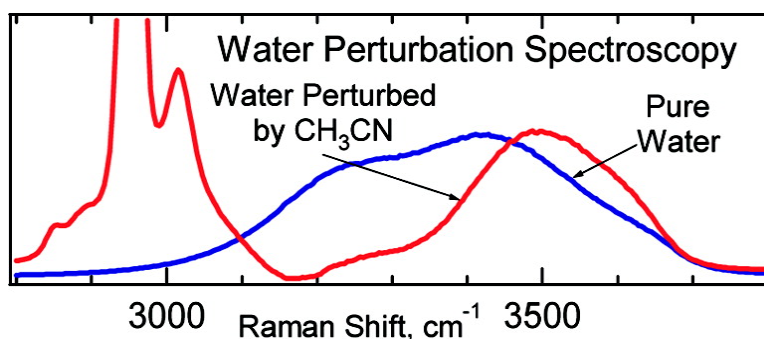## Communication

Solute-Induced Perturbations of Solvent-Shell Molecules Observed Using Multivariate Raman Curve Resolution

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Solute-Induced Perturbations of Solvent-Shell Molecules Observed Using Multivariate Raman Curve Resolution

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The biological, environmental, and industrial importance of liquid solutions depends essentially on intermolecular interactions. Such interactions can induce large changes in chemical equilibria and dynamics, as exemplified by water-induced changes in the structure and function of proteins. Previous experimental studies of solute−solvent interactions have focused primarily on changes in *solute* properties. Here we demonstrate a new approach to probing liquid intermolecular interactions by measuring the influence of a solute on *solvent* structure. The results reveal vibrational spectroscopic changes in solvation-shells composed of either water or 1,2-dichloroethane (DCE) around various solutes, thus providing a new view of solvation, and a challenge to theoretical and simulation modeling strategies. Moreover, the present approach compliments recent femtosecond 2D IR experiments aimed at tracking vibrational energy migration, dephasing, and relaxation processes in water and other systems.[1]

The present method differs in important respects from previous difference,[2] solvent-shell,[3,4] and solvent perturbation spectroscopies.[5,6] In particular, the present approach makes no assumptions regarding the spectral shape of either the solvent or the solute-induced spectra. Moreover, unlike traditional difference spectroscopies, the extracted spectra contain only positive spectral features corresponding to solute-induced vibrational bands. Also, the present method yields spectral features associated with the solvation-shell around isolated (dilute) solute molecules and so are not in general equivalent to spectra obtained from high concentration solutions.[7,8] More specifically, the solute-induced spectra contain vibrational features arising both from the solute itself *and from any solvent molecules whose vibrational spectra are significantly perturbed by the solute*.

The input Raman spectra are obtained from a series of solutions of different concentrations (typically 1−5 wt %). Multivariate curve resolution (MCR)[9] is used to extract bulk solvent and solute-induced spectra from each such series of solution spectra. The following key assumptions are invoked in applying MCR to extract solute-correlated (solvent perturbation) contributions to the measured spectra. Each set of spectra is assumed to consist of a linear combination of two components, each of which have non-negative spectral intensities and weights; one of the two spectral components is necessarily equivalent to the pure solvent (zero solute concentration) spectrum, while the other contains solute-correlated spectral features. The assumption that there are only two spectral components implies that the solute concentration is sufficiently low and that solute−solute interactions are negligible. The validity of this assumption is confirmed by the success of the MCR procedure, as additional components would be required to describe the input spectra if solute−solute interactions were significant. Further details of the experimental and MCR procedures are provided as Supporting Information.

