The effect of an anti-hydrogen bond on Fermi resonance: A Raman spectroscopic study of the Fermi doublet $\nu_1-\nu_{12}$ of liquid pyridine*

Li Dong-Fei(李东飞)[a)b)], Gao Shu-Qin(高淑琴)[b)], Sun Cheng-Lin(孙成林)[a)b)], and Li Zuo-Wei(里佐威)[a)b)†]

[a)] *State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun* 130012, *China*
[b)] *College of Physics, Jilin University, Changchun* 130012, *China*

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The effects of an anti-hydrogen bond on the ν_1–ν_{12} Fermi resonance (FR) of pyridine are experimentally investigated by using Raman scattering spectroscopy. Three systems, pyridine/water, pyridine/formamide, and pyridine/carbon tetrachloride, provide varying degrees of strength for the diluent-pyridine anti-hydrogen bond complex. Water forms a stronger anti-hydrogen bond with pyridine than with formamide, and in the case of adding non-polar solvent carbon tetrachloride, which is neither a hydrogen bond donor nor an acceptor and incapable of forming a hydrogen bond with pyridine, the intermolecular distance of pyridine will increase and the interaction of pyridine molecules will reduce. The dilution studies are performed on the three systems. Comparing with the values of the Fermi coupling coefficient W of the ring breathing mode ν_1 and triangle mode ν_{12} of pyridine at different volume concentrations, which are calculated according to the Bertran equations, in three systems, we find that the solution with the strongest anti-hydrogen bond, water, shows the fastest change in the ν_1–ν_{12} Fermi coupling coefficient W with the volume concentration varying, followed by the formamide and carbon tetrachloride solutions. These results suggest that the stronger anti-hydrogen bond-forming effect will cause a greater reduction in the strength of the ν_1–ν_{12} FR of pyridine. According to the mechanism of the formation of an anti-hydrogen bond in the complexes and the FR theory, a qualitative explanation for the anti-hydrogen bond effect in reducing the strength of the $\nu_1 - \nu_{12}$ FR of pyridine is given.

Keywords: Fermi resonance, Raman spectrum, anti-hydrogen bond

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1. Introduction

The phenomenon of hydrogen bonding is omnipresent in nature. Hydrogen bonds, for instance, stabilize the secondary and tertiary structures of proteins and are thought to play a major role in molecular recognition, binding, and enzymatic catalysis.[1] Nucleic acid base pairs of polyphosphodiesters, such as of ribonucleic acid (RNA) and deoxyribonucleic acid (DNA), are stabilized by hydrogen bonds between the pyrimidine and purine bases.[2] Hydrogen bonding has been an important and intensely studied subject in chemistry, physics, and biology.[3−5] It is well known that the formation of H-bonding may lead to the change in the electronic structures and physical chemistry properties of both the proton donor and acceptor.[3,6,7] As far as the frequency shift of the X–H stretch vibration in the H-bonding proton donor is concerned, the consequences can be classified into red-shifted and blueshifted X–H vibrations.[8] Red-shifted H-bonds are characteristic of the elongation of the HX bond and the decrease in the frequency of the HX stretching vibration, while the characteristic feature of blue-shifted H-bond is contraction of the HX bond with a concomitant increase in XH stretching frequency, which is also called anti-hydrogen bond.[9] Recently, the problem of the effect of hydrogen bonding on the proton acceptor has attracted considerable attention. It seems, however, that there are few studies which deal with the quantitative interpretation of the hydrogen bond effect, especially anti-hydrogen bond, on the FR in hydrogen-bonded species.

As is well known, FR is a very common phenomenon in complex molecules. FR plays an important role in molecular spectra, energy transfer, and internal conversion, and reaction dynamics.[10,11] Fur-

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†Corresponding author. E-mail: zuowei_li@163.com

