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RAMAN SPECTROSCOPIC CHARACTERIZATION OF GAS MIXTURES. I. QUANTITATIVE COMPOSITION AND PRESSURE DETERMINATION OF CH_4, N_2, AND THEIR MIXTURES

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ABSTRACT. Raman spectral parameters for pure CH_4 and N_2 and their mixtures have been determined as a function of pressure (up to 700 bars) at room temperature. The spectral parameters include peak height (maximum intensity), area (integrated intensity), width (at half height), and position. These parameters can be exploited to provide quantitative analysis of both the composition and pressure (or density) of a CH_4–N_2 fluid at room temperature. At a fixed pressure, the peak position of each endmember gas is changed significantly by the addition of a second component, and the peak positions of CH_4 and N_2 in pure and mixed fluids shift to lower relative wavenumbers as a function of increased pressure. The peak position thus can be used to determine the pressure of a fluid whose composition is known. The relative peak heights of CH_4 and N_2 in binary mixtures are very sensitive to composition and somewhat less sensitive to pressure. Likewise, the relative peak area ratio in a mixture is very sensitive to composition but, above about 75 bars, is insensitive to pressure. The determination of composition by reference to relative peak areas is supported by spectroscopic theory, but, in some practical applications, there are advantages to referencing relative peak heights. The individual peak widths of pure CH_4 and N_2 and their mixtures vary as a function of increased pressure (broaden and narrow, respectively) and, to a lesser extent, composition. Thus, peak width ratios may be used as a monitor of fluid pressure. The internal consistency of these methods has been confirmed by the determination of the compositions and internal pressures in a suite of natural CH_4–N_2 fluid inclusions.

INTRODUCTION

There is increasing application of spectroscopic techniques to the characterization of geologic materials, because they probe materials on their molecular, atomic, and/or subatomic level (Kieffer and Navrotsky, 1985; Hawthorne, 1988). Raman spectra reflect the vibrational energetics of covalent bonds, thereby providing information on bond strengths and molecular structure, as well as the physical (for example, density, molecular mass) and chemical (for example, matrix composition) parameters that affect covalent bonds.

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Of all the analytical techniques applied to fluid inclusions, only Raman spectroscopy and microthermometry can provide information on both composition and pressure of an individual inclusion. Unfortunately, in microthermometry, the inference of those two parameters is not uniquely determined from actual measurements (see Burruss, 1981). As demonstrated below, in Raman spectroscopic analysis of a mixed-volatile fluid, there are sufficient independently measured parameters to determine uniquely both composition and pressure/density of a fluid inclusion. Utilization of those parameters for quantitative fluid analysis requires knowledge of the spectroscopic behavior of the molecular species as a function of the molecular environment (in this case, pressure and composition). In addition, accurate determination of those parameters requires reference to calibration standards.

Many studies have illustrated the striking difference between the spectrum of a low-density vapor and more condensed phases (liquid and solid). The Raman band for a gas species can be described by its spectral position and band shape. As the density of the gas is increased, the spectrum is subject to shifts in frequency (peak position), broadening or narrowing of the band, and changes in intensity. These modifications clearly illustrate the effect of the molecular environment (including pressure, temperature, and composition) and intermolecular forces on the intramolecular properties (for example, vibrational frequency, bond polarizability). In the past, studies of gases have addressed the effect of the molecular environment on the Raman spectra of gas species in order to elucidate the nature of molecular interactions in a fluid (May and others, 1961, 1964; Srivastava and Zaidi, 1979).

More recent studies on the quantitative Raman analysis of gas-bearing fluid inclusions have indicated the usefulness of a systematic investigation of gas mixtures of the composition and pressure of those found in fluid inclusions (Pasteris and others, 1990; Fabre and Oksengorn, 1992). The main goal of our investigation of C–O–H–N–S gas mixtures is to document the effects of pressure and composition on the measured spectral parameters of gases for use in the quantitative determination of the composition and pressure of mixed-volatile fluid inclusions. This paper presents a study of the CH_4–N_2 system up to 700 bars pressure at room temperature.