Figure 1 shows results obtained from solutions of acetonitrile (CH₃CN) in water (H₂O). The lower two Raman spectra are those of the corresponding pure liquids (both collected under identical
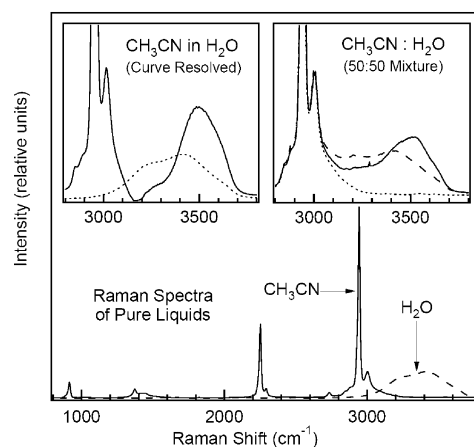

Figure 1. Vibrational (Raman) spectra derived from pure acetonitrile and water (lower panel) are compared with those obtained from aqueous acetonitrile solutions (upper panels). The new higher frequency OH peak appearing in both upper spectra is that of about one water molecule associated with each acetonitrile (see text for details).

conditions). Thus, the relative areas of the broad water OH stretch band (peaked at ∼3400 cm⁻¹) and the acetonitrile CH stretch band (peaked at ∼2942 cm⁻¹), combined with the concentrations of each of the pure liquids (55.55 and 19.15 M, respectively), imply that the effective Raman cross section (area) of the acetonitrile CH band is approximately 1.74 times larger than that of the water OH band. The spectra in the two upper panels are obtained from solutions containing both acetonitrile and water (solid curves) as well as pure water and pure acetonitrile (dotted curves) and an equimolar arithmetic sum of the two pure liquid spectra (dashed curve). The intensity of the pure acetonitrile and pure water spectra (dotted curves) in the upper panels are scaled to appear as they would if the two pure liquids had the same molarity (i.e., the CH/OH band area ratio is 1.74).

The solid curve in the upper-left panel in Figure 1 is the acetonitrile-induced spectrum extracted from the dilute aqueous solutions using MCR. This spectrum evidently contains features associated with acetonitrile as well as a new OH band of higher frequency and narrower width than that of bulk water. The relative intensities of the pure water and acetonitrile-induced OH bands implies that the perturbed water OH band arises from approximately one (more precisely ∼1.2) water molecule per acetonitrile molecule (assuming that the OH Raman cross section is approximately constant, as confirmed below). The higher frequency of the new OH band suggests that this special (perturbed) water molecule has a weaker hydrogen bond than in pure water.

The solid curve in the upper-right panel in Figure 1 is the raw Raman spectrum of a solution containing an equimolar mixture of acetonitrile and water. The equimolar spectrum clearly differs from that of the arithmetic sum of the two pure liquid spectra (dashed
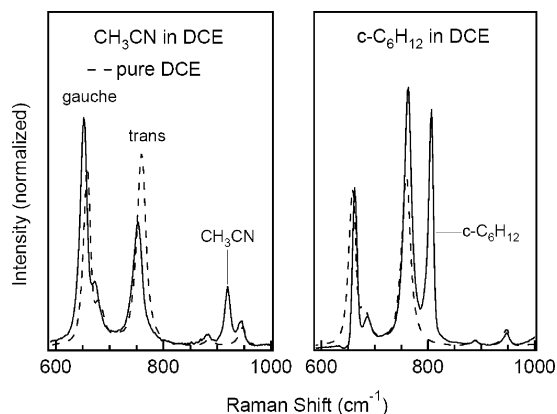
Figure 2. Vibrational (Raman) spectra derived from solutions of either acetonitrile or cyclohexane in DCE. The solid curves are solute-induced spectra (and the indicated peaks correspond to solute vibrational bands). The dashed spectra pertain to pure DCE (see text for details).

curve). Note that the OH band in the equimolar mixture spectrum contains a higher frequency feature reminiscent of that in the solute-induced spectrum obtained from dilute acetonitrile solutions (upper left panel). Thus, although the water associated with acetonitrile in these two systems is in a different environment (i.e., at a different acetonitrile concentration), in both cases the water evidently is in a more weakly hydrogen bonded state. Note that the comparable intensities of the two OH bands in the upper-right panel confirm that the OH Raman cross section is approximately independent of acetonitrile concentration (since the relative areas of these two bands reflect the relative Raman scattering intensities of an OH in pure water and in an equimolar mixture of water and acetonitrile).

