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UNUSUAL SPECTRAL BEHAVIOUR OF ETHANOL USING SIMPLE XENON LAMP EXCITATION SOURCE

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Abstract: Raman scattering technique has been used in every field of research to determine purity of compounds or materials in different environments because every compound or material has the characteristic vibrations. In water and alcohol mixture, Raman scattering technique can be used. However, the behaviour of Raman scatterings was not addressed much when wavelength of excitation (λ_{exc}) was considered at $2(\lambda_{\mathrm{exc}})$ or $(\lambda_{\mathrm{exc}})/2$. Excitations corresponding to $2(\lambda_{\mathrm{exc}})$ and $(\lambda_{\mathrm{exc}})/2$ are taken as the second order excitation and second harmonic excitation, respectively. Here, we report the following interesting observations in pure ethanol: (1) Raman scattering intensities after consideration of excitation at wavelength of second harmonic is slightly more than those of the direct excitation and (2) the peak intensity corresponding to wavelength of 2nd harmonic or 2nd order is very much less than that of Raman scattering. Spectral intensity decreases with increase of water content in ethanol. These observations are explained on basis of possible causes such as Raman or inelastic scattering from ethanol as well as photoluminescence from additive or foreign impurities present in ethanol.

Keywords: Inelastic Scattering, Elastic Scattering, 2nd Harmonic, Ethanol, Fluorescence

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1 Introduction

The Raman phenomenon was observed by C. V. Raman and K. S. Krishnan in 1928 using sunlight as source of excitation on organic liquids [1]. Since then, Raman spectroscopy is used in every field of sciences particularly in analytical chemistry. This technique is non-destructive and any form of substances such as gaseous, liquid and solid samples can be applied. When light is interacting with molecules, the Raman effect takes place after perturbation of the electronic conformation of molecule to an unstable virtual state. It is to be noted that excitation wavelength is much more than size of molecule. After interaction of light with molecules, two types of scattered lights occur namely; those with same wavelength of light are of elastic type and a few fractions (a few orders of 1 in 10^6) are of inelastic type [2]. As compared to incoming light, the first type of scattered light does not change energy, while the latter type of scattered light gains energy from or lose energy to vibrations of molecule. The first type is considered as Rayleigh scattering and the second type is considered as Raman scattering. Based on gain and loss of energy to vibrations of molecule, anti-Stokes and Stokes shifts occur in Raman spectra. Any molecule can show Raman effect only when it has non-zero polarizability (i.e., excitation photon must produce deformation of the electron configuration of a molecule).

Molecules containing O-H functional are highly Infra-red (IR) active, but poor Raman active [2]. Because of this, Raman spectra in water are recorded in most studies of molecules/tissues/cells in biology as compared to FTIR spectra (Fourier transform infrared). Water can have 4 H-bonds per molecule of water, whereas ethanol can have one H-bond. When water and ethanol solvents are mixed, they form non-ideal solution, (i. e. their hydrogen bonds and viscosity do not follow with the concentration of ethanol in water) [3]. Maximum H-bonds are observed when ethanol to water weight ratio is of 10-20 as compared to that of water. The bending vibration of water occurs at 1630 cm^{-1} and the -O-H stretching vibrations occur at 3200-3400 cm^{-1}. The peaks at 3200 cm^{-1} and 3400 cm^{-1} are assigned to strong and weak H-bonds, respectively. This can be seen in both water and ethanol. The stretching frequency of the free OH group without H-bond is 3650 cm^{-1}. There are experimental evidences for vibrations of water at higher frequencies (3600-12159 cm^{-1}) arising from combination of frequencies or overtones, but their peak intensities are very weak [4, 5]. It means that it can have vibration bands up to dissociation energy of H-O (41145 cm^{-1}) [6]. In low concentration of ethanol in water, it forms $C_2H_5OH.nH_2O$ (n = 3-6) and at higher concentration, it forms $C_2H_5OH.1H_2O$. This is considered as hydration number or a clathrate type. It was reported that solvents have sensitive vibrational bands in Raman spectra. For example, solvents such as acetonitrile, ethanol and methanol have strong bands at 921 (C-C) cm^{-1}, 879 (C-C) cm^{-1} and 1019 (C-O) cm^{-1}, respectively [7]. Because of these, they can be identified after mixing. The Raman technique is used in the purity study of alcoholic beverages to identify components such as water and alcohols present in it [2, 8].

In luminescence study of compounds soluble in solvents, several Raman peaks arising from solvents could be observed. These Raman peaks are very complex because of low resolution of detector, but excitation intensity is much higher than those of Raman peaks. When 2nd order of excitation wavelength is considered, will it follow the same trend as of the first order? That is, when wavelengths of excitation are λ_{exc} = 600 nm, 550 nm and 500 nm, the wavelengths of second harmonic from grating (instrument) are $(\lambda_{\text{exc}})/2$ = 300 nm, 275 nm and 250 nm, respectively. In the literature, this was not addressed much to the best of our knowledge.

Here, we have studied the observation of higher intensity of Raman peaks as compared to 2nd harmonic excitation or 2nd order intensity using simple Xe excitation sources. Also, Raman intensity of ethanol is reduced significantly in the presence of a few percentages of water. Many high frequency peaks (3500 – 10000 cm^{-1}) with significant intensities are observed.

2 Experimental Section

Deionized water was used. Ethanol was obtained from two sources. Ethanol(1) had purity of 99.9%, procured from Changshu Yangyuan Chemical, made in China. Batch number of this ethanol (1) is XK-13-201-00185. Possible impurities present in ethanol (1) were water (0.1%), residue on evaporation (0.001%), alkaline (0.01) and methanol (0.05%), which were written in catalogue/label of bottle. Whereas, ethanol(2) had purity of about 95% (H_2O: 5%), which was prepared by distillation in our laboratory. Solution of ethanol (1) and water was prepared in 40:60%.

Spectra of materials were carried out using an Edinburgh Instrument FLS920 and a 450 W Xe lamp was used as the excitation source. Angle between excitation source and detector was kept at 90°. In order to get monochromatic light (λ_{exc}), the gratings were used in instrumental set-up. It follows the Bragg's law, $2d\sin\theta = n\lambda$, where d is interplanar distance of grating, θ is the Bragg's angle, n is number and λ is the wavelength of excitation. n = 1, 2, 3 are the 1st, 2nd and 3rd order of reflection or diffraction, respectively. n = $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{4}$ are 2nd, 3rd and 4th harmonic, respectively. Quartz cuvette was used as sample holder. Empty cuvette was checked for its purity. Experiment was performed at ambient atmosphere. Figure A.7 (see Appendix A) showed spectral behaviour of empty cuvette at 10 nm slit width for excitation and emission modes. Irish was kept at 1% in 200-800 nm. In order to check the response of detector, the corrected emission spectra after excitation at 300 nm at different slit widths (1-10 nm) and 1% Irish were recorded (figure A.8). Two peaks originated from elastic scatterings at 300 nm and 600 nm were observed. The latter one corresponds to the second order of excitation wavelength ($2\lambda_{\text{exc}} = 2 \times 300\,\text{nm} = 600$ nm) from grating used in instrument. Any kind of filter was not used before and after sample. It is found that intensity increases with increase of slit width. Also, excitation intensity of 300 nm peak is more than that of 600 nm. Difference in intensity is more at 10 nm slit width. The line width at half maximum intensity (LWHM) increases with increase of slit width, i.e., resolution decreases with increase of slit width. This suggests the good response of detector.

3 Results and Discussion

Figure 1 shows the spectra of ethanol (1) at three different excitation wavelengths 500 nm, 550 nm, and 600 nm. Pure ethanol is not expected to have luminescence peaks from absorption through the electronic transitions

($\sigma - \sigma^*$, $\pi - \pi^*$, n-σ^* of CH_3CH_2-O-H) at these excitation wavelengths because excitation energy is much lower than the required absorption energy. The UV-visible absorbance cut-off wavelength for ethanol is 205 nm, and above this wavelength, there is no effect. However, we have seen spectral peaks. To explain these peaks, we have considered two possible processes: 1. Raman scatterings from ethanol and 2. Photoluminescence from additive or foreign impurity present in ethanol.

