

Calibration of Raman shifts of cyclohexane for quantitative analyses of methane density in natural and synthetic fluid inclusions

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Raman shifts of cyclohexane were calibrated at room temperature based on two Ne emission lines near the ν_1 peak of CH_4 around 2918 cm^{-1} . These calibrated Raman shifts of cyclohexane can be used as reference standards for obtaining accurate methane ν_1 peak positions and, therefore, the pressures (or densities) of CH_4 in natural or synthetic fluid inclusions. Copyright © 2015 John Wiley & Sons, Ltd.

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Introduction

Cyclohexane is one of the eight materials adopted by ASTM (American Society for Testing and Materials) subcommittee on Raman spectroscopy as Raman shift standards.^[1] Raman spectra of these materials were obtained by at least six different labs with both Fourier transform and dispersive Raman spectrometers, and for each of the standards, peak wavenumbers with standard deviations of less than 1 cm^{-1} were established as an ASTM standard for calibrating the Raman shift axis of Raman spectrometers. However, the quantitative analyses of methane in fluid inclusions (in terms of pressure or density) require accurate CH_4 ν_1 peak wavenumber measurements, with standard deviations much less than 1 cm^{-1} .^[2,3] In order to establish a reliable Raman shift standard, Raman shifts of cyclohexane were calibrated in this study at room temperature based on the Ne emission lines near the ν_1 peak of CH_4 around 2918 cm^{-1} .

Experimental

The experimental apparatus and procedures used in this study are identical to those employed previously.^[2–5] Cyclohexane was purchased from J. T. Baker Chemical Co. (Lot No. 403057) without further purification, and it was loaded in a fused silica capillary (300 μm OD, 100 μm ID and 18 mm long) with two ends sealed with a hydrogen flame. The Ne emission lines were generated from NE-1 Neon Calibration Light Source purchased from Ocean Optics (www.oceanoptics.com).

Raman spectra of cyclohexane and Ne emission lines were acquired using a JY/Horiba LabRam HR Raman system, with the following settings: 532.06 nm (frequency doubled Nd:YAG) laser excitation; a 40 \times Olympus objective lens with 0.25 numerical aperture; and a 1800 grooves/mm grating with a spectral resolution of about 1 cm^{-1} . Approximately 20-mW laser light was focused on a central level of the horizontal tube to generate cyclohexane Raman signals during the measurement. Spectra were collected in a single window between 2825 and 3172 cm^{-1} , which covers the ν_1 peak of methane around 2918 cm^{-1} , two large reference peaks of

cyclohexane at room temperature reported by the McCreery research group at 2852.9 and 2938.3 cm^{-1} , and the Ne–He emission line at 2992.52 cm^{-1} . All of these measured spectra were fitted with the program PeakFit v. 4.0 (AISN software Inc.) using Gaussian functions. No smoothing nor baseline corrections were applied to the spectra before peak fitting procedures, and the resolution can be enhanced to 0.03 cm^{-1} by using a curve fitting technique.^[6]

Results

The measured Raman spectra are shown in Fig. 1, with major peak positions marked; these marked peak positions were obtained by using the LabSpec 5 general data acquisition and data analysis software. The actual peak positions for the emission lines of both Ne (626.649 and 630.479 nm) and Ne–He (632.817 nm) based on the 532.06-nm laser excitation are listed in Table 1. The measured peak positions for these emission lines listed in Table 1 were obtained by using the PeakFit Program mentioned above. Similarly, the measured and calibrated Raman shifts for cyclohexane and Ne–He emission line are listed in Table 2; the calibrations were based on the two Ne emission lines at 2836.976 and 2933.916 cm^{-1} .

Discussion

As emphasized by McCreery,^[1] Raman shift standards are easier to use than wavelength standards (such as atomic emission lines) and do not depend on laser wavelength. The cyclohexane standard can be used directly under the microscope for calibration purposes, and it is not necessary need to be sealed in a fused silica capillary tube,

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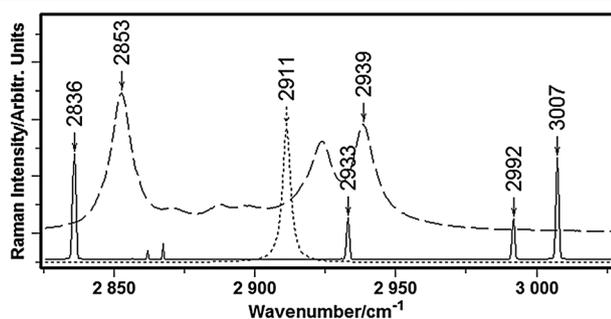


Figure 1. Raman spectra for cyclohexane (dashed line with the maximum peak at 2853 cm^{-1}) and methane vapor (dotted line; peak at 2911 cm^{-1}), which coexists with methane hydrate and aqueous phase at room temperature in a fused silica capsule. Also shown is the spectrum for Ne emission lines and the one Ne–He line at 2992 cm^{-1} (solid line with the maximum peak at 2836 cm^{-1}). The marked peak positions were obtained by using the LabSpec 5 general data acquisition and data analysis software. For details, see text.

