

Technical Notes

Development and Validation of Spectroscopic Methods for Monitoring Density Changes in Pressurized Gaseous and Supercritical Fluid Systems

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The further development of new processes utilizing liquid or supercritical CO₂ as a solvent will benefit from the rational design of new CO₂-philes. Understanding solvation structures and mechanisms of these molecules is an important part of this process. In such studies, determining the change in density as a function of the measured thermodynamic conditions (pressure and temperature) provides an excellent means of directly monitoring the solution conditions in the detection volume for a given technique. By integrating spectroscopic peaks, changes in area can be used to determine changes in analyte concentration in the detection volume, and thus, it should be possible to monitor the system density in situ. In the present study, we examine the utility of Raman and NMR spectroscopy as a means of following changes in solution density conditions and validate this approach in pure fluids and gases (N₂ and CO₂) and supercritical fluid mixtures (acetaldehyde vapor in N₂). In addition, we present the design of a simple, inexpensive cell for conducting Raman and NMR measurements under moderate pressure conditions.

Supercritical fluids (SCFs) possess a variety of unique physical properties, making them attractive as solvents for a variety of analytical and synthetic processes and many other applications.^{1–7} Depending on their thermodynamic state, these systems are both gaslike and liquidlike. Like gases, they have low viscosities and are highly compressible. However, like liquids, they are relatively dense and can be used to dissolve a wide variety of compounds. The density, viscosity, and solvating power of the supercritical

fluid solvent can be “tuned” by simply changing the system pressure or temperature, thus allowing control of molecular partitioning, reaction rates, and product distributions. SCFs can be used to reduce the amount of hazardous organic waste in industrial processes by replacing conventional solvents.

A major issue that is relevant to the feasibility of more widespread use of fluid- and gas-based processes is the insolubility of the majority of materials in these media. Although the past decade has focused almost exclusively on the enhanced solubility of fluorocarbon and silicon containing materials in CO₂, the expense of the majority of these systems is prohibitive to their widespread use in industrial processes. A recent focus of this area is the development of hydrocarbon-based CO₂-philes, including surfactants and metal chelating agents. An understanding of the fundamental interactions between these molecules and CO₂, such as the solvation structure and dynamics, are crucial to the design and development of future CO₂-based processes.

Spectroscopic studies provide one of the best approaches for studying these interactions and validating computational results and theoretical models. In such studies, monitoring the solution conditions (temperature, pressure, and density) in the probed volume is necessary to ensure reliability in the interpretation of the spectroscopic results. One example of this is the “density augmentation” phenomenon in which many authors have proposed that solvent molecules cluster around solute molecules, causing an enhanced local density relative to the bulk density under the appropriate solution conditions.^{8–11} This is generally illustrated by plotting some observable (e.g., Stokes shift⁹ or absorbance measurements^{10,11}) as a function of the solution density, which is typically determined through calculations using an equation of state for the fluid of interest. However, it is important to realize that uncertainties in the density calculations (due to pressure or temperature gradients) for a given set of conditions can result in erroneous conclusions. An example of

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this was recently given in the case of the measured NMR chemical shielding of hexane dissolved in CO₂ by Kanakubo et al.¹² In this study, a nonlinearity in the chemical shielding as a function of density was observed. These authors concluded that the nonlinearity was due to inhomogeneous temperature deviations in the sample, although the measured temperature remained constant. NMR has been shown to be an excellent tool for monitoring phase separation in supercritical fluid solutions.^{13–15} However, to the best of our knowledge, no study has examined the utility of using the integrated peak areas from Raman or NMR spectroscopy as a means of monitoring the density changes that occur in gaseous or supercritical fluid states upon changing thermodynamic conditions.

