RAMAN SPECTROSCOPIC CHARACTERIZATION OF GAS MIXTURES. I. QUANTITATIVE COMPOSITION AND PRESSURE DETERMINATION OF CH₄, N₂, AND THEIR MIXTURES

JEFFERY C. SEITZ*, JILL DILL PASTERIS**, and I-MING CHOU***

ABSTRACT. Raman spectral parameters for pure CH₄ and N₂ 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 CH₄–N₂ 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 CH₄ and N₂ 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 CH₄ and N₂ 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 CH₄ and N₂ 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 CH₄–N₂ 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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Author's Note: Any use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.
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 \( \text{CH}_4 \) and \( \text{N}_2 \) peak positions were referenced against the Ar emission lines at 605.2723 nm (2912.8 \( \text{cm}^{-1} \) in vacuo) and 586.0310 nm (2370.51 \( \text{cm}^{-1} \) in vacuo) in the regions of the (Q-branch) symmetric stretch (\( \nu_1 \)) of \( \text{CH}_4 \) and \( \text{N}_2 \), respectively. Note that all peak positions are in vacuo values, recorded in relative wavenumbers (\( \text{cm}^{-1} \)), 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 \( \text{cm}^{-1} \).

Analyses typically were performed with 0.5 \( \text{cm}^{-1} \) 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 \( \mu \text{m} \), corresponding to a theoretical spectral resolution of about 4.4 \( \text{cm}^{-1} \) (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>
<thead>
<tr>
<th>Slit width (( \mu \text{m} ))</th>
<th>Band pass (( \text{cm}^{-1} ))*</th>
<th>Band pass (( \text{cm}^{-1} ))*</th>
<th>Band pass (( \text{cm}^{-1} ))*</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.4</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>2.7</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>3.4</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

* 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 CH₄—N₂ inclusions. The best approach is to evaluate and compare the results derived from several measured parameters, as discussed in detail below.

<table>
<thead>
<tr>
<th>Spectral parameter</th>
<th>Coupled with</th>
<th>Inferred parameter</th>
<th>Comments and caveats</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position</td>
<td>Composition</td>
<td>Pressure</td>
<td>More precise for CH₄-rich fluids. Compositional sensitivity.</td>
</tr>
<tr>
<td>Peak width ratio</td>
<td>Composition</td>
<td>Pressure</td>
<td>Slight compositional sensitivity.</td>
</tr>
<tr>
<td>Peak height ratio</td>
<td>Pressure and composition</td>
<td>Composition</td>
<td>Small compositional sensitivity.</td>
</tr>
<tr>
<td>Peak area ratio</td>
<td>Composition</td>
<td>Pressure</td>
<td>Large pressure sensitivity.</td>
</tr>
<tr>
<td>Peak shape (area/height)</td>
<td>Composition</td>
<td>Pressure</td>
<td>Pressure sensitivity below about 75 bars.</td>
</tr>
</tbody>
</table>

CH₄ peak most useful.
BINARY MIXTURES

Previous spectroscopic work has addressed the effects of pressure on pure gases, such as \( \text{H}_2 \) (May and others, 1961, 1964), \( \text{CO}_2 \) (Wang and Wright, 1973; Wright and Wang, 1974; Bertran, 1983; Garrabos, Eschartgui, and Marsault-Herail, 1989), \( \text{N}_2 \) (Varghese, ms as referenced by Gray and Welsh, 1971; May, Stryland and Varghese, 1970) and \( \text{CH}_4 \) (May, Stryland, and Welsh, 1959; Fabre and Couty, 1986). For instance, Fabre and Couty (1986) determined the Raman spectral peak position of \( \text{CH}_4 \) up to 3 kb pressure, making it possible to infer the pressure of pure \( \text{CH}_4 \) fluid inclusions from their Raman spectra. However, the effect of the presence of other gases on the \( \text{CH}_4 \) 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 \( \text{CH}_4 \), 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 \( \text{CH}_4 \, v_1 \) 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 \( \text{CO}_2 \), dramatically decrease

