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Citation: Review of Scientific Instruments **69**, 3645 (1998); doi: 10.1063/1.1149153
View online: https://doi.org/10.1063/1.1149153
View Table of Contents: http://aip.scitation.org/toc/rsi/69/10
Published by the American Institute of Physics

A novel divided cell for quantitative Raman and resonance Raman spectroscopy

Musilli M. Mitambo, Shuliang L. Zhang,[a] and Glen R. Loppnow[b]
Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

(Received 29 May 1998; accepted for publication 24 July 1998)

A novel four nuclear magnetic resonance (NMR)-tube holder is described for quantitative Raman and resonance Raman spectroscopy. This cell has advantages over other divided cell designs in producing high precision quantitation and eliminating off-axis errors. Raman spectra were obtained for both absorbing and nonabsorbing solutions, and the results compared to those obtained using a single tube holder. The relative Raman intensities in a 1:1 mixture of benzene and chloroform taken in the single holder were within 6% of those of the pure solvents taken with the four NMR tube holder. The resonance Raman scattering cross section of chromate was determined to be within 6% of the value obtained from a single-tube holder. All of these errors in accuracy and precision are within the errors normally associated with the quantitative measurement of Raman cross sections. These results show that the four-tube holder can be used for precise and accurate measurement of both Raman and resonance Raman scattering. © *1998 American Institute of Physics.* [S0034-6748(98)04510-9]

I. INTRODUCTION

The determination of Raman spectral band intensities and relative cross sections is normally made with respect to a reference band.[1] The reference band can either be from an internal standard, in which a small amount of the reference substance is introduced into the sample at a known concentration, or from an external standard,[1] in which the reference substance sits in a separate solution. There are advantages and disadvantages to each method. The main advantage of the internal standard method, which is most commonly used,[2–9] is that the chemical composition of the sample and standard is the same throughout, i.e., whatever factors affect the spectrum of the species under study also affect the standard in a similar fashion. On the other hand, this method cannot be used where the standard is chemically incompatible with the species of interest or in cases where the standard may change the Raman properties under study.[10–12] The use of an external standard is attractive when chemical compatibility is an issue. However, matching the spectroscopic properties of the sample and reference, and the resulting signal levels from each present formidable challenges. For example, the number of molecules in the sample and reference excited by the laser as well as the coupling of the Raman scattered light to the detector should be equivalent in the two for accurate, quantitative measurements. This constraint is particularly important in resonance Raman spectroscopy, where the incident laser beam is absorbed by the sample.

External standards have been used in Raman spectroscopy before by making use of divided cells.[13–16] The main advantage of using a divided cell is the elimination of alignment errors during sample cell substitution. Using such divided cells can be difficult however, in producing quantitative intensities or cross sections. Matching the Raman signal from the two halves, having a good optical surface at the divider, and controlling the spinning axis, are all potential problems. In this article, we describe a cell holder for quantitative Raman spectroscopy. In this novel design, a spinning holder with four nuclear magnetic resonance (NMR) tubes containing the same or different solutions yields the Raman spectrum of all components simultaneously. This design alleviates many of the problems associated with divided cells. We present results for Raman and resonance Raman that show this four NMR tube holder can be applied for quantitative determination of relative Raman scattering cross sections with an external standard.

II. EXPERIMENT

Raman spectra of benzene and chloroform were obtained by spherically focusing 200 mW of 488 nm light from an Ar ion laser (Coherent, Santa Clara, CA) into the sample in a 135° backscattering geometry. Resonance Raman spectra of chromate and dichromate were obtained similarly by using 20 mW of 406.7 nm light from a Kr ion laser (Coherent, Santa Clara, CA). The absorption spectra were measured using a diode array spectrophotometer (Hewlet-Packard, Sunnyvale, CA). Multichannel detection of Raman scattering was obtained as described previously.[2,12] Spectral slit widths were 8 cm^{-1}. The spectra were analyzed as described previously.[2,12]

The absolute Raman cross sections of chromate were determined from the relative integrated intensities using[6]

$$\sigma_{CrO_4^{2-}}=\sigma_{NO_3^-}\frac{[(1+2\rho)/(1+\rho)]_{CrO_4^{2-}}[NO_3^-]I_{CrO_4^{2-}}S_{i,NO_3^-}}{[(1+2\rho)/(1+\rho)]_{NO_3^-}[CrO_4^{2-}]I_{NO_3^-}S_{i,CrO_4^{2-}}}, \quad (1)$$