High-pressure spectroscopic experiments such as these require the use of specialized cells that are costly, complex to set up, and are generally designed for one spectroscopic technique. In particular, performing IR spectroscopy at elevated pressures is often difficult, since the most commonly used high-pressure spectroscopic windows, quartz and glass, strongly absorb IR radiation. Diamond windows can be used, but these windows are often prohibitively expensive. These considerations make Raman spectroscopy an attractive alternative technique for examining gaseous and supercritical fluid solutions.¹⁶ In Raman spectroscopy, both the excitation and scattered radiation are generally in the visible region, allowing the use of more economical glass, quartz, and sapphire windows. Like IR spectroscopy, Raman spectroscopy provides information concerning the vibrational and reorientational dynamics in a system.¹⁷

Although spectroscopic techniques are the methods of choice for determining structural and dynamical information, it is often challenging to design and construct spectroscopic cells that are able to withstand not only corrosion but also the temperatures and pressures of supercritical fluid environments. Many of the optical spectroscopic cells that have been reported previously utilize metal alloy pressure vessels with either sapphire or diamond spectroscopic windows.^{16,18–19} These cells are able to accommodate, in some cases, pressures up to 3.0 kbar and temperatures in excess of 400 °C. However, they are usually rather complex in design and expensive with respect to assembly time and materials cost. Howdle et al.^{20,21} and Yonker et al.^{22–24} addressed these concerns by developing spectroscopic cells that

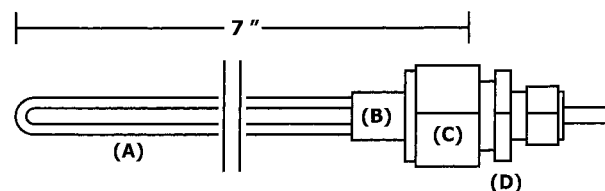


Figure 1. Schematic diagram of the 3-piece HPR-NMR cell: (A) 7-in.-thick walled 5-mm NMR tube (Wilmad), (B) protective nylon sheath, (C) 0.25 in. Swagelok nut and ferrule assembly, and (D) 0.25–0.125 in. Swagelok reducing union

utilize inexpensive, commercially available materials such as fused-silica capillaries for Raman and NMR studies. These methods have been successfully used by other research groups.^{25,26} Fused-silica capillaries can withstand extremely high pressures, are fairly inexpensive, and are extremely safe to use as a result of their small volume. However, unless very efficient collection geometries are employed or the capillary is folded several times to increase sample volume in the detection region,²⁰ the signals are often very weak. Other groups have developed simple NMR and Raman cells that use single-axis, ultrapure sapphire tubes in the detection region.^{27–29} These cells can withstand a wide range of pressures and temperatures, but these specially made tubes are quite expensive. More recently, our group designed and utilized a high-pressure NMR PEEK cell that is economical and quite capable with respect to the pressures and temperatures of CO₂ solutions.¹⁵ However, direct optical access is not possible in this system without the use of fiber-optic feed-throughs. With these considerations in mind, we have developed a simple 3-piece spectroscopic cell for the study of gaseous and supercritical systems that is not only economical and easy to assemble, but also can be used for both Raman and NMR spectroscopic measurements under moderate pressure conditions.

EXPERIMENTAL SECTION

Reagents. Nitrogen (National Welders' Supply Co.) and SFE-grade carbon dioxide (Scott Specialty Gases, Inc.) were used as received. Acetaldehyde, 99.5% (Aldrich Chemical Co.) was dried over activated 4 Å molecular sieves (Fisher Scientific) prior to use.

Cell Design and Experimental Setup. A schematic representation illustrating the design of the simple, 3-piece high-pressure Raman-NMR (HPR-NMR) cell is presented in Figure 1. The spectroscopic cell portion of the design is a commercially available, thick-walled 5 mm borosilicate glass NMR tube (Wilmad, 522-PP). This tube (Figure 1A) is connected to the pressurization system by means of a 0.25 in. Swagelok nut (Figure 1C) attached to a piece of 0.25 in. stainless steel tubing through a reducing union (Figure 1D). To cushion the glass tube from over-

