Investigation of inter-molecular hydrogen bonding in the binary mixture (acetone + water) by concentration dependent Raman study and *ab initio* calculations*

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This paper reports that vibrational spectroscopic analysis on hydrogen-bonding between acetone and water comprises both experimental Raman spectra and *ab initio* calculations on structures of various acetone/water complexes with changing water concentrations. The optimised geometries and wavenumbers of the neat acetone molecule and its complexes are calculated by using *ab initio* method at the MP2 level with 6-311+G(d,p) basis set. Changes in wavenumber position and linewidth (fullwidth at half maximum) have been explained for neat as well as binary mixtures with different mole fractions of the reference system, acetone, in terms of intermolecular hydrogen bonding. The combination of experimental Raman data with *ab initio* calculation leads to a better knowledge of the concentration dependent changes in the spectral features in terms of hydrogen bonding.

Keywords: Raman spectra, intermolecular hydrogen bond, *ab initio* caluculations
PACC: 3120, 3220E

1. Introduction

Hydrogen-bonding is an extensively investigated phenomenon,[1,2] especially due to its importance for biological systems,[3] soft materials of hydrogen-bonding molecular systems, and chemical reactions in hydrogen-bonding solutions. Therefore, various experimental methods are employed to characterize hydrogen bonds.[4−8] For the liquid state, where the formation and cleavage of such complexes occur rapidly, vibrational spectroscopy such as infrared (IR) and Raman are ideally suited to detect hydrogen-bonding because they cover both structural and dynamic aspects.[9−11] The wavenumber position of a vibrational band, which relates to the corresponding internuclear force constants, is dependent on electronic structure and bonding. The line width contains information about molecular dynamics. As compared to IR spectroscopy, Raman spectroscopy can reveal additional information from a line width analysis.

The study of the acetone/water system is very important for understanding binary mixtures leading to powerful solvents with applications in physics and chemistry.[12] Therefore, numerous investigations on water–acetone mixtures have been performed by the spectroscopic method[13−18] and *ab initio* calculations.[15,19] Experimentally, the spectroscopic results suggest that hydrogen bonding plays an important role in water–acetone mixtures. Theoretically, the interpretation of Raman spectroscopic data can be expanded in conjunction with an appropriate theoretical model that correlates the experimentally observed spectral features with explicit molecular structures presented in the liquid. In this respect, modern quantum chemical approaches can strongly contribute to our understanding of the hydrogen bond.[20,21] Although there has been some successful theoretical treatments and experiment, a detailed analysis of the hydrogen bond interaction known to exist between acetone and water, is still lacking.

In this study, Raman spectra of liquid acetone and its binary mixtures is recorded and analysed to influence the hydrogen bond formation in neat acetone as well as in binary mixtures (acetone+H_2O). The *ab initio* calculations for optimised geometries and wavenumbers of the different normal modes are also made in order to understand and explain the

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spectral features observed in the binary mixture with varying mole fraction of the reference system. This work can be useful to study the nature of the hydrogen bonding and the structures of hydrogen-bonded complexes.

2. Methods

2.1. Samples and procedures

The sample of acetone is obtained from Aldrich Co. and is used without further purification. For preparing the binary mixture, triple distilled water is used as solvent. The binary mixtures of acetone in water (H_2O) is prepared for various mole fractions of the solute.

2.2. Instruments and measurement

The micro Raman spectrometer (Renishaw In-Via Raman microscope) is equipped with a 514.5 nm Ar^+ ion excitation laser (Spectra Physics 163-M42). The 20×objective (LEICA DMLM 0.12NA) is used for both laser illumination and Raman backscattering detection. The excitation power of 7.5mW and exposure time of charge coupled devices (CCD integration times) of 20s are used to collect all Raman spectra. All the experiments were performed at room temperature.

