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Influence of absorption on quantitative analysis in Raman spectroscopy

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Abstract

Absorption of both the excitation and Raman scattered light by the sample (self-absorption) is common in UV Raman spectroscopy and sometimes in visible and FT-Raman spectroscopy due to electronic or vibrational excitation. Self-absorption affects Raman bands and usually results in a non-linear relationship between the Raman intensity and sample concentration. This paper compares quantitative analysis methods for Raman measurements of absorbing liquid and solid samples. Methods based on both internal and external standards can be used to correct for self-absorption. Examples including both liquid (1-methylnaphthalene/isooctane) and solid (V/δ-Al_2O_3) systems were used to compare the effectiveness of these methods. The results show that as long as certain restrictions on the use of these analysis methods are satisfied, the self-absorption problem in Raman spectroscopy can be accurately corrected.

Keywords: Raman spectroscopy; Quantitative analysis; Absorption; Scattering; Internal standard; External standard; Diffuse reflectance; Correction

1. Introduction

Raman spectroscopy has experienced rapid development in recent years due to improvements in lasers, spectrometers, and detectors [1]. It is one of the most powerful tools for the atomic/molecular level investigation of catalytic materials and surfaces especially under reaction conditions [2–10]. Raman spectroscopy also has a number of potential advantages for quantitative analysis [11]. For example, Raman spectra can be measured from both solids and liquids with little or no sample preparation. Raman spectra are often simpler than infrared spectra with only small contributions from water, CO_2, and overtone or combination bands. However, in spite of these features, Raman spectroscopy is associated more with qualitative analysis than with quantitative analysis. This is due to difficulties in obtaining reproducible spectra or absolute Raman intensity along with uncertainties in Raman scattering cross-sections. Both instrumental and sample-related factors can affect the measured Raman band intensity, making it difficult to determine the intrinsic intensity that is proportional to species concentration [11]. Consequently, quantitative information requires the use of internal [10,12–14] or external standards [5,10,15]. The internal standard can be the solvent in a liquid mixture, the support in supported catalysts, or an added component. The laser line or a plasma line can be used as an external standard.

Among the sample-related factors, optical absorption by the sample can affect Raman bands intensities by attenuating both the excitation and Raman intensities. This effect, termed self-absorption, occurs with samples whose UV–vis–NIR absorption bands coincide with the wavelengths of excitation and Raman scattering, resulting in a non-linear relationship between sample concentration and band intensity [1,5,10,13,16–22]. If the sample absorbance varies with wavelength, which is usually the case, self-absorption may affect some parts of the Raman spectrum more than others. Under these circumstances, quantitative analysis becomes more complicated than for non-absorbing samples. As an example, Fig. 1a and b show the UV-excited Raman spectra of 1-methylnaphthalene dissolved in isooctane and vanadium oxide supported on δ-Al_2O_3, respectively. Although isooctane is the major component in the mixture (>99.8 mol%), the spectrum

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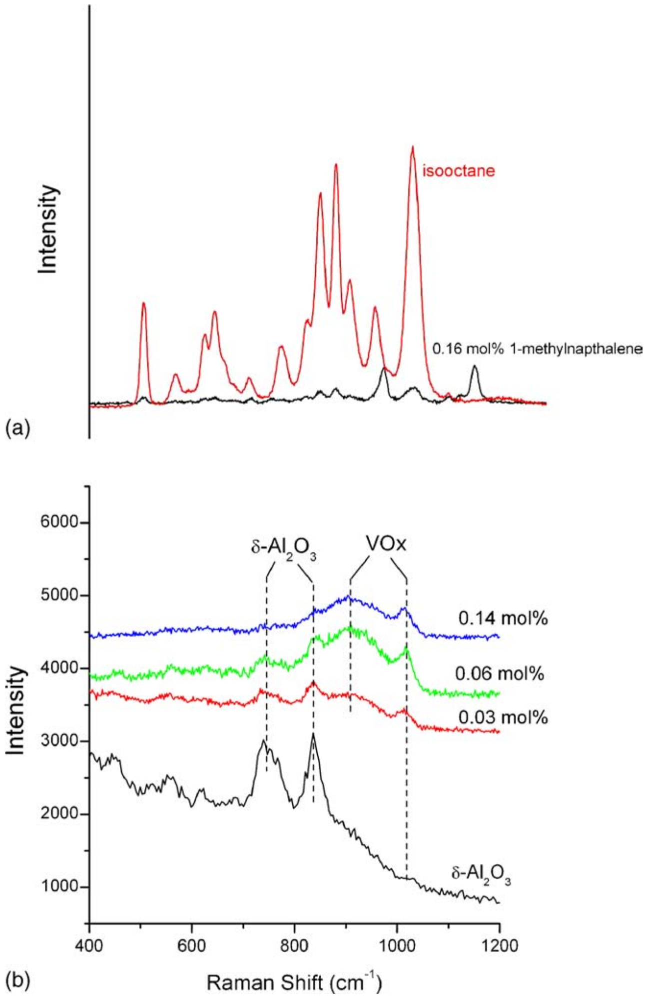

