

High-efficiency stimulated Raman scattering from alcohols: theory and experiments

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The coherent Raman emission from primary alcohols [CH₃(CH₂)_nOH, *n* = 0–10], 2-propyl alcohol and *tert*-butyl alcohol was studied using a frequency-doubled Nd:YAG pump laser (532 nm). We show that increases in the chain length (CH₂ groups) and the number of CH₃ groups in the alcohols (CH₃ > CH₂) enhance the Raman emission efficiency. Theoretical density functional theory (DFT) calculations and frequency scaling allow one to associate the vibrational wavenumbers with the molecular fragment responsible for the vibration. We obtained good agreement between the observed phenomena and the predictions of the theory. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: stimulated Raman scattering; primary alcohols

INTRODUCTION

Stimulated Raman scattering (SRS) has been widely studied during the last 20 years for its potential applications in the improvement of the beam quality of laser light,¹ temperature measurement in oceanic and atmospheric studies² and generation of coherent light different from the source light.³ Because of its very large gain coefficient, the vibrational transition of gases such as H₂ at a pressure of several atmospheres and a temperature of ~300 K has been an attractive candidate for the efficient Raman conversion of a laser to a Stokes wavenumber shift.^{4,5} Other liquid substance has been tested in SRS, such as water.⁶ In this case, high efficiency (~13%) has been reported.⁷ Consequently, when stimulated by using a high-gain medium or a cavity, a Raman source can provide a high-gain light output at wavenumbers difficult to achieve through other means.⁸ This way of generating coherent light is particularly useful in medical applications, as, for example, the important application in laser photo-dynamic therapy (PDT).⁹

Raman spectroscopy and quantum mechanical calculation methods have found widespread application in recent years in both academic and industrial research and

development.¹⁰ High-level electronic and vibrational structure calculation methods have found increasing use in optical properties studies.¹¹

Despite this evident success, there are still unanswered questions concerning the SRS efficiency of different kinds of materials and how the molecular structure must be changed in order to make better SRS materials. Alcohols have a particularly interesting behavior. In a short-chain alcohol, the interactions between molecules are dominated by hydrogen bonds. However, in long-chain alcohols, the OH group is strongly attracted to water, but the long carbon chain is repelled. They exhibit characteristic intense Raman bands in the region around 2900 cm⁻¹. For this reason, long-chain alcohols are potential SRS generators in the red and near-infrared region of the spectra when pumping by a visible laser. Alcohols have been used as SRS generators before, but the relations between molecular properties and SRS generation has not been considered before in these systems.

In this work, we performed an experimental and theoretical study of SRS generation by liquid alcohols [CH₃(CH₂)_nOH, *n* = 0–10] excited by frequency-doubled Nd:YAG laser radiation. We show that the efficiency of SRS generation is improved by two factors: the chain length (CH₂ groups) and the number of CH₃ groups within the alcohol molecule. The SRS efficiency can be enhanced linearly with the number of CH₂ groups added to the chain and nearly doubles for each CH₃ group added. Calculations performed using density functional theory

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(DFT) confirmed the experimental observations. The DFT calculations reproduce fairly well the Raman spectra of the alcohols and allow one to assign the characteristic bands associated with the mechanisms of the SRS effect.

THEORETICAL

Raman scattering is the result of an inelastic collision between a photon and a particle. A Raman-active medium is able to couple wavenumbers that differ by the wavenumber of the molecular vibrations. This corresponds to the more familiar quantum mechanical interpretation of Raman scattering, in which the energy absorbed by the molecules is the difference in energy between the absorbed pump and the emitted Stokes photons.¹² Energy transfer between the particle and photon leads to absorption of the photon and emission of another.¹³ The wavenumber of the emitted photon can be lower (a Stokes transition) or higher (an anti-Stokes transition) depending on the physical properties of the system. The difference in the energies of the incident and the emitted photons corresponds to the vibrational and rotational energy levels of the molecule ($\nu_V = \nu_P - \nu_S$).

