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Accurate wavenumber and intensity calibration for standardization of Raman Spectroscopy

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Abstract

Accurate wavenumber and intensity calibration are requisite for the standardization of spectroscopic techniques. Infrared spectroscopy ensures high wavenumber accuracy due to Fourier-transform spectrometers and accurate intensity scale in the unit of absorbance. Raman spectroscopy still needs improvements in wavenumber and intensity accuracies and better methods for calibration of Raman spectrometers are needed. Accurately calibrated Raman spectrometers are useful for experiments on the determination of absolute Raman cross-sections and quantitative Raman spectroscopy.

In the present work, intensity and wavenumber calibration of a Raman spectrometer is performed using the pure rotational ($\Delta v = 0$, $\Delta J = \pm 2$) Raman bands of H_2 , HD and D_2 and the vibration-rotation bands ($\Delta v = 1$, $\Delta J = \pm 2$) of O_2 . For wavenumber calibration, theoretical and experimental wavenumbers¹ accurately determined for H_2 and D_2 , HD and O_2 are used as standards. Accurate polarizability anisotropy calculated by us previously² is used to determine the intensities of the rotational Raman bands of H_2 , HD and D_2 as intensity standards. Relative experimental intensities for bands originating from common rotational states³, and the corresponding accurate theoretical ratios are used with a non-linear least-squares fitting procedure to obtain the wavelength dependent sensitivity for intensity calibration. Polarization dependence of the spectrometer has been corrected by comparing the observed depolarization ratio, ρ , with the pure rotational Raman bands (H_2 , HD, D_2) and vibration-rotation bands (O_2), having the theoretical value of $\rho = 0.75$.

A laboratory built Raman spectrometer with 532 nm excitation has been calibrated for the spectral range from -1034 cm^{-1} to 1700 cm^{-1} with wavenumber accuracy of $\pm 0.6\text{ cm}^{-1}$ determined as $3\sigma_{n-1}$. Temperature determination using anti-Stokes to Stokes intensity ratio has been used to estimate the accuracy of the sensitivity curve to be less than 2%. Standard Raman spectra of several organic liquids including benzene, carbon tetrachloride, cyclohexane, and toluene, have been determined on this calibrated Raman spectrometer.⁴ They are highly useful as the secondary standards for straightforward wavenumber and intensity calibration of any kind of Raman spectrometers.

Keywords: Raman spectroscopy, intensity calibration, wavenumber calibration

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