EXPERIMENTAL METHOD

Raman spectra were obtained with a 1983-model, single-channel, Jobin-Yvon RAMANOR U-1000 (Instruments SA) dispersive spectrometer interfaced with a modified Olympus BH-2 microscope (located at Washington University). The spectrometer consists of a 1-meter, double monochromator with two plane holographic gratings (1800 grooves/mm). A half-wave plate (polarization rotator) is required in the instrument between the microscope and the monochromator to provide optimum transmission of the gratings. The 514.532 nm line of a 5-watt, Ar-ion laser (Coherent Innova 90-5) was used to provide about 15 mW

excitation at the surface of the optical cell. The focusing of the laser beam as well as the collection of the Raman scattered light was done with an Olympus 50x ultra-long-working-distance objective with a numerical aperture of 0.55. The photon detector is a thermo-electrically cooled RCA C31034 photomultiplier tube.

The optical cell is based on a silica glass tube of 3 mm O.D. × 1 mm I.D., as described in detail in Chou, Pasteris, and Seitz (1990). Independently certified gas mixtures of known composition (±1 relative percent) were loaded into the sample cell. The pressure was controlled with a mechanical piston and monitored on-line with a standard pressure transducer (±1 relative percent). Our analytical methodology assumes that the optical cell, as well as the host mineral of an inclusion, is uniformly transparent to the Raman bands of the various gas species.

Due to the non-linear behavior of monochromators, the spectrometer position must be monitored in each spectral region of interest to insure accuracy in the measurement of peak positions. The positions of argon emission lines were routinely measured between every few analytical runs. The CH_4 and N_2 peak positions were referenced against the Ar emission lines at 605.2723 nm (2912.8 Δcm^{-1} *in vacuo*) and 586.0310 nm (2370.51 Δcm^{-1} *in vacuo*) in the regions of the (Q-branch) symmetric stretch (ν_1) of CH_4 and N_2, respectively. Note that all peak positions are *in vacuo* values, recorded in relative wavenumbers (Δcm^{-1}), representing the displacement of the Raman band from the frequency of the exciting laser line. The good agreement between duplicate data sets recorded in different analytical sessions establishes the validity of this method. Estimated accuracy and reproducibility in recorded peak positions are approx 0.3 cm^{-1}.

Analyses typically were performed with 0.5 cm^{-1} scanning steps and 3 to 10 sec counting time per step, but the scanning parameters were adjusted to optimize the signal-to-noise ratio with the minimum analysis time. The spectrometer slit widths were 500 μm, corresponding to a theoretical spectral resolution of about 4.4 cm^{-1} (Paroli and Butler, 1990). Table 1 gives our actual band passes (full peak width at half height) measured on spectra of the reference Ar emission lines, using various spectrometer slit widths. The analytical set-up and scanning procedures

TABLE 1

Full peak width (half height) for Ar emission lines measured on the Ramanor U-1000

Slit width (μm)	Band pass (cm^{-1})*	Band pass (cm^{-1})**
200	1.4	1.2
400	2.7	2.4
500	3.4	3.0

* measured on 586.0310 nm Ar emission band
** measured on 605.2723 nm Ar emission band

used in the gas experiments are very similar to those routinely used in our laboratory for the analysis of fluid inclusions. The chosen optical configuration and scan parameters are not appropriate for the determination of the absolute values of spectral parameters describing the band shape (for example, intrinsic peak width, et cetera) and fine spectral features (for example, rotational bands).

The parameters measured in our study include the spectral peak positions and both the absolute values and the ratios of Raman peak heights, areas, and widths. Data were collected, processed, and analyzed using the PRISM® software of Instruments S.A. From plots of the spectra, the following parameters were manually derived: spectral peak position and full peak width as determined at half height and peak height (maximum intensity) as determined by subtracting an appropriate background from the maximum value. The software was used to calculate peak areas (above the background) between given limits of integration. Plots of the variations and co-variations in these spectral parameters as a function of pressure and composition permit evaluation of the usefulness of individual parameters in the quantitative analysis of natural fluid inclusions. No single measured parameter can provide both compositional and pressure information.