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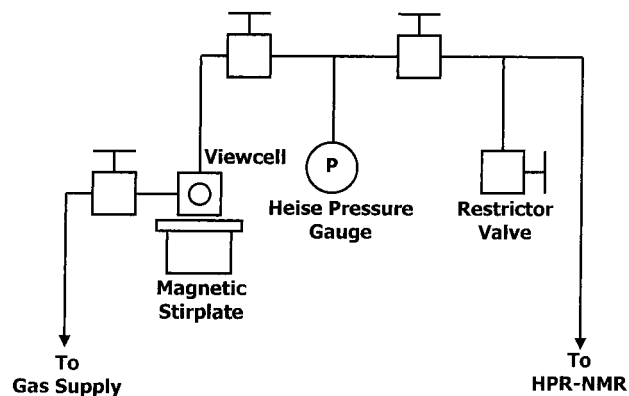


Figure 2. Schematic drawing of high-pressure experimental setup.

constriction by the ferrule and to make up the difference in diameter between the 5 mm tube and the 0.25 in. Swagelok fitting, a protective sheath made from a small piece of 0.25 in. o.d. nylon tubing (Figure 1B) was placed on the open end. To aid in the insertion of the tube into the sheath, the open end of the NMR tube was beveled using a quartz wheel, and a small amount of vacuum grease was applied. Once the NMR tube has been started into the polymer tube, the nylon is heated under a stream of hot water to soften it just enough to allow the glass to slip through. The sheath material must be a fairly rigid polymer, such as nylon, because if the polymer is very flexible, such as polyethylene, it will stretch upon insertion of the NMR tube, and the Swagelok fittings required to connect the cell to the pressurization system will no longer slide over the sheath. Since no machining is required, the only costs associated with the construction of this cell are the material costs of purchasing the thick-walled NMR tube, a small piece of nylon tubing, and a Swagelok nut and ferrule (currently a total cost of approximately \$15 U.S.).

A diagram of the system setup is shown in Figure 2. The cell can be connected either directly to a gas supply (when investigating neat gas or fluid systems) or indirectly through a mixing cell (when investigating gas or fluid mixtures). If the mixing cell is used, the sample of interest can be thoroughly mixed with the gas before the vapors are bled into the cell. Once the system has been pressurized to the maximum density, the mixing cell is isolated from the gas supply. Raman and NMR measurements are then taken at various pressures by bleeding off the excess pressure through a restrictor. In systems that contain several components, this ensures that the studies are performed under constant concentration (i.e., mole fraction) conditions.

Instrumentation. All Raman measurements were made using an argon ion laser (Spectra Physics model 2020-05), operating at 60 mW on the 514.5 nm line. Plasma lines were removed from the beam by filtering through a Pellin-Broca prism system with a spatial filter. Temperature control was achieved by placing the cell in a homemade copper block equipped with resistive heating elements regulated by a PID controller (Omega Engineering CN76000) with temperature determined using a platinum RTD. All data in the present study were collected at 25.0 ± 0.2 °C. Raman scattered light, using a 90° collection geometry, was sent through a 1.0 m additive double monochromator (Jobin-Yvon U1000) with 1800-groove density gratings. The entrance slit was set at a width of 20 μm and slit height of 2 mm. Each spectrum

was acquired over a 30 s integration time using a liquid nitrogen-cooled CCD camera (Princeton Instruments NTE-400EB). Spectra were subsequently calibrated using the plasma lines from the Ar^+ laser employing the method of Carter et al.³⁰ Pressures were generated using a manual high-pressure syringe pump in the case of N_2 (HIP model 50-6-15) or an automated syringe pump in the CO_2 studies (ISCO model 100DX). Pressures were measured with a Bourdon type gauge (Heise H43315) with uncertainties of ± 5 psig.