The generation of stimulated Raman scattering is characterized by exponential light amplification described by

$$I_S(l) = I_S(0)e^{g_S I_P(0)l - \alpha l} \quad (1)$$

where I_S is the Raman emission, g_S is the Raman gain factor, I_P is the pump laser, l is the interaction length, α is the linear absorption coefficient and $I_S(0)$ is the spontaneous Stokes contribution. Large amplification values are commonly observed, bringing the scattered intensity up to the level of the laser intensity. In fact, conversion efficiencies of laser into scattered light of up to 90% have been measured.¹⁴ As can be seen from Eqn (1), the amplification is determined by the gain factor g_S , the incident light and the length of the medium. As we show below, increasing the length of the chain and the number of CH₃ groups in the alcohols molecules enhances the Raman conversion efficiency.

The vibrational spectra of alcohols have been investigated for many years. They are relatively complicated owing to their size and also anharmonic effects giving rise to the mixing of vibrations. Moreover, the occurrence of hydrogen bond vibrations influences the structure of the spectra in the high-wavenumber region. In the case of alcohols, overtones of vibrations of the CH₃ group are located very close to the fundamental vibrations observed for CH₃ and CH₂ groups and they have the same symmetry, which results in Fermi resonance (FR) effects. In this work, we performed experimental investigations on the liquid primary alcohols in the homologous series to explain the changes in these optical properties along with the increasing number of substituted CH₂ groups. Other alcohols, secondary (2-propyl) and tertiary (*tert*-butyl), were studied in order to describe the influence of the ramifications in the principal chain and the number of CH₃ groups.

To confirm the experimental findings, we performed DFT calculations. All DFT calculations were carried out by using Gaussian 98 package.¹⁵ The 6-31G + +G(d,p) basis set was used with the B3-LYP exchange correlation functional. As B3-LYP at the level used overestimates the vibrational wavenumbers by about 5%, we applied the appropriate scaling factor. The scaling factor suggested in the literature for the B3-LYP functional corresponds to a frequency scale factor of 0.963.¹⁶

In a first step, DFT calculations (geometry optimization and vibrational wavenumber) were performed in order to obtain the Gaussian 98 output file for all alcohols used in the experiments. In a second step, using the previously estimated Gaussian 98 output file, the Raman spectral data were calculated by applying the SWizard program,¹⁷ revision 3.1, and the pseudo-Voigt model. The half-bandwidths, $D_{1/2,1}$, were taken to be equal to 10 cm⁻¹. Subsequently, the vibrational bands were assigned using the ALP-Vibro program,¹⁸ revision 1.14, and the Raman band calculated by SWizard on the same Gaussian 98 output file.

EXPERIMENTAL

Figure 1 shows the experimental set-up used for SRS relative measurements. The measurement of SRS emission in alcohols was related to the Raman emission of water (648.02 nm). The excitation source was a Q-switched Nd:YAG laser (Continuum Surlite II) with pulses of 10 ns and wavelength 532 nm. The mean energy per pulse was ~10 mJ. With a 50:50 beamsplitter, two beams with approximately the same energy were obtained; these beams were collimated into the test and reference samples using lenses L₁, L₂, L₃ and L₄. Behind the samples, we used a pass-band optical filter in order to attenuate the excitation beam. Thanks to these filters, the photodiodes D₁ and D₂ (Thorlabs Det-110) detected only the stimulated Raman emission.

We used a digital scope to record the maximum stimulated Raman emission intensity generated by the

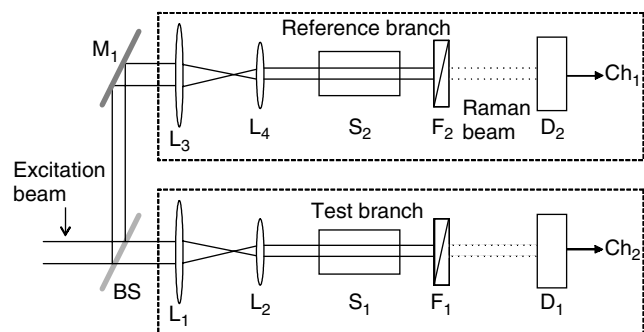


Figure 1. Experimental set-up consisting of a reference and sample branch, a beamsplitter (BS), a mirror (M₁), collimating lenses (L₁, L₂, L₃ and L₄), sample and reference cells, interference filters (F₁ and F₂) and semiconductor detectors (D₁ and D₂).

reference and test cells. Test samples were contained in a glass cell of 10 cm pathlength.