The accuracy in the composition (or pressure) inferred from a measured Raman parameter reflects the sensitivity of that parameter (that is, range in spectral values) to variations in composition (or pressure). Some spectral parameters are more sensitive within a specific range of composition or pressure and simultaneously may be affected by the other factors (pressure or composition). Thus, the choice of the optimum spectral parameters as well as the accuracy of the inferred pressure or composition will vary over P-X space. Table 2 summarizes our evaluation of the usefulness of individual spectral parameters in the analysis of CH_4—N_2 inclusions. The best approach is to evaluate and compare the results derived from several measured parameters, as discussed in detail below.

TABLE 2

Useful spectral parameters to monitor for the determination of composition and pressure in CH_4-N_2 fluids

Spectral parameter	Coupled with	Inferred parameter	Comments and caveats
Peak position	Composition	Pressure	More precise for CH_4-rich fluids. Compositional sensitivity.
Peak width ratio	Composition	Pressure	Slight compositional sensitivity.
Peak height ratio	Pressure and composition	Composition	Small compositional sensitivity. Large pressure sensitivity.
Peak area ratio		Composition	Pressure sensitivity below about 75 bars.
Peak shape (area/height)	Composition	Pressure	Small compositional sensitivity. CH_4 peak most useful.

BINARY MIXTURES

Previous spectroscopic work has addressed the effects of pressure on pure gases, such as H_2 (May and others, 1961, 1964), CO_2 (Wang and Wright, 1973; Wright and Wang, 1974; Bertran, 1983; Garrabos, Eschargui, and Marsault-Herail, 1989), N_2 (Varghese, ms as referenced by Gray and Welsh, 1971; May, Stryland and Varghese, 1970) and CH_4 (May, Stryland, and Welsh, 1959; Fabre and Couty, 1986). For instance, Fabre and Couty (1986) determined the Raman spectral peak position of CH_4 up to 3 kb pressure, making it possible to infer the pressure of pure CH_4 fluid inclusions from their Raman spectra. However, the effect of the presence of other gases on the CH_4 peak position was unknown, thus limiting the applicability of this method in the interpretation of compositionally more complex fluid inclusions.

For analysis of multicomponent fluid inclusions containing CH_4, of major concern are the effects of "contaminant" gases and whether these effects are compositionally sensitive. The results of our reconnaissance study of these effects are shown in figures 1 and 2, plotted in terms of the directly determined variables, composition and pressure, rather than density (which can be inferred). Figure 1 illustrates the effect of composition on the CH_4 ν_1 peak position in four different equimolar gas mixtures as a function of pressure. The compositional effects of the four gases are quite different, emphasizing the need for investigation of individual binary systems. Note that all the gases, except CO_2, dramatically decrease

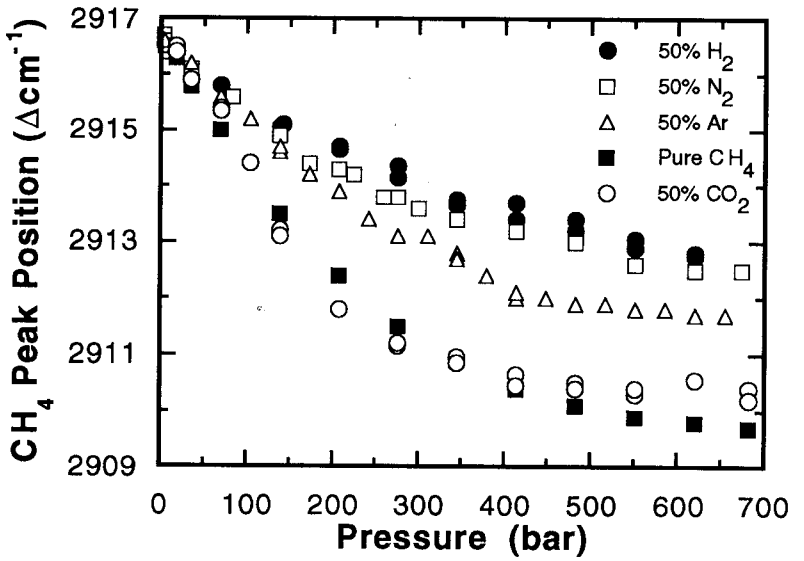


Fig. 1. CH_4 peak position (ν_1) versus total gas pressure for pure CH_4 and equimolar mixtures of CH_4 with H_2, N_2, Ar, and CO_2.