3.1 Raman/Inelastic scatterings from ethanol

At 500 nm excitation, a broad spectrum in the range 560–800 nm along with a peak at 535 nm was observed. These are related to phonon scattering/inelastic scattering from alcohol molecules. Possible peaks can be assigned to the broad spectrum (figure 2a, table S1). The Stokes shifts (difference between excitation wavelength at 500 nm and inelastic scattering of phonon) are 1308 cm^{-1}, 2906 cm^{-1}, 4252 cm^{-1}, 5612 cm^{-1}. The wavelength of the second harmonic of excitation is 250 nm ($\lambda_{exc}/2$ = 500/2 nm = 250 nm). From this excitation, a broad spectrum in the range 270–450 nm was observed. This is related to phonon scattering from alcohol molecules. Possible peaks can be assigned to the broad spectrum (figure 2b, table S1). The Stokes shifts are 7213 cm^{-1}, 8652 cm^{-1}, 11014 cm^{-1}, 15124 cm^{-1}. The reported Raman peaks for ethanol were 893 cm^{-1} (vs), 1060 cm^{-1} (s), 1095 cm^{-1} (s), 1458 cm^{-1}, 2940 cm^{-1} (vs), 3000–3300 cm^{-1} [9]. Some of the Stokes shifts are much higher than Raman active modes for ethanol (C-H, O-H). These will be related to combinations and overtones of phonons [10, 11]. But these modes should not exceed the dissociation energy of C-H (32200 cm^{-1}) and O-H (36700 cm^{-1}) of ethanol [12, 13].

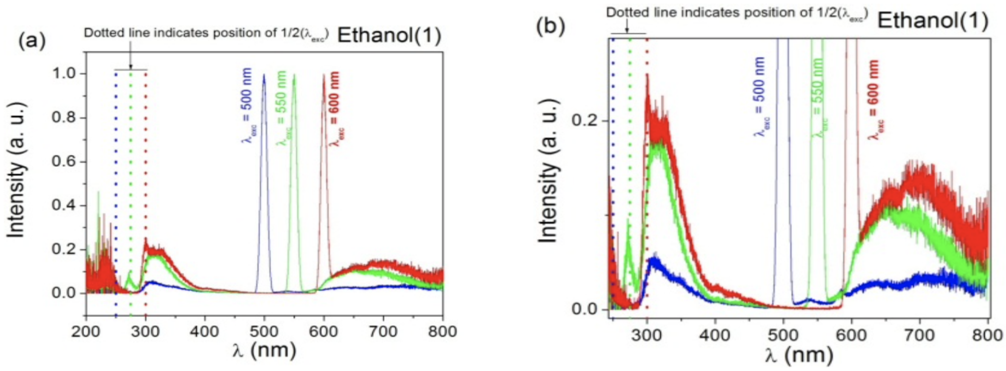


Figure 1: (a) Normalized spectra of ethanol (1) after excitations at 500 nm, 550 nm, or 600 nm. The second harmonic wavelengths of excitations are shown as dotted lines (= $\lambda_{exc}/2$ = 250 nm, 275 nm, or 300 nm). (b) Their expanded spectra.

For excitation at 550 nm, Stokes shifts are found to be 1515 cm^{-1}, 2105 cm^{-1}, 2821 cm^{-1}, 3710 cm^{-1}, 4705 cm^{-1} (figure 2c, table S1). The wavelength of the second harmonic of excitation is 275 nm ($\lambda_{exc}/2$ = 550/2 nm = 275 nm). Stokes shifts are found to be 3577 cm^{-1}, 5114 cm^{-1}, 6952 cm^{-1} (figure 2d, table S1).

For excitation at 600 nm, Stokes shifts are found to be 1139 cm^{-1}, 2381 cm^{-1}, 3190 cm^{-1} (figure 2e, table S1). The second harmonic wavelength of excitation is 300 nm ($\lambda_{exc}/2$ = 600/2 nm = 300 nm). Stokes shifts are found to be 1282 cm^{-1}, 2752 cm^{-1}, 4431 cm^{-1}, 8395 cm^{-1}, 10131 cm^{-1}, 11258 cm^{-1} (figure 2f, table S1).

In general, the Raman active modes are very strong as compared to other possible modes of combinations and overtones. Nonetheless, it is not followed in this study. In some cases, the mode of O-H could not be observed. Instead, other modes are observed and very strong (figure 2b, table S1). Here, inelastic scattering intensities are significant, i.e., distinct peaks could be observed even without the expansion of the spectrum. Elastic scattering intensity from direct excitation is more than those of inelastic scattering. That is, intensity at 500 nm, 550 nm, or 600 nm is more than those of scattering. However, the elastic scattering from the wavelength of the second harmonic of excitation has lower intensity than those of phonon/inelastic scattering, which is quite unexpected.

It is difficult to get pure ethanol. In most cases, some water molecules are associated. Distinction between pure ethanol and mixture with water can be identified by Raman spectra. Figure 3 shows the scattering spectra of the solution of ethanol (1) and water (about 40% + 60%) at different excitation wavelengths 500 nm, 550 nm, and

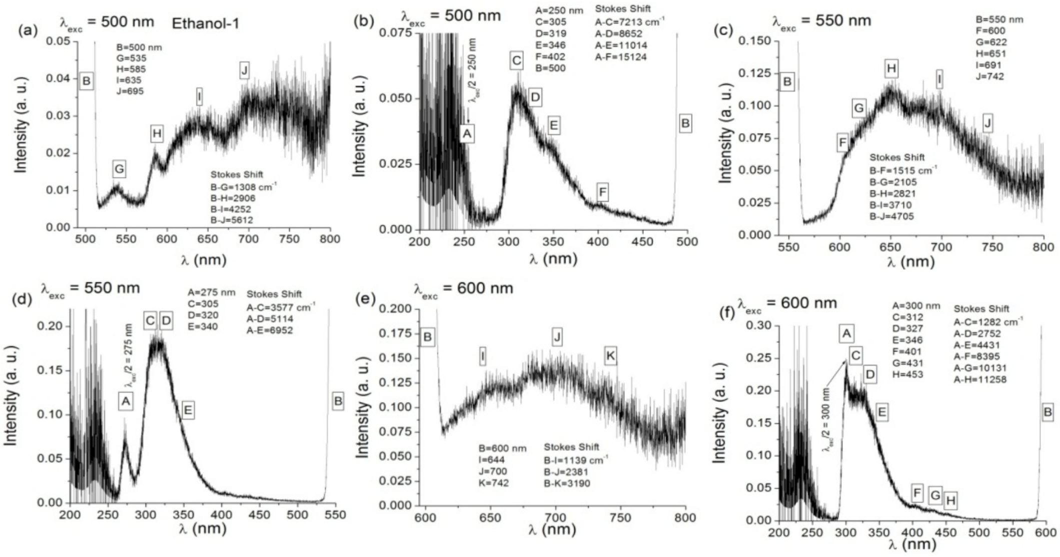


Figure 2: Expanded spectra of ethanol (1) (figure 1) after excitations at 500 (a, b), 550 **(c, d)**, or 600 nm (e, f). The symbol (A) stands for the position of the second harmonic wavelength of excitation (= $\lambda_{exc}/2$), and the symbol (B) stands for the position of the direct excitation wavelength (= λ_{exc}). The possible phonon peaks/inelastic scatterings are assigned (C, D, E, F, G, H, I, J, K in nm). Possible Stokes shifts are calculated (expressed in cm^{-1}).