The alcohols used in the experiments were of analytical grade (Merck). The reference sample was a 10 cm distilled water column. All measurements were performed relative to the water sample. The wavelength of the SRS emission was determined by using an optical fiber spectrometer.

RESULTS AND DISCUSSION

The SRS Stokes emission wavelength measured with the optical fiber spectrometer is shown in Table 1. Using these values, we obtained the experimental vibrational wavenumbers ν_V which correspond to the difference in the energies of the incident and emitted photons (see Fig. 2). Figure 2 also shows the vibrational wavenumbers calculated using the DFT approximation. We obtained good agreement between the theoretical predictions and the experimental results. These values are also in good agreement with previous measurements.¹⁹ The correlation between the

Table 1. SRS emission wavelengths for the different alcohols studied

| Alcohol | Wavelength nm |
|---------|---------------|
| Methyl | 626.31 |
| Ethyl | 629.66 |
| Propyl | 627.98 |
| Butyl | 627.31 |
| Hexyl | 627.98 |
| Heptyl | 626.98 |
| Octyl | 627.31 |
| Nonyl | 626.64 |
| Decyl | 626.98 |

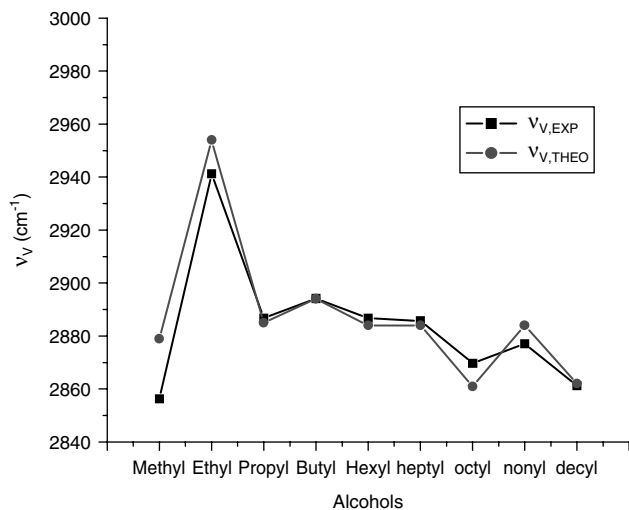


Figure 2. Wavenumber displacement with the alcohol length measured with the optical fiber spectrometer.

calculated and observed vibrational wavenumbers allows confident assignment of the values of the fundamental bands in the fingerprint region using the ALP-Vibro program.

Figure 3 shows schematics of the molecular structures of methyl (A), ethyl (B), decyl (C), 2-propyl (D) and *tert*-butyl (E) alcohols. Methyl alcohol has a symmetrical vibration at ~ 2830 cm⁻¹, which corresponds to CH₃ stretching as shown in Fig. 3(A). For ethyl alcohol, vibration modes of the CH₃ stretching appear at ~ 2927 cm⁻¹.

They exhibit a modest coupling with the CH₂ stretching mode [Fig. 3(B)]. Starting with propyl alcohol, the CH₂ stretching vibration becomes more important as the length of the chain increases. The CH₂ stretching is coupled with the length of the chain acting as a tuned oscillator [Fig. 3(C)]. When adding CH₃ groups such as 2-propyl [Fig. 3(D)] and *tert*-butyl alcohols [Fig. 3(E)], the stronger vibrational coupling increases the Raman efficiency. In Figure 4(A) shows the theoretical calculations of the Raman band strength for different alcohols relative to OH symmetric stretching vibrations. The theoretical calculations predict an increase in the vibrational intensity per added CH₂. This effect can be crucial to the enhancement in the SRS emission. In fact, the experimental result confirms this prediction. Figure 4(B) plots experimental SRS emission strength values relative to water for alcohols with increasing numbers of CH₂ groups. The efficiency of the SRS emission increases nearly linearly with the number of CH₂ groups added. For comparison with the results obtained for alcohols, we also performed measurements of the relative Raman emission efficiency of alkanes [see Fig. 4(B)]. These molecules exhibit a larger relative Raman efficiency and a similar dependence on the number of CH₂ groups. We also note that for alkanes no changes in the stimulated Raman emission wavelength are observed. The different molecules emit at 625 nm independently on the number of CH₂ groups. The larger efficiency and the wavelength independence are understood