Additional results have been obtained for aqueous solutions of acetone, pyridine, and tetrahydrofuran (see the Supporting Information). The acetone solution results are quite similar to those in Figure 1, with a new OH band of comparable magnitude and width but a slightly lower frequency than that shown in the upper-left panel of Figure 1. The aqueous pyridine and tetrahydrofuran solutions are more interesting as they each reveal the presence of two new OH bands. The intensities of the new OH bands suggest that together they again correspond to roughly one special water molecule per solute. Previous computer simulation studies of aqueous pyridine indicate that water hydrogen bonds primarily to N (rather than to the aromatic ring),[10] thus the two OH bands we have observed may correspond to the two inequivalent hydrogens of that one water molecule. However, since the spectrum of water perturbed by acetonitrile has only a single OH band (as illustrated in Figure 1), our solute-induced spectra imply that there is a significant structural and/or dynamic difference between the water molecules that are associated with the N atoms of acetonitrile and pyridine. Further experimental and theoretical studies are clearly needed to distinguish various solute-induced water perturbation mechanisms in these and other aqueous solutions.

Figure 2 shows results obtained for solutions in which 1,2-dichloroethane (DCE) is the solvent, with either a polar (acetonitrile) or a nonpolar (cyclohexane) solute. Note that pure liquid DCE (dashed spectrum) contains a mixture of gauche and trans conformers, each of which give rise to a distinct C−Cl stretch band (and the ratio of the intensities of the two bands is approximately equal to the corresponding conformer concentration ratio).[11] The solid

curves represent the solute-induced spectra extracted from the two dilute solutions (scaled so that all the spectra have approximately the same integrated C−Cl intensity). The different relative intensities of the gauche and trans C−Cl bands in the two solute-induced spectra clearly indicate that the DCE molecules in the solvation shell around acetonitrile have an enhanced gauche population, while those associated with cyclohexane have a higher trans population. Thus, the polar solute (acetonitrile) shifts the DCE equilibrium toward the dipolar gauche state (which has a dipole moment of ~3.12 D), while the nonpolar solute (cyclohexane) shifts the DCE equilibrium toward the nondipolar trans conformer. The relative areas of the solvent and solute bands imply that in both cases only about one DCE molecule in the solvation-shell around each solute has a spectrum that significantly differs from that of pure DCE (more specifically, the integrated area ratios imply that around acetonitrile and cyclohexane there are on the average about 0.74 and 1.35 perturbed DCE molecules, respectively, assuming that the total C−Cl stretch Raman cross sections are approximately the same in both solutions).

In conclusion, multivariate Raman curve resolution has been used to uncover vibrational spectroscopic features associated with perturbations of solvent molecules (water or DCE) by various solutes (acetonitrile, acetone, pyridine, tetrahydrofuran, and cyclohexane). The results reveal new OH stretch bands arising from water molecules associated with polar solutes. The higher frequency of these OH bands suggests that they are more weakly hydrogen bonded than an average bulk water molecule. In some cases, two well resolved OH bands are evident, which may either be due to two inequivalent water structures or two inequivalent hydrogen atoms on a single water molecule. Polar and nonpolar solutes in DCE are found to perturb the gauche−trans isomerization equilibrium of solvent-shell molecules in opposite directions. Further work aimed at better characterizing and understanding the observed solvent-perturbation spectra is in progress, including studies of aqueous salt solutions which compliment recently reported spectroscopic and theoretical studies.[12]

Supporting Information Available: Experimental and MCR analysis details and additional water perturbation spectral results. This material is available free of charge via the Internet at http://pubs.acs.org.

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