Table 1. Positions of measured and actual emission lines (in cm^{-1}) of Ne and Ne–He based on the 532.06-nm laser excitation. Extra digits were given for the wavenumbers for calibration purposes

	Ne	Ne	Ne–He
Measured	2835.892	2933.154	2991.985
Actual	2836.976	2933.916	2992.516

Table 2. Measured and calibrated Raman shifts (in cm^{-1}) for cyclohexane and Ne–He light based on the 532.06 nm laser excitation. Extra digits were given for the wavenumbers for calibration purposes

	Cyclohexane	Cyclohexane	Ne–He
Measured	2852.787	2938.668	2991.985
Calibrated	2853.815	2939.412	2992.554*

* Calculated from:

$2836.976 + (2991.985 - 2835.892) (R)$,
where $R = (2933.916 - 2836.976) / (2933.154 - 2835.892)$.
All wavenumbers used are from Tables 1 and 2.

although the sealed standard makes it easier to operate and also prevents possible contamination during repeated usage.

For the Raman shift of cyclohexane at 2852.9 cm^{-1} reported by McCreery,^[1] the calibrated wavenumber is 2853.815 cm^{-1} , and the one for 2938.3 cm^{-1} reported by McCreery is 2939.412 cm^{-1} (Table 2). Even though these differences are near the 1 cm^{-1} standard deviation associated with McCreery's values,^[1] they tend to generate considerable uncertainties. For example, if the McCreery's^[1] numbers are used for cyclohexane, then the calibrated Ne–He line locates at 2991.207 cm^{-1} , which is 1.309 cm^{-1} lower than the expected value of 2992.516 cm^{-1} (Tables 1 and 2). However, if the current calibrated values for cyclohexane are used, the calibrated Ne–He line locates at 2992.554 cm^{-1} (see footnote of Table 2), which is only 0.038 cm^{-1} lower than the expected value. Note that the Ne–He line at 2992.516 cm^{-1} is outside of the bracket between the two chosen reference standard Raman shifts of cyclohexane (Fig. 1); therefore, the uncertainties associated with methane ν_1 peak positions within the cyclohexane calibration bracket should be smaller than 0.038 cm^{-1} . Furthermore, according to

Eqn (3) of Lu *et al.*^[2] for the calculation of methane pressures in fluids, it was the difference between two measured methane ν_1 peak positions being used, one near 0.1 MPa and the other at unknown elevated pressure. Therefore, the derived uncertainties for the calculated pressures tend to be very small. The calibrated Raman shifts for cyclohexane have been applied to evaluate the effect of pressure (or density) and temperature on the Raman shifts of methane ν_1 peak positions.^[3]

Finally, it should be pointed out that Raman shifts for the same material obtained in different laboratories are usually not the same. For example, the differences in wavenumbers for CH_4 near zero pressure and near room temperature ($20\text{--}30\text{ }^\circ\text{C}$) reported in different laboratories can be as large as 2.21 cm^{-1} (Table 2 and Fig. 1 of Lu *et al.*^[2]). Because these differences are not a result due to the small difference in temperatures of these samples,^[3] therefore, calibration of each Raman spectroscopic system is needed to minimize the effects of other unknown factors on the measured Raman shifts. Also, it is absolutely necessary to use the same instrument setting and software to determine the position of Raman bands for both the sample and the calibrant. To further improve the accuracy of gas density measurements, similar to the method of Lu *et al.*^[2] described above for CH_4 pressure measurements, the difference between two Raman bands instead of a single Raman band should be used, such as the use of Fermi diad splits of CO_2 , based on the well-established Raman bands of benzonitril at 1192.6 and 1598.9 cm^{-1} ,^[1] to obtain the density of CO_2 sample.^[4]

Conclusions

Raman shifts of cyclohexane were calibrated at room temperature based on He emission lines for two peaks with wavenumbers near the methane ν_1 peak position of about 2918 cm^{-1} . These calibrated Raman shifts of cyclohexane can be used as reference standards for obtaining accurate methane ν_1 peak positions and, therefore, the pressures (or densities) of CH_4 in natural or synthetic fluid inclusions.

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