600 nm. For excitation at 500 nm, the phonon scattering peaks are observed at 1818 cm^{-1} and 3607 cm^{-1} (Stokes shift). For $\lambda_{exc}/2$ = 500/2 nm = 250 nm, Stokes shifts are 7742 cm^{-1}, 11429 cm^{-1}, 13333 cm^{-1}, 17011 cm^{-1}, 17778 cm^{-1}. Details can be obtained in figure A.9 and table S2. The bending vibration of water occurs at 1630 cm^{-1}, and the -O-H stretching vibrations occur 3200–3400 cm^{-1} [3]. Dissociation energy values of H-O in water and ethanol are 36700 cm^{-1} and 41145 cm^{-1}, respectively [6, 13]. The values of Stokes shifts apart from Raman active modes are less than those of their dissociation energies and thus these are related to the combinations and overtones of the phonons.

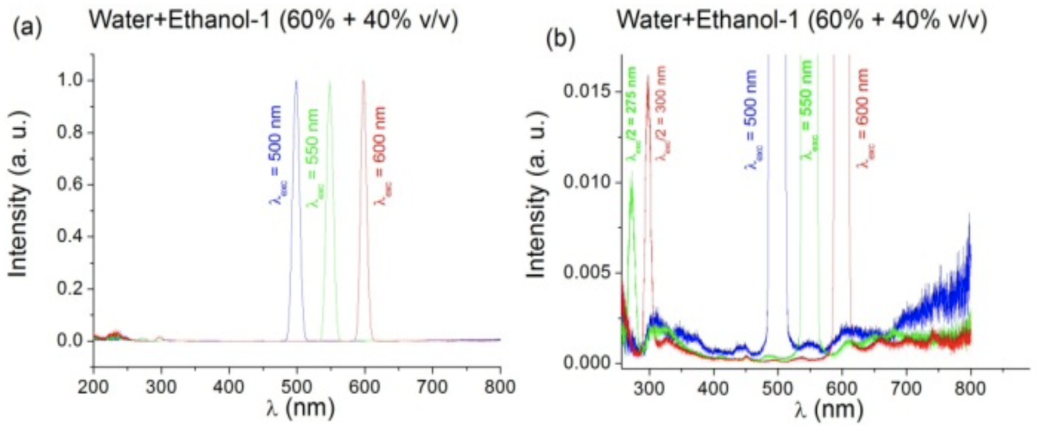


Figure 3: (a) Normalized spectra of Water + Ethanol (1) (60% + 40%, v/v) after excitations at 500 nm, 550 nm, or 600 nm and (b) their expanded spectra. The second harmonic wavelengths of excitations are also shown ($\lambda_{exc}/2$ = 275 or 300 nm). Here, phonon scattering peaks are observed.

For excitation at 550 nm (λ_{exc}), the phonon scattering peaks are 1922 cm^{-1}, 2797 cm^{-1}, 3476 cm^{-1} (Stokes shift). For $\lambda_{exc}/2$ = 550/2 = 275 nm, Stokes shifts are 3361 cm^{-1}, 5595 cm^{-1}, 12033 cm^{-1}, 14142 cm^{-1}, 15745 cm^{-1}.

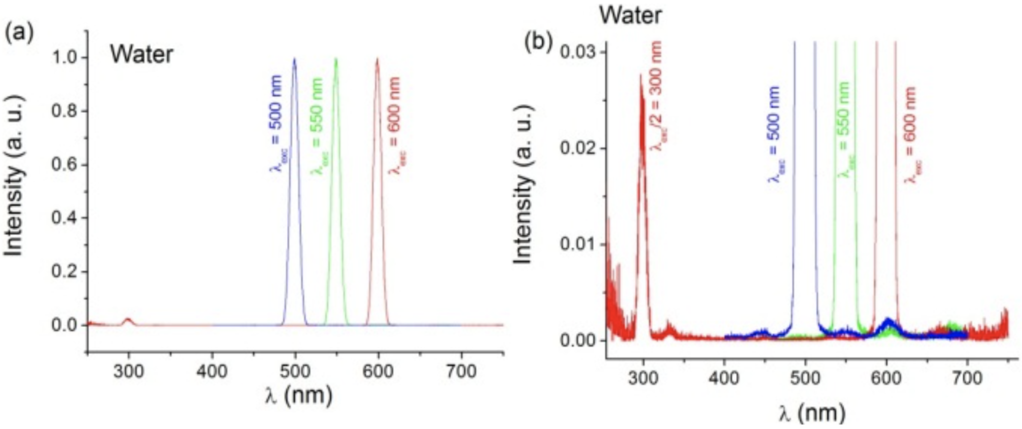


Figure 4: (a) Normalized spectra of Water after excitations at 500 nm, 550 nm, or 600 nm and (b) their expanded spectra. The second harmonic wavelength of excitation is also shown ($\lambda_{\text{exc}}/2$ = 300 nm). Here, phonon scattering peaks are observed.

Details can be obtained in figure A.9 and Table S2. In case of excitation at 600 nm, the phonon scattering peaks are 1515 cm^{-1}, 2381 cm^{-1}, 3172 cm^{-1} (Stokes shift). For the wavelength of the second harmonic of excitation at 600/2 nm = 300 nm, the scattering peaks are 2564 cm^{-1}, 8943 cm^{-1}, 10077 cm^{-1}, 11111 cm^{-1}, 13131 cm^{-1} 14641 cm^{-1} (Stokes shift). Details can be obtained in figure A.9 and table S2.

Intensities for phonon scattering from ethanol (2) (discussed later) and the water-ethanol (1) mixture are less than those of ethanol (1). Raman scattering is very strong in the case of pure ethanol. Also, the number of hydrogen bonds present in ethanol is one, whereas that in water is four. Thus, the kinetic energy of ethanol molecules is more than that of water.

Figure 4 shows the scattering spectra of water at three different excitation wavelengths 500 nm, 550 nm, and 600 nm, and their expansion spectra are shown in figure 4b and figure A.10. For direct excitation at 500 nm, Stokes shifts are 1818 and 3471 cm^{-1}, which are close to the reported Raman peaks (1640 cm^{-1} for bending and 3240–3400 cm^{-1} for stretching) for water [3, 14]. Slight variations from reported values are due to uncertainties in the assignment of peaks on the spectrum. In the case of direct excitation at 550 nm, Stokes shifts are 1654 cm^{-1} and 3477 cm^{-1}. In the case of direct excitation at 600 nm, the Stokes shift is 1630 cm^{-1}. The excitation at the second harmonic wavelength at 300 nm shows Stokes shifts at 3213 cm^{-1}, 11111 cm^{-1}, and 14642 cm^{-1}. Details of peaks assignment are given in table S3. The order of intensities of phonon scattering of the medium is ethanol (1) $>>$ ethanol (1) + water $>$ water. It means that enhanced phonon modes are found in ethanol. Due to the presence of water, the intensities of phonons are reduced.

Figure 5a shows the scattering spectra of ethanol (2) at two different excitation wavelengths 550 nm and 600 nm, and their expanded spectra are shown in figure 5b and figure A.11. Stokes shifts at 1515 cm^{-1}, 2796 cm^{-1}, and 3367 cm^{-1} are observed after direct excitation at 550 nm. In the case of the second harmonic excitation wavelength at 275 nm, Stokes shifts are 3031 cm^{-1}, 5595 cm^{-1}, 11974 cm^{-1}, and 13108 cm^{-1}. For excitation at 600 nm, Stokes shifts are 1400 cm^{-1} and 2874 cm^{-1}. The second harmonic excitation wavelength at 300 nm gives Stokes shifts at 2374 cm^{-1}, 5401 cm^{-1}, 8642 cm^{-1}, 10077 cm^{-1}, and 11111 cm^{-1}. Table S4 gives the detailed peak assignment of ethanol (2). The intensities of phonon scatterings are less than those of ethanol (1), but are more than those of ethanol (1) + water mixture or water. Also, there are similar features in both ethanol (1) and (2) for Raman peak assignment. In studies of various solvents, it is noticed that peak intensities of Raman scattering observed from the second harmonic excitation ($\lambda_{\text{exc}}/2$) are higher than those observed from direct excitation (λ_{exc}). However, the peak intensity of second harmonic excitation is very much less than that of direct excitation.