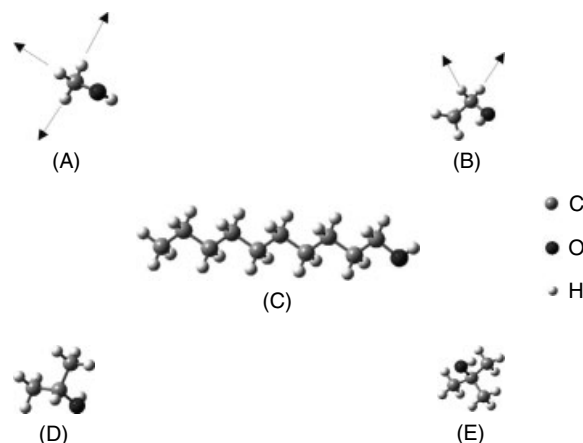


Figure 3. Molecular structures of (A) methyl, (B) ethyl, (C) 2-propyl, (D) *tert*-butyl and (E) decyl alcohols. The direction of the main stretching mode are indicated in (A) and (B).

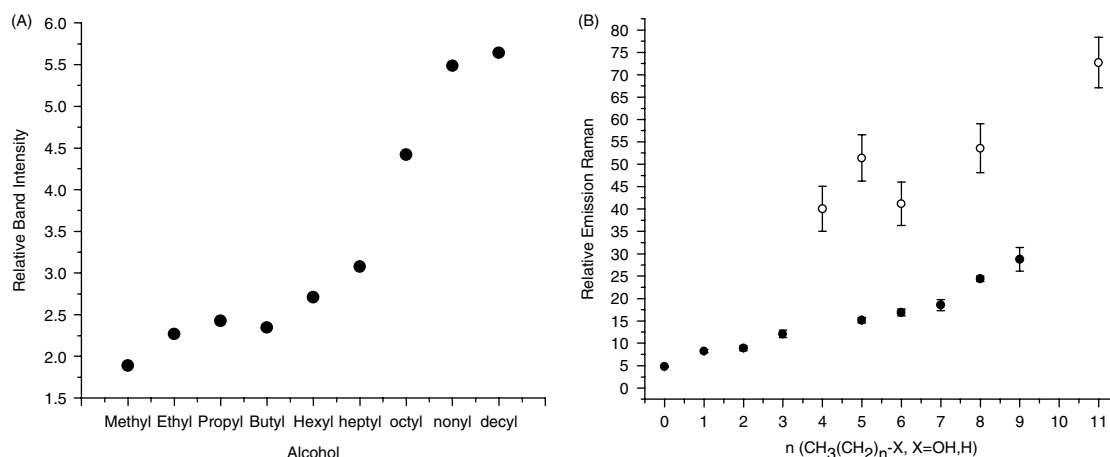


Figure 4. (A) Theoretical Raman intensity values related to the SRS process and relative to the OH symmetric stretching vibration of water. (B) Experimental relative efficiency values of SRS in alcohols (●) and alkenes (○). An increase in the emission with the length of the chain is observed.