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thermore, FR can also cause an accelerated rate of population or energy transfer between the vibrational modes, thus influencing the dynamical behaviour of molecules and the fate of chemical reactions.[12] FR occurs when two vibrational modes having the same symmetry and comparable vibrational frequencies are coupled by an anharmonic term in the interatomic potential, which was recognized first by Fermi in the case of CO_2.[13] Because of its importance in spectrum analysis, the studies of FR remain an active area of research, both experimentally and theoretically.[14−21] FR can occur for triatomic and polyatomic molecules, the spectrum of pyridine providing a good example. Pyridine is a molecule with permanent dipole moment (2.25 D) of relatively high symmetry ($C_{2\nu}$),[22] and there is an FR between the symmetric ring breathing mode ν_1 at approximately 990 cm^{-1} and the so-called triangle mode ν_{12} at approximately 1030 cm^{-1}, which is sensitive to changes of external parameters like pressure, temperature, and solvent.[23] Pyridine can also act as the proton acceptor using its lone pair electrons n(N) or its π-electrons to form H-bonds with proton donors, and this H-bonding interaction will change geometrical and electronic structures[9] and influence vibrational spectra of pyridine (thus varying the FR conditions). Therefore, pyridine is ideally suited for studying the effects of hydrogen bond on the FR. Additionally, pyridine itself is an important component in many powerful pharmaceuticals[9] and biologically important compounds such as nicotine, niacin, vitamin B6, and related compounds. Understanding the FR changes induced on pyridine during hydrogen bonding should provide an insight into many areas of its biochemistry.

In the present work, we investigate the ν_1–ν_{12} FR of pyridine at different concentrations in the presence of carbon tetrachloride, or formamide, or water using Raman spectroscopy. The choice of these diluents is to provide varying degrees of strength for the diluents-pyridine anti-hydrogen bond complex. In light of the Bertran equations, we calculate the values of the Fermi coupling coefficient W of the Raman bands ν_1 and ν_{12} of pyridine dilution with different diluents from the spectral parameters Δ and R, and study their variations with the change of concentration of pyridine in different mixtures. In particular, comparing with the values of Fermi coupling coefficient W of the Raman bands ν_1 and ν_{12} of pyridine at different concentrations in the three systems, it is found that the stronger diluent-pyridine anti-hydrogen bond effect will cause a faster reduction in Fermi coupling coefficient value with pyridine concentration deceasing. Finally, we give a qualitative explanation for the anti-hydrogen bond effect in reducing the strength of the ν_1–ν_{12} FR of pyridine.

2. Experiment

All samples were purchased and used without further purification: pyridine (99.9%, Aldrich Chemical), carbon tetrachloride (99.9%, Aldrich Chemical), formamide (99+%, Aldrich Chemical), and high-purity water (> 99.9%, Romil Chemicals). Stock solutions of pyridine and diluent were prepared at various volume concentrations. The volume concentration range of pyridine was from 10% up to 100% in steps of 10%.

Raman spectra of the solutions were obtained using a Renishaw in Via Raman Microscopic instrument with excitation by a Spectra Physics 160M Ar^+ laser using 514.5-nm radiation. The power of the laser beam in the sample was ca. 6 mW, and the typical accumulation time for each spectrum was 20 s. The spectra were collected in the range 100 cm^{-1}–4000 cm^{-1} at a spectral resolution of 1 cm^{-1}. A Leica microscope with a 20× objective lenses enables measurements in the backscattering geometry. For Rayleigh rejection, the scattered light passed through an edge filter. All Raman spectra were recorded immediately after the mixtures had been prepared and placed inside a quartz scattering cell. The spectral wavenumbers were calibrated with the Si line and are believed to be accurate to 1 cm^{-1}. All measurements were conducted at room temperature and atmospheric pressure.

3. Results

3.1. Dilutions with carbon tetrachloride

The Raman spectra of pyridine/carbonate tetrachloride system with varying volume concentrations of pyridine from 10% up to 90% in steps of 10% and of pure pyridine and pure carbonate tetrachloride were recorded in the frequency range 100 cm^{-1}–4000 cm^{-1} shown in Fig. 1. It should be noted that we focus mainly on two regions in the Raman spectra of the three systems in the present study: (i) 970 cm^{-1}–1050 cm^{-1} and (ii) 3000 cm^{-1}–3120 cm^{-1} due to the fact that the hydrogen bonding causes significant spectral changes in these two regions. As shown in Fig. 1, two Raman bands at approximately 990 cm^{-1} and