Possible anti-Stokes shifts are observed (table S1-S4). In a few cases, there are comparable peak intensities for both Stokes and anti-Stokes scatterings (figure A.9-Sa). For example, peaks at F, G, and H are comparable in terms of intensities. Similarly, scattering peak intensities at D and E are comparable (figure A.10-Sa). In general, intensities of anti-Stokes peaks are very weak and are even difficult to observe, whereas intensities corresponding

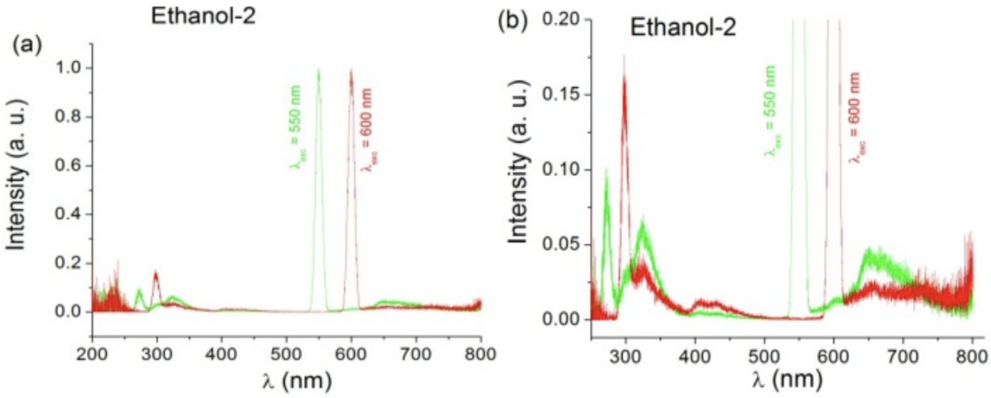


Figure 5: (a) Normalized spectra of ethanol (2) after excitations at 550 nm or 600 nm and (b) their expanded spectra. The second harmonic wavelengths of excitations are also shown ($\lambda_{\text{exc}}/2$ = 275 nm or 300 nm). Here, phonon scattering peaks are observed.

to Stokes peaks are strong. It is to be noted that Stokes shifts observed at higher frequencies above 11000 cm^{-1} in all spectra may be from anti-Stokes shifts because peaks are close to the excitation wavelength.

The higher phonon scattering intensities of pure ethanol as compared to water can be related to the following: (i) Increase of H- - O-H (H-bond) from 1 (ethanol) to 4 (water); (ii) Decrease of kinetic energy (KE) of molecules from ethanol to water; (iii) increase of partition functions from water to ethanol (Z = the ratio of the total number of molecules in a system to the number of particles in the lowest energy state); (iv) Hot band excitation in the case of pure ethanol since the molecules have higher KE. These result in different deformation of electron clouds in both cases when the same light intensity interacts with molecules.

Also, we have recorded the spectrum of ethanol (1) after direct excitation at 300 nm (figure 6). Spectral intensity is almost the same as the excitation intensity (λ_{exc} = 300 nm). In the case of the second order of excitation ($2\lambda_{\text{exc}}$ = 600 nm), the spectral intensity is higher than that of excitation. The wavelength corresponding to direct excitation in figure 1 is 600 nm, whereas that in figure 6 is 300 nm. However, the spectral patterns are almost the same in both cases.

We have tested other solvents having polar and non-polar properties, such as methanol, isopropanol, and hexane. However, we do not find observations similar to ethanol (1) wherein a significant increase of phonon scattering intensity after excitation at the second harmonic wavelength as compared to the peak intensity of excitation is observed. Generally, phonon scattering intensity is much less than the peak intensity of excitation.

3.2 Photoluminescence from additive or foreign impurity present in ethanol

Even if additives are added to ethanol (1) to obtain 99.9% (anhydrous), there is a possibility to observe fluorescence peaks from additives in the range of 250–400 nm. However, ^{1}H and ^{13}C NMR studies could not find extra peaks apart from ethanol (figures A.12, A.13). It needs to be further understood why such high spectral intensity is observed in ethanol (1) as compared to excitation intensity.

4 Conclusion

This study provides understanding of Raman scattering of molecules having H-bonding as well as behaviour of Raman scattering when direct and 2^{nd} harmonic excitations are considered. Raman scattering intensity for pure ethanol is very high. When water is present, intensity decreases significantly. Raman scattering intensities after consideration of excitation at wavelength of second harmonic are slightly more than those of the direct excitation, whereas the peak intensity corresponding to wavelength of second harmonic is very much less than that of direct excitation. Several Stokes shifts at higher frequencies which are more than fundamental modes are observed.

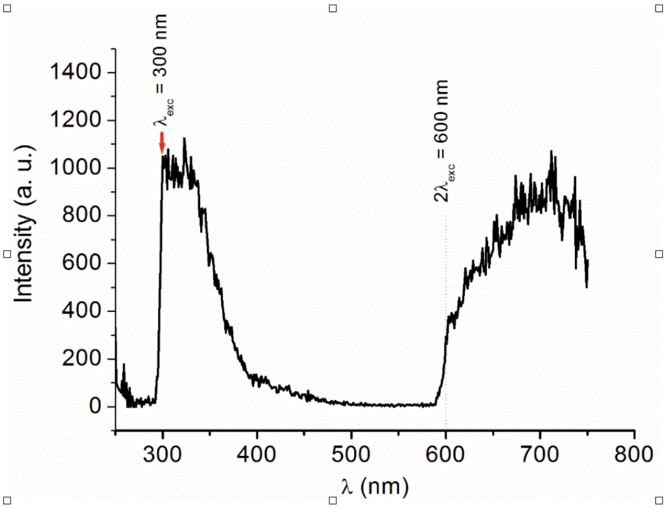


Figure 6: Spectrum of ethanol (1) after excitation at 300 nm. The second order wavelength of excitation is $2\lambda_{\text{exc}}$ = 600 nm.

These may be related to combination of vibrations or overtones. But, these may be assigned to anti-Stokes shifts since peaks are nearer to excitation peak. The partition functions (Z in terms of translational, rotational and vibrational modes) of molecules need to be considered in scattering phenomena in addition to Raman scattering modes.

A Supplementary data

Tables for peak position, Stokes shift and anti-Stokes shift calculated from ethanol, water, water-ethanol mixture, spectrum of empty cuvette after excitation, intensity versus slit width for empty cuvette, expanded spectra of water, ethanol, water and ethanol mixture, NMR data.

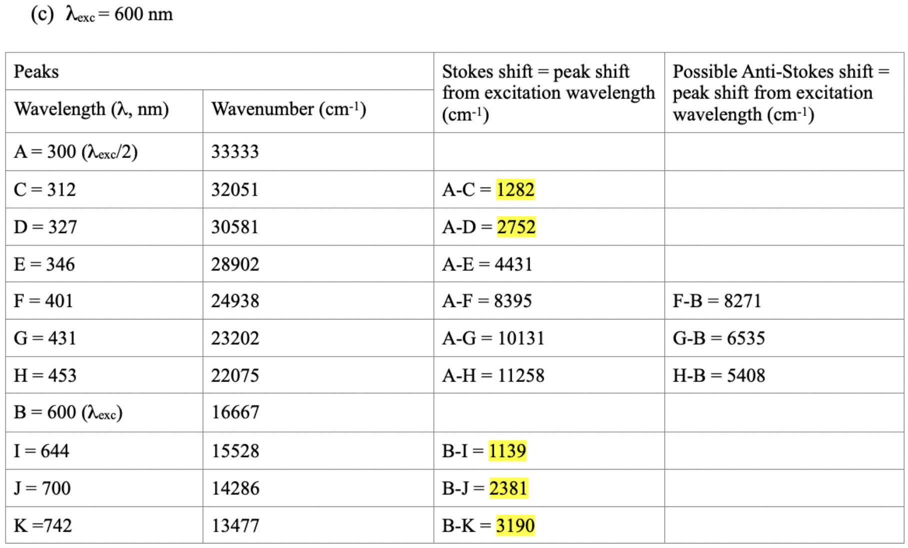
(a) λ_{exc} = 500 nm

Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
A = 250 ($\lambda_{exc}/2$)	40000		
C = 305	32787	A-C = 7213	
D = 319	31348	A-D = 8652	D-B = 11348
E = 346	28986	A-E = 11014	E-B = 8986
F = 402	24876	A-F = 15124	F-B = 4876
B = 500 (λ_{exc})	20000		
G = 535	18692	B-G = 1308	
H = 585	17094	B-H = 2906	
I = 635	15748	B-I = 4252	
J = 695	14388	B-J = 5612	