Fig. 1. (a) UV Raman spectra of isooctane and 0.16 mol% 1-methylnaphthalene in isooctane; (b) UV Raman spectra of dehydrated V/δ-Al_2O_3 with surface VO_x concentration range 0.03–0.14 mol%.

of the solution is dominated by the Raman bands due to the minor component, 1-methylnaphthalene, and the bands due to the isooctane solvent decrease dramatically compared to the pure liquid. Similarly, the major component in the solid VO_x/δ-Al_2O_3 system, δ-Al_2O_3, shows attenuated Raman bands even when the VO_x concentration is only 0.14 mol% (surface VO_x density is 0.16 V/nm^2) which is far below the monolayer value for VO_x on Al_2O_3 [7]. Meanwhile, the intensity of the band at ca. 1015 cm^{-1} due to V=O vibrations in surface VO_x [7,23] exhibits no changes in intensity despite the fact that the concentration increases from 0.03 to 1 mol%. Strong absorption by 1-methylnaphthalene and VO_x species in the UV region are responsible for these "distorted" spectra. Darkening of a catalytic material by coking or reduction can also lead to the self-absorption problem in Raman studies [5,10].

Self-absorption is a more common problem for UV Raman measurements than visible-excited Raman and FT-Raman because most materials show electronic absorption in the UV region. A good example is the huge difference in Raman band intensities observed for TiO_2 excited by different laser lines [24,25]. However, self-absorption can also occur in visible- and FT-Raman studies when electronic absorption extends into the visible region or when absorption is caused by vibrational excitation [5,10,19]. As a result, procedures to correct the Raman intensities for self-absorption have been developed for both liquid [13,16–19] and solid systems [5,10,20–22]. In this paper we compare the quantitative analysis procedures for liquid and solid samples. After a review of the quantitative analysis methods for absorbing samples, the systems shown in Fig. 1 are used to evaluate the effectiveness of these methods.

2. Background

2.1. Liquid samples

The effect of self-absorption on the intensity of Raman bands has been considered previously [1,13,16–19]. For the 180° backscattering collection geometry, the intensity, I_x, of Raman scattering emanating from the front face of an absorbing sample is given by [13]:

$$I_x = \frac{I_0 J_x C_x}{2.303C(\varepsilon_e + \varepsilon_x)}\{1 - \exp[-2.303(\varepsilon_e + \varepsilon_x)Cb]\} \qquad (1)$$

where I_0 is the incident laser intensity, J_x, the Raman cross-section for line x, C and C_x, the concentration of the absorber and the species responsible for the line x, respectively, b, the depth of Raman cell, and ε_e and ε_x are the sample absorptivity (base 10) at the wavelengths of the laser radiation and Raman scattered radiation, respectively. When the sample is weakly absorbing, $1 - \exp[-2.303(\varepsilon_e + \varepsilon_x)Cb] = 2.303(\varepsilon_e + \varepsilon_x)Cb$, then

$$I_x = I_0 J_x C_x b = k_1 C_x \qquad (2)$$

where k_1 is a constant. I_x is linearly proportional to the sample concentration, similar to the case of non-absorbing samples. At high absorbance values, $1 - \exp[-2.303(\varepsilon_e + \varepsilon_x)Cb] = 1$ and

$$I_x = \frac{I_0 J_x C_x}{2.303C(\varepsilon_e + \varepsilon_x)} \qquad (3)$$

When there is one type of absorber in the solution and this is the species of interest, $C = C_x$, and I_x is a constant ($I_x = I_0 J_x/2.303(\varepsilon_e + \varepsilon_x) = k_2$). The intensity of a Raman band from the absorber in the sample will approach a plateau when the concentration is high.

When the sample concentration is within the working range of the Lambert–Beer law, an internal standard can be employed to do the quantification. The quantity r, the intensity ratio between the Raman bands of the sample, I_x, and the standard, I_i, can be written as:

$$r = \frac{I_x}{I_i} = \frac{J_x C_x(\varepsilon_e + \varepsilon_i)[1 - \exp(-2.303(\varepsilon_e + \varepsilon_x)Cb]}{J_i C_i(\varepsilon_e + \varepsilon_x)[1 - \exp(-2.303(\varepsilon_e + \varepsilon_i)Cb]} \qquad (4)$$

where ε_i is the sample absorptivity at the wavelength of the Raman scattered radiation from the internal standard and C_i is the concentration of the internal standard. Applying the

Lambert–Beer law ($A = \varepsilon CL$) to expression (4), r can be expressed as:

$$r = k_3 C_x \frac{(A_\mathrm{e} + A_i)[1 - \exp(-2.303(A_\mathrm{e} + A_x)]}{(A_\mathrm{e} + A_x)[1 - \exp(-2.303(A_\mathrm{e} + A_i)]} \tag{5}$$

where k_3 is a proportionality constant that includes the Raman cross-sections of the sample and internal standard lines and the concentration of internal standard. When the sample absorbance is the same at the wavelengths of the sample and standard Raman bands, i.e., $A_x = A_i$, $r = k_3 C_x$, then the corrected band intensity of the sample, I_c, is defined as:

$$I_\mathrm{c} = I_x \frac{I_{i0}}{I_i} = r I_{i0} = k_3 I_{i0} C_x = k_4 C_x \tag{6}$$