1030 cm^{-1} in the region 970 cm^{-1}–1050 cm^{-1} are assigned, respectively, to the ring breathing mode ν_1 and triangle mode ν_{12} in pyridine,[24,25] while a very strong band around 3056 cm^{-1} in the region 3000 cm^{-1}–3120 cm^{-1} can be attributed to the totally symmetric C–H stretching mode ν_2 of pyridine.[22,26] With concentration of pyridine decreasing, the intensities of the Raman bands ν_1, ν_2, and ν_{12} become weaker; the positions of the ring breathing mode ν_1 and triangle mode ν_{12} remain practically unchanged, but the C–H stretching vibration mode ν_2 shows a slight increase in frequency. Since the ring breathing vibration ν_1 of pyridine around 990 cm^{-1} is very sensitive to hydrogen-bonding between nitrogen-containing heterocycles and H-donor solvents,[25,27] we conclude that there is no hydrogen bonding formation between pyridine and carbonate tetrachloride. It is interesting to note that, however, the CH stretching bands of pyridine exhibit a linear dependence of frequency shift on the concentration of pyridine as shown in Fig. 2. As is well known, in the pure pyridine liquid, the C–H bond will be elongated due to the pyridine–pyridine hydrogen bond forming effect, which will result in a decrease in the shift of the C–H stretching mode vibrational wavenumber, whereas as the carbonate tetrachloride is added into pure pyridine, which just directly affects the hydrogen bong formation between pyridine–pyridine molecules, the hydrogen bond between pyridine molecules will be broken and the C–H bond will no longer be elongated and, hence resulting in the blue-shift of the C–H stretching mode ν_2 as the concentration of carbonate tetrachloride increases. Therefore, the increase of the C–H stretching mode ν_2 Raman shift in the pyridine–carbonate tetrachloride solution shown in Fig. 2 can be attributed to the dilution effect which breaks the hydrogen bond between pyridine–pyridine molecules.

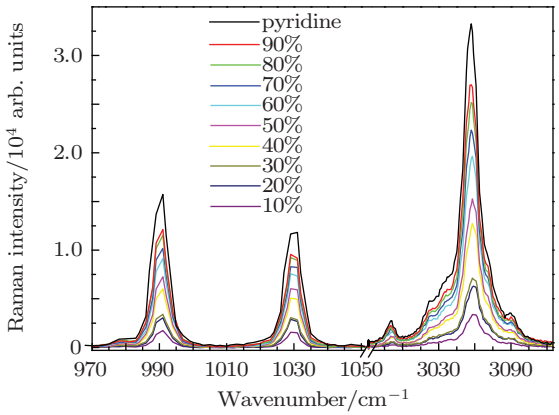


Fig. 1. (colour online) Raman spectra of pyridine–carbon tetrachloride mixture at different volume concentrations.

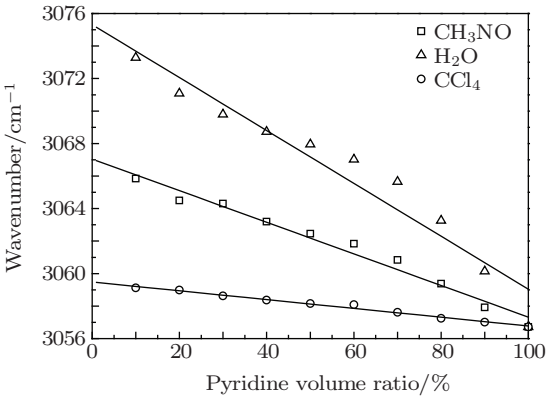


Fig. 2. C–H stretching mode Raman shifts of pyridine each as a function of pyridine volume concentration in solvents (◯) CCl_4, (□) CH_3NO, (△) H_2O.

Pyridine is an interesting sample to study, not only because of its hydrogen-bonding properties, but also due to the fact that the bands ν_1 and ν_{12} in the Raman spectrum are both in FR.[23] FR occurs when two nearly degenerate vibrational bands are of the same symmetry, and thus may couple to each other through anharmonic terms in the vibrational Hamiltonian, which leads to a frequency splitting, as well as a drastic change in the relative intensity of the two bands.[28] This resonance interaction is well documented and has been studied in detail by Bertran *et al.*[29] who have given a method of determining the FR parameters based on the perturbation theory, and described the FR by the following equations:

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

$$R = \frac{I_{\nu_1}}{I_{\nu_{12}}} = \frac{\Delta + \left(\Delta^2 - 4W^2\right)^{1/2}}{\Delta - \left(\Delta^2 - 4W^2\right)^{1/2}}, \tag{2}$$

where Δ is the wavenumber separation between the perturbed levels in the presence of FR; Δ_0 is the wavenumber separation between the perturbed harmonic levels in the absence of FR; W is the Fermi coupling coefficient; R is the ratio between Raman integrated intensities of FR components; I_{ν_1} is the Raman integrated intensity of the band ν_1 in the Raman spectrum of pyridine; $I_{\nu_{12}}$ is the Raman integrated intensity of the band ν_{12} in the Raman spectrum of pyridine.