(b) λ_{exc} = 550 nm

Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
A = 275 ($\lambda_{exc}/2$)	36364		
C = 305	32787	A-C = 3577	C-B = 14605
D = 320	31250	A-D = 5114	D-B = 13068
E = 340	29412	A-E = 6952	E-B = 11230
B= 550 (λ_{exc})	18182		
F= 600	16666	B-F = 1515	
G = 622	16077	B-G = 2105	
H = 651	15361	B-H = 2821	
I = 691	14472	B-I = 3710	
J= 742	13477	B-J = 4705	

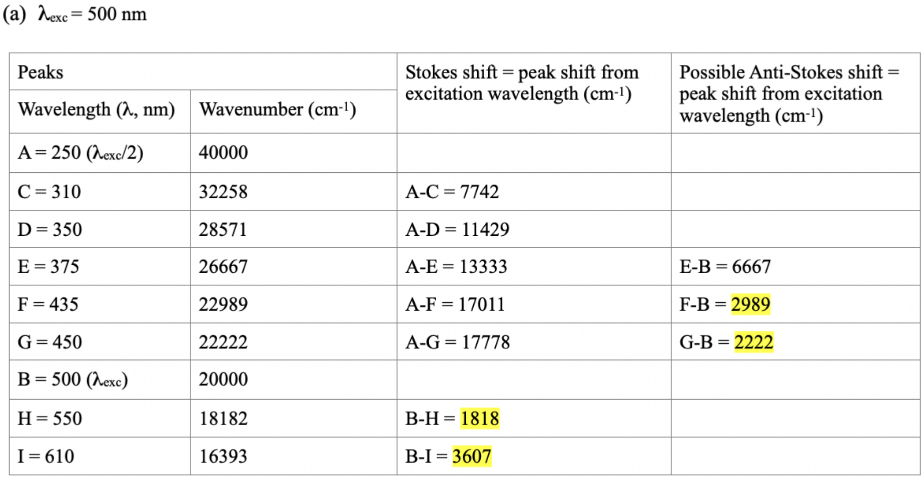
Table S1 (part 1): Peak position, Stokes shift and Anti-Stokes shift calculated from ethanol (1) after excitation at different wavelengths: (a) 500 nm, (b) 550 nm. Here, ”A” represents the second harmonic wavelength of excitation (B).



(c) $\lambda_{exc} = 600$ nm

Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
A = 300 ($\lambda_{exc}/2$)	33333		
C = 312	32051	A-C = 1282	
D = 327	30581	A-D = 2752	
E = 346	28902	A-E = 4431	
F = 401	24938	A-F = 8395	F-B = 8271
G = 431	23202	A-G = 10131	G-B = 6535
H = 453	22075	A-H = 11258	H-B = 5408
B = 600 (λ_{exc})	16667		
I = 644	15528	B-I = 1139	
J = 700	14286	B-J = 2381	
K =742	13477	B-K = 3190	

Table S1 (part 2): Peak position, Stokes shift and Anti-Stokes shift calculated from ethanol (1) after excitation at different wavelengths: (c) 600 nm. Here, ”A” represents the second harmonic wavelength of excitation (B).

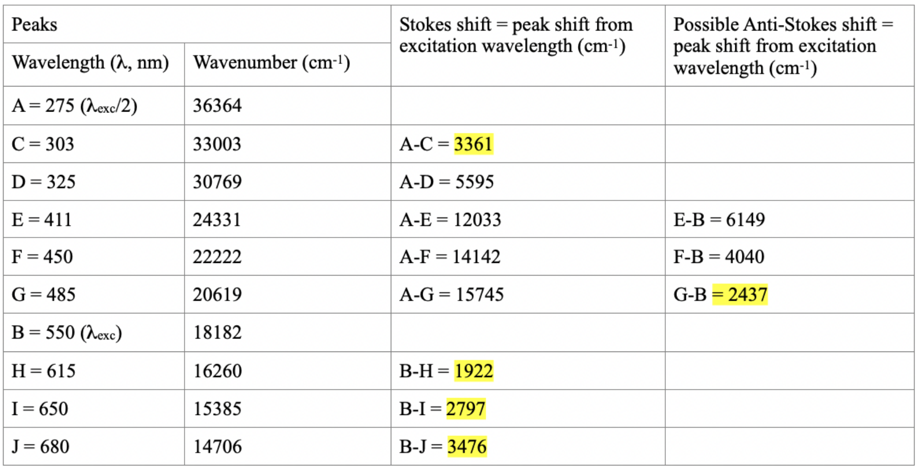


(a) $\lambda_{exc} = 500$ nm

Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
A = 250 ($\lambda_{exc}/2$)	40000		
C = 310	32258	A-C = 7742	
D = 350	28571	A-D = 11429	
E = 375	26667	A-E = 13333	E-B = 6667
F = 435	22989	A-F = 17011	F-B = 2989
G = 450	22222	A-G = 17778	G-B = 2222
B = 500 (λ_{exc})	20000		
H = 550	18182	B-H = 1818	
I = 610	16393	B-I = 3607	

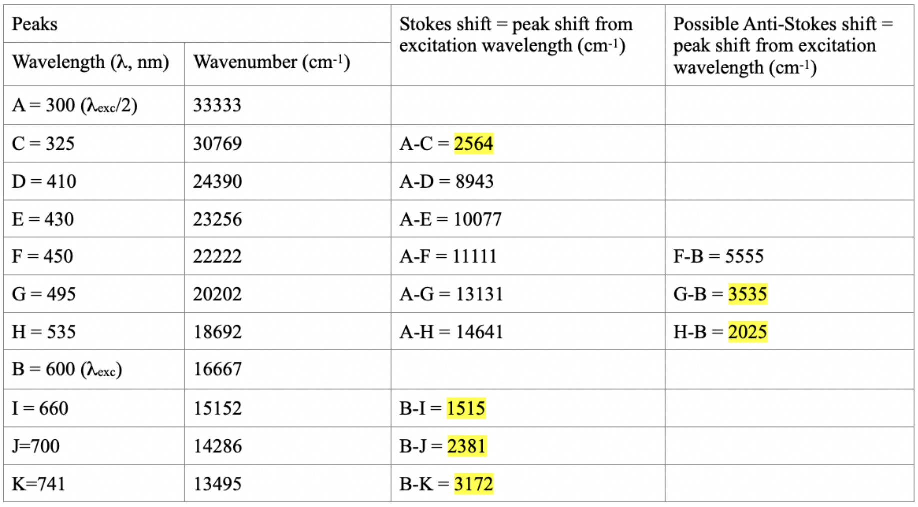
Table S2 (part 1): Peak position, Stokes shift and Anti-Stokes shift calculated from solution of ethanol (1) and water (about 40% + 60%) after excitation at different wavelengths: (a) 500 nm. Here, ”A” represents the second harmonic wavelength of excitation (B).