2.3. Computational methods

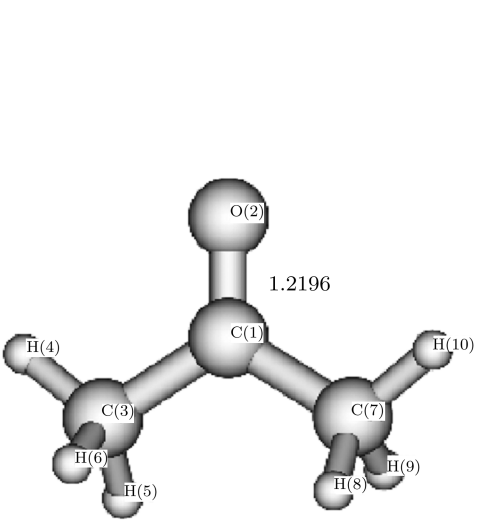
The ground state geometries for acetone and its various hydrogen bonded complexes are optimised at the second order level of closed shell MΦller-Pleset (MP2) perturbation theory employing the 6-311+G(d, p) basis set. All calculations are performed by using the GAUSSIAN 03 programme.[22] Internal coordinates are generated using the MOLDEN programme, by starting from acetone and then successively adding water molecules.

3. Results and discussion

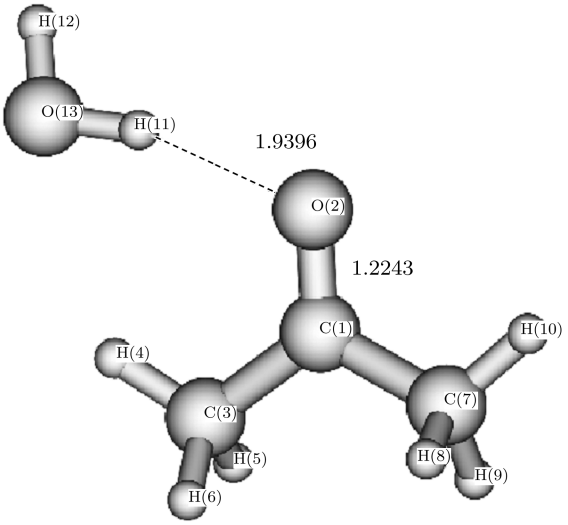
3.1. Optimised geometries of the neat and binary mixtures

In the binary acetone/ water (W) system, many different hydrogen-bonded complexes can be simultaneously shown. Therefore, we calculate the structures of various Acetone W_x clusters with stoichometric ratios $1 : x$ ranging from 1 : 1 to 1 : 3. The basic aim of optimised geometries is to understand the spectral features of neat acetone and its several complexes with the H_2O. The ground state geometries for neat acetone and several complexes with H_2O are optimised by the gradient procedure at the second order level of perturbation theory and the 6-311+G(d, p) basis set using the Gaussian 03 programme package. The optimised geometries obtained from the *ab initio* calculations for acetone and all other structures are presented in Fig. 1.

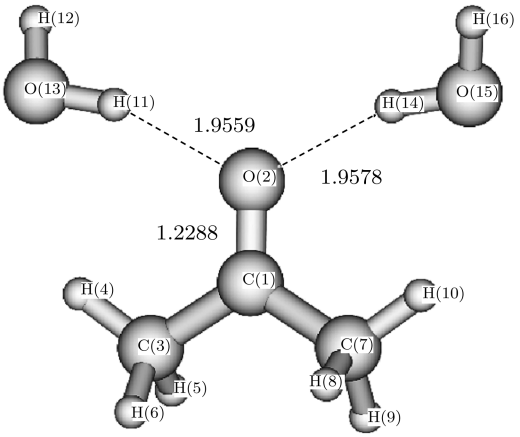
The total energies of the H_2O monomer is calculated to be –76.27472 Hartree (not shown in Fig. 1). The total energies for the monomers, acetone and H_2O, and the hydrogen-bonded complexes of acetone quoted in Hartree in the optimised structures are depicted in Fig. 1. The total energies for the monomers and the hydrogen-bonded complex are less than the sum of energies of the individual monomers, which clearly indicates that stable complexes are formed. The hydrogen-bonded complex of acetone with one water molecule is calculated as shown in Fig. 1(b). In the complex, the hydrogen bond is formed between H atom of water molecule and O atom of the acetone molecule, the hydrogen bond length is 1.9396 Å (1 Å = 0.1 nm). Hydrogen-bonding of two water molecules to acetone may lead to complexes shown in Figs. 1(c) and 1(d), respectively. In the acetone $W_{2(2+0)}$ complex (Fig. 1(c)), the H atom of the OH group of two water molecules form hydrogen bonds with the same O atom of the reference molecule acetone, the hydrogen bond lengths in this case are 1.9559 Å and 1.9578 Å, respectively. In the acetone $W_{2(1+1)}$ complex (Fig. 1(d)), the H atom of the OH group of one water molecule forms hydrogen bond with the O atom of the reference molecule acetone, and the H atom of the OH group of the water molecule forms hydrogen bond with the O atom of other water molecule. Similar to the 1:2 stoichiometry, hydrogen-bonding of three water molecules to acetone can result in the formation of the two acetone W_3 clusters depicted in Fig. 1(e) and 1(f), respectively. The acetone W_x complexes have two structures, which can be interpreted as the result of two effects. One is the dipole–dipole interaction. The other is the directional character of sp^2 hybridization of the lone pair of the oxygen at the C=O end.[19] This has a very intriguing influence on the spectral features in solution, which will be discussed in detail in the relevant sections.