In Fig. 1, the experimental observables in the FR doublet are the ratio of Raman integrated intensities R and the wavenumber separation between the values of peak Δ. Therefore, with the values of R and Δ we can calculate the values of Fermi coupling coefficient W of pyridine in carbonate tetrachloride at different volume concentrations, which are plotted in Fig. 3. As can be seen from Fig. 3, with the pyridine

volume concentration decreasing, the Fermi coupling coefficient W of pyridine in carbonate tetrachloride is practically unchanged. Consequently, we can conclude that dilution of pyridine with carbonate tetrachloride will break only the hydrogen bond between pyridine molecules and result in the ν_2 mode shifting toward higher frequency, but cannot affect the FR coupling between ν_1 and ν_{12} of pyridine.

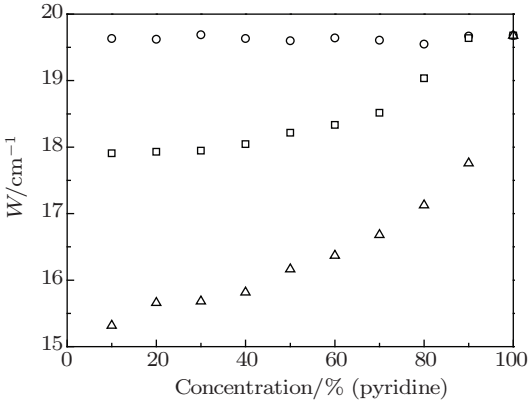


Fig. 3. (colour online) Values of Fermi coupling coefficient W of pyridine in (◯) CCl_4, (□) CH_3NO, (△) H_2O solutions.

3.2. Dilutions with formamide

Formamide is a hydrogen bond donor (and also acceptor) through an N–H and, hence forms a weaker hydrogen bond with pyridine.[25] With carbonate tetrachloride, ten different volume concentration mixtures of pyridine and formamide are studied and their Raman spectra are shown in Fig. 4. As can be seen from Fig. 4, with the concentration of pyridine decreasing, the intensities of the CH stretching band ν_2 and the Fermi doublet ν_1 and ν_{12} of pyridine become much weaker, and all shift toward higher frequency to different extents. It is well known that hydrogen bonding causes significant spectral changes in the ring stretching mode of pyridine, and particularly the ring breathing mode ν_1 at 990 cm^{-1} is much more affected than the triangle mode ν_{12} at 1030 cm^{-1}.[30–32] Since the FR effect is extremely sensitive to the slight modification of vibrational frequency, thus it is expected that once the pyridine forms hydrogen bonded complexes with formamide, the FR coupling between the Raman bands ν_1 and ν_{12} of pyridine should be affected. According to Eqs. (1) and (2), we calculate the Raman band ν_1 and ν_{12} Fermi coupling coefficient W of pyridine in formamide at different concentrations. Figure 2 illustrates the Raman bands ν_1 and ν_{12} Fermi coupling coefficient W of pyridine in formamide at different concentrations, and as can be seen, with the concentration of pyridine decreasing, the Fermi coupling coefficient W decreases, which indicates that the FR coupling of the Raman bands ν_1 and ν_{12} of pyridine becomes weaker. Besides, in the region of 3000 cm^{-1}–3120 cm^{-1}, the band of the CH stretching band ν_2 around 3056 cm^{-1} of pyridine shows a frequency shift toward higher wavenumbers with the concentration of pyridine decreasing. The changing tendency of the C–H stretching mode ν_2 Raman shift of pyridine in formamide at different volume concentrations is plotted in Fig. 2. As shown in Fig. 2, with the concentration of pyridine decreasing, the shift of the C–H stretching mode ν_2 of pyridine in formamide is much faster than in carbonate tetrachloride, which can be interpreted as the fact that the anti-hydrogen bond forming effect between pyridine and formamide is much stronger.