(b) λ_{exc} = 550 nm



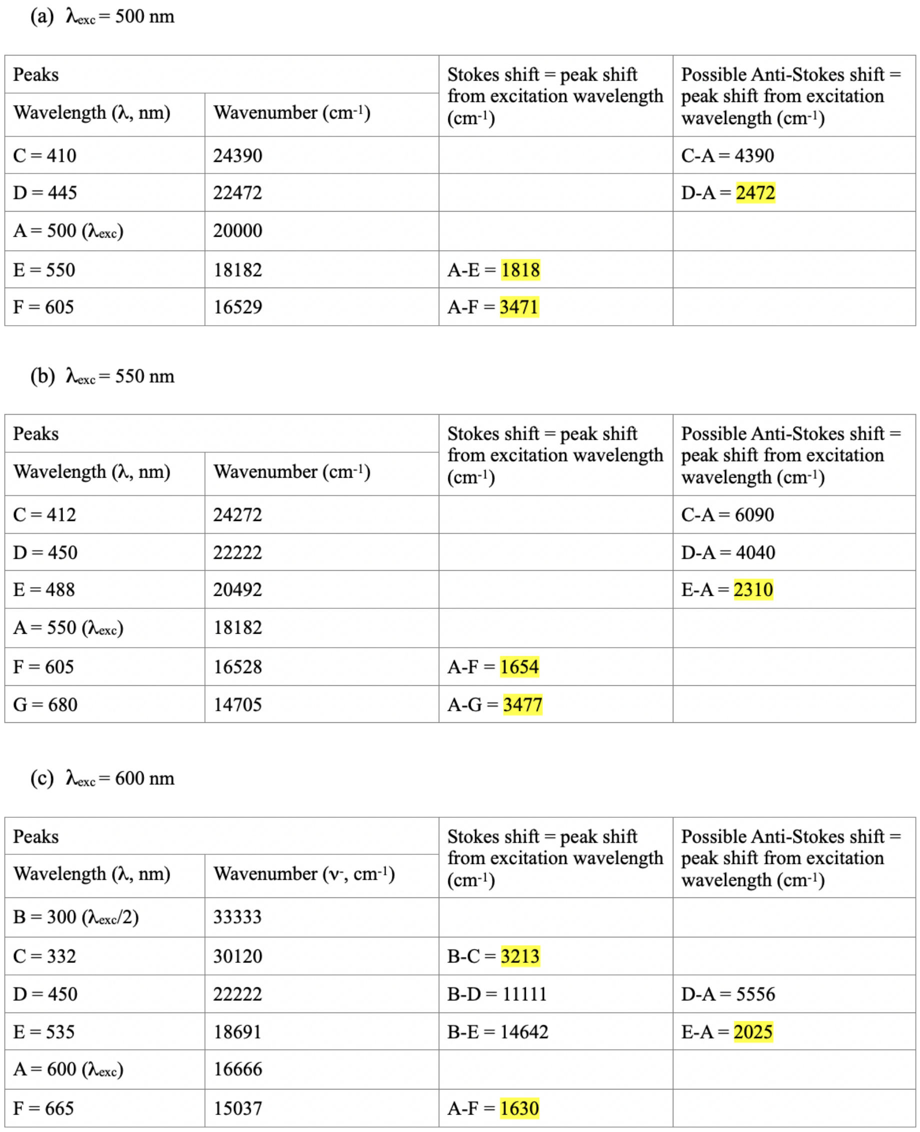
Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
A = 275 (λ_{exc}/2)	36364		
C = 303	33003	A-C = 3361	
D = 325	30769	A-D = 5595	
E = 411	24331	A-E = 12033	E-B = 6149
F = 450	22222	A-F = 14142	F-B = 4040
G = 485	20619	A-G = 15745	G-B = 2437
B = 550 (λ_{exc})	18182		
H = 615	16260	B-H = 1922	
I = 650	15385	B-I = 2797	
J = 680	14706	B-J = 3476	

(c) λ_{exc} = 600 nm



Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
A = 300 (λ_{exc}/2)	33333		
C = 325	30769	A-C = 2564	
D = 410	24390	A-D = 8943	
E = 430	23256	A-E = 10077	
F = 450	22222	A-F = 11111	F-B = 5555
G = 495	20202	A-G = 13131	G-B = 3535
H = 535	18692	A-H = 14641	H-B = 2025
B = 600 (λ_{exc})	16667		
I = 660	15152	B-I = 1515	
J=700	14286	B-J = 2381	
K=741	13495	B-K = 3172	

Table S2 (part 2): Peak position, Stokes shift and Anti-Stokes shift calculated from solution of ethanol (1) and water (about 40% + 60%) after excitation at different wavelengths: (b) 550 nm (c) 600 nm. Here, ”A” represents the second harmonic wavelength of excitation (B).



(a) $\lambda_{exc} = 500$ nm

Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
C = 410	24390		C-A = 4390
D = 445	22472		D-A = 2472
A = 500 (λ_{exc})	20000		
E = 550	18182	A-E = 1818	
F = 605	16529	A-F = 3471	

(b) $\lambda_{exc} = 550$ nm

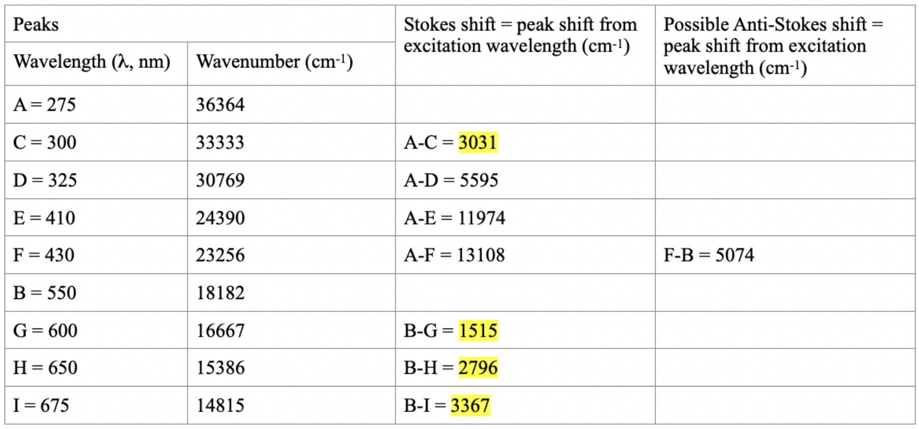
Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
C = 412	24272		C-A = 6090
D = 450	22222		D-A = 4040
E = 488	20492		E-A = 2310
A = 550 (λ_{exc})	18182		
F = 605	16528	A-F = 1654	
G = 680	14705	A-G = 3477	

(c) $\lambda_{exc} = 600$ nm

Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber ($\bar{\nu}$, cm^{-1})		
B = 300 ($\lambda_{exc}/2$)	33333		
C = 332	30120	B-C = 3213	
D = 450	22222	B-D = 11111	D-A = 5556
E = 535	18691	B-E = 14642	E-A = 2025
A = 600 (λ_{exc})	16666		
F = 665	15037	A-F = 1630	

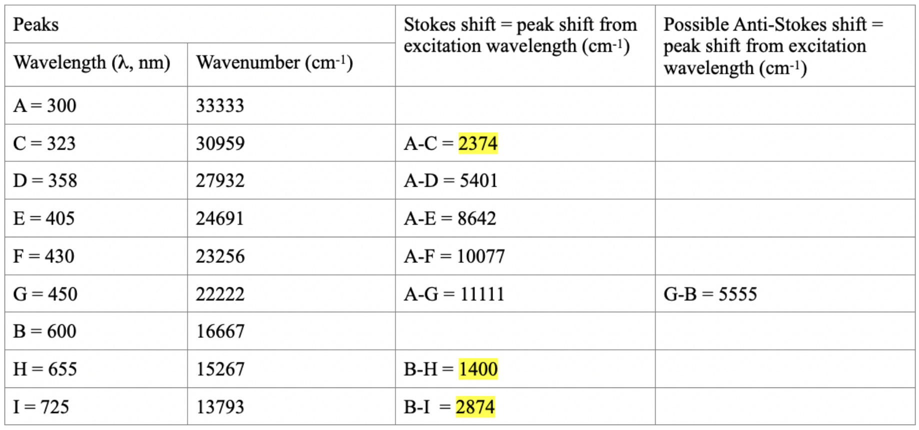
Table S3: Peak position, Stokes shift and Anti-Stokes shift calculated from water after excitation at different wavelengths: (a) 500 nm, (b) 550 nm (c) 600 nm. Here, ”B” represents the second harmonic wavelength of excitation (A).

