Comparison between IR Absorption and Raman Scattering Spectra of Liquid and Supercritical 1-Butanol

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Raman spectra of 1-butanol have been obtained at a constant pressure of 500 bar up to 350 °C and along isotherms 250, 300, and 350 °C up to 600 bar. The purpose of the experiment was to compare responses of Raman and IR absorption spectroscopy to the forming of O−H···O bonds in alcohols. As a result, some important inferences were drawn from the experiment. In particular, it has been estimated quantitatively how the intensity of Raman scattering in the region of the OH band depends on the extent of hydrogen bonding. As might be expected, the dependence is much weaker than in the case of the IR absorption. As was shown, the ratio of integrated intensities of bonded molecules in the absorption and scattering spectra is a constant and does not depend on temperature and density. The effect of cooperativity of hydrogen bonds is confirmed. It was also found that even at high pressures, a noticeable amount of nonbonded molecules exists at room temperature.

Introduction

The nature of H-bonded substances, in particular, water, alcohols, organic acids, etc. and their behavior at high temperatures and pressures has attracted much attention especially during the last two decades.[1−8] Apart from promising practical applications of these fluids,[9−13] there is the need to improve our fundamental understanding of the structure of H-bonded fluids and the very phenomenon of hydrogen bonding. Simple alcohols are suitable objects for investigating the effect of temperature and pressure on the extent and character of hydrogen bonding because H-bonded aggregates should have less intricate structures than those, for example, in water or more complex alcohols. Nevertheless, discussion about the probable forms of the aggregates seems to be very far from complete. Approaches have included the use of computer simulations[1,3,5,18−21] that were intensively used as well as diffraction,[4,14−17] NMR,[6,8,18−20] and spectroscopic[5,22−30] techniques. The inferences drawn from these experimental and theoretical studies can be roughly classified into two categories. Some authors predict the existence of relatively small H-bonded clusters, while others believe that H-bonding leads to the formation of long chains of bonded molecules, so that small clusters are only possible at low densities. In this work, we prefer to avoid the discussion of the size and configuration of H-bonded aggregates. Our desire is only to better understand how temperature and pressure influence the extent of hydrogen bonding and how hydrogen bonds reveal themselves in the infrared and Raman spectra of liquid and supercritical alcohols.

Experimental Procedures

High-temperature high-pressure (HTHP) Raman spectra of 99.8% pure 1-butanol (Fisher) were obtained with an Almega (Thermo Nicolet) Raman spectrometer. The spectra were excited by a DPSS laser emitting at 532 nm. A miniature cell with a single sapphire window (8 mm o.d.) based on backscattering (180°) geometry was fixed on the *XYZ* stage in the sample compartment of the spectrometer. The cell has been already described in detail elsewhere.[31,32] It can withstand such severe conditions as 500 °C at 1500 bar. In this work, however, we exploited the cell only up to 375 °C because of the noticeable decomposition of butanol at 400 °C. The spectra were obtained along the isobar at 500 bar up to 375 °C and along three isotherms at 250, 300, and 350 °C up to 600 bar. All the spectra were corrected on the system spectral response and wavelength dependence of the intensity of scattering.

The high-temperature spectra of butanol were complicated by fluorescence arising at temperatures higher than 150−200 °C. Unfortunately, it is a rather frequent case in HTHP Raman experiments. The intensity of the very broad fluorescence band is usually much higher than the intensity of weak Raman scattering, so that a Raman spectrum can be, at worst, completely obscured by the statistical noise from fluorescence. In some cases, this troublesome effect can be diminished, if a sample under study (i.e., some water systems) is exposed for a sufficient time to a temperature above 500 °C. In the case of alcohols, it is not possible because of thermal decomposition at lower temperatures. It was necessary to greatly extend the exposure time at high temperatures to decrease the fluorescence noise. The fluorescence background was eliminated from raw spectra after simulation of the baseline by a polynomial regression, as Figure 1 shows. It is important that all the spectra in the series should be processed exactly in the same way.

The processed spectra were normalized by reducing them to equal areas in the range of 2400−3200 cm^{-1}, in which the stretching modes of C−H groups occur. This step is advisable to account for different exposure times, a change in conditions of scattering at different temperatures and pressures, and

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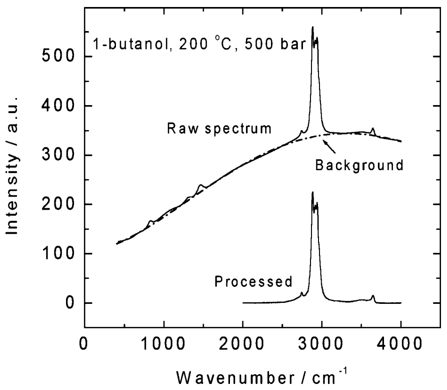

Figure 1. Example of the procedure for removing the fluorescence background from a Raman spectrum.