![Graph showing CH₄ peak position (v₁) versus total gas pressure for pure CH₄ and equimolar mixtures of CH₄ with H₂, N₂, Ar, and CO₂.](image)

Fig. 1. \( \text{CH}_4 \) peak position \((v₁)\) versus total gas pressure for pure \( \text{CH}_4 \) and equimolar mixtures of \( \text{CH}_4 \) with \( \text{H}_2, \text{N}_2, \text{Ar}, \) and \( \text{CO}_2 \).
Fig. 2. CH₄ peak widths (ν₁) at half height versus total gas pressure for pure CH₄ and equimolar mixtures of CH₄ with H₂, N₂, Ar, and CO₂.

the total range of CH₄ peak positions. At any given total gas pressure, dilution of CH₄ by H₂, Ar, or N₂ shifts the CH₄ peak to higher relative wavenumbers. Figure 2 illustrates the differential effects of the same four gases on the peak width of ν₁ of CH₄. For this parameter, H₂ and CO₂ have a large effect, but in opposite directions.

As expected, the CH₄ peak positions and widths converge to single values at low pressure for all the mixtures. This value represents the fundamental value for a single CH₄ molecule, unperturbed by other (CH₄ or different) molecules. For instance, our data indicate that the fundamental frequency of CH₄ is 2916.8 ± 0.1 Δcm⁻¹ (in vacuo), which agrees well with the literature value of 2917.0 Δcm⁻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 CH₄ and N₂ in various CH₄–N₂ 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 CH₄ (May, Stryland, and Welsh, 1970; Fabre and Couty, 1986) and N₂ (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 N₂ at low pressure.]

Our experimental data on the peak position of the ν₁ band (Q-branch) of CH₄ in various CH₂-N₂ 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 CH₄ 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 CH₄ peak (compared to the 1-bar position) are sufficient (given an uncertainty of ±0.3 cm⁻¹) for pressure-determinations of natural inclusions.

![Graph showing CH₄ peak position (ν₁) versus total gas pressure for pure CH₄ and various CH₂-N₂ mixtures (mole percent).](image_url)
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. Furthermore, 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 $v_1$ 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

![Graph showing N$_2$ peak position ($v_1$) 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:

$$I_m \propto N I_o \Sigma \xi \eta$$  \hspace{1cm} (1)

where $N$ is the number of target molecules in the excitation volume, $I_o$ is the excitation power (intensity of laser), $\Sigma$ is defined as a constant and represents the inherent scattering efficiency of an unperturbed molecule, $\xi$ is a general term describing the effects of the molecular environment on that molecular scattering efficiency ($\Sigma$), and $\eta$ 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, $\xi$ 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.
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 ±0.3 cm$^{-1}$ uncertainty in peak position, as illustrated in figure 12A and B.
and mole fractions of the species. If the measured peak height or area ratio of CH\textsubscript{4} to N\textsubscript{2} varies as a function of pressure for a single gas mixture, then, the effective scattering efficiencies for one or both species must change as a function of pressure, since all other parameters (instrumental, compositional, et cetera) have remained the same.

The value of the analytically determined peak height ratio for species 1 and 2 (H\textsubscript{1}/H\textsubscript{2}) can be described by a modified Placzek relation:

\[ G_1/G_2 = (H_1/H_2)(C_2/C_1) \tag{2} \]

where G is a "Raman quantification factor", and C is the concentration of a species in a binary mixture. The Raman quantification factor, G, is analogous to the F-factor for peak area ratios, as developed in Wopenka and Pasteris (1987) and Seitz, Pasteris, and Wopenka (1987); like the F-factors, the G-factor incorporates the molecular and instrumental efficiencies. The effect of plotting the G-factor ratio (see fig. 6) rather than the ratio of the measured relative intensities is to reveal how the ratio of the molecular efficiency parameters changes as a function of pressure. It is neither possible nor necessary to know the absolute value of the G-factor for a single gas species. Only the ratio of the G-factors for two or more components are obtainable, which is sufficient for relative quantification in the analysis of fluid mixtures.