(a) $\lambda_{exc} = 550$ nm



Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
A = 275	36364		
C = 300	33333	A-C = 3031	
D = 325	30769	A-D = 5595	
E = 410	24390	A-E = 11974	
F = 430	23256	A-F = 13108	F-B = 5074
B = 550	18182		
G = 600	16667	B-G = 1515	
H = 650	15386	B-H = 2796	
I = 675	14815	B-I = 3367	

(b) $\lambda_{exc} = 600$ nm



Peaks		Stokes shift = peak shift from excitation wavelength (cm^{-1})	Possible Anti-Stokes shift = peak shift from excitation wavelength (cm^{-1})
Wavelength (λ, nm)	Wavenumber (cm^{-1})		
A = 300	33333		
C = 323	30959	A-C = 2374	
D = 358	27932	A-D = 5401	
E = 405	24691	A-E = 8642	
F = 430	23256	A-F = 10077	
G = 450	22222	A-G = 11111	G-B = 5555
B = 600	16667		
H = 655	15267	B-H = 1400	
I = 725	13793	B-I = 2874	

Table S4: Peak position, Stokes shift and Anti-Stokes shift calculated from ethanol (2) after excitation at different wavelengths: (a) 550 (b) 600 nm. Here, ”A” represents the second harmonic wavelength of excitation (B).

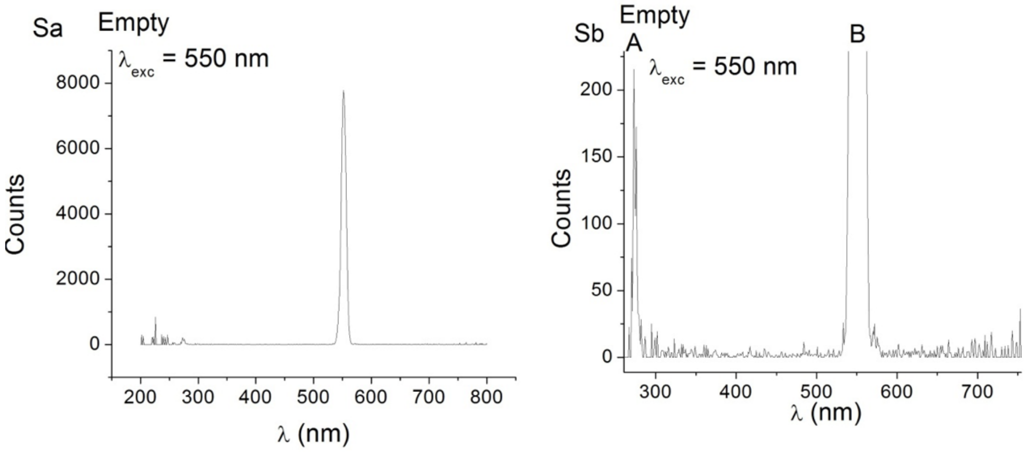


Figure A.7: Spectrum (Sa) of empty cuvette after excitation at 550 nm and its expanded form (Sb). The symbol (A) stands for the position of the second harmonic wavelength of excitation, and the symbol (B) stands for the position of the direct excitation. An appreciable phonon emission peak could not be observed.

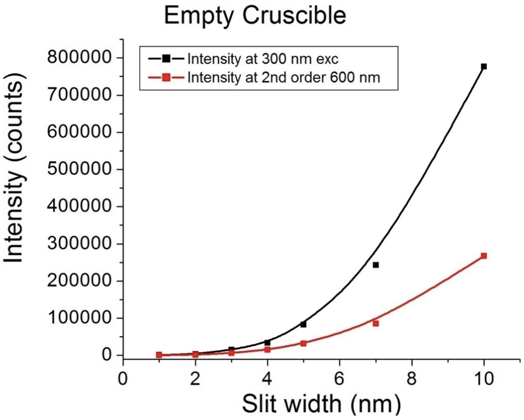


Figure A.8: Intensity versus slit width for an empty crucible. The wavelength for direct excitation is fixed at 300 nm, and the wavelength for second order excitation is 600 nm. Intensity increases with slit width, and intensity obtained after direct excitation is more than that after second order excitation.

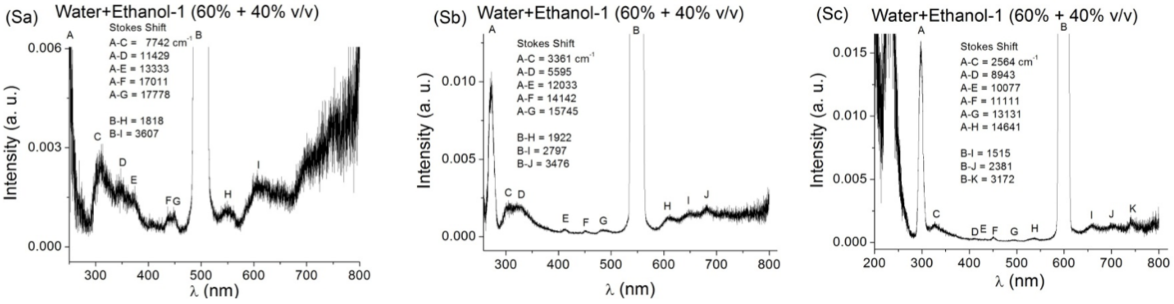


Figure A.9: Expanded spectra of Water + Ethanol (1) (60% + 40%, v/v) (figure 3) after excitations at 500 (Sa), 550 (Sb), or 600 nm (Sc). The symbol (A) stands for the position of the second harmonic wavelength of excitation, and the symbol (B) stands for the position of the direct excitation wavelength. The possible phonon peaks are assigned (expressed in nm (C, D, E, F, G, H, I, J, K)). Stokes and Anti-Stokes shifts are calculated (expressed in cm^{-1}).

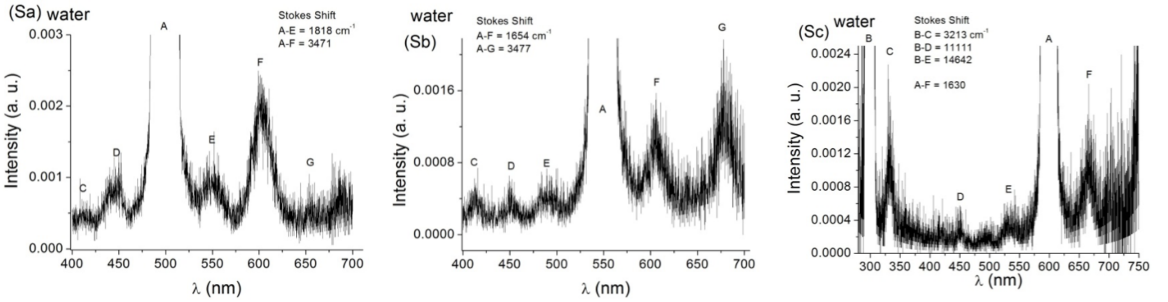


Figure A.10: Expanded spectra of Water (figure 4) after excitations at 500 nm (Sa), 550 nm (Sb), or 600 nm (Sc). The symbol (B) stands for the position of the second harmonic wavelength of excitation, and the symbol (A) stands for the position of the direct excitation wavelength. The possible phonon peaks are assigned (expressed in nm (C, D, E, F, G)). Stokes and Anti-Stokes shifts are calculated (expressed in cm^{-1}).

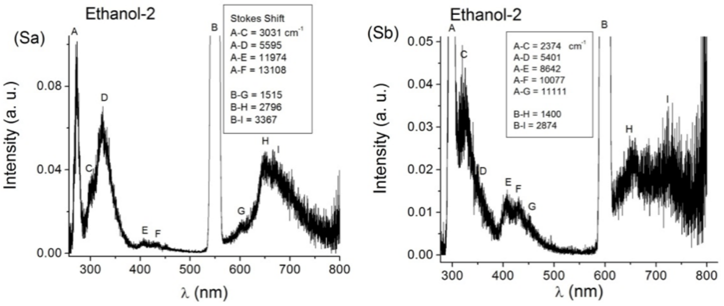


Figure A.11: Expanded spectra of Ethanol (2) (figure 5) after excitations at 500 nm (Sa), 550 nm (Sb), or 600 nm (Sc). The symbol (A) stands for the position of the second harmonic wavelength of excitation, and the symbol (B) stands for the position of the direct excitation wavelength. The possible phonon peaks are assigned (expressed in nm (C, D, E, F, G, H, I)). Stokes and Anti-Stokes shifts are calculated (expressed in cm^{-1}).