I_{i0} is the band intensity of internal standard in one of the samples. An observed linear response of the corrected Raman intensity to the species concentration implies that the internal standard successfully corrects for self-absorption. When the sample absorbance is different at the wavelength of the sample and standard Raman bands, i.e., $A_x \neq A_i$, then the internal standardization method cannot fully correct for self-absorption effect without independently determined values of A_x and A_i. These can be obtained either by direct measurement or from the species concentrations and absorptivities. The former is equivalent to the application of an external standard, as we show below. The latter often amounts to the information sought by performing the Raman measurement. Obviously, the error introduced by the internal standard method will increase with the difference between A_x and A_i. Therefore, the internal standard method is accurate under two assumptions: (a) $A_x = A_i$; and (b) the sample concentration should be in the range where the linearity implied by the Lambert–Beer law holds, so that Eq. (5) can be derived from Eq. (4). The sample concentration typically needs to be less than 0.01 M.

2.2. Solid samples

The internal standard method described above for liquid samples can also be applied to solids. However, it is often inconvenient or impossible to provide an internal standard in catalyst samples. In these circumstances an external standard method, based on measurements of the sample absorption, can be employed.

When a solid system is opaque due to strong absorption or scattering, a direct measurement of the sample absorbance by transmission becomes difficult. Alternatively, absorption together with scattering can be characterized by the diffuse reflectance of the solid, as measured by UV–vis–NIR spectroscopy [5,10,20–22]. An approximate relationship between the diffuse reflectance from an infinitely thick sample, R_∞, and the Raman intensity, ψ_∞, is based on the Kubelka-Munk formalism [26]:

$$\psi_\infty = \frac{\rho I_0}{\sqrt{k(k+2s)}}(1+R_\infty)^2 = \frac{\rho I_0}{s}\frac{R_\infty(1+R_\infty)}{(1-R_\infty)} = \frac{\rho I_0}{s} G(R_\infty) \tag{7}$$

where ρ is the coefficient of Raman generation (Raman cross-section), k, the absorption coefficient and s is the scattering coefficient which depends only on the particle size at a given excitation wavelength. Both the Raman generation coefficient and the absorption coefficient depend linearly on the concentration of the absorber. Eq. (7) is useful for correcting intensities for self-absorption if three restrictions are satisfied: (a) the scattering coefficient s does not change among a series of sample measurements. For supported catalysts, it is common that the particle size of the support is much larger than the supported phase so that s is usually determined by the particle size of the support. s is, likewise, constant for a catalytic reaction when there is no severe sintering or aggregation of catalyst particles during the reaction. (b) The sample is not too strongly absorbing. If the sample is strongly absorbing, the diffuse reflectance R_∞ of the sample approaches zero, and the Raman intensity ψ_∞ approaches $\rho I_0/k$, which is independent of concentration. This is similar to the case of absorbing liquid samples at high concentrations. (c) The diffuse reflectance R_∞ must be identical at the excitation wavelength and the wavelength of the Raman bands. This is typically obeyed since the wavelength range for Raman scattering is narrow compared to the broad diffuse reflectance bands observed for most solid systems. Under these conditions, the corrected (true) Raman intensity I_c can be calculated as:

$$I_\mathrm{c} = \psi_\infty / G(R_\infty) = \frac{\rho I_0}{s} = K C_x \tag{8}$$

where K is considered as a constant when the laser intensity, scattering coefficient, and Raman cross-section of the sample do not change. Thus, the self-absorption effect is taken into account by the $G(R_\infty)$ function that can be derived from the measured diffuse reflectance of the solid sample. This method, classified as an external standardization, cannot compensate for instrumental variations or changes in optical alignment. It is best suited for Raman measurements on a fixed sample that undergoes color changes (diffuse reflectance changes). A catalyst subjected to reduction or a coke formation reaction is such an example.

3. Experimental

3.1. Sample preparation

Two sample systems, as shown in Fig. 1, were prepared for Raman measurements. For 1-methylnaphthalene/isooctane solutions, 1-methylnaphthalene (97%, Acros) was dissolved in isooctane (99%, Acros) to produce concentrations in the range of 10^{-5} to 10^{-2} M. The supported VO_x samples were prepared by incipient wetness impregnation of δ-Al_2O_3 (Johnson Matthey, UK, $S_\mathrm{BET} = 101\ \mathrm{m^2/g}$) using aqueous

NH_4VO_3 (99+%, Aldrich) solutions. The surface VO_x concentration varies in the range 0.01–12.2 mol%, corresponding to surface VO_x density of 0.01–14.2 V/nm^2. The detailed preparation procedure can be found elsewhere [23].