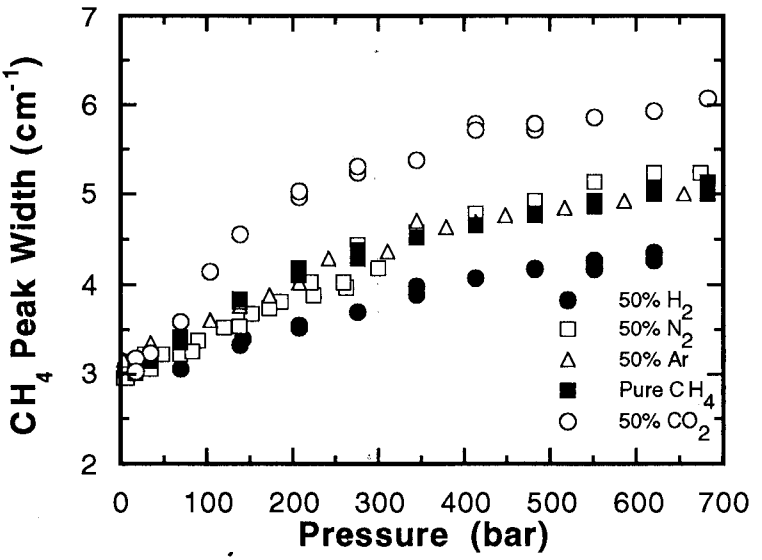


Fig. 2. CH_4 peak widths (ν_1) at half height versus total gas pressure for pure CH_4 and equimolar mixtures of CH_4 with H_2, N_2, Ar, and CO_2.

the total range of CH_4 peak positions. At any given total gas pressure, dilution of CH_4 by H_2, Ar, or N_2 shifts the CH_4 peak to higher relative wavenumbers. Figure 2 illustrates the differential effects of the same four gases on the peak width of ν_1 of CH_4. For this parameter, H_2 and CO_2 have a large effect, but in opposite directions.

As expected, the CH_4 peak positions and widths converge to single values at low pressure for all the mixtures. This value represents the fundamental value for a single CH_4 molecule, unperturbed by other (CH_4 or different) molecules. For instance, our data indicate that the fundamental frequency of CH_4 is $2916.8 \pm 0.1\ \Delta cm^{-1}$ (*in vacuo*), which agrees well with the literature value of $2917.0\ \Delta cm^{-1}$ (Shimanouchi, 1972).

Figures 1 and 2 demonstrate that the effects of molecular interactions on the spectra of gases are very complex and that it is not possible to predict accurately the effect of the perturbation of other molecules on the spectrum of a given molecular species. Thus, experimental determinations are necessary. In the following sections, we will discuss the effects of pressure and composition on the spectral parameters of CH_4 and N_2 in various CH_4–N_2 mixtures, with the ultimate goal of applying these data to the quantitative determination of composition and pressure of fluids.

PEAK POSITION

The spectral peak position reflects the frequency of a specific vibrational mode of a molecule. Its total Raman spectrum thereby uniquely

identifies a molecular species, making this technique useful in the qualitative analysis of complex mixtures. However, the exact vibrational frequency (and thus, the Raman peak position) may change as a function of the physical and chemical state of the molecular environment, which, in the case of a fluid, includes composition and density. It has been shown that the peak positions of CH_4 (May, Stryland, and Welsh, 1970; Fabre and Couty, 1986) and N_2 (May, Stryland, and Welsh, 1970) shift to lower relative wavenumbers as density increases. [The measured peak position of a strongly asymmetric peak may shift as a function of the spectral resolution of the spectrometer (Seitz, Pasteris, and Morgan, 1993). This is most critical for N_2 at low pressure.]

