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Wavenumber Calibration of CCD Detector Raman Spectrometers Controlled by a Sinus Arm Drive

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Abstract

The calibration procedures needed for use of dispersive Raman spectrometers have been reviewed. Like other high-precision spectrometers incorporating moving gratings, Raman spectrometers are subject to problems with wavenumber scale accuracy. Commercially available Raman Spectrometers of types "DILOR-HORIBA LabRam" and "RENISHAW System 1000" have been examined for wavenumber scale stability, linearity and reproducibility. For reliable use of the wavenumber data, daily calibration is a necessity. A procedure to examine the linearity of such mechanical drive systems is presented. A new finding was that the examined spectrometers give wavenumber calibration errors that were quite reproducible from day to day at a given temperature in the laboratory but depended markedly on the selected setting of the gratings. Knowledge of this linearity problem is essential for obtaining a reliable calibration. The most correct calibration was obtained by the use of certain "golden" settings of the sinus drive at a constant temperature of the laboratory. In this way, the examined spectrometers could be used with better precision, without daily calibration, provided the temperature of the room was constant or corrected for. A procedure for correction of these errors by the software is suggested.

Key Words: Instrumentation, Raman spectroscopy, Wavenumber scale calibration, CCD detector, Reproducibility.

1. Introduction

In recent years, charge coupled device (CCD) detector cameras have improved Raman spectrometric measurements dramatically. A certain part of the spectrum is normally recorded for a fixed position of the dispersive element, usually an optical grating. With such a system it is possible to investigate unstable or very sensitive compounds in much shorter time than previously. But there are still some problems to consider. There are limitations of the spectral length according to the dimensions of the array and the resolution, but first of all the abscissa calibration is a key issue in a Raman spectrometer.

The subject of wavelength calibration of such multichannel Raman spectrometers has received considerable attention in the literature, and a wealth of general reports dealing with the calibration of Raman spectrometers have appeared, [1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16] and even an ASTM standard has been established[17]. The steps to be taken in the calibration process has been extensively described in the very readable review by Hamaguchi [2].

Translation of the multichannel detector image into a Raman spectrum requires a means of assigning the position of a particular detector element (a pixel) to a Raman shift value. Sometimes only a projection of a column of pixels is used, obtained by the so-called "binning" process. The wavelength at each pixel is determined by the position of that detector element at the focal plane of the monochromator and hence the position and tilt of the grating. The grating setting is normally determined by the software of the system. Because of the rather small size of the pixels (typically 25 micrometers) most spectrometer systems have a hard job to reproduce the situation after a grating movement or an elapsed time. Thus

spectrometers must be recalibrated to obtain the desired accuracy. The precision of the resulting calibration depends on the quality of the standards used as well as on the quality of the spectrometer [10]. Robust instrument calibration is essential [18].

Since the Raman emission spectrum is a frequency shift phenomenon, absolute wavelength calibration of the dispersive spectrometer alone is not sufficient. It is just as important to know the excitation laser wavelength. While gas lasers such as He-Ne and Ar$^+$ emit precisely known atomic emission lines, the wavelength of a solid state laser, such as the doubled Nd-YAG laser, is less accurately known. It is able to and likely to shift its frequency substantially with time and temperature, e.g. the laser wavelength drifts with temperature on the order of 0.0025 to 0.1 nm/^{o}C [18], [19], and start-up mode jumps of ±0.2 nm have been found for a 532 nm Nd-YAG laser [18], [19], [20], also in our laboratory [16].

In principle it is possible to calibrate the Raman shift axis directly by exciting a known Raman standard material, such as cyclohexane, and observing the pixel image positions of the precisely known bands. But the number of available Raman bands is limited, compared to the number of atomic emission lines available from Ne or Ar lamps; and precise values of their lines have been given for neon [21], [22], [23], [24], argon [10], [25] and krypton lines [26]. Fountain et al. [13] studied the calibration with neon lines in detail. A convenient and reliable means of calibration is to obtain the lines from a detuned laser, and this method has been often used to get the absolute wavenumber response of Raman spectrometers [8], [18], [24], [27], [28], [29], [30], [31].

Notch filters in the Raman collection path are specifically designed to block the laser line. Therefore in such systems, the determination of the laser position is slightly more complicated because typically the notch filter should be removed, and the light level reduced not to saturate the detector, when the position of the laser line is determined. A practical alternative to such a laser line determination has been suggested by Kaiser Optical Systems [18] involving taking out a fraction of the laser light and injecting it downstream of the notch filter. The advantage is that every Raman spectrum recorded contains a wavelength peak of the very same laser line that was used, and if the laser wavelength happens to shift it is directly detected. A third way to determine the laser position is to record a Raman standard spectrum (e. g. of cyclohexane) and calculate the laser line position from its known values [16], [18].

The position of the sample on the optical axis is quite important and considerable errors might arise if the sample position is slightly off axis, as has been discussed [9]. As the position of the sample can have significant effect on wavelength accuracy, it is advisable to duplicate the positioning for both the standard and the sample [12]. Wavelength calibration thus is most accurate if e.g. neon light is fed into the spectrograph via the same optical path that is used for the collection of the Raman data, although this may be impractical in some set-ups [18].