3.2. UV Raman measurements

The UV excitation at 244 nm is produced by a Lexel 95 SHG (second harmonic generation) laser equipped with an intracavity non-linear crystal, BBO (beta barium borate: BaB_2O_4) that frequency doubled visible radiation into the mid-ultraviolet region. Raman spectra of 1-methylnaphthalene in isooctane were collected by an ellipsoidal mirror and focused into a fiber bundle that is coupled to a Triax 550 single grating spectrograph with a UV-enhanced CCD detector. A UV edge filter (Omega Optical) was used to block Rayleigh scattering. For each measurement, precisely 1.00 ml (±0.05 ml) of solution was loaded into a cylindrical quartz cell to provide a consistent sample position. During the measurement, the cell was covered with a UV transparent quartz window and a stirring magnet was used to stir the solution to minimize interference from laser heating or photochemistry. An integration time of 15 s with two accumulations was used for the measurements of liquid samples. The Raman spectra of dehydrated V/δ-Al_2O_3 were measured in a fluidized bed reactor on the UV Raman instrument described previously [23,25,27,28]. The V/Al_2O_3 samples were heated in the fluidized bed reactor in flowing 5% O_2/N_2 (60 ml/min) at 823 K for 2 h to remove adsorbed moisture. Raman spectra were then taken at room temperature in flowing He (>100 ml/min). The fluidized bed reactor was designed as following: the catalyst, in the form of a loose powder with a certain size (~150 μm), was placed on a quartz porous disk located near the end of a vertical quartz tube, which also served as the gas inlet. The quartz tube assembly was surrounded by a concentric quartz tube with the top end sealed by a UV-transparent window for Raman spectroscopic measurements. The space between the inner quartz tube and the outer quartz tube served as the gas outlet. An oven surrounded the entire assembly to provide heating for catalyst pre-treatment and elevated reaction temperatures. Gas flow and mechanical vibration were adjusted to produce stirring of the catalyst powder without lifting the powder bed off the porous disk. Detailed information on the measurement is provided in previous papers [23,28]. The Raman spectra of V/δ-Al_2O_3 were normalized to the same integration time of 5500 s. All Raman spectra were collected using a laser power of 2 mW at the sample position.

In quantitative analysis, the Raman band intensities were determined by spectral fitting using the program PeakFit v4.11. In the case of V/δ-Al_2O_3 where the Raman bands of surface VO_x overlap with those from the support, the program PeakFit was also used for peak separation.

3.3. UV–vis measurements

UV–vis spectra were measured in the range of 200–800 nm on a Varian Cary 1E UV–vis spectrophotometer. The spectra for 1-methylnaphthalene/isooctane samples were acquired in the transmission mode using a 1-cm path length. For the V/δ-Al_2O_3 samples, diffuse reflectance spectra were collected using a diffuse reflectance attachment, with MgO as a reference. For details, please see Ref. [23].

4. Results and discussions

4.1. Internal standard method

Fig. 2a presents the UV Raman spectra of 1-methylnaphthalene/isooctane in the concentration range 10^{-5} to 10^{-2} M. The observed Raman intensities of 1-methylnaphthalene (the band at 1612 cm^{-1}) and isooctane (the band at 1450 cm^{-1}) from Fig. 2a versus the concentration ($-\log c$) of 1-methylnaphthalene are plotted in Fig. 2b. Although the mole percentage of isooctane in the mixture is nearly constant (>99.8 mol%) in all samples, the band intensity decreases by several orders of

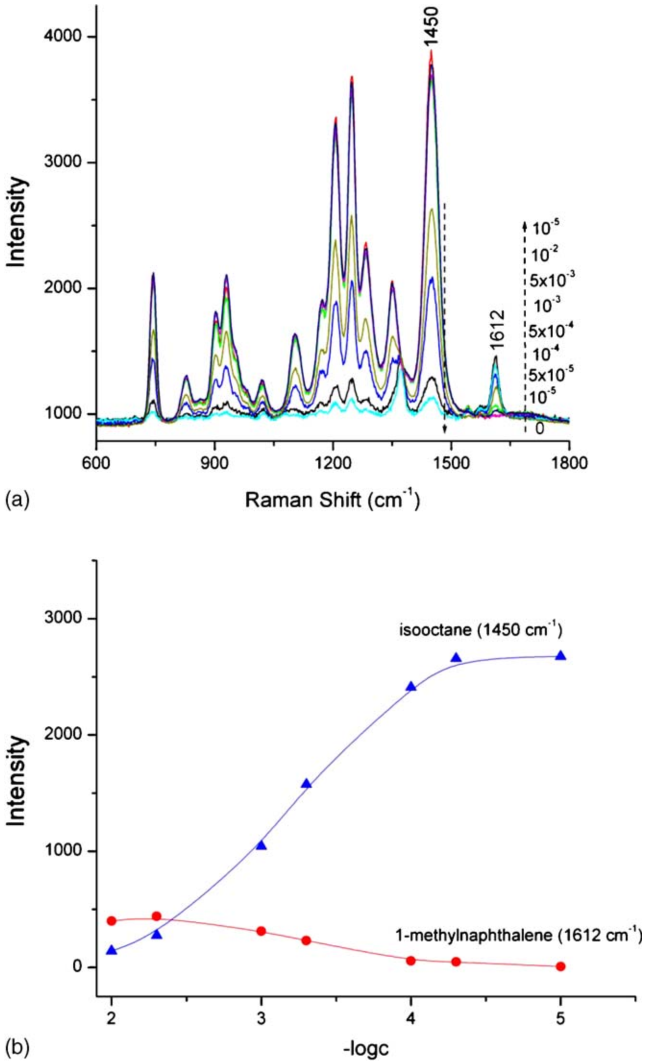

Fig. 2. (a) UV Raman spectra of 1-methylnaphthalene in isooctane in the concentration range 10^{-5} to 10^{-2} mol/L. (b) Observed Raman intensity of isooctane (1450 cm^{-1}) and 1-methylnaphthalene (1612 cm^{-1}) as a function of concentration.