Our experimental data on the peak position of the ν_1 band (Q-branch) of CH_4 in various CH_4–N_2 mixtures are presented in figure 3 as a function of pressure. There are two observations of particular significance to fluid-inclusion analysis. First, is the fact that our measured peak positions (using a resolution of 4.4 cm^{-1}) for the pure CH_4 system are indistinguishable from those of Fabre and Couty (1986), who made their measurements with much higher spectral resolution (0.35 cm^{-1}). Secondly, the magnitudes of the pressure-dependent displacements of the CH_4 peak (compared to the 1-bar position) are sufficient (given an uncertainty of ± 0.3 cm^{-1}) for pressure-determinations of natural inclusions.

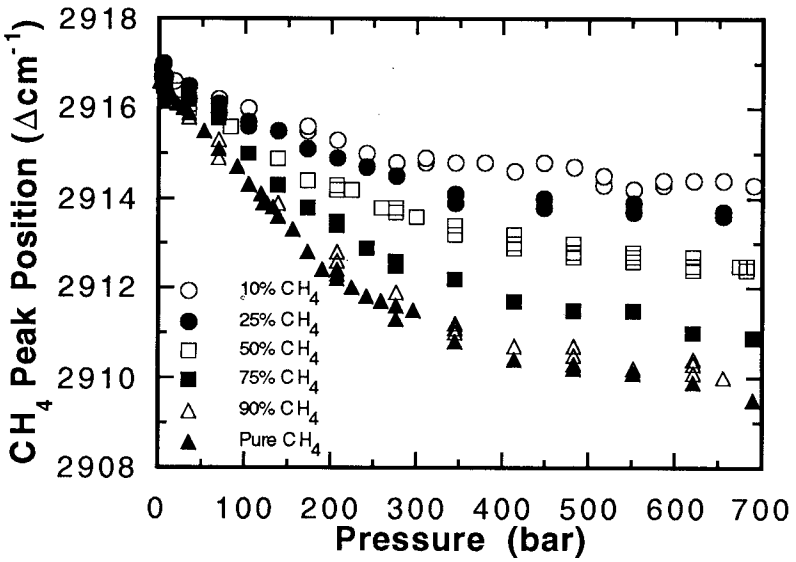


Fig. 3. CH_4 peak position (ν_1) versus total gas pressure for pure CH_4 and various CH_4–N_2 mixtures (mole percent).

The CH_4 peak positions for all the mixtures converge to the same value (2916.8 Δcm^{-1}) at low pressure; the presence of N_2 causes the CH_4 peak position to be shifted to higher relative wavenumbers compared to pure CH_4 for all of the mixtures, as predicted from figure 1. Futhermore, this "dampening" effect of N_2 on the pressure-sensitivity of the CH_4 peak position increases with the concentration of N_2. Of significance to fluid-inclusion analysis is the fact that the CH_4 peak position becomes an increasingly less sensitive function of pressure in mixtures with increasing proportions of N_2.

Figure 4 shows the peak positions for the ν_1 mode of N_2 in the same CH_4–N_2 mixtures, as a function of total pressure. Note that the N_2 peak positions converge to 2328.2 ± 0.2 Δcm^{-1} for all the mixtures at low pressure, which agrees with the value of 2328.2 Δcm^{-1} determined by Wang and Wright (1973) for pure N_2 at zero density. Our data on 50–50 mixtures of CH_4–N_2 also agree very well (that is, well within our 0.3 cm^{-1} uncertainty) with those of Fabre and Oksengorn (1992) for 55–45 mixtures. Wang and Wright (1973) demonstrated that the peak shift is a linear function of density and concluded that the dispersion force (induced dipole-instantaneous dipole force) between molecules is the major interaction mechanism that gives rise to the observed peak shift.