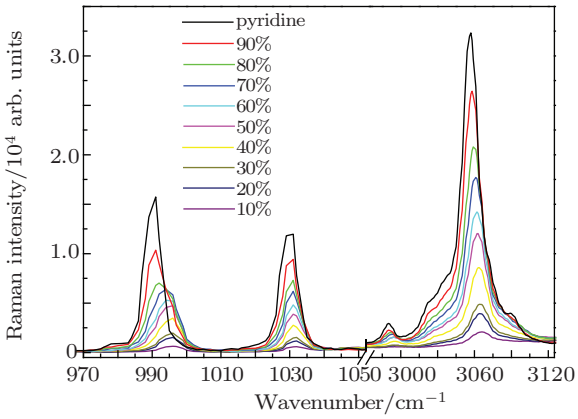


Fig. 4. (colour online) Raman spectra of pyridine-formamide mixture at different volume concentrations.

3.3. Dilutions with water

Figure 5 shows the Raman scattering spectra of the Fermi doublet ν_1 and ν_{12} and the C–H stretching mode ν_2 of pyridine in water at different concentrations. As shown in Fig. 5, with the concentration of pyridine decreasing, the intensities of the Raman bands ν_1, ν_2, and ν_{12} become weaker; the positions of the ν_1, ν_2, and ν_{12} all shift toward higher frequency, resulting from the intermolecular anti-hydrogen bond formed between water and pyridine, and the blue-shift of the ring breathing mode ν_1 is much faster than the triangle mode ν_{12}. With the concentration of pyridine decreasing, the hydrogen bond between pyridine and water becomes stronger, and the stronger hydrogen bond-forming effect will cause a greater blue-shift in the C–H stretching mode ν_2 of pyridine. The Raman

bands ν_1 and ν_{12} FR coupling coefficient W of pyridine in water at different volume concentrations are calculated based on the Bertran equations shown in Fig. 3. As shown in Fig. 3, with the concentration of pyridine decreasing, the Raman bands ν_1 and ν_{12} Fermi resonance coupling coefficient W of pyridine in water decreases. Therefore, we can conclude that the decreasing of concentration of pyridine enhances the strength of anti-hydrogen bond between pyridine and water, the strength of ring breathing mode ν_1 and triangle mode ν_{12} FR coupling of pyridine becomes weaker. As water is added into the pure pyridine liquid, the Raman shift of the C–H stretching mode ν_2 increases as the pyridine concentration decreases, which can be attributed to the effect of the anti-hydrogen bond formed between water and pyridine as shown in Fig. 2. The shift of the C–H stretching mode ν_2 of pyridine in water is the fastest in the three systems.

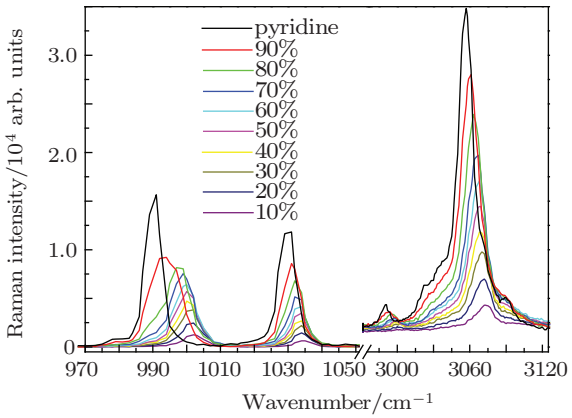


Fig. 5. (colour online) Raman spectra of pyridine-water mixture at different volume concentrations.

4. Discussion

The pyridine mixtures with carbonate tetrachloride, formamide, and water represent varying degrees of "hydrogen bondedness". With N–H used as a donor in formamide, the anti-hydrogen bond with the nitrogen of pyridine is relatively weak. The strength of the anti-hydrogen bond increases with the O–H donor of water increasing. Finally, the carbonate tetrachloride, which is neither a donor nor a acceptor, just can affect the hydrogen bond formation between pyridine molecules in the dilution process. The result presented in this work shows that diluting the pyridine with non-polar solvent carbonate tetrachloride which is incapable of forming hydrogen bond with pyridine, the FR coupling coefficient W of the ring breathing mode ν_1 and the triangle mode ν_{12} of pyridine is nearly constant, whereas, diluting the pyridine with water or formamide which is capable of forming anti-hydrogen bond to a different extent, the FR coupling coefficient W of the ring breathing mode ν_1 and the triangle mode ν_{12} of pyridine, instead of instant, decreases by forming anti-hydrogen bond with diluents, and the stronger the hydrogen bond is, the smaller the Fermi coupling coefficient W becomes. The decreasing of the FR coupling coefficient W indicates that the FR is weakened. The result implies that the FR coupling between ν_1 and ν_{12} of the pyridine is sensitive to the formation of anti-hydrogen bond. Since the FR effect is extremely sensitive to the slight modification of vibrational frequency and symmetry, and the ν_1 and ν_{12} vibrational modes of pyridine are more sensitive to the intermolecular hydrogen bond. Adding different solvents into the pyridine will certainly induce drastic changes in anti-hydrogen bond and hence the FR coupling between ν_1 and ν_{12} of pyridine.