[a]Present address: Unilever Research US, Edgewater, NJ 07020.
[b]Author to whom correspondence should be addressed; electronic mail: glen.loppnow@ualberta.ca

where σ is the cross section, ρ is the depolarization ratio of the scattered light, $[CrO_4^{2-}]$ and $[NO_3^-]$ are the concentrations of chromate and nitrate, $I_{CrO_4^{2-}}$ and $I_{NO_3^-}$ are the integrated intensities of the chromate and nitrate vibrational bands, and S_{i,NO_3^-} and $S_{i,CrO_4^{2-}}$ are the correction factors for self-absorption of the scattered light at the nitrate and chromate vibrational frequencies, respectively. The self-absorption correction[17] was found to be $\leqslant 2\%$ for the experiment described here and was not considered further. The depolarization ratio for chromate was difficul to measure at 406.7 nm due to lack of a well-define signal at the parallel orientation of the analyzer. Based on our signal-to-noise ratio, we estimate an upper limit of $\rho_{CrO_4^{2-}}$ as 0.03. The nitrate cross section was determined at the laser wavelength by using[6,18]

$$\sigma_{NO_3^-} = \frac{8\pi}{3}\left(\frac{1+2\rho}{1+\rho}\right) K \nu_0 \nu^3 \left(\frac{\nu_e^2+\nu_0^2}{(\nu_e^2-\nu_0^2)^2}+C\right)^2, \qquad (2)$$

where $\rho = 0.04$, ν_0 is the incident photon energy in cm^{-1}, ν is the scattered photon energy in cm^{-1}, $\nu_e = 51\,940\ cm^{-1}$, $K = 9.647\times10^{-13}$ Å^2/molecule, and $C = 4.504\times10^{-10}$ cm^2. The calculated value for the 1049 cm^{-1} nitrate band cross section at 406.7 nm was $\sigma_{NO_3^-} = 3.902\times10^{-12}$ Å^2/molecule.

III. RESULTS AND DISCUSSION

The main objective of this work was to develop a precise, accurate, and simple method for quantitating Raman and resonance Raman intensities with an external standard. We initially tried previous designs of divided cells,[13–16] but encountered problems with several aspects of the design when applied to absorbing samples. For example, the spinning axis must be coincident with the center axis of the cell to very small tolerances when highly absorbing solutions are used in a backscattering geometry, such as used here. If not, the slit image may move in and out of focus and change position, significantl decreasing the signal and altering the relative intensities of the standard and unknown Raman bands. Additionally, scattering from the divider contributes to a strong Rayleigh line, overwhelming the low-frequency bands. Finally, matching the volumes and surface areas exposed to the laser from both halves within a reasonable experimental error proved difficult

Because of these problems, a novel four NMR tube holder (Fig. 1) was designed. The top view shows the four NMR tube cavities. The use of NMR tubes, which are designed for high tolerances, ensured equal volumes in each compartment. The four NMR tube holder is made of black Delrin to reduce any stray light from the cell dividers. During the collection of Raman scattering the holder is spun by a compressed stream of air in order to avoid sample heating. This spinning exposes the sample and the standard to the incident excitation laser beam for equal times. The window, through which the NMR tubes are exposed to the laser line, was machined to expose half the circumference of each tube. This window is necessary to avoid reflection of the incident light by the other tubes and ensures that the beam strikes a single NMR tube at a time. The NMR tube cavities have to