In figure 6, it can be seen that the ratio of the effective scattering efficiencies (G\textsubscript{CH\textsubscript{4}}/G\textsubscript{N\textsubscript{2}}) is a sensitive function of pressure but also a

![Figure 6](image_url)  
**Fig. 6.** G-factor ratios (CH\textsubscript{4}/N\textsubscript{2}) for two different CH\textsubscript{4}–N\textsubscript{2} mixtures. G-factor ratio, related to peak heights, was calculated from eq (2) (see text).
function of the composition of the mixture. The effective scattering efficiency of CH₄ is slightly enhanced in N₂-dominated fluids, but the change in the G-factor ratio due to pressure (at constant composition) is an order of magnitude greater than the effect of composition.

**PEAK WIDTH**

Changes in the peak width represent changes in the rotational states of the molecules as a function of density and composition. There is a rotational component involved in all vibrational Raman scattering events in gases. Appropriate spectral resolution would reveal that the Gaussian-shaped vibrational Raman bands actually consist of individual discrete (quantized) peaks, each one representing the same vibrational state, but different rotational transitions of the molecule (a function of the rotational quantum number, J). In the analysis of mixtures containing H₂, we have observed the individual lines of the Q-branch, even at coarse spectral resolution; for very light gases, the rotational state of the molecule has a large effect on the vibrational frequency. Thus, the individual lines of the Q-branch (each one representing the same vibrational mode but with different initial rotational states) are easily resolvable. However, for heavier gases, such as N₂, the rotation-vibration interaction is so small that the individual lines of the Q-branch overlap (small separation in frequency), and the observed peak represents the width of the entire Q-branch (Gray and Welsh, 1971).

The intrinsic peak widths and peak positions of the individual lines of the Raman bands change as a function of the density of the gas, because the frequency of intermolecular collisions increases with density, which affects the rotational state of the molecules. The peak width of a gas such as N₂ or CH₄ is related to the separation of the individual rotational lines of the Raman band. As the density of the gas increases, the width of the peak may increase by a mechanism known as collision damping (Gray and Welsh, 1971). Further increase in density causes the individual lines of the Q-branch to overlap progressively, producing frequency degeneracy. The eventual outcome of this process in high-density gases is that the molecule may move through many different rotational states during one scattering event because of the increased frequency of collisions. Thus, the molecules scatter light at an average frequency, rather than at the individual frequencies of the different rotational lines of the Raman band. Such eventual frequency degeneracy results in collision- or motional-narrowing of the peak width (Gordon, 1966; Allin and others, 1967).

Narrowing of the N₂ band with increase in density was first observed by Vargheese (1967, as referenced by Gray and Welsh, 1971). In addition, May, Stryland, and Vargheese (1970) noted that the peak is asymmetric for low-density N₂ but becomes more symmetric with increased density. Presumably, the individual components of the Q-branch of N₂ are very close in frequency (nearly degenerate), and thus, collision narrowing commences immediately upon an increase in density. In contrast, Fabre and Couty (1986) showed that collision damping causes broadening of
the CH$_4$ band for the pure component to continue with increasing density up to 0.447 g/cm$^3$, that is, to 3 kb, the maximum pressure of their experiments.

The peak widths of CH$_4$ and N$_2$ increase and decrease, respectively, as pressure increases for binary mixtures. Figure 7 illustrates that the peak width ratio is a sensitive function of pressure for a single mixture, but that it is relatively insensitive to composition (variation due to composition is generally $<$ 10 relative percent). These features make the width ratio a useful pressure monitor in fluid inclusions.

The recorded peak width of an individual species (band) is a function of the spectral resolution of the instrument, as well as the inherent band shape. The effect on the CH$_4$ peak width of adding 45 mole percent N$_2$ has been investigated by Fabre and Oksengorn (1992). Their reported widths differ from ours due to the difference in the spectral resolution in their instrumental set-up.