Now, we turn to a discussion of the strength of anti-hydrogen bond formed by the dependence of dilute and pyridine on the FR coupling coefficient W. Since W represents the degree of resonance coupling between the two modes through anharmonic terms in the Hamiltonian, the obvious interpretation of the W value decrease is that the anharmonicities in the vibration modes ν_1 and ν_{12} become less with the increase of the strength of anti-hydrogen bond.[28] We propose that the most reasonable physical explanation of the less anharmonicity at lower concentration of pyridine where the anti-hydrogen bond is strongest, is that the formation of anti-hydrogen bond between pyridine and diluent affects the FR conditions of the ν_1 and ν_{12} of pyridine.

Without the hydrogen bond, the free pyridine has a lone pair of electrons in an sp^2 hybrid orbital localized on the nitrogen atom. Due to the relatively large spatial extent of the orbital of the nonbonded lone pair electrons, the delocalized π molecular orbital becomes "squeezed" out of the region and this destabilizes the π contribution to the ring bonds with respect to a hypothetical scenario where there is no lone pair of electrons on the nitrogen. When hydrogen bonding occurs, some of the lone pair electrons are drawn out by the hydrogen, thereby releasing the "squeeze" on the π orbital. This allows better delocalization of the π electrons and stabilizes the system, resulting in the blue shifts of the ν_1 and ν_{12} mode and the decrease of anharmonicity in the vibration modes ν_1 and ν_{12}.[25] The fact that the W decreases from for-

mamide to water can be explained as the fact that a stronger hydrogen bond will draw out more lone pair electrons, this relieves the squeezing of the π molecular orbital to a greater degree, causing more stabilization and less anharmonicity in the vibration modes ν_1 and ν_{12}. Therefore, we can conclude that the hydrogen bond formation is deeply affect the anharmonicities in the ring stretching mode ν_1 and triangle mode ν_{12} of pyridine which are in the FR, and hence affect the FR coupling.

In addition, no matter whether carbonate tetrachloride, formamide or water is used to dilute the pyridine, all the C–H stretching mode ν_2 of pyridine will shift toward higher frequency as the concentration decreases. This result can also be explained according to the formation of the anti-hydrogen bond effect. As noted above, when the carbonate tetrachloride is added into pure pyridine, the hydrogen bond between pyridine molecules will be broken and the C–H bond will no longer be elongated, hence result in the smooth blue-shift of the C–H stretching mode ν_2 as the concentration of carbonate tetrachloride increases. While adding the diluent, water or formamide, which can form anti-hydrogen bond with pyridine, the hydrogen bond between pyridine–pyridine molecules will be broken and the new anti-hydrogen bond between pyridine with water or formamide will form, and the latter is much stronger. When the anti-hydrogen bond between the pyridine and water or formamide forms, the C–H bond of pyridine is no longer elongated but is shortened, hence the frequencies increases. The stronger the anti-hydrogen bond is, the more the C–H bond is shortened and the frequency is increased.

5. Conclusion

In the present paper, we use Raman scattering spectroscopy to study the effects of anti-hydrogen bond formation on the ν_1–ν_{12} FR of pyridine at different concentrations in three systems, pyridine/water, pyridine/formamide, pyridine/carbonate tetrachloride, which can provide varying degrees of strength for the diluent-pyridine anti-hydrogen bond complex. The values of FR coupling coefficient W of the ring breathing mode ν_1 and the triangle mode ν_{12} of pyridine in carbonate tetrachloride, water, and formamide at different concentrations are calculated based on the Bertran equation. The result shows that the solution with the strongest anti-hydrogen bond, water, shows the fastest change in the Fermi coupling coefficient W of the ring breathing mode ν_1 and the triangle mode ν_{12} of pyridine as the volume concentration varies, followed by the formamide and carbonate tetrachloride solutions. In addition, we also find that no matter whether the carbonate tetrachloride, formamide or water is used to dilute the pyridine, all the C–H stretching mode ν_2 of pyridine will shift toward higher frequency as the concentration decreases, and the only difference is that the stronger the anti-hydrogen bond is, the faster the C–H stretching mode shifts. Finally, we give a qualitative explanation for the anti-hydrogen bond effect in reducing the strength of the ν_1–ν_{12} FR and increasing the frequency of the C–H stretching mode of pyridine.