All NMR measurements were made using a broad-band 10 mm probe equipped with a proton-decoupling channel on a Bruker Avance spectrometer equipped with an 11.75 T superconducting magnet operating at 500.1 MHz for the ^1H nucleus. The cell was placed inside a standard 10-mm NMR tube that contained CDCl_3 as the lock solvent and external standard. Spectra were collected as the average of 128 transients at each pressure point. Since the longitudinal relaxation times (T_1) of the vapor phase samples were quite long (several seconds in range), a 30° pulse length acquisition sequence was used to avoid having to wait $5T_1$, with a total acquisition/delay time of 3 s between transients. This ensured that the areas were quantitative with respect to the experimental relaxation parameters. All NMR experiments were performed at 25.0 ± 0.1 °C and controlled using the air bath and temperature controller (Eurotherm BVT3000) provided with the spectrometer.

Important Safety Considerations. This cell has the potential to cause serious injury upon failure if it contains pressurized gases. Experiments conducted to determine the safe operation range at room temperature (6 cells were tested) indicate that the cells have a mean burst pressure of 2500 ± 500 psig. It was noted that the common causes of failure were by rupturing at the ferrule constriction point on the nylon sheath and by the slipping of the glass tube out of the nylon sheath. In the cells that failed at the ferrule constriction point, it is possible that over-tightening of the Swagelok fitting caused extra stress on the glass. Therefore, the authors feel that it is extremely important to tighten the fitting only to the point where it will adequately hold the pressure as instructed by the Swagelok manufacturer. Our experience indicates that this cell can be safely and routinely pressurized to 800 psig without failure. We do not recommend routine use above 1000 psig unless adequate safety precautions are taken, including examination for stresses in a cross-polarizer and thorough pressure testing prior to use. We note, however, that through the use of quartz tubing, it may be possible to extend the range of pressures beyond 30 000 psi.³¹

RESULTS AND DISCUSSION

Raman Results. The cell developed for this study proved to be very easy to set up and was extremely robust for moderate pressure work. A single cell was pressurized routinely up to 800 psig for the entire experimental run without failure. One concern was the possibility of a large fluorescence background, since the cell is made of borosilicate glass and not high-purity quartz or sapphire. However, as shown in Figure 3A, a relatively small background was observed which could be easily subtracted from the spectrum using standard spectroscopic software. For the present measurements, the baseline of the background was

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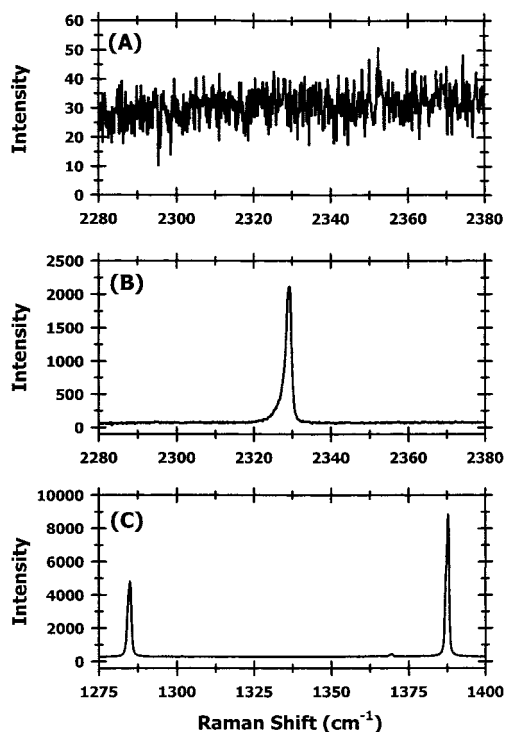


Figure 3. (A) Representative Raman spectrum of blank cell indicating no substantial fluorescence background, (B) representative Raman spectrum of pressurized N_2 (615 psi, 25.0 °C) showing the ν_1 vibrational band at 2329 cm^{-1} , and (C) representative Raman spectrum of CO_2 (615 psi, 25.0 °C) showing the ν_1 and $2\nu_2$ bands at 1388 and 1285 cm^{-1} , respectively.