Although N_2, like CH_4, undergoes a downshift in relative wavenumbers as pressure is increased, there are important differences between figures 3 and 4. First, the maximum range of peak positions for CH_4 between 1 and 700 bars is about 7.5 cm^{-1}, whereas the value is only about

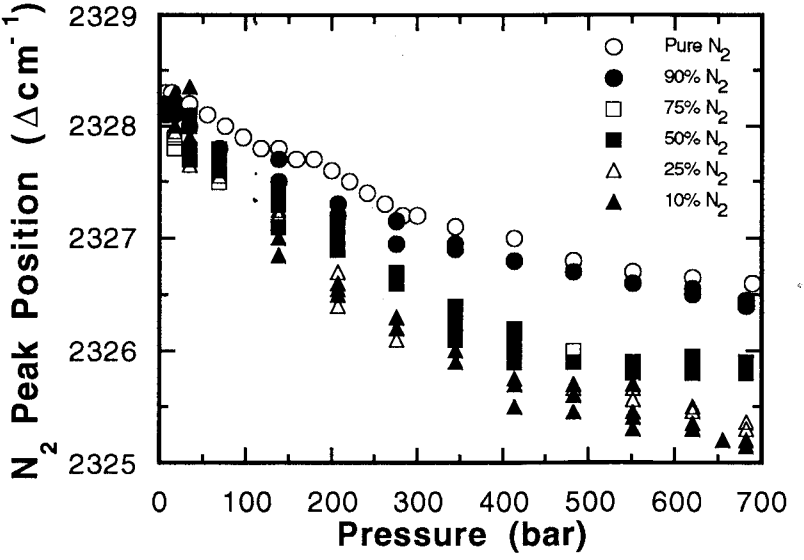


Fig. 4. N_2 peak position (ν_1) versus total gas pressure for pure N_2 and various N_2–CH_4 mixtures (mole percent).

3.0 cm^{-1} for the N_2 peak position. Secondly, for N_2, the effect of adding the second component (CH_4) at constant pressure is to shift the N_2 peak to lower relative wavenumbers, thereby increasing the total range of N_2 peak positions relative to pure N_2. The N_2 peak position thus becomes a more sensitive function of pressure as CH_4 content increases in the mixture.

In figure 5A and B, the data on the CH_4 and N_2 peak positions have been reprojected in terms of the variables that can be measured or inferred. These figures are convenient for determining the internal pressure of a CH_4–N_2 fluid inclusion if the composition (determined by Raman spectroscopy, microthermometry, et cetera) and the CH_4 or N_2 Raman peak position are known. Given an appropriate equation of state, the density of the fluid may then be calculated, since the composition, pressure, and temperature (room temperature) have been uniquely determined.

PEAK HEIGHT

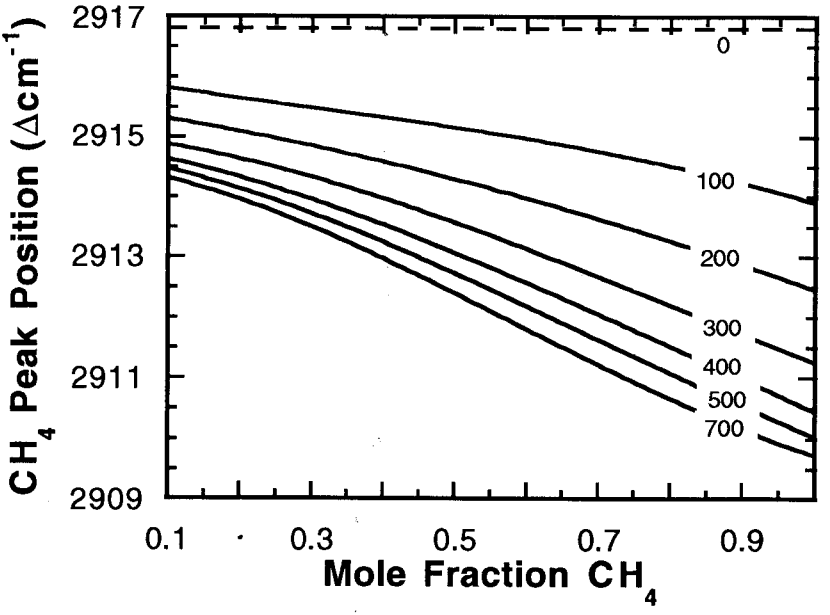
The peak height represents the maximum band intensity and, in a simplistic sense, is proportional to the number of molecules of the Raman-scattering species present in the irradiation volume of the sample. For a fixed optical and instrumental configuration, the absolute heights of individual peaks in a mixture will vary as a function of pressure (or density) at constant composition due to the compressibility of gases.