**PEAK AREA**

The integrated peak intensity, that is, peak area, is another parameter that monitors the intensity of the Raman signal (in addition to the peak height). The comparison of peak areas of species is the classical approach to determination of molar proportions of species in a multicomponent fluid (Placzek, 1934; Dhamelincourt and others, 1979; Seitz,

In figure 8, the normalized peak areas for pure \(N_2\) and \(CH_4\) indicate that the measured peak areas vary differently as a function of pressure. The dominant effect relating the peak area of a species to its pressure or density is the increase in the number of target molecules, \(N\), in the excitation volume. Wang and Wright (1973) found that the integrated intensity (peak area) for \(N_2\) is nearly a linear function of density, which agrees well with our data. They concluded from the linear behavior that the major contribution to scattering intensity probably arises from uncorrelated single \(N_2\) molecules (suggesting negligible molecular interactions). By analogy, the nonlinear behavior of \(CH_4\) suggests higher-order interactions, such that scattering from \(CH_4-CH_4\) pairs and \(CH_4-CH_4-CH_4\) triplets may contribute to the effective scattering efficiency of methane. The differences between the spectroscopic behavior of \(CH_4\) and \(N_2\) are related to the different ways that these species respond to their molecular environment. Clearly, \(CH_4\) appears to be more sensitive to molecular interactions, and thus its effective scattering efficiency changes. On the other hand, there does not appear to be significant interaction between \(N_2\) molecules up to 300 bars (\(\rho = 10.60\) mole/liter), thereby leaving the effective scattering efficiency essentially constant.

In figure 9, the peak area ratio (\(CH_4/N_2\)) for a 10 mole percent \(CH_4\) (90 mole percent \(N_2\)) mixture is plotted as a function of the total pressure.

![Graph showing normalized peak areas for \(CH_4\) and \(N_2\) as a function of fluid density (calculated from Ely, 1988). Peak areas for each gas species were normalized to peak area measured at 6.9 bars.](image)

Fig. 8. Normalized peak areas for pure \(CH_4\) and \(N_2\) as a function of fluid density (calculated from Ely, 1988). Peak areas for each gas species were normalized to peak area measured at 6.9 bars.
Fig. 9. Plot of data for 10 percent CH$_4$ (90 percent N$_2$) mixture; left vertical scale indicates raw peak area ratio (CH$_4$/N$_2$), and right vertical scale indicates F-factor ratio (CH$_4$/N$_2$) for the same data. F-factor ratio, related to peak areas, was calculated using eq (3) (see text).

There is a dramatic rise in the peak area ratio as pressure is increased to about 75 bars. At higher pressures, the ratio remains approximately constant. Similar experiments by Fabre and Oksengorn (1992) confirm the constancy of the peak area ratio at elevated pressure (up to 3 kbs). The data in figure 9 also are plotted in terms of the F-factor ratio (F$_{CH_4}$/F$_{N_2}$), which, as discussed in Seitz, Pasteris, and Wopenka (1987) and Pasteris, Wopenka, and Seitz (1988), incorporates both the molecular and instrumental efficiencies pertinent to measurements of peak areas. In terms of eq (1), the F-factor represents the product of the instrumental efficiency ($\eta$) and the molecular parameters ($\Sigma\xi$). The exact value of individual F-factors cannot be determined, but the ratio of the F-factors for species 1 and 2 can be evaluated by the relation:

$$\frac{F_1}{F_2} = \frac{A_1}{A_2}\frac{C_2}{C_1} \quad (3)$$

Thus, through monitoring of the F-factor ratio (as in fig. 9), the change in the relative scattering efficiencies of the two components can be monitored as a function of the molecular environment, since all other parameters (composition, $I_0$, $\eta$) are held constant or are normalized. Because the F-factors are normalized for composition, they may be compared directly in different mixtures. Figure 9 suggests that, at low pressure (0–75 bars), the effects of molecular interactions are significant. In other words, the
value of $\xi$ is a sensitive function of pressure. However, the effect of the molecular interactions on the ratio of the effective scattering efficiencies reaches its maximum at about 75 bars and does not significantly change at pressures up to 3 kb. The F-factor ratio does not appear to be a sensitive function of composition in the CH$_4$–N$_2$ system. To test this conclusion, we determined the F-factor ratio in five different CH$_4$–N$_2$ mixtures four times each on two different days (for a total of 8 determinations) at a standard pressure (150 bars). The variation in the F-factor with composition is not significant within our analytical uncertainty (compare fig. 9, this study and fig. 6 of Chou, Pasteris, and Seitz, 1990). Taken as a single population ($n = 40$), the average value of the F-factor ratio is $7.39 \pm 0.20$. It is interesting to compare this value to the literature values of the relative normalized (to N$_2$) differential Raman scattering cross section for CH$_4$, which range from 8.7 to 9.3 (Schrötter and Klöckner, 1979), and the relative Raman scattering cross section for CH$_4$, which is 7.57 with respect to the Ar laser line at 514.5 nm (calculated by Dubessy, Poty, and Ramboz, 1989). Both latter values were determined for CH$_4$ at about 1 atm pressure. The F-factor ratio $(F_{CH_4}/F_{N_2})$ derived experimentally by Wopenka and Pasteris (1987) is 6.7 in various gas mixtures at total pressure of about 15 atm.

**PEAK SHAPE**

Several of the figures discussed above represent aspects of the spectral band shape. One simple representation of the peak shape, that is, the ratio of the peak area to the peak height, also can be used to describe the variations in the Raman spectra of gas mixtures as a function of composition and pressure. Although the peak area ratios remain constant at pressures above 100 bars, the ratios of the other spectral parameters do change significantly. The decrease in the maximum intensity (peak height) of the CH$_4$ peak relative to N$_2$ is inversely related to the broadening of the CH$_4$ peak. Essentially, the two gas peaks change their shapes, but the relative areas remain constant: the CH$_4$ peak broadens and undergoes a relative decrease in maximum intensity, whereas the N$_2$ peak becomes more narrow, and the maximum intensity increases relative to CH$_4$. Figure 10 illustrates how the shapes of the CH$_4$ and N$_2$ peaks change as a function of composition and pressure. Note the difference in vertical scale on the two plots. Clearly, the dominant effect on peak shape is pressure, CH$_4$ being much more sensitive than N$_2$. The bulk composition of the gas has a moderate effect on the peak shape of CH$_4$ but appears to have little or no effect on N$_2$ (within analytical uncertainty). Thus, the peak shape (area/height), particularly that of CH$_4$, can be used as a monitor for the pressure of the gas.

**DISCUSSION**

Each spectral parameter varies differently in response to composition and pressure. Some are very sensitive to either composition or pressure, whereas other parameters are sensitive to both, as illustrated in
Fig. 10 (A and B). Plots showing change in ratio of area/height for CH₄ and N₂, respectively, in three different CH₄–N₂ mixtures. Area/height ratio reflects overall peak shape.
the above figures. These differences in response can be used to quantify both the composition and pressure of an unknown fluid by reference to two or more measured spectral parameters. Application of the figures in this paper and recognition of the uncertainties shown on them indicate the best procedure for analysis of CH$_4$–N$_2$ inclusions. Table 2 outlines some caveats in this procedure, and the next section demonstrates the application of these data to the quantitative analysis of natural fluid inclusions.

It may appear that measurement of the relative peak areas is the superior method to determine the composition of an unknown fluid; that is, G-factor ratios are sensitive to composition and pressure, whereas the F-factor ratios are insensitive to these parameters. However, it is often difficult to measure precisely the peak area ratio in CH$_4$-dominated mixtures because CH$_4$ is a much stronger scatterer than N$_2$. For instance, in a 90 percent CH$_4$ (10 percent N$_2$) mixture, the CH$_4$ peak area would be about 66 times greater than the N$_2$ peak area. If there is a ±5 relative percent analytical uncertainty in the measured CH$_4$ peak area, this value represents a total uncertainty that is more than 3 times greater than the total N$_2$ peak area!