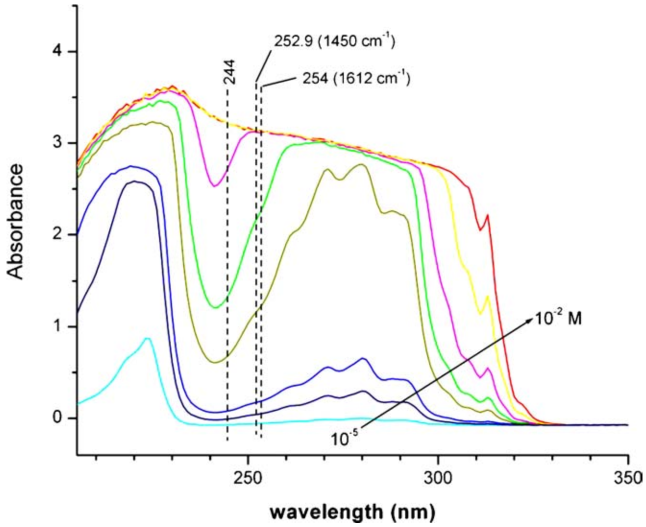

Fig. 3. UV–vis spectra of 1-methylnaphthalene in isooctane in the concentration range 10^{-5} to 10^{-2} mol/L.

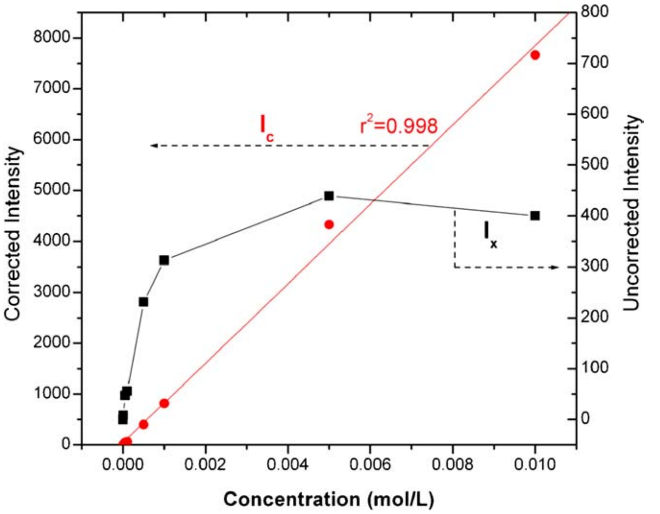

Fig. 4. Uncorrected and isooctane-corrected Raman intensity of 1-methylnaphthalene (1612 cm^{-1}) as a function of concentration.

magnitude. The band intensity for 1-methylnaphthalene increases gradually and non-linearly at low concentrations and reaches a plateau at concentration higher than 5×10^{-3} M. The intensity of 1-methylnaphthalene shows the trend predicted by Eq. (1) for an absorbing sample. Since the concentration of isooctane can be considered constant in the series of mixtures, it is possible to use isooctane as an internal standard to correct for the self-absorption of 1-methylnaphthalene.

The UV–vis absorption spectra of the liquid mixtures are presented in Fig. 3. The absorptivity of 1-methylnaphthalene in isooctane is calculated to be 1291 M^{-1} cm^{-1} using the Lambert–Beer law relationship, showing that 1-methylnaphthalene is strongly absorbing. The absorbance values at the wavelengths corresponding to the bands at Raman shifts of 1450 cm^{-1} (for isooctane) and 1612 cm^{-1} (for 1-methylnaphthalene) are nearly equal, which makes it possible to use the band at 1450 cm^{-1} to normalize the spectra based on Eq. (6). Other sets of Raman bands from 1-methylnaphthalene and isooctane (e.g., 1373 cm^{-1} from 1-methylnaphthalene and 1351 cm^{-1} from isooctane) could have been selected provided their absorbance values are also nearly equal. Since the two bands at 1450 and 1612 cm^{-1} do not overlap with each other, selection of this set of bands makes the standardization process simple and accurate. The corrected intensity of the band at 1612 cm^{-1} is plotted in Fig. 4 as a function of 1-methylnaphthalene concentration. The plot of uncorrected intensity versus concentration is also included for comparison. Clearly, the corrected Raman band intensity accurately follows a linear relationship with respect to concentration using isooctane as an internal standard even at concentrations where the Raman intensity from 1-methylnaphthalene has reached a constant value.