References

[1] Kirby A J 1997 *Acc. Chem. Res.* **30** 290

[2] Hobza P and Sponer J 1999 *Chem. Rev.* **99** 3247

[3] Jeffrey G A 1997 *An Introduction to Hydrogen Bonding* (New York: Oxford University Press)

[4] Vinogradov S N and Linnell R H 1971 *Hydrogen Bonding* (New York: Van Nostrand Reinhold)

[5] Pimentel G C and McClellan A L 1960 *The Hydrogen Bond* (San Fransisco: W. H. Freeman)

[6] Scheiner S 1997 *Hydrogen Bonding* (New York: Oxford University Press)

[7] Desiraju G R and Steiner T 1999 *The Weak Hydrogen Bond in Structural Chemistry and Biology* (Oxford: Oxford University Press)

[8] Hobza P and Havlas Z 2000 *Chem. Rev.* **100** 4253

[9] Li A Y, Ji H B and Cao L J 2009 *J. Chem. Phys.* **131** 164305

[10] Baer T and Hase W L 1996 *Unimolecular Reaction Ddynamics* (New York:: Oxford University Press)

[11] Wyatt R E and Zhang J Z H 1996 *Dynamics of Molecules and Chemical Reaction* (New York: Marcel Dekker)

[12] Fujisaki H, Yagi K, Hirao K and Straub J E 2007 *Chem. Phys. Lett.* **443** 6

[13] Fermi E 1931 *Z. Phys.* **71** 250

[14] Andrzej Hacura 1997 *Phys. Lett.* A **227** 237

[15] Denis Ostrovskii, Magnus Edvardsson and Per Jacobsson 2003 *J. Raman Spectrosc.* **34** 40

[16] Kiyoshi Yagi, So Hirata and Kimihiko Hirao 2008 *Phys. Chem. Chem. Phys.* **10** 1781

[17] Aoki K, Yamawaki H and Sakashita M 1995 *Science* **268** 1322

[18] Viktor V Struzhkin, Alexander F Goncharov, Russell J Hemley and Ho-Kwang Mao 1997 *Phys. Rev. Lett.* **78** 4446

[19] Song M, Yamawaki H, Fujihisa H, Sakashita M and Aoki K 1999 *Phys. Rev.* B **60** 12644

[20] Jiang X L, Yang G, Li D F, Zhou M, Sun C L, Gao S Q and Li Z W 2010 *Chin. Phys.* B **19** 103301

[21] Cao B, Zuo J, Li Z W, Ouyang S L, Gao S Q, Lu G H and Jiang Y H 2009 *Acta Phys. Sin.* **58** 3538 (in Chinese)

[22] Charles H K and John T 1944 *J. Chem. Phys.* **12** 300

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

[24] Thomas W Bell, Alisher B Khasanov and Michael G B Drew 2002 *J. Am. Chem. Soc.* **124** 14092

[25] Erik R Berg, Sarah A Freeman, Daniel D Green and Darin J Ulness 2006 *J. Phys. Chem.* A **110** 13434

[26] Kreyenschmidt M, Eysel H H and Asthana B P 1993 *J. Raman Spectrosc.* **24** 645

[27] Dheeraj K Singh, Shivangi Mishra, Animesh K Ojha, Sunil K Srivastava, Schlucker S, Asthana B P, Popp J and Ranjan K Singh 2011 *J. Raman Spectrosc.* **42** 667

[28] Schwartz M and Wang C H 1973 *J. Chem. Phys.* **59** 5258

[29] Bertran J F, Ballester L and Dobrihalova L 1968 *Spectrochimica Acta* **24** 1765

[30] Asthana B P, Takahashi H and Kiefer W 1983 *Chem. Phys. Lett.* **94** 41

[31] Schlucker S, Heid M, Singh R K, Asthana B P, Popp J and Kiefer W 2002 *Z. Phys. Chem.* **216** 267

[32] Schlucker S, Singh R K, Asthana B P, Popp J and Kiefer W 2001 *J. Phys. Chem.* A **105** 9983