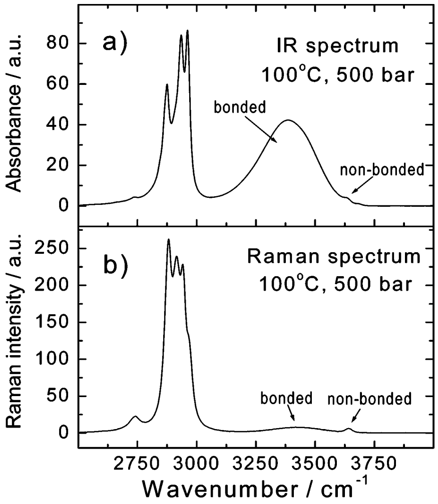

Figure 2. Comparison of IR and Raman spectrum of 1-butanol at identical conditions.

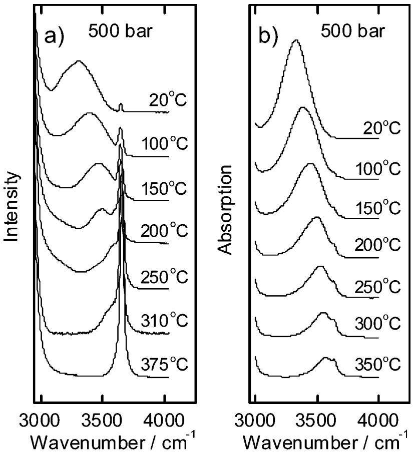

Figure 3. (a) Processed and normalized Raman spectra of 1-butanol in the region of OH stretching vibrations at isobaric heating. (b) IR spectra at practically the same conditions.

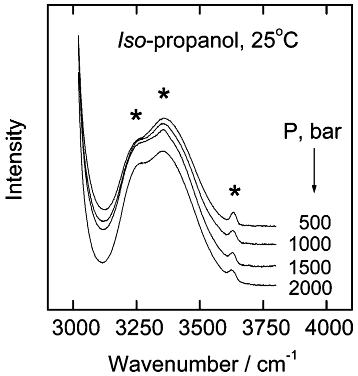

Figure 4. Raman spectra of 2-propanol at room temperature and high pressure. Asterisks indicate specific features of the contours.

deviations from ideal setup geometry because of thermal deformations.

Results and Discussion

Studying a series of simple alcohols with the use of infrared absorption spectroscopy, we were able to describe quantitatively how the extent of hydrogen bonding depends on the parameters of state.[30] Our methodological approach to the problem was based on treating the intensity of the C−H stretching band as an internal standard. It allowed us to find the mole fraction of H-bonded molecules as a function of temperature and pressure, to determine temperature and pressure trends for the absorption coefficient of H-bonded molecules, and to confirm the effect of cooperativity of hydrogen bonds. A valuable feature of the approach is that it is not necessary to know density values and path lengths in the IR cell to obtain the important information.

Despite some important advantages, Raman scattering (unlike absorption spectroscopy) is not a quantitative technique. It does not operate with absolute intensities of scattering, except in specially designed experiments. One can only measure relative intensities either about a line in a spectrum or about an internal or external standard. Besides, the intensity of Raman scattering depends on many factors, which are very difficult if not impossible to control or to make corrections. Therefore, it is a challenging task to find whether the results of the infrared study can be confirmed with the Raman scattering spectroscopy. The task is not simple because the intensity of OH vibrations in the Raman spectrum is much lesser the intensity of OH bands in the infrared spectrum, as is seen in Figure 2. The situation becomes worse for high-temperature spectra as the probability of hydrogen bonding decreases.

Figure 3 demonstrates absorption and scattering spectra in the region of the O−H stretch in the full temperature range. One can see a striking difference in the intensity and shape of the O−H stretching modes obtained with these two methods. Nevertheless, these are vibrational spectra of the same substance at the same parameters of state. It is interesting that IR spectra do not clearly reveal the existence of nonbonded butanol molecules at room temperature and at a pressure of 500 bar, while Raman spectra show this unambiguously. It is also worth mentioning that IR spectra do not show any signs of resolution in the contour of a broad band corresponding to bonded O−H groups. However, the contour is asymmetrical and cannot be approximated with only one symmetrical distribution function. As is seen in Figure 3a, a shoulder at ~3250 cm^{-1} is observed in the Raman spectrum at room temperature (see also Figure 5). That allows us to suggest that there are at least two distinguishable components in the energy distribution of bonded alcohol molecules. The low-frequency shoulder is also observed in other alcohols.[33] It is especially well-manifested in the Raman spectra of 2-propanol obtained at room temperature and at different pressures (Figure 4).[31] The fact of the nonuniform distribution of hydrogen bonds in alcohols has been discussed earlier,[33] but the Raman spectra show it most explicitly. Thus, when studying the phenomenon of hydrogen bonding, the Raman spectroscopy reveals a rather unexpected advantage over IR absorption spectroscopy due to the lower sensitivity of the intensity and width of the OH stretching band to the strength of hydrogen bonds. On the other hand, manifestations of bonded