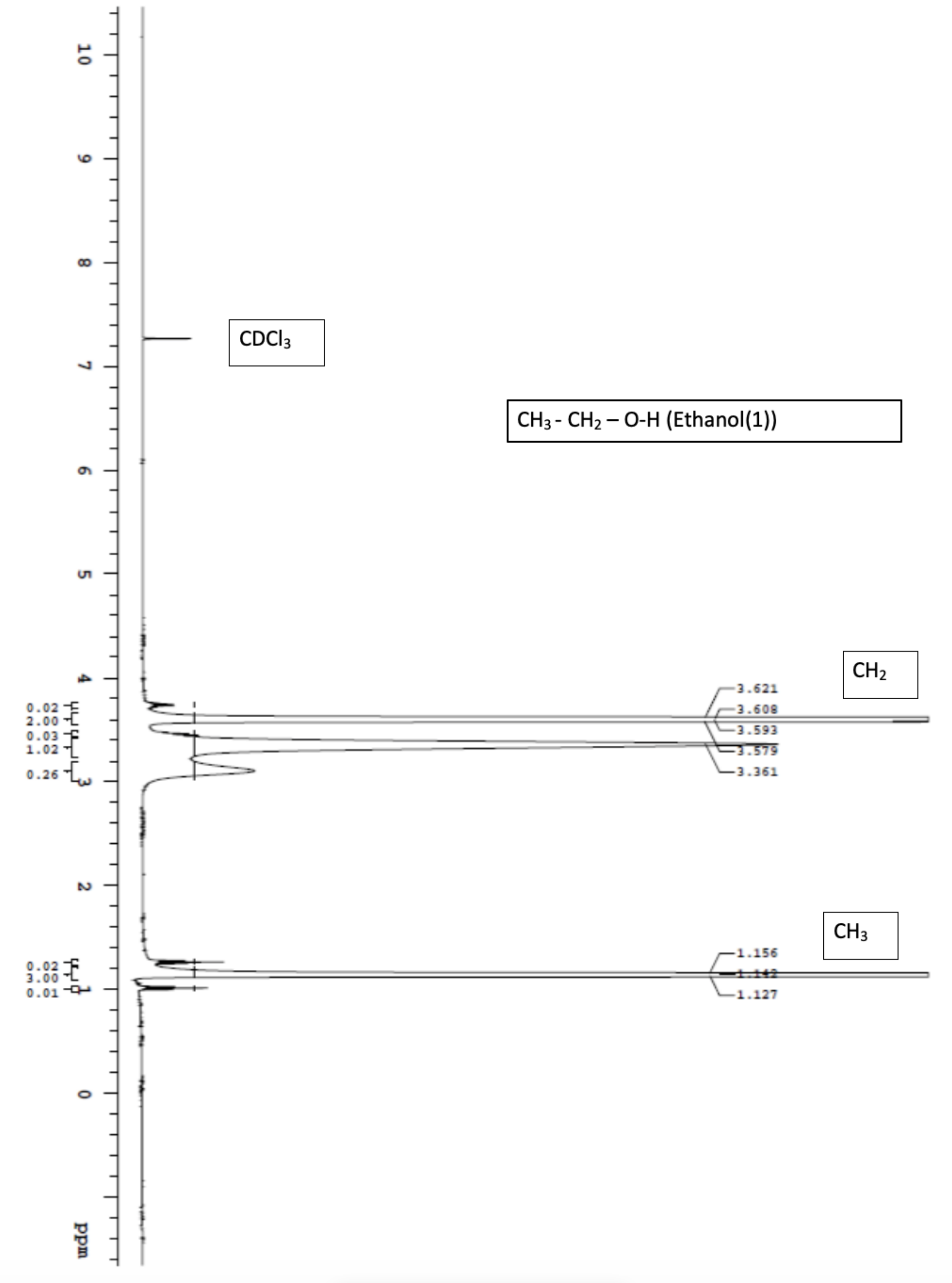


Figure A.12: ^{1}H NMR data of ethanol (1) in CDCl$_3$ medium.

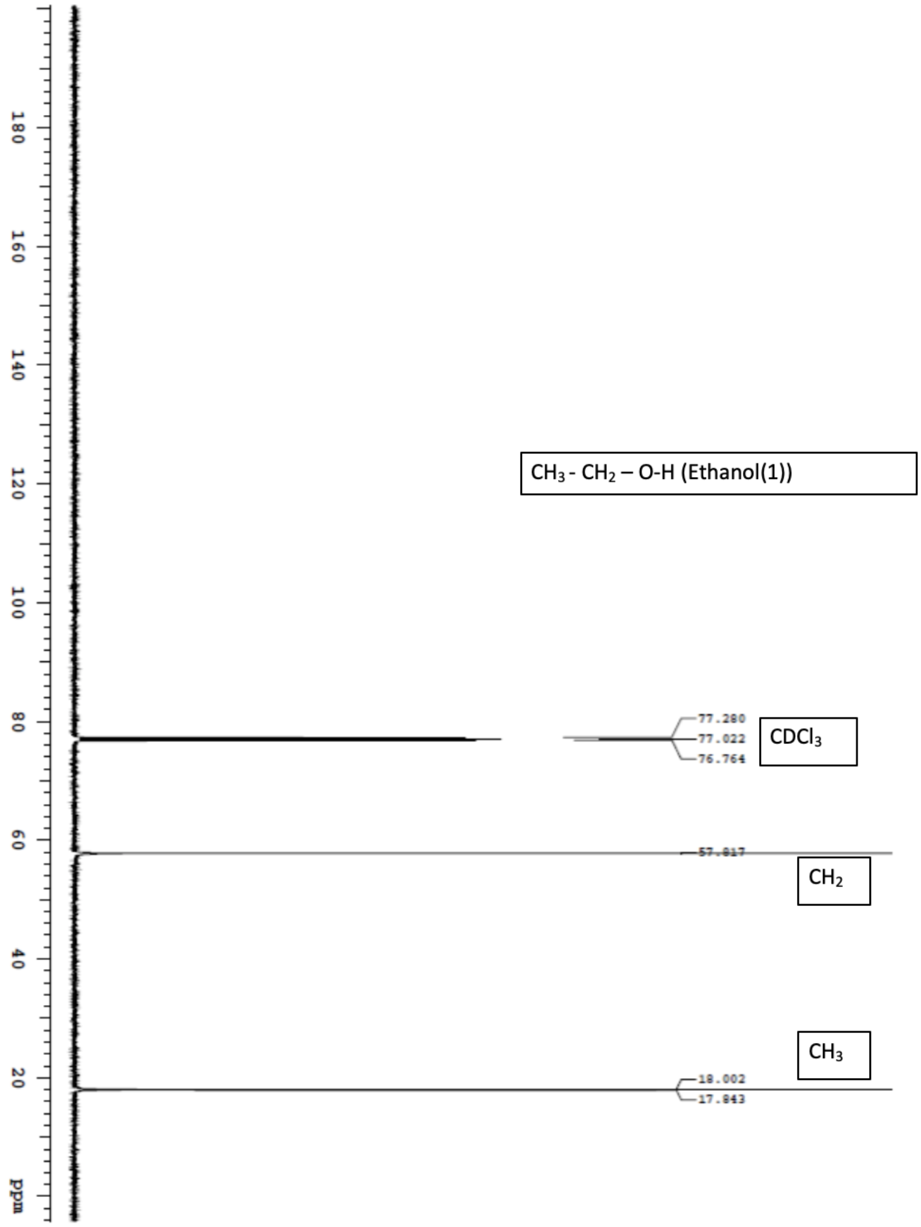


Figure A.13: ^{13}C NMR data of ethanol (1) in $CDCl_3$ medium.

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