sufficiently constant to allow an offset integration of the peak without background subtraction. Figure 3B,C illustrates the typical Raman spectrum obtained for nitrogen and carbon dioxide in which one observes the ν_1 vibrational band of N_2 at 2329 cm^{-1} and the ν_1 and $2\nu_2$ Fermi dyad bands of CO_2 at 1388 and 1285 cm^{-1} , respectively. Both spectra have been offset slightly from the baseline for clarity. In the latter system, the appearance of the Fermi dyad is an important consideration in monitoring density, since it has previously been shown to be density-dependent³² and could substantially affect the integrated areas as intensity is transferred from the Raman active ν_1 vibration to the $2\nu_2$ vibration through mixing of the energy levels.

One goal of our research is to quantify the specific interaction of CO_2 with various CO_2 -philic materials. This can be accomplished by comparing the observed spectra of these materials in CO_2 to spectra obtained in a gas that should have no specific interaction, such as N_2 . This necessitates the development and validation of a method to determine the amount of gas present in the system. Since it is difficult to predict the effect that a specific molecular interaction will have on the Raman scattering cross-section, direct measurement of the peak intensity or peak area to determine the absolute concentration of a species in environments that have

different degrees of intermolecular interactions may contain an inherent error due to perturbations in molecular geometry and polarizability. However, since all of the molecules in a particular environment should be perturbed in the same manner, all molecules should experience the same, if any, in the Raman scattering cross section in a given experiment. Therefore, by comparing the area of a Raman band at an arbitrary reference pressure, any change in the area at subsequent pressures should reflect a change in the molar amount of material present in the excitation volume, assuming that the other factors that could affect the peak area remain constant.

To demonstrate that this method is valid for determining changes in volume concentration (density) as a function of pressure, gaseous N_2 and CO_2 were studied. These gases were chosen for two reasons in the present study. First, the gases have substantially different densities as a function of pressure, and in fact, N_2 is supercritical under the conditions examined. Second, as mentioned previously, in future studies of CO_2 -philic molecules, the N_2 data will be the baseline to which the CO_2 data will be compared. In all of these experiments, 65 psi (50 psig) was arbitrarily selected as the pressure to which all other pressures were referenced. To normalize and compare the integrated areas to the reference point, eq 1 was used

$$\Delta n = \frac{A_x}{A_{65}} - 1 \quad (1)$$

where Δn is the percent molar increase of the analyte in the detection volume, A_x is the integrated Raman or NMR peak area obtained at a particular pressure point, and A_{65} is the integrated Raman or NMR peak area at 65 psi. Presenting the data in this manner results in the percent molar increase in analyte as compared to the molar amount present at 65 psi. The results of these calculations are shown for neat N_2 and CO_2 in Figure 4, parts A and B, respectively. The solid lines represent the percent molar increase for values of gas density calculated at 25.0 °C from equations of state for N_2 and CO_2 using the National Institute of Standards and Technology (NIST) website.³³ The data points plotted against this line are the values obtained from the Raman peak areas, and the error bars represent the 95% confidence interval obtained from triplicate measurements. The data obtained from the Raman measurements follow the calculated NIST values almost exactly for both N_2 and CO_2 , and the calculated values fall well within the error bars of the measurements. The slopes of the lines generated for N_2 from the NIST calculations (0.0154) and Raman peak integration data (0.0150) agree well, having only a 2.7% difference. The measurements obtained for CO_2 also agree well with equation of state calculations, with the a, b, and c parameters of the quadratic fit having deviations of 2.1, 3.8, and 1.7%, respectively. It is clear from these data that the Raman integration method provides an excellent means of following the density changes in the system. This indicates that changes in the Raman scattering cross section as a function of pressure within the supercritical N_2 and gaseous CO_2 environments are not significant and that the density-dependent response of the Fermi dyad of CO_2 does not interfere with the ability to determine density changes in this system.