In a similar manner, δ-Al_2O_3 can serve as an internal standard to correct for self-absorption in the Raman spectra of surface VO_x species at concentration below 1 mol% where the Raman bands due to δ-Al_2O_3 are still observable (see Fig. 5). Fig. 6 depicts the UV–vis diffuse reflectance spectra of dehydrated V/δ-Al_2O_3. It is evident that the diffuse reflectance (absorbance) value for the band at 845 cm^{-1} due to δ-Al_2O_3 is nearly equal to that for the band at ca. 1015 cm^{-1} due to surface VO_x species. Consequently, attenuation of the two bands by self-absorption is similar and an internal standardization using δ-Al_2O_3 should be effective. The normalized results are present in Fig. 7 together with uncorrected results. The corrected Raman intensity of VO_x species shows a linear dependence on the surface concentration, in contrast to the non-linear relationship between the intensity and surface concentration without standardization. As with the liquid sample, this procedure is effective at concentrations where the Raman intensity for VO_x has leveled off. The results show that Eqs. (5) and (6) can be used for correction of the self-absorption effect in both liquid and solid samples.

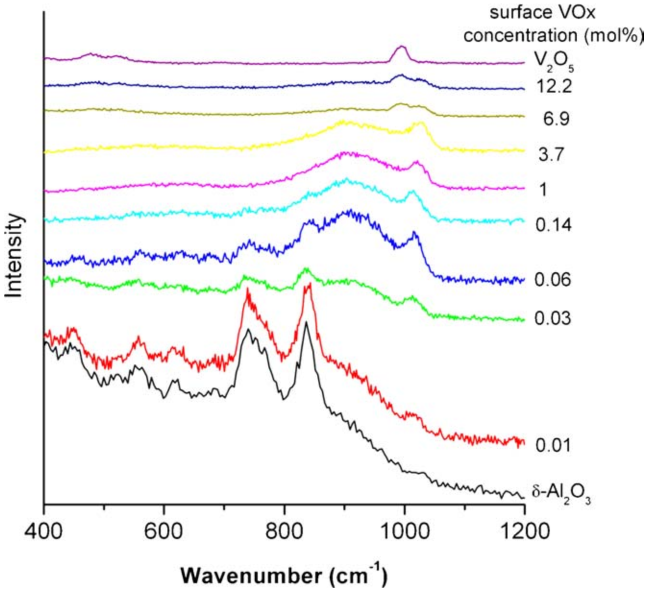

Fig. 5. UV Raman spectra of dehydrated V/δ-Al_2O_3 with VO_x concentration range 0.03–12.2 mol%. The spectra were normalized to the collection time of 5500 s.

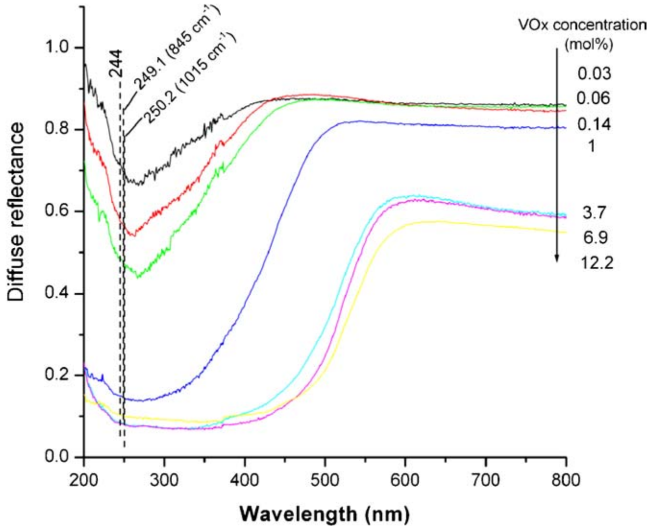

Fig. 6. UV–vis spectra of dehydrated V/δ-Al_2O_3 with VO_x concentration range 0.03–12.2 mol%.

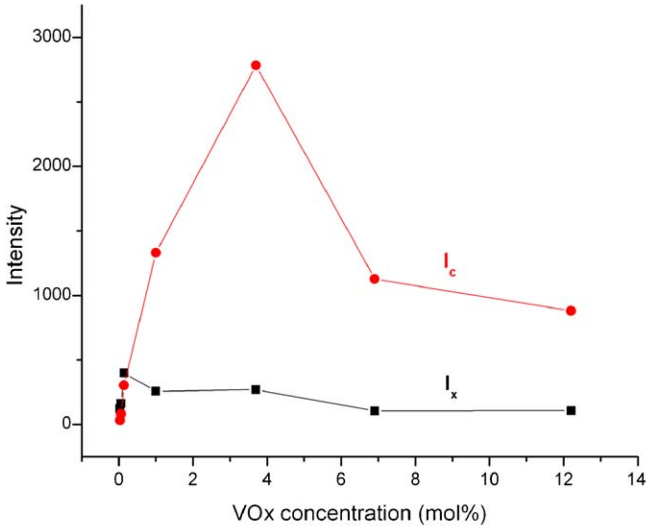

Fig. 8. Uncorrected and $G(R)$-corrected Raman intensity of surface VO_x ($\sim$1015 cm^{-1}) as a function of VO_x concentration.