In addition, the peak shapes of CH$_4$ and N$_2$ change as a function of pressure, which can complicate analysis. The base of the CH$_4$ peak broadens more rapidly with pressure than does the width at half height. In figure 11 the base of the CH$_4$ peak is shown for a high-pressure

![Intensity vs. Δcm$^{-1}$](image)

**Fig. 11.** Full-scale and blow-up view of spectrum of CH$_4$ at 150 bars pressure, indicating extensive area in wings of peak.
CH₄–N₂ mixture (at different vertical scales). Significant portions of the total peak area are contained in the wings of the peak. Thus, (1) the limits of integration for a high-pressure CH₄ mixture need to be increased relative to the integration limits at lower pressure, and (2) the choice of the specific integration limits is very important to the compositional analysis.

If the integration limits for the CH₄ peak are increased, this leads to two distinct analytical difficulties. First, there is a dramatic increase in analysis time if a scanning monochromator is used. At low pressure, a 30 cm⁻¹ spectral window may be sufficient, whereas, at higher partial pressures of CH₄, the spectral window may be well over 150 cm⁻¹. Secondly, the signal-to-noise ratio is much worse in the wings of the peak. This limits the precision with which the peak area ratio can be measured. Both problems can become acute in high-density, CH₄-dominated mixtures (Seitz, Posteris, and Morgan, 1993).

Consideration of these problems for CH₄-dominated fluids suggests there may be instances in which it is more advantageous to use relative peak heights to quantify the composition of a mixture. For instance, the peak height ratio can be determined with much higher precision than the peak area ratio. Thus, quantification using the relative peak heights avoids the complication produced by changes in peak shape. However, the height ratio is a sensitive function of the pressure of the mixture (see fig. 6). This complication can be overcome by estimating a nominal pressure and then using that value to determine an appropriate value for the G-factor ratio. Since the G-factor ratio is not a sensitive function of composition, the true composition can be determined iteratively.

With Raman microsampling spectroscopy, the reproducibility of a spectral measurement is sensitive to instrumental factors (for example, coupling of the monochromator), as well as sample-specific factors (for example, composition, depth of the inclusion, fluorescence). For instance, the standard deviation of the CH₄/N₂ peak area ratio for duplicate analyses increases from about 1.5 relative percent for a 10 mole percent CH₄ mixture to over 3 relative percent for a 90 mole percent CH₄ mixture at approx 150 bars total pressure. Thus, in order to evaluate precisely the uncertainty of a compositional determination, one needs to know the analytical uncertainty associated with the peak area (or height) ratio. If instrumental and sample parameters are optimized, peak area, height, and width ratios can be determined to within less than 3 relative percent uncertainty. The corresponding uncertainty in pressure or compositional determinations from the measured spectral parameters will depend on the exact relationship between the spectral parameter and the unknown variable.

APPLICATION TO NATURAL FLUID INCLUSIONS

The complexity of low-temperature phase equilibria in gaseous systems (Kerkhof, ms and 1990) and the extremely low temperatures required to freeze CH₄⁻ or N₂-rich fluid inclusions (in many cases,
impossible in practice), hinder microthermometric analysis and interpretation of such inclusions.

The calibrated spectral parameters presented in this paper have been applied to several dozen CH$_4$-N$_2$ fluid inclusions in igneous rocks from the Duluth Complex in northern Minnesota. This mafic body consists of multiple intrusives injected during a rifting event about 1.1 BY ago (Weiblen and Morey, 1980). Drill core samples from the Fish Lake area, along the southwest contact of the Complex with the carbonaceous Virginia Formation, show abundant evidence of fluid-rock interaction: replacement of mafic igneous minerals by amphibole and chlorite, interstitial quartz, and graphite spherulites up to 2 mm in diameter. Petrologic study of the quartz grains has revealed abundant fluid inclusions, with both aqueous (minor) and volatile-bearing (dominant) populations. Raman microprobe analyses show that the volatile-bearing inclusions consist of CH$_4$ + N$_2$ ± CO$_2$ (Pasteris, 1990).