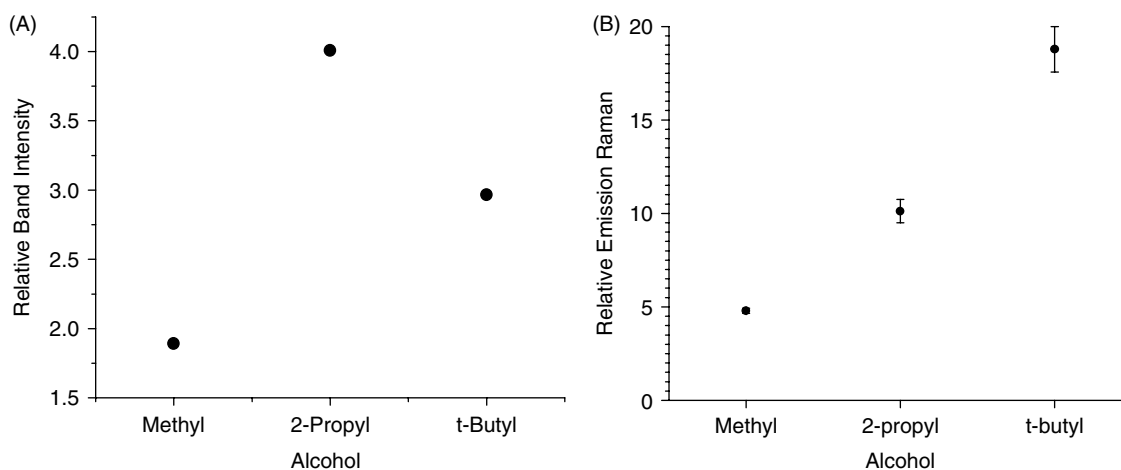


Figure 5. (A) Theoretical Raman intensity values related to the SRS process and relative to the OH symmetric stretching vibration of water. (B) Experimental relative efficiency values of SRS in alcohols. An increase in the emission with number of CH₃ groups is observed.

as the effect of the CH₃ group on each extreme of the molecule and the symmetry of the alkanes compared with the alcohols.

For alcohols, the SRS efficiency is enhanced when the number of CH₃ groups increases. Figure 5(A) shows the theoretical predictions of the Raman band strength for the primary, secondary and tertiary alcohols. Figure 5(B) plots the SRS emission strength values relative to water for alcohols with increasing numbers of CH₃ groups. We observe that adding one CH₃ group doubles the SRS efficiency. A fourfold increase is observed on adding two CH₃ groups. Although the theoretical model does not reproduce exactly the observed increase, the general growing dependence is shown.

We associate the increase in the SRS efficiency with increasing number of CH₂ and CH₃ groups to the increase in strength of the Raman band of the molecule and

also to the intermolecular interaction in alcohols. The OH group can form hydrogen bonds as usually happens with water molecules. The structural and dynamic properties of methyl, ethyl and propyl alcohols are strongly influenced by intermolecular hydrogen bonding and it significantly affects solvent properties such as solubility, boiling-points and surface tension. Because of this in small alcohols, linear winding chains basically constitute the structure of the liquid with averages of close to two hydrogen bonds per molecule.²⁰ In contrast, large alcohol molecules are somewhat frustrated by packing and steric effects in making these hydrogen bonds.²¹ In fact, in alcohols with a larger chain, the solubility in water decreases because the hydrophobic part of the molecule dominates the intermolecular interaction (dispersion forces). Dispersion forces not only bring molecules together but also tend

mutually to align or orient them (molecular ordering in liquids), although this orienting effect is usually weak. However, even in the liquid state large molecules are still very much restricted in their motion and in the way they can position themselves with respect to each other. The 16% increase in the available space corresponds to only a 5% increase in the mean intermolecular separation and, as a consequence, the tendency to pack into an ordered lattice persists in the liquid. Experimentally, it is found that for straight-chain alcohols, the cohesive energy increases by between 6 and 7.5 kJ mol⁻¹ per added CH₂ group. These values are confirmed by the theoretical calculations showing near additivity.²² This near additivity was also found here in the relative emission efficiency measurements. The observed tendency for packing of large-chain molecules enhances the coherent interaction of the molecular system with the electromagnetic field increasing the efficiency of SRS generation in comparison with the situation with more disordered small molecules.

CONCLUSIONS

A high conversion efficiency of SRS at ambient temperature from alcohols was observed and analyzed. The DFT calculations reproduce successfully the Raman spectra of the alcohols and allow the assignment of the characteristic bands associated with the mechanism of the SRS effect. We found two factors that affect the emission in these molecules. The efficiency of SRS is increased nearly linearly with each CH₂ group added along the chain and is nearly doubled with each CH₃ group added. We propose that large-chain alcohols with positions substituted with CH₃ groups can be very efficient in frequency conversion. Additionally, this coherent emission of red light is a low-cost alternative in a number of studies that use laser dyes, including medical applications such as photodynamic therapy (PDT). Further work along these lines will be concentrate on synthesizing new molecules with the previously mentioned characteristics and analyzing other effects such as the increase in the length cell and the use of resonant chambers.

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