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NMR Results. The system studied in this experiment was the vapor of a CO₂-philic molecule (acetaldehyde) in a pressurized N₂ atmosphere. This experiment was conducted to determine if the same concentration (density) change obtained for the neat gas by Raman measurements could be obtained by monitoring the integrated ¹H NMR signal of a dilute solute species dissolved in the gas. This was necessary because neither of the solvent gases has an NMR active nucleus that is readily utilized for the quantitative determination of spin populations in a reasonable amount of time. The validation of this method will be of particular importance to future studies of the nature of CO₂-CO₂-phile interactions, since much more information concerning local molecular interaction can be obtained from the ¹H chemical shift of a dilute solute than by directly monitoring the chemical shift of the solvent (gas) itself. By starting the mixture at the highest pressure and gradually decreasing until ambient conditions are reached, the mole fraction of solute to solvent is kept constant. Therefore, assuming there are no specific interactions between the N₂ and acetaldehyde, any change in Δn of the acetaldehyde vapor in the system should be proportional to the molar changes in the N₂ solvent. The acetaldehyde methyl proton peak was first integrated and then ratioed to the chloroform external reference peak at each pressure in order to remove any effects due to peak intensity variation caused by the spectrometer response. Equation 1 was then used to calculate the Δn as it was in the Raman experiment from the appropriate integrated peak areas.

The results of this experiment are shown in Figure 5. As illustrated, the Δn increase of acetaldehyde as a function of system pressure closely follows the Δn of neat N₂ gas obtained from the NIST calculations,³³ validating the NMR method as a means of following density changes in pressurized gaseous systems and the data manipulation method used in the Raman results discussed previously. What is important to note about this result is that the slope obtained from the NMR peak integration (0.0150) matches the slope obtained from the Raman peak integration (0.0150), showing that both methods are capable of providing reliable in situ measurements of changes in system density. This NMR result is also significant, because it shows that experiments with a soluble, nonspecifically interacting chemical species introduced into the system can be used to monitor the pressure-induced density behavior of the system as a whole. This means that in future studies, it may be possible to use the deviation of density changes from ideal behavior to identify a specific interaction between two chemical species as well as to determine the magnitude of the interaction by quantifying the degree of deviation.

One important experimental aspect to consider when making this type of comparison is the T_1 of the sample. If the T_1 of the sample changes substantially throughout the course of the experiment and the delay times between transient collection are not long enough to allow complete relaxation of the magnetization vector, then the integrated areas of the peaks and subsequent analysis will be erroneous. In N₂, the T_1 values were determined to change substantially as a function of pressure, varying by a factor of ~ 3 in the range of pressures studied. Since the relaxation times in the gas phase are on the order of several seconds, this variation is quite substantial. Therefore, it is necessary to show that the experimental acquisition/delay time was sufficiently long

