCl_4	218	3.03	8.5	
	314	7.29	10.1	
	459			

Table 1(b). Pressures on C_6H_6 in binary solution and in pure liquid at Raman spectral line splitting (P/GPa).

liquid name	wavenumber/cm^{-1}	first splitting	second splitting
mixed C_6H_6	606	3.45	
	992		
pure C_6H_6	606	4.61	9.9
	992	1.22	

4. Conclusions

The FR behaviours in binary solution in the present work are quite different from their counterparts in pure liquid with pressure increasing. In binary solution, with the intermolecular distance shortening when samples are mixed together, solvent effects such as intermolecular interaction, etc. lead to the increase in intermolecular interaction potential compared with that in pure liquid. Consequently, the parameters, i.e., the intensity ratio R, coupling coefficient W, etc., change more markedly than in pure liquid; when samples are compressed, the shift rate of Raman band increase more dramatically; the value of Δ_0 between the unperturbed harmonic levels changes more markedly; the spectral line splitting occurs much ahead of that in pure liquid; the FR intensity ratio R as well as the coupling coefficient W decreases more rapidly, especially in the solution whose molecules are of the same polarity. Moreover, the FR phenomenon does disappear at a much lower pressure than in pure liquid.

References

[1] Zhang G Y and Jin Y D 2008 *Acta Phys. Sin.* **57** 132 (in Chinese)

[2] Wang W N 2009 *Acta Phys. Sin.* **58** 7640 (in Chinese)

[3] Adachi M, Yoneyama M and Nakamura S 1992 *Langmuir* **8** 2240

[4] Shimizu H and Matsumoto K 1984 *J. Phys. Chem.* **88** 2934

[5] Lipinska-Kalita K E, Pravica M G and Nicol M 2005 *J. Phys. Chem.* B **109** 19223

[6] Kavitha G and Narayana C 2006 *J. Phys. Chem.* B **110** 8777

[7] Thiery M M, Besson J M and Bribes J L 1992 *J. Chem. Phys.* **96** 2633

[8] Thiery M M, Besson J M and Bribes J L 1988 *J. Chem. Phys.* **89** 4255

[9] Cansell F, Fabre D and Petitet J 1993 *J. Chem. Phys.* **99** 7300

[10] Harada I and Shimanouchi T 1965 *J. Chem. Phys.* **44** 2016

[11] Akella J and Kennedy G C 1971 *J. Chem. Phys.* **55** 793

[12] Ciabini L, Santoro M, Bini R and Schettino V 2001 *J. Chem. Phys.* **115** 3742

[13] Ciabini L, Santoro M, Bini R and Schettino V 2002 *Phys. Rev. Lett.* **88** 085505

[14] Pravica M, Grubor-Urosevic O, Hu M, Chow P, Yulga B and Liermann P 2007 *J. Phys. Chem.* B **111** 11635

[15] Chen Y, Zhou Y Q and Ni P 2006 *Rock and Mineral Analysis* **25** 211 (in Chinese)

[16] Meng Q T, Zheng Y J and Ding S L 2000 *Int. J. Quantum Chem.* **81** 154

[17] Bertran J F, Ballester L, Dobrihalova L, Sanchez N and Arrieta R 1968 *Spectrochim. Acta* **24** A 1765

[18] Ishibashi Y, Mishina T and Nakahara J 2006 *Physica Status Solidi* (b) **243** 1159

[19] Zakin M R, Grubb S G, King Jr H E and Herschbach D R 1986 *J. Chem. Phys.* **84** 1080