4.2. External standard method

The above-mentioned examples use an internal standard to correct for self-absorption. However, internal standards are not always available for samples of interest in the Raman studies, especially for solid systems. For example, in the V/δ-Al_2O_3 system, using δ-Al_2O_3 as an internal standard is impossible when the VO_x concentration is higher than 1 mol% (1.2 V/nm^2) since the Raman bands due to δ-Al_2O_3 are no longer observable (see Fig. 5). Moreover, many supports, such as γ-Al_2O_3 or amorphous silica, do not exhibit detectable Raman bands. Another example comes from the catalytic coke formation process where the Raman spectra are dominated by bands due to coke species on the catalyst, and the bands due to catalyst are undetectable. While it is sometimes possible to introduce an internal standard by adding an inert component to the catalyst sample [10,14,29], there are some disadvantages to this procedure. The internal standard should have a particle size that is similar to the catalyst sample, and the two components should be mixed homogenously so that Raman signal can be picked up simultaneously from the catalyst and the internal standard. As an alternative, an external standard, produced by a plasma line from the laser [5] or combining UV–vis absorption and Raman spectroscopy measurements [10], has recently been shown to effectively correct for self-absorption in solid catalytic systems. The correction is based on Eq. (7) and makes use of a value for the $G(R_\infty)$ function obtained from the measured diffuse reflectance of the catalyst. From the measured UV–vis diffuse reflectance spectra of the V/δ-Al_2O_3 system (Fig. 6), we can employ the $G(R_\infty)$ function to correct for self-absorption and compare the results with the internal standard procedure. Fig. 8 presents the corrected and uncorrected Raman intensities of VO_x (band at ca. 1015–1026 cm^{-1}) as a function of surface VO_x concentration. At VO_x concentrations <1 mol% (1.2 V/nm^2), the corrected intensity is linearly proportional to the surface VO_x concentration, in agreement with the results from the internal standard. The corrected intensity versus VO_x concentration is no longer linear as the surface VO_x concentration increases to 1 mol% and above. This non-linearity is not due to the breakdown of the three requirements for using the $G(R_\infty)$ function. The scattering coefficient s does not change since it mainly depends on the particle size of δ-Al_2O_3 which is on the order of micrometers. The diffuse reflectance at 1 mol% is above 0.15. The diffuse reflectance R_∞ is nearly equal for the excitation wavelength (244 nm) and the wavelength (250.2 nm) corresponding to the Raman bands (1015 cm^{-1}).

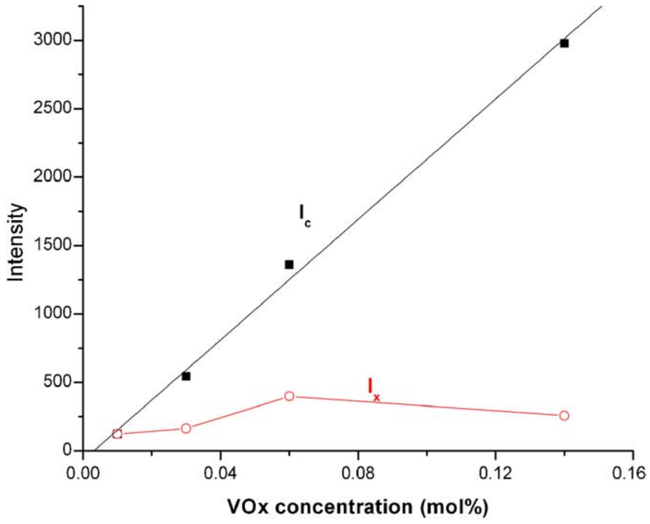

Fig. 7. Uncorrected and δ-Al_2O_3-corrected Raman intensity of surface VO_x ($\sim$1015 cm^{-1}) as a function of VO_x concentration.

One possible explanation for this non-linear relationship is in agreement with the conclusions of our recent paper [23]. It has been shown that VO_x species are present in a distribution of cluster sizes on δ-Al_2O_3 and UV excitation exclusively detects isolated or less-polymerized VO_x species on the surface due to selective resonance enhancement. At VO_x concentrations of 1 mol% and above only a fraction of the vanadia species are detected by UV Raman spectroscopy so that the plot in Fig. 8 is not expected to be linear. Under these circumstances, the plot in Fig. 8 would be indicative only of the concentration of VO_x species detected by UV resonance Raman spectroscopy. This species increases linearly at low surface VO_x concentration (consistent with the intensity corrected by the internal standard method in Fig. 7) and decreases at high VO_x concentrations. However, another contributing factor to the non-linear relationship between corrected Raman intensity and VO_x concentration could also be changes in the Raman cross-section of surface VO_x as the concentration increases. It is expected that the Raman cross-section of VO_x species changes when the surface VO_x cluster size and structure vary with concentration. Under these circumstances it is not possible to quantify the surface VO_x species by the Raman intensity without accounting for changes in the Raman cross-section. The present results do not allow us to distinguish between these two contributions.