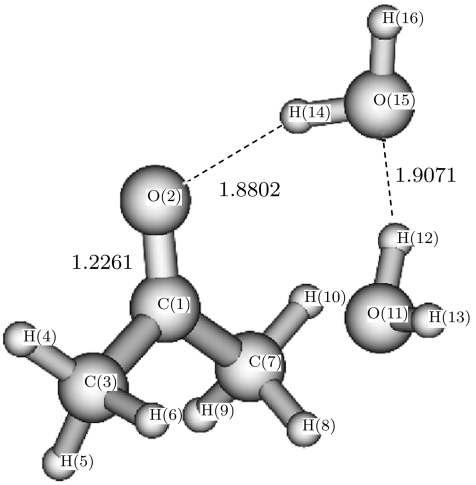
(a) $E = -192.570817$ hartree



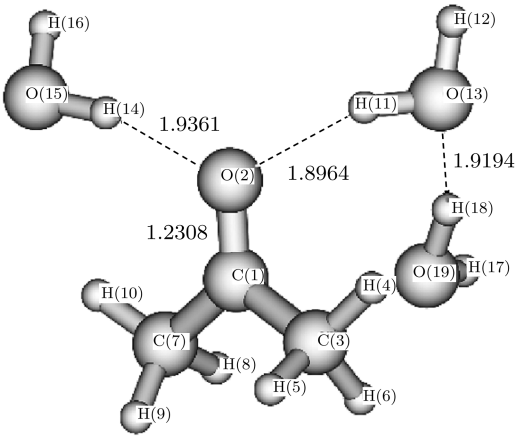
(b) $E = -268.831471$ hartree



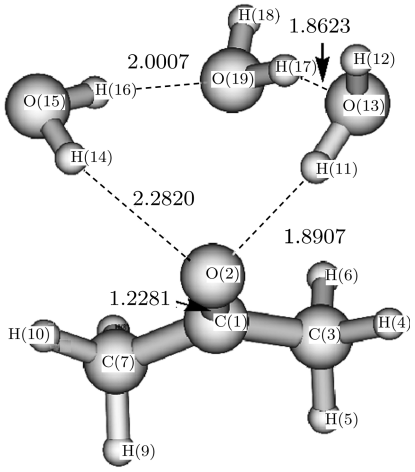
(c) $E = -345.091501$ hartree



(d) $E = -345.096229$ hartree



(e) $E = -421.356320$ hartree



(b) $E = -421.358676$ hartree

Fig. 1. (a)–(f) Optimised geometries of various hydrogen-bonded acetone/W complexes (acetoneW_x) with different stoichiometric ratios. The *ab initio* calculationed O . . . H distances and C=O distances are indicated. Selected distances (Å) are indicated. (1 hartree = 110.5×10^{-21} J)