As discussed in Wopenka and Pasteris (1987) and Seitz, Pasteris, and Wopenka (1987), absolute quantification of Raman spectra is difficult, if not impossible. However, relative quantification can be achieved by comparing either the relative areas or the relative peak heights of the bands for two or more species in a fluid. Some spectral aspects of CH_4-bearing fluids may make measurement of peak intensities more desirable than peak areas, as explained below.

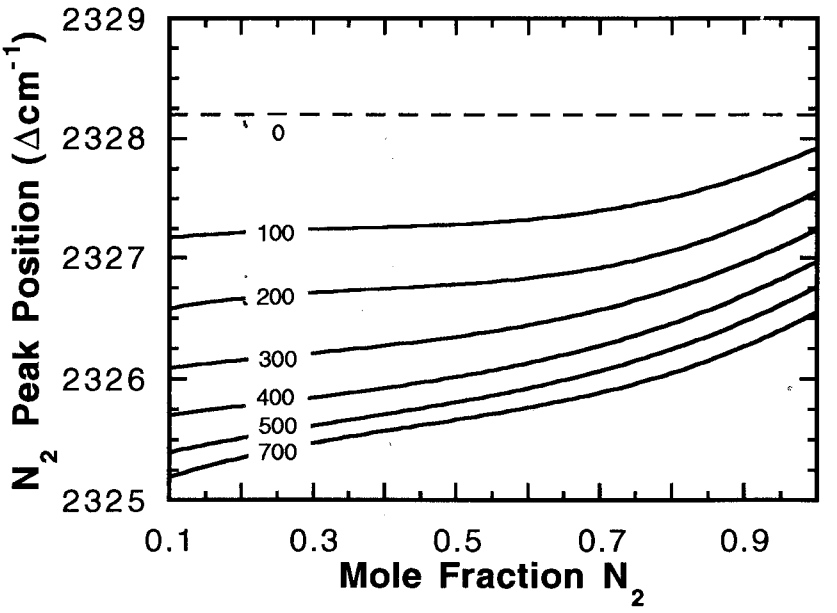
Qualitatively, the measured intensity (peak height or area) of a Raman band, I_m, can be represented as follows:

$$I_m \alpha N I_o \Sigma \xi \eta \quad (1)$$

where N is the number of target molecules in the excitation volume, I_o is the excitation power (intensity of laser), Σ is defined as a constant and represents the inherent scattering efficiency of an unperturbed molecule, ξ is a general term describing the effects of the molecular environment on that molecular scattering efficiency (Σ), and η is the wavelength-dependent efficiency of the instrument (Placzek, 1934; Dhamelincourt and others, 1979; Pasteris, Wopenka, and Seitz, 1988). In this study, the *effective scattering efficiency* is defined as the product ($\Sigma\xi$). It represents a property of the molecule in its particular chemical environment, independent of the instrumental efficiency. At the limit of zero density, ξ for an unperturbed molecule is equal to unity. In the Raman analysis of a fluid of fixed composition, the ratio of the intensities of the peaks therefore is proportional simply to the ratios of the effective scattering efficiencies



A.



B.

Fig. 5 (A and B) Plots showing CH_4 and N_2 peak positions, respectively, in terms of measurable parameters (fluid composition versus peak position). Curves represent isobars (in bars). In each plot, region above 0-bar isobar (higher relative wavenumbers) is unattainable. Uncertainties in pressure vary as a function of $\pm 0.3\ cm^{-1}$ uncertainty in peak position, as illustrated in figure 12A and B.