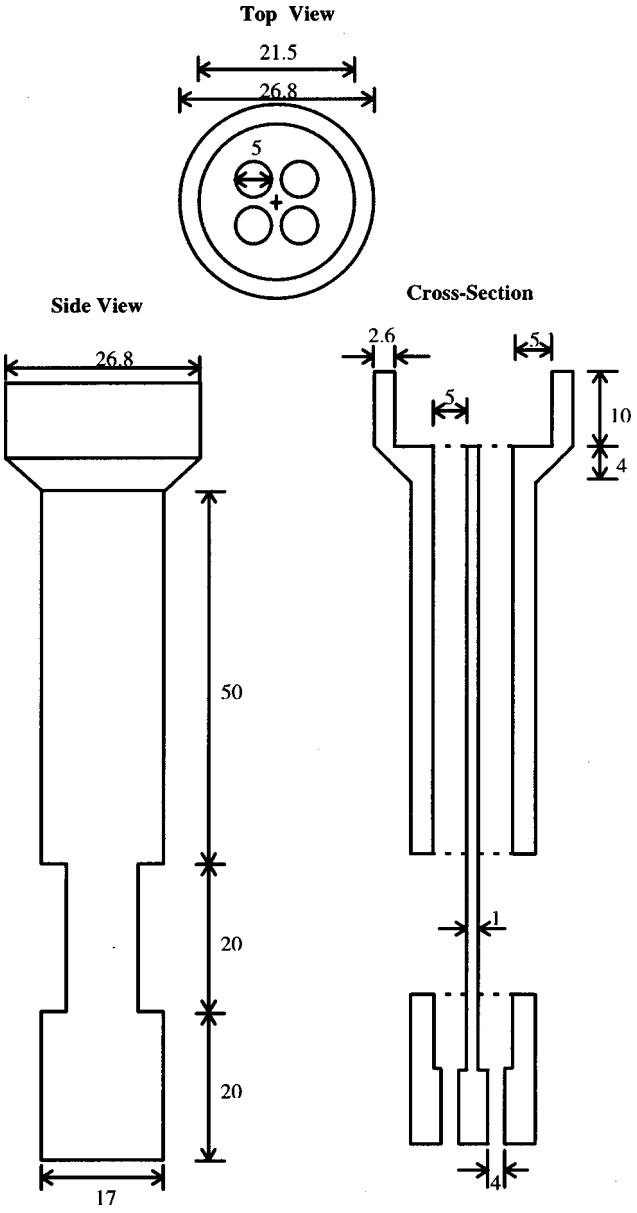

FIG. 1. The four NMR tube holder design. Dimensions are given in mm.

be on a radius equidistant from the spinner axis to avoid systematic errors that would result from changes in the focal point of the Raman scattering being collected at the detector. The choice of four NMR tubes was based on the need for a design relatively insensitive to small changes in rotations around axes perpendicular to the spinning axis.

To validate the use of the new spinner, it was tested for both Raman and resonance Raman scattering methods. In the Raman experiment, a 1:1 (v/v) mixture of benzene and chloroform was used in the single NMR tube spinner and the pure solvents were used in the four NMR tube spinner. The resulting Raman spectra are shown in Fig. 2. The ratio of the integrated benzene band at 992 cm^{-1} to the integrated chloroform band at 667 cm^{-1} is 3.253 ± 0.004 in the single-tube spinner and 3.453 ± 0.007 in the four NMR tube holder. However, to compare the intensities of the pure solvents used in the four NMR tube holder and the solution used in the single tube, two corrections must be performed on the

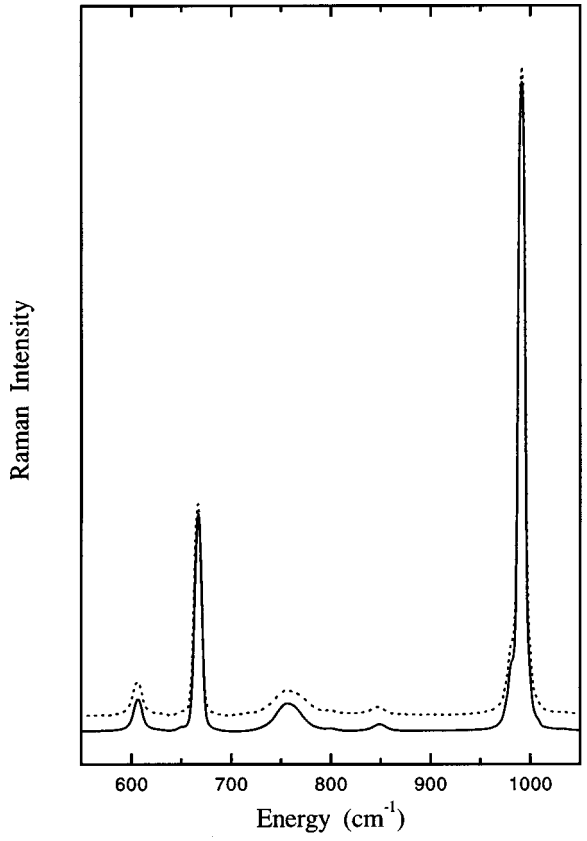

FIG. 2. A region of the Raman spectrum of benzene and chloroform excited at 488 nm. The dashed (---) line is a spectrum of the 1:1 mixture taken in a single NMR tube and the solid (—) line is a spectrum of pure benzene and chloroform in the four-tube holder. The spectrum of the mixture has been slightly offset from that of the pure solvents.

observed intensities to correct for internal fiel and geometric effects. For the local fiel factor, the intensities were divided by $L^4=[(n^2+2)/3]^4$ for each solvent.[19–21] For the geometric correction, the intensities were multiplied by n, the refractive index.[22] Using $n=1.5011$ and $n=1.4459$ for benzene and chloform, respectively, a correction factor of 0.89 is obtained which must be multiplied by the intensity ratio to yield 3.073 ± 0.007 for the four NMR tube holder. The experimental errors are the standard deviations in three measurements, which give a precision of 0.1% and 0.2% for the single-tube and four-tube spinners, respectively, when used with transparent solutions. The intensities differ by 6%, which may arise from slightly lower signal-to-noise ratios in the four-tube spinner spectrum.