3.2. Concentration dependence of wavenumber shift for the v (C=O) stretching mode

In Fig. 2 the Raman spectra are recorded in the region, 1600–1800 cm^{-1} for the neat as well as for ten different mole fractions, $C = 0.17$, 0.21 0.25, 0.28, 0.33, 0.4, 0.5, 0.66, 0.8 and 1.0 of the reference system, acetone in the binary mixture (acetone + H_2O). This mode has been assigned to the v (C=O) stretching following reports in the earlier work.[23]

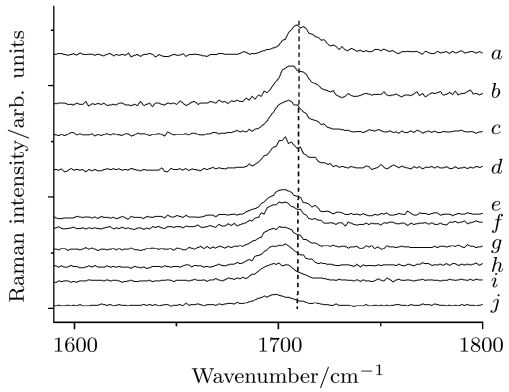


Fig. 2. The Raman spectra in the region 1600–1800 cm^{-1} for neat acetone and its binary mixture at ten mole fractions (C) of acetone, curve j: $C = 0.17$; curve i: $C = 0.21$; curve h: $C = 0.25$; curve g: $C = 0.28$; curve f: $C = 0.33$; curve e: $C = 0.4$; curve d: $C = 0.5$; curve c: $C = 0.66$; curve b: $C = 0.8$ and curve a: $C = 1.0$.

It shows an almost continuous downshift in wavenumber position with dilution as presented in Table 1.

Table 1. Peak positions and linewidths [full width at half maximum] of the peak corresponding to v (C=O) of neat acetone and its hydrogen bonded complexes.

mole fraction (C) of acetone	peak position /cm^{-1}	linewidth (FWHM) /cm^{-1}
1.0	1709.02	24.05
0.8	1708.6	25.2
0.66	1707.55	24.83
0.5	1704.6	23.75
0.4	1703.14	23.04
0.33	1701.67	22.06
0.28	1701.2	22.56
0.25	1700.02	19.5
0.21	1700.0	19.1
0.17	1698.13	18

In the binary mixture (acetone + water), the O atom of the C=O group of acetone forms hydrogen bonds with the H atom of the water molecules as shown in Fig. 1. The optimised structures with formation of hydrogen bonds and solvent molecules are obtained as described in foregoing section. In neat acetone, the length of the C=O group of acetone is 1.2196 Å. When water is added into the solute, it will form OH...O=C type hydrogen bond. When more water is added, more number of solute molecules will be hydrogen bonded. Therefore, the lengths of the C=O group of acetone stretch from 1.2243 to 1.2308 Å in Fig. 1, due to hydrogen bond formation in the binary mixture. Hence, it can be concluded that the C=O group, after hydrogen bond formation with water, withdraws some charge density from the group and thereby decreases the force constant of the C=O group which leads to decreases v(C=O) stretching frequency.

3.3. Variation of the linewidth of the v (C=O) stretching mode of acetone with concentration

The variation of the linewidth of the v (C=O) stretching mode of acetone with concentration shows a decrease upon dilution, and the results are presented in Fig. 3.

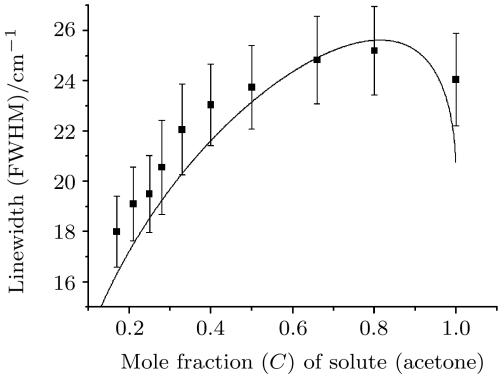


Fig. 3. The experimental data points for the Raman linewidth varying with concentration of the solute (acetone) at mole fraction C for the v (C=O) stretching mode in the binary mixture and the solid line represents the fit obtained by using Eq. (2).