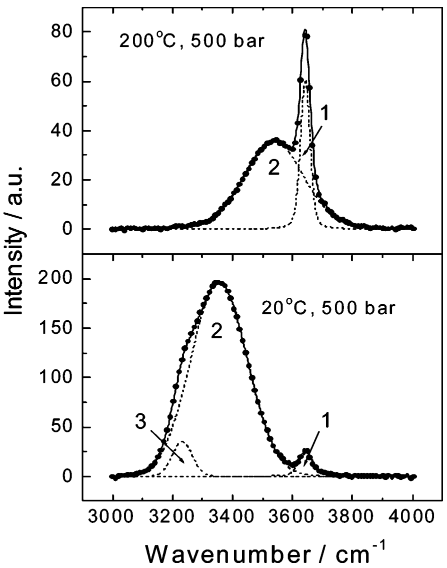

Figure 5. Examples of curve-fitting procedure.

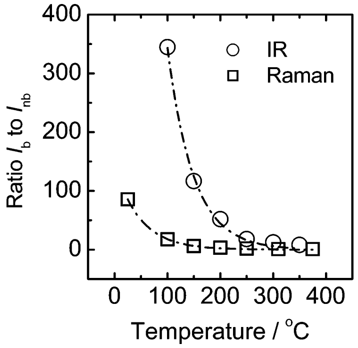

Figure 6. Intensity of absorption and scattering in the region of OH stretching modes of 1-butanol as a function of temperature at a pressure of 500 bar.

molecules in the Raman band of the OH stretching mode are very weak at high temperatures. Hence, the Raman scattering and IR absorption spectroscopy provide truly complementary information on the hydrogen-bond situation.

It is well-known that the intensity of IR absorption is the most sensitive characteristic of the strength of hydrogen bonds.[34] For example, the coefficient of integrated absorption for water decreases by a factor of 25−30 from the state with all H-bonds realized (ice) to the state with practically no hydrogen bonds (water vapor at low density). However, the situation with Raman scattering is uncertain. In general, it is accepted that the intensity of scattering decreases with the weakening of hydrogen bonding. But to what extent? Here, we have an opportunity to compare IR and Raman responses to the change in strength of hydrogen bonding. Let us consider the value $R = (I_b/I_{nb})$ as a characteristic of the strength of hydrogen bonding in butanol. Here, I_b is the integrated intensity of IR absorption or Raman scattering for H-bonded molecules, and I_{nb} is the integrated intensity for nonbonded ones. The values of R for IR absorption can be extracted from our earlier study.[30] To find R for the Raman scattering spectra shown in Figure 3a, we have to apply a curve-fit procedure. Examples of using the procedure are presented in Figure 5. As is seen in Figure 6, the intensity of Raman scattering depends on the probability of hydrogen bonding to a much lesser degree than for IR absorption. Each trend can be accurately described by the exponential function

$$R_{\mathrm{IR,\,Ram}} = A \exp(-t/B) \qquad (1)$$

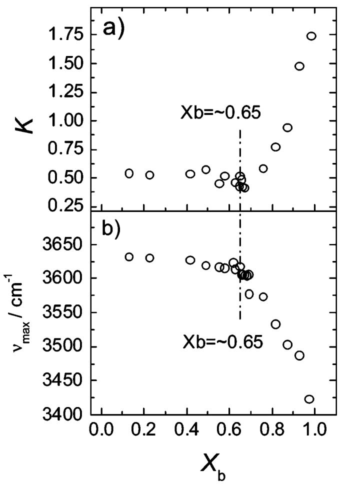

Figure 7. (a) Coefficient of scattering as a function of the extent of hydrogen bonding X_b. (b) The behavior of band positions for bonded molecules.

where t is temperature. For the IR absorption, $A = 2662 \pm 260$ and $B = 49.2 \pm 2.2$, while for the Raman scattering $A = 144 \pm 2.4$ and $B = 48.3 \pm 1.3$.