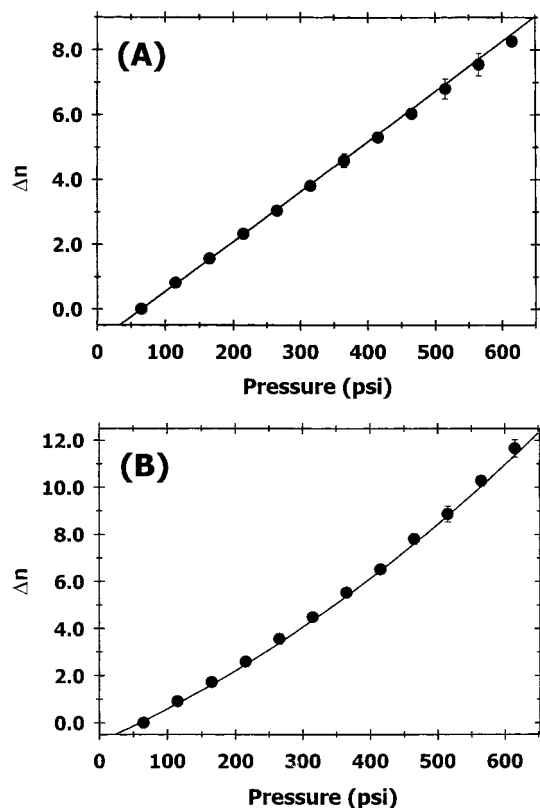


Figure 4. Comparison of density values for N₂ obtained experimentally from integration of Raman bands (●) at 25.0 °C to values obtained from the NIST database³³ (solid line) for (A) N₂ and (B) CO₂. Fitting parameters obtained from linear regression of the experimental N₂ data were $m = 0.0154$, $b = -0.9191$, and $R^2 = 0.9999$; and for the NIST data were $m = 0.0154$, $b = -1.0074$, and $R^2 = 1.0000$. Fitting of the CO₂ data required the use of a quadratic fit, resulting in parameters for the experimental results of $a = 1.1146 \times 10^{-5}$, $b = 0.0133$, $c = -0.8192$, and $R^2 = 0.9997$; and for the NIST data, $a = 1.1377 \times 10^{-5}$, $b = 0.01283$, $c = -0.8052$, and $R^2 = 0.9999$.

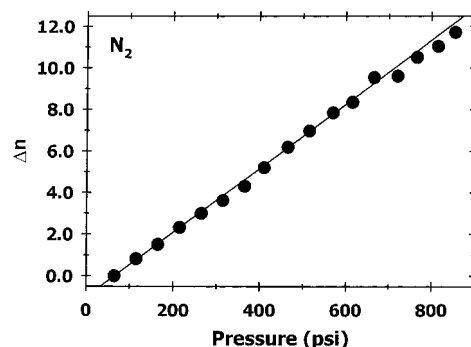


Figure 5. Comparison of density values for N₂ solutions obtained experimentally from integration of acetaldehyde NMR peaks (●) at 25.0 °C to values obtained from the NIST database³³ (solid line). Linear regression of the experimental data gave fitting parameters ($m = 0.0150$, $b = -0.933$, $R^2 = 0.9973$) that agreed well with those obtained from the Raman measurements and NIST data presented in Figure 4.

to allow complete magnetization vector relaxation between transient spectrum collection.

The NMR experiments performed in this study utilized a 30° pulse sequence, which decreases the directionality of the magnetic vector along the z-axis by only 14%. As a result, it is not necessary to wait the usual $5T_1$ delay time between the collection of transient

spectra. Two observations support the assertion that the 3 s acquisition/delay time between transient spectra is sufficient to allow the sample to relax back to equilibrium. First, and most convincingly, when the sample free-induction decay (FID) is directly observed, the oscillation intensity drops off to 0 at ~ 0.8 and 0.4 s for the high and low pressure limits, respectively. This means that the 3-s acquisition/delay time is sufficiently long in all cases to allow quantitative analysis of the peak areas. Second, the fact that the measured areas fall so close to the predicted values from the NIST equation of state calculations strongly indicates that the sample has had ample time to relax. If the delay time had been too short, then the higher pressures values (which have the higher T_1 values) would have deviated substantially from the predicted values.

CONCLUSIONS

In the present study, we have developed a simple 3-piece pressure cell for both Raman and NMR measurements and demonstrated its utility for routinely recording spectra using these two techniques at moderate pressures. The data collected using this cell show the validity of the Raman and NMR peak integration methods as a means of determining and comparing the density increase (percent molar increase) of both a neat gaseous or supercritical fluid system and a dilute solute dissolved in a supercritical fluid. To the best of our knowledge, this method represents a novel approach for the in situ determination of changes in density of a system as a function of pressure while

simultaneously investigating the molecular interactions through the use of the same spectroscopic technique. This method could be valuable for monitoring the stability of a system in supercritical fluid processes. In addition, in the case of a dilute solute dissolved in a fluid, deviations from the expected density dependence could provide a means of identifying a specific molecular interaction between solvent and solute. This approach may be important in determining the solvation structure and mechanism of specific CO_2 -philic molecules and lead to improved CO_2 -philic materials for use in industrial processes and chemical separations.

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