The C=O group of acetone involves hydrogen bonding with the solvent molecule between the H atom of the water and the O atom of acetone. The motion of the reference molecule, acetone, is constrained owing to this hydrogen-bond formation with the solvent molecule. This would give rise to the phenomenon of motional narrowing as discussed by Oxtoby,[24] according to which the dipolar interaction and resonant energy transfer are mainly responsible

for motional narrowing. An empirical model has been recently proposed by Ojha *et al.*[25] According to the model, the changes in the linewidth is not only due to the concentration fluctuation as in the model given by Bondarev and Mardaeva,[26] but also due to the change of the microviscosity at different relative concentrations of the solute and the solvent as well as the effect of concentration fluctuation as the microlevel. The viscosities of the different mixtures can be calculated by using the relation:

$$\eta_{\rm mix} = \eta_{\rm solute} C + \eta_{\rm solvent}(1 - C), \tag{1}$$

where C is the mole fraction of the solute, and $\eta_{\rm solute}$ and $\eta_{\rm solvent}$ are the bulk viscosities of the solute and the solvent, respectively. The effect of viscosities can be visualized by comparing the viscosities of the solute and the solvent. The viscosities of acetone and water are 0.32×10^{-3} Pa$\cdot$s and 1.002×10^{-3} Pa$\cdot$s, respectively. The variation of the linewidth with the concentration is given by the relation

$$\Gamma(C) = \Gamma_{\rm C} + \Gamma_i(\eta_{\rm C}), \tag{2}$$

where $\Gamma_{\rm C}$ is the contribution due to the concentration fluctuation and $\Gamma_{\rm i}$ is the intrinsic linewidth, given by

$$\Gamma_{\rm i}(\eta_{\rm C}) = \Gamma_{\rm i} \exp\left[-a\left(1 - \frac{\mu_2 \eta_{\rm C}}{\mu_1 \eta_{\rm solute}}\right)\right], \tag{3}$$

$$\Gamma_{\rm C} = 2\sqrt{2\ln 2}\Delta\Omega\sqrt{\frac{C(1-C)}{n}}, \tag{4}$$

$$\eta_{\rm m} = \eta\left[0.16 + 0.4\left(\frac{r_1}{r_2}\right)\right], \tag{5}$$

where μ_1, μ_2 are microfriction parameter for neat liquid as well as the mixture, respectively, $\Delta\Omega$ is the amplitude of the wavenumber shift between the neat liquid and infinite dilution, n is the number of the neighbouring molecules influencing the reference mode. In the case of hydrogen-bonded system, the value of the van der Waals radius of the terminal atom through which the hydrogen bonding takes places was taken as the solute radius r_1, and similarly the value of the van der Waals radius of the terminal atom of the solvent involved in the hydrogen bonding was taken as the solvent radius r_2 for calculating microviscosity $\eta_{\rm mix}$ by using Eq. (5). The parameter a in Eq. (3) is an adjustable parameter which is basically vibrational mode dependent, and depends upon the polarisability of the vibrational mode under investigation. Therefore, it contributes to the linewidth. If $a = 1$ is substituted in Eq. (3), it still fits the qualitative trend, but by adjusting this parameter one can get a quantitative agreement with the experimental data. In this study, although concentration fluctuation may be an important factor, the concentration dependence of both v (C = 0) and $\Gamma(C)$ showed a departure from what is expected on the basis of the concentration fluctuation model. It is concluded that the departure from the expected trend may be due to microviscosity.

4. Conclusions

In the present study, the Raman spectra of acetone has been recorded and the solvent effects on acetone discussed in terms of hydrogen bonding. The peak position and Raman linewidth of the vibrational mode of acetone have been investigated. It can be concluded from this study that both the frequency shift and the line width of acetone are affected by hydrogen bonding, and that viscosity is the main contributing factor to the linewidth of acetone. The optimised geometries obtained by the *ab initio* calculations have supported the changes in the spectral features upon changing the concentration of the solute molecules in the binary mixtures. The results reported here are important for better understanding the role of hydrogen bonding in determining the properties of molecule within hydrophilic environments.

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