One can see that in the limits of experimental errors, the exponential factor is, in fact, the same for both methods. Evidently, it is independent of the technique used. Therefore, the ratio R_{IR}/R_{Ram} is simply a constant equal to 18.5 ± 1.9. Obviously, this fundamental experimental fact reflects the ratio of probabilities of IR absorption and Raman scattering on the molecular level. Roughly speaking, the increase in the intensity of IR absorption due to the forming of hydrogen bonds is by a factor of 18−20 higher than in the case of Raman scattering. A theoretical estimate of the difference in the intensities of absorption and scattering can be found in ref 5.

The strong dependence of the absorption intensity on the energy of hydrogen bonds allowed us to demonstrate the phenomenon of the cooperativity of H-bonding.[30] The effect means that each additional molecule added to a chain of bonded molecules enhances the average energy of bonding and, correspondingly, the absorption coefficient.[35] The effect is very important for understanding the behavior of the hydrogen-bonded structural species at high temperatures. With every molecule detached from an H-bonded molecular aggregate under the influence of thermal energy, the further destruction of the aggregate becomes increasingly easier. Thus, we can consider destruction of hydrogen-bonded species as an autocatalytic process.

As shown previously, the dependence of the intensity of Raman scattering on the extent of H-bonding is much weaker. It is interesting to question whether the effect of cooperativity may be demonstrated by analyzing the intensities in Raman spectra.

To answer this question, we need a parameter that characterizes the intensity of scattering per unit of concentration. As stated previously, we cannot use absolute intensities of scattering. However, we can operate relative values. It is easy to see that the parameter $\alpha(I_b/X_b)$ has the same meaning as the absorption coefficient. Here, I_b is again the integrated intensity of scattering by bonded molecules; X_b is their mole fraction; and α is a coefficient that involves density, scattering volume, losses of scattered radiation, and geometry of experiment, in short, everything that influences the intensity of Raman scattering. Obviously, the coefficient of scattering for nonbonded species is $\alpha(I_{nb}/1 - X_b)$. Assuming that the coefficient for nonbonded species is independent of the state of hydrogen bonding, we consider the ratio $K = (I_b(1 - X_b)/I_{nb}X_b)$ as a dimensionless characteristic of the intensity of scattering for bonded OH groups. In this way, we eliminate the influence of all unknown variables and measuring uncertainties. The corrections for wavelength-dependent factors are introduced at the preliminary processing of the spectra.

The behavior of K as a function of the mole function X_b is shown in Figure 7a, which clearly demonstrates the effect of cooperativity. Moreover, despite a larger scatter of experimental points, the effect is even more pronounced than in the case of IR absorption spectroscopy.[30] In the range X_b from 0 to 0.6−0.7, K changes very little or not at all, which may mean that the intensity of scattering for small aggregates, most likely dimers, does not essentially differ from that for monomers.

Exactly as in our IR study,[30] the effect is confirmed by the behavior of the maximum of the O−H band ν_{max} presented in Figure 7b. When $X_b > 0.6-0.7$, as long chains or large rings are formed, the intensity of scattering increases rapidly.

Conclusion

In the conclusion, we wish to draw attention to a few points we were able to clarify. We have confirmed that the intensity of Raman scattering depends on the strength of hydrogen bonds to a much slighter degree than the intensity of IR absorption. However, just this circumstance allowed us to suggest that at low temperatures, even at high pressures, a noticeable amount of nonbonded OH groups exists. Such groups are not seen in IR absorption spectra because they are masked by the strong absorption of bonded OH. It is shown quantitatively that the increase in the intensity of IR absorption due to the forming of hydrogen bonds is by a factor of 18−20 higher than in the case of Raman scattering.

Another inference drawn from the experiment is the fact that the energy distribution of bonded molecules is certainly discrete. At least two distinguishable species may be recognized at low temperatures in the contours of the OH stretching bands of H-bonded 1-butanol and 2-propanol. Unfortunately, we cannot definitively state the nature of these species. Perhaps, the low-frequency, high-energy component indicates the presence of rings in which the effect of cooperativity should be rather strong.

Despite a weaker dependence of the Raman scattering intensity on the energy of hydrogen bonds, the Raman spectra confirm the existence of the cooperativity effect. The coefficient of scattering K, which we suggested in this study to use as a characteristic of the intensity of scattering, shows accelerated growth as the mole fraction of the bonded OH groups exceeds 0.6−0.7. It seems that above this value, an avalanche-like process of forming long chains or large rings takes place. Such a phenomenon resembles very much the surmounting of a percolation threshold.

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Supporting Information Available: Raman and IR spectra of 1-butanol at high pressures and temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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