The precision with which the peak wavenumber can be determined is limited by the resolution of the spectrometer, again depending on the line density of the grating, the spectrometer focal length, the slit width and the pixel size, as considered in ref. [9]. Yet another factor that influences the precision of the spectrometer is non-uniformity of pixel size, as discussed by Hamaguchi [2].

The question of what Raman shift calibration standard to use has been addressed by many. The use of indene as a *shift* calibration standard in combination with Ar$^+$ and Kr$^+$ laser plasma lines was explored by Hendra [24], Wollman and Bohn [7], Sharma et al. [1] and Carter et al. [10]. Mann et al. [32], [33] studied transfer of data from one instrument to another using as references cyclohexane and neon lines. Cyclohexane is a particularly popular standard substance [34] and data from several laboratories have been compared at ASTM [17]. The effects of sample temperature (over a range of 7 to 73 ^{o}C) on 14 liquid state cyclohexane Raman bands were studied by Pelletier [20] who used neon and mercury atomic emission spectra and a third order polynomial (sub-pixel interpolation) to fit the lines. Also naphthalene, 50/50 v/v toluene/acetonitrile, polystyrene, sulphur, silicon, diamond, 4-acetamidophenol (active ingredient of

Tylenol), indene and others have often been used as Raman shift standard substances [2], [12], [17], [28], [30], [31], [34].

       The relationship between peak position (or pixel number) and wavelength has been much discussed. Conversions of pixel to wavelength or wavenumber have typically been accomplished with the use of *fitting polynomials*. The lowest order of a satisfactory polynomial fitting function should preferably be used to give the most reliable calibration [10], and a third order (cubic) expression is perhaps the best one t use [7]. For compact Raman spectrometers, Vickers et al. [6], [11], [13], [14] studied wavenumber axis calibration procedures, such as interpolation between pixels by use of fifth order polynomials, to determine the exact positions of peaks aiming at a better than 0.1 cm^{-1} accuracy. Problems with the abscissa accuracy were discussed, and the physical parameters of the monochromator have been studied [3]. It was concluded that the precision of the abscissa calibration degraded markedly each time the grating had been moved [13].

       The interpolation between pixels to recover a nearly true band shape has been the theme in several of the papers and a method known as Fourier-domain zero-filling has been developed, see e.g. [35]. Improvements in spectral line shape detection have been obtained by slanting the image on the CCD and a simple algorithm has been proposed to convert the two-dimensional data into a one-dimensional spectrum [36]. Also one can use an alternative procedure that involves directly scanning the spectra across the CCD camera but it requires that one has a very accurate spectrometer drive (precision less than 0.1 cm^{-1}) that is not easily obtainable [4], [5].

       Yet another key element to good calibration of dispersive Raman instruments that needs to be mentioned is the spectral intensity response of the instrument (also called the white light calibration) [18], [37], [38], [39], [40]. With intensity-axis correction even low-cost CCD detectors can be used to get Raman spectra with signal-to-noise ratios approaching those obtainable with the most expensive "scientific" ones [40]. Large errors owing to the inability to reposition the spectrometer precisely and to temperature fluctuations were found [6], [9].

       The use of a socalled reduced intensity format R(ω) should also be encouraged [41], [42]. The intensity form I(ω) of Raman data mostly given is dependent on the excitation frequency (ω is the Raman shift in wavenumber from the laser line at ω_o). A software procedure should ideally be applied to correct for the fourth power dependence of the scattering activity on the frequency and to correct for the Bose-Einstein temperature factor, B = [1-exp(-*h*cω/*k*T)] (*h*, *k*, c and T are Planck's and Boltzmann's constants, the speed of light in vacuum and the absolute temperature, respectively). In this way the reduced R(ω) spectrum is obtained that is directly proportional to a point by point relative scattering activity, in the double harmonic approximation. The R(ω) format most closely approaches the vibrational density of states [41] [42]. The relationship between the I(ω) and R(ω) formats of the spectra is given by the equation, Eq. (1):

$$R(\omega) \;=\; I(\omega)(\omega_o - \omega)^{-4}\,\omega\,B \qquad\qquad (1)$$

       One should prefer to plot the spectrum in the R(ω) format because the Bose-Einstein factor removes the state dependent temperature factor of the excited state transitions and leaves the essential Raman spectrum.

2. Examination of Raman Spectrometer Systems

2.1 The DILOR-HORIBA "LabRam" Type

This kind of spectrometer was delivered by DILOR S.A., France. The spectrometer was incorporated into a larger Raman XY-spectrometer system, having the choice between two spectrometers of different focal length. This so called "*LabRam*" or "second" monochromator, is schematically depicted in Fig. 1. It is equipped with two interchangeable gratings (with 150 and 600 grooves/mm) mounted on a common shaft. The shaft is turned by a so called *sinus arm* driven by a computer controlled stepping motor. The path of Raman scattered light, after being collected by a lens, filtered by passing a notch filter and focused, is visualised in Fig. 1. This figure is showing the rays from the slit to the CCD detector (256 x 1024 pixels), as well as the essential parts of the mechanism controlling the tilting movement of the selected grating. The focal length of the spectrometer was 300 mm (both lenses) and the slit width was normally set to 0.1 mm. As the stepping motor revolves the spindle, the metal block carrying a small mirror (used as a flat surface) moves slowly back and forth, pushing the sinus arm, that is tilting the grating and consequently shifting the position of Raman light on the CCD. We tried this kind of spectrometer in two modifications (in short called DH1and DH2).
