

QUANTITATIVE ANALYSIS OF FLUID INCLUSIONS WITH RAMAN SPECTROSCOPY

by

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Raman spectroscopy is the inelastic scattering of photons and can be taken as a fingerprint of molecules. Within a linear approximation the relative concentration $x = n_a/(n_a+n_b)$ of two Raman active species, a and b, in the same phase of a fluid inclusion may be obtained from measurements of the corresponding peak areas, A_a and A_b , of the Raman bands (PLACZEK 1934).

However, inclusions in minerals are known over a wide density range (0.003 to 0.025 mole/cm³) and even pure gases of one component are reported to show nonlinear Raman response with density (SEITZ 1996, WANG 1973). In order to compensate for such effects sophisticated calibration methods have been used which base on a direct comparison of an artificial mixture of the same components at a density comparable with the individual inclusion (SEITZ 1996; KERKHOF 1993). Such methods are demanding with regard to the preparation of mixtures at several densities and restrict the standard application of a quantitative micro-Raman analysis. Furthermore, it is impossible to produce all the artificial mixtures at exact the same conditions as found in natural inclusions; this causes a remaining systematic error.

We developed an algorithm that accounts for nonlinear Raman behavior within a consistent framework using only the measured Raman efficiency $S_a(\omega_a)$, the differential Raman scattering cross section of a molecule $\sigma_a(\omega_a)$, and the number of molecules per volume n_a . Values of the differential Raman scattering cross sections for the Q branch of N₂ and CH₄ at standard conditions (760 Torr, 298 K, 514.5 nm laser excitation) are:

$$\sigma_{N_2}(2331\text{cm}^{-1}) = 43 \times 10^{-32}\text{cm}^2\text{sr}^{-1},$$

$$\sigma_{CH_4}(2917\text{cm}^{-1}) = 3.2 \times 10^{-30}\text{cm}^2\text{sr}^{-1} \text{ (SCHRÖTTER 1979).}$$

In a real experiment we do not see a single molecule but a certain volume with a large number of particles. As long as there is no interaction between the molecules the Raman efficiency (units of cm⁻¹sr⁻¹) increases linearly with the molecule density $S_a(\omega_a) = n_a\sigma_a(\omega_a)$. However, molecule-molecule interactions will disturb this simple behavior and we may write instead a power series in n_a, n_b, n_c, \dots . It is still a straight forward calculation by using an iterative algorithm to obtain the concentrations $n_{a,b,c,\dots}$ of the individual species as long as the absolute Raman efficiencies S_a are known. The coefficients of the polynomial in n_a, n_b have to be determined from an artificial gas mixture. The experimental values of the absolute Raman efficiencies $S_a(\omega_a)$ of a Raman band (ω_a) generally can be obtained by proper correcting the Raman spectrum (PRESSL 1996).

In geological and mineralogical sciences absolute Raman efficiencies can not be obtained as a standard procedure, even if one considers the complicated surrounding conditions (geometrical shape, refractive index, etc.) of fluid inclusions. Therefore, we have to consider that only relative efficiencies are known. This fact does not matter in the relative concentration $x = n_a / (n_a + n_b)$; but, the nonlinear Raman response is a function of the absolute particle concentrations. Additional information as e.g. Raman frequency shifts, line shapes, etc. is required in order to solve the nonlinear problem. However, a rather simple algorithm can be achieved if we consider the homogenization temperature T_h (observed in micro-thermometry) which relates the relative composition x to the total density ρ . For the binary subsystem the relations of the total density with relative composition for several homogenization temperatures $d(x, T_h)$ can be obtained from the thermodynamic properties.

Our proposed algorithm for nonlinear Raman response works as follows: First the relative compositions x_i are determined by Raman analysis with a first guess of the absolute concentrations n_i of the inclusion. (It is assumed that the Raman investigations are performed at a temperature above the homogenization temperature with the same density of the inclusion as at T_h . For most cases this will be true for room-temperature Raman analyses.) Secondly, the homogenization temperature is determined by micro-thermometric measurements. With the help of the relations $d(x_i, T_h)$ for the specific binary subsystems the density ρ of the inclusion is determined. Then the absolute concentrations $n_i = \rho x_i$ are obtained and enter into the next iteration step for the Raman analysis.

The relevant question for the application of this method on geological problems is how the accuracy can be improved. In order to estimate the error of the Raman analysis we consider the N_2 - CH_4 subsystem and take the nonlinear Raman response as obtained by SEITZ (1996) and WANG (1973). As long as the density of the inclusion is lower than around 0.005 mole/cm^3 the linear approximation will work with an error less than 20% and slightly better than our proposed nonlinear method. At higher densities the error of the linear interpretation raises significantly and is far above 100% at 0.02 mole/cm^3 . For this high density inclusion the error of our nonlinear method is down at 7% which is the statistical limit for an estimated Raman accuracy of 10%.

This work has been supported by the FWF project P11 583.

References

- KERKHOF, A.M.V.D. & KISCH, H.J. (1993): CH_4 -rich inclusions from quartz veins in the Valley-and-Ridge province and the anthracite fields of the Pennsylvania Appalachians - Reply. - *Amer. Min.*, 78, 220-224.
- PLACZEK, G. (1934): Rayleigh-Streuung und Ramaneffekt. - In: Marx, E. (eds), *Handbuch der Radiologie*, Leipzig, Akademische Verlagsgesellschaft, p. 205-374.
- PRESSL, M., MAYER, M., KNOLL, P., LO, S. HOHENESTER, U. & HOLZINGER-SCHWEIGER, E (1996): Magnetic Raman Scattering in Undoped and Doped Antiferromagnets. - *J. Raman Spec.*, 27, 343-349.
- SCHRÖTTER, H.W. & KLÖCKNER, H.W. (1979): Raman Scattering Cross-Sections in Gases and Liquids. - In: Weber, A. (eds), *Raman Spectroscopy of Gases and Liquids*, p. 123-166.
- SEITZ, J.C, PASTERIS, J.D. & CHOU, I.M. (1996): Raman spectroscopic characterization of gas mixtures. 2. Quantitative composition and pressure determination of the CO_2 - CH_4 system. - *Am. J. Sci.*, 296, 577-600.
- WANG, C.H. & WRIGHT, R.B. (1973): Effect of density on the Raman scattering of molecular fluids. I. A detailed study of the scattering polarization, intensity, frequency shift and spectral shape of gaseous N_2 . - *J. Chem. Phys.*, 59, 1706-1712.