The pertinent Raman spectral parameters for five (CO$_2$-absent) inclusions, all from a single sample, are presented in Table 3. The bottom row of the table indicates the pertinent figure used to infer the values given in each column. In column 2, the composition of each inclusion ($X^A_{CH_4}$) was calculated from the relative peak areas of CH$_4$ and N$_2$ and an F-factor of 7.39, using eq (3). Column 3 lists the composition ($X^H_{CH_4}$) of each inclusion as determined from the relative peak heights. [As indicated in figure 6, the G-factor is a sensitive function of pressure and, to a lesser extent, a function of composition. The appropriate G-factor for each inclusion was determined from the internal pressure (columns 4–7).

<table>
<thead>
<tr>
<th>Inclusion</th>
<th>$X^A_{CH_4}$</th>
<th>$X^H_{CH_4}$</th>
<th>$P^A_{CH_4}$</th>
<th>$P^0_{N_2}$</th>
<th>$P^W_{CH_4}$</th>
<th>$P^{A/H}_{total}$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0.827</td>
<td>0.836</td>
<td>185</td>
<td>140</td>
<td>180</td>
<td>170</td>
<td>7.88</td>
</tr>
<tr>
<td>A4</td>
<td>0.917</td>
<td>0.884</td>
<td>100</td>
<td>70</td>
<td>90</td>
<td>90</td>
<td>4.18</td>
</tr>
<tr>
<td>A5</td>
<td>0.756</td>
<td>0.754</td>
<td>220</td>
<td>145</td>
<td>200</td>
<td>175</td>
<td>8.29</td>
</tr>
<tr>
<td>M4</td>
<td>0.444</td>
<td>0.461</td>
<td>285</td>
<td>225</td>
<td>190</td>
<td>190</td>
<td>9.02</td>
</tr>
<tr>
<td>M11</td>
<td>0.285</td>
<td>0.271</td>
<td>155</td>
<td>85</td>
<td>140</td>
<td>110</td>
<td>5.04</td>
</tr>
<tr>
<td>Reference figure</td>
<td>6</td>
<td>5A</td>
<td>5B</td>
<td>7</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$X^A_{CH_4}$ = CH$_4$ mole fraction as calculated from the relative peak areas.

$X^H_{CH_4}$ = CH$_4$ mole fraction as determined from the relative peak heights.

$P^A_{CH_4}$ = Total internal pressure (bars) as determined from the CH$_4$ peak position.

$P^0_{N_2}$ = Total internal pressure (bars) as determined from the N$_2$ peak position.

$P^W_{CH_4}$ = Total internal pressure (bars) as determined from the relative peak widths.

$P^{A/H}_{total}$ = Total internal pressure (bars) as determined from the area/height ratio for CH$_4$.

$\rho$ = Density (mole/liter) calculated from equation of state of Ely (1988).

Reference figure refers to the figure in the text from which the composition or pressure was inferred from the Raman spectral parameters.
and composition (as determined from the peak areas, column 2). Then the composition given in column 3 was recalculated using eq (2). There is sufficient independence of the spectral parameters to justify using an estimate of the composition (from peak areas) in order to recalculate the composition as determined from the peak heights. The agreement among all the values in a single row demonstrates the internal consistency of these methods; note that compositional analyses from column 3 differ in both a positive and negative sense from those in column 2.

Although the $G$-factor is a function of the composition of the fluid, it is much less sensitive to this parameter than to the pressure of the inclusion. To illustrate this point, consider inclusion A1, whose $\text{CH}_4$ and $\text{N}_2$ peak positions are plotted on figure 12. Figure 6 indicates that at 170 bars (an average pressure-determination), depending on the exact fluid composition, the appropriate $G$-factor ratio would be between approx 5.5 and 6.7. From eq (2), the calculated $\text{CH}_4$ mole fraction would lie between 0.842 and 0.814. Reference to column 2 of table 3 provides an independent compositional analysis. From this value, an appropriate $G$-factor ratio ($G_{\text{CH}_4}/G_{\text{N}_2} = 5.7$) can be interpolated from figure 6. The final composition is calculated as $X_{\text{CH}_4} = 0.836$, which is in good agreement with the value in column 2.