For the resonance Raman experiment, the sample choice becomes much more important. To ensure that equal numbers of molecules are probed in the sample and reference, the external intensity standard must sit in a solution that is absorbance matched to the sample of interest at the excitation wavelength. This is to maintain an equal optical pathlength for the incident beam through the two solutions. Criteria that an absorbance-matching species must meet are: (1) high extinction coefficient in the spectral region of interest, (2) minimum number of Raman allowed vibrations, particularly in the vibrational region of interest, and (3) chemical compatibility with a Raman intensity standard. The use of this cell for absorbing samples was demonstrated on an aqueous

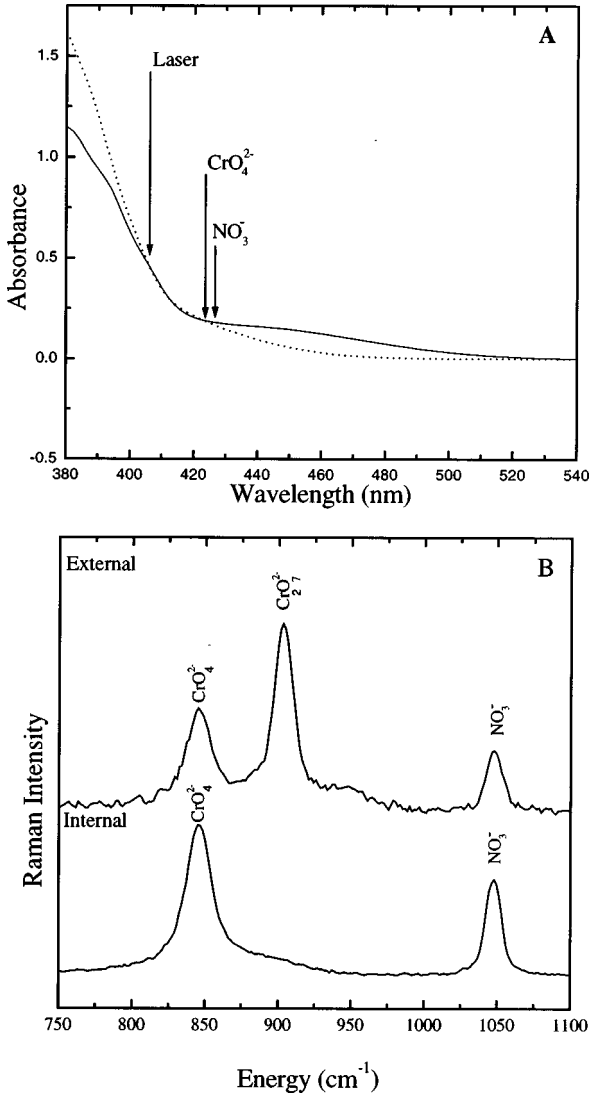

FIG. 3. (A) Absorption spectra of 0.0382 M chromate and 0.0334 M dichromate solutions taken in a 0.01 cm cell. The dashed (---) line is for chromate and the solid (—) line is for dichromate. The arrows indicate the 406.7 nm excitation (laser), 424 nm chromate scattering (CrO_4^{2-}), and 428 nm nitrate (NO_3^-) scattering wavelengths used for this sample. (B) Resonance Raman spectra of chromate taken with nitrate as an external standard in dichromate solution (top) and with nitrate as an internal standard (bottom). Excitation was at 406.7 nm. The peaks are assigned to the chemical species contributing the vibrations.

solution of chromate. For this test, chromate was an ideal choice, since dichromate is readily available and has a similar absorption spectrum and extinction coefficien to chromate. The absorption spectra for chromate and dichromate solutions used in the experiments here are presented in Fig. 3(A). The resonance Raman spectra of chromate with an external and internal intensity standard is shown in Fig. 3(B). Note that the dichromate band is relatively well separated from the chromate and nitrate bands, and should not interfere significantl with the quantitative determination of chromate's resonance Raman cross section. Note also that the relative intensities of the chromate and nitrate peaks are similar in the two spectra. The resonance Raman scattering cross sections of chromate for the 845 cm^{-1} band calculated from Eq. (1) are $\sigma_{CrO_4^{2-}}=(9.144\pm0.120)\times10^{-10}$ Å^2/molecule

for the single tube holder and $\sigma_{CrO_4^{2-}}=(8.645\pm 0.828)\times 10^{-10}$ Å^2/molecule for the four-tube holder (a difference of 6%). This difference is within the random error of measurements normally associated[2,4,6,8,9,14] with quantitation of Raman and resonance Raman cross sections. These results demonstrate that the four-tube spinner yields precise and accurate results for Raman and resonance Raman spectra.

ACKNOWLEDGMENTS

The authors wish to extend their appreciation to the Department of Chemistry at the University of Alberta, NSERC, and the Alberta Heritage Foundation for Medical Research for financia support. They would also like to thank D. Starke for machining the four-tube holder.

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