Another factor to consider is experimental. At high surface VO_x concentration the measured diffuse reflectance is small (0.08–0.1). In this regime a small offset in the absolute measured diffuse reflectance, e.g. by a shift in the zero level, produces a significant error in I_c. We investigated, numerically, the sensitivity of I_c to offset errors in R_∞. By introducing an offset of 0.05 it was possible to extend the linearity of I_c up to VO_x concentrations as high as 3.7 mol%, but no adjustments in offset could produce linearity up to higher concentrations. This analysis indicates that the decrease in I_c at higher VO_x concentrations is not due to measurement error. Finally, the possible influence of changes in optical alignment and sample position on the Raman intensities were considered since the measurements were performed on different samples. However, the fact that the correction for self-absorption by internal and external standards agrees for the low loading samples, where they would be expected to agree, is strong evidence that the observed deviations from linear behavior are not due to experimental artifacts.

The case study of V/δ-Al_2O_3 suggests that accurate quantification is difficult for heterogeneous systems where the nature of the species of interest undergoes transformation. In coke formation reactions, the chemical nature of the coke species usually changes with reaction time, and the Raman cross-section of surface coke species are expected to change with coke composition. Unfortunately, the Raman cross-section values of the compounds contributing to coke are not known. Therefore, the Raman intensity of coke species after correction for sample absorption cannot be assumed to be linear in the amount of coke. In our opinion the direct transformation of corrected Raman intensity into coke content in a recent report of propane dehydrogenation on a Cr/Al_2O_3 catalyst [10] has not been proven.

In the data presented here application of the $G(R_\infty)$) function to correct for self-absorption required the combination of in situ UV–vis diffuse reflectance and Raman spectroscopy [10]. Ideally this combination of measurements would be performed with UV–vis and laser beams having the same diameter and irradiating the same spot on the sample. However, as long as the two beam diameters are much larger than the sample particle size and the distribution of materials is homogeneous, then irradiation by different beam diameters and at different locations should not invalidate the measurements. Since the laser beam diameter is often larger than tens of microns and the UV–vis beam diameter is even larger, the measurements average over many particles and both criteria can be met. However, when Raman microscopy is used to collect the Raman signal, the beam size can be of the same order as the particle size. If the sample is composed of several phases, it is possible that Raman microscopy detects scattering from one of the phases while UV–vis spectroscopy measures an average diffuse reflectance value. For example, in the Raman microscopic study of MoVW-mixed oxide catalyst reported by Mestle [4], the spectra from different portions on a 40 μm × 40 μm area of the sample show the presence of two or more oxide phases. By using a principle component analysis method, the author concluded that MoO_{3-x}- and V_2O_5-type oxides are present and inhomogeneously distributed in the sample. In this case, a combination of UV–vis and Raman microscopy would result in an inaccurate quantitative analysis. The discrepancy between measured and actual compositions becomes worse as the difference between the diffuse reflectance of the two phases increases. In our Raman study of the V/δ-Al_2O_3 system, the diameter of the laser beam is ca. 50 μm. As the particle size of δ-Al_2O_3 is several microns and the cluster size of dispersed VO_x is much smaller, the combination of UV–vis and Raman spectroscopy should sample the same distribution of species.

When the combination of in situ UV–vis and Raman spectroscopy is not possible, the diffuse-reflected intensity of a plasma line [5] from the laser can also be used to correct for self-absorption in solids. This is feasible for solid powders where specular reflectance is negligible. With our new Raman instrument (single grating spectrograph + fiber bundle + edge filter), we are able to measure the Rayleigh and Raman scattering intensities simultaneously from the sample. With this capability it is possible to correct for self-absorption using the diffuse-reflected Rayleigh scattering. For one sample subject to a color change process (reduction, coke formation, etc), the analysis procedure could be as follows: (a) measure the Rayleigh scattering intensity, I_i, of MgO which is typically used as white standard in UV–vis diffuse reflectance measurements of solid samples. Its diffuse reflectance value, R_i, can be considered as unity. (b) Measure the Rayleigh scattering intensity, I_x, simultaneously with the Raman intensity of the sample during the reaction. (c) Use the relationship $I_x/I_i = R_x/R_i$ to calculate R_x. (d) Employ $G(R_\infty)$ function to correct the Raman intensity as in Eq. (8).

5. Conclusions

The effect of self-absorption on Raman spectra has been compared for both liquid and solid systems. The effect of self-absorption can be taken into account using either an internal standard or external standard method as long as some restrictions are satisfied. When an internal standard is used, the standardization requires that sample absorbance is the same at the wavelengths of the sample and standard Raman bands, i.e., $A_x = A_i$, and the sample concentration should be in the working range of the Lambert–Beer law, usually not higher than 10^{-2} M. The internal standardization corrects self-absorption effectively for both liquids and solids. For external standardization, the correction is made based on the diffuse reflectance, R_∞, of the solid sample. The scattering coefficient s must be constant, and the diffuse reflectance R_∞ must be identical for the excitation wavelength and the wavelengths corresponding to the Raman bands. The combination of in situ UV–vis diffuse reflectance and Raman spectroscopy and the measurement of the diffuse-reflected laser line or plasma lines fall into this category. As long as the Raman cross-sections of the absorbers remain constant, quantitative analysis can be performed for absorbing samples by using either the internal or external methods.

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