In columns 4 and 5, the internal pressure of each inclusion ($P_{\text{total}}^{\text{CH}_4}$ and $P_{\text{total}}^{\text{N}_2}$) was determined from the $\text{CH}_4$ and $\text{N}_2$ peak positions, respectively. The pressures may be determined from the compositions of the inclusions (column 2) and the respective peak positions by reference to figure 5. This method is illustrated in figure 12 on which the error bars represent an uncertainty of $\pm 0.3 \text{ cm}^{-1}$ in the determination of the peak position. Thus, the pressure-determinations from the peak positions of the individual gases agree within analytical uncertainty.

The pressures determined from the $\text{N}_2$ peak positions are generally lower than those for $\text{CH}_4$; the reason for this apparent bias is unknown. Columns 6 and 7 are tabulations of the internal pressures of the inclusions as determined from the relative peak widths ($P_{\text{total}}^{\text{W}}$) by reference to figure 7 and the $\text{CH}_4$ peak area/height ratio ($P_{\text{total}}^{\text{A/H}}$) by reference to figure 10A, respectively. These values generally agree well with the pressures determined from the peak position data. It should be noted that each of these determinations of the internal pressure of an inclusion can be derived from the same spectrum but that each is somewhat independent of the other. Simultaneous determination of pressure and composition at room temperature permits one to calculate the density of the fluid. Column 8 of table 3 is a list of densities calculated using the equation of state of Ely (1988).

The application of quantitatively determined spectral parameters to this suite of inclusions clearly illustrates the inherent advantages of Raman microsampling spectroscopy for the analysis of fluid inclusions. Bulk analytical techniques, such as gas chromatography and mass spectrometry, are incapable of detecting the compositional variability within a single population of inclusions. In addition, no other technique, besides
Fig. 12 (A and B) Plots illustrating method to determine internal pressures of fluid inclusions from CH$_4$ and N$_2$ peak positions, respectively. Fluid inclusions (in quartz) are from single sample from Duluth Complex (MN). Data for these inclusions listed in table 3. Error bars represent ±0.3 cm$^{-1}$ uncertainty in measurement of peak position. Compositions derived from peak area ratios.
microthermometry, is capable of determining quantitatively the pressure (or density) of individual inclusions. Moreover, these particular inclu-
sions represent a case for which microthermometric analysis would not be possible due to the very low temperatures at which the pertinent phase transitions occur in this system.

CONCLUSION

Our experiments provide the Raman spectral parameters (position, width, height, and area) for \( \text{CH}_4, \text{N}_2 \), and their mixtures as a function of pressure up to about 700 bars. Raman spectroscopic determination of composition in a mixed-volatile fluid inclusion can be accomplished by relative quantification of the ratios of peak area and height. The F-factor ratio \((F_{\text{CH}_4}/F_{\text{N}_2})\), based on peak areas, is independent of composition; above 75 bars, it is also independent of pressure or density. On the other hand, the G-factor ratio, based on peak heights, is a sensitive function of pressure, and to a lesser extent, of the bulk composition. The spectral peak positions and peak widths of \( \text{CH}_4 \) and \( \text{N}_2 \) can be used to determine the internal pressure of natural fluid inclusions given the bulk composition. Additionally, the measured peak widths and peak shapes (area/height) in mixtures vary dominantly as a function of pressure and, to a lesser extent, as a function of the bulk composition. Thus, these parameters also can be used to determine the pressure of an unknown fluid.

The data presented in this paper can be applied to spectra collected in other laboratories. The \( \text{CH}_4 \) and \( \text{N}_2 \) peak positions represent absolute measurements referenced to argon emission lines to insure accuracy. Thus, these data can be applied directly, without correction, to any Raman spectra calibrated for wavelength. Our peak width, area, and height data cannot be applied directly to the spectra of unknown fluids analyzed in other laboratories, since the instrumental parameters can strongly affect their measurement (Wopenka and Pasteris, 1987; Fabre and Oksengorn, 1992). However, our data illustrate general trends and can be used to develop a calibration strategy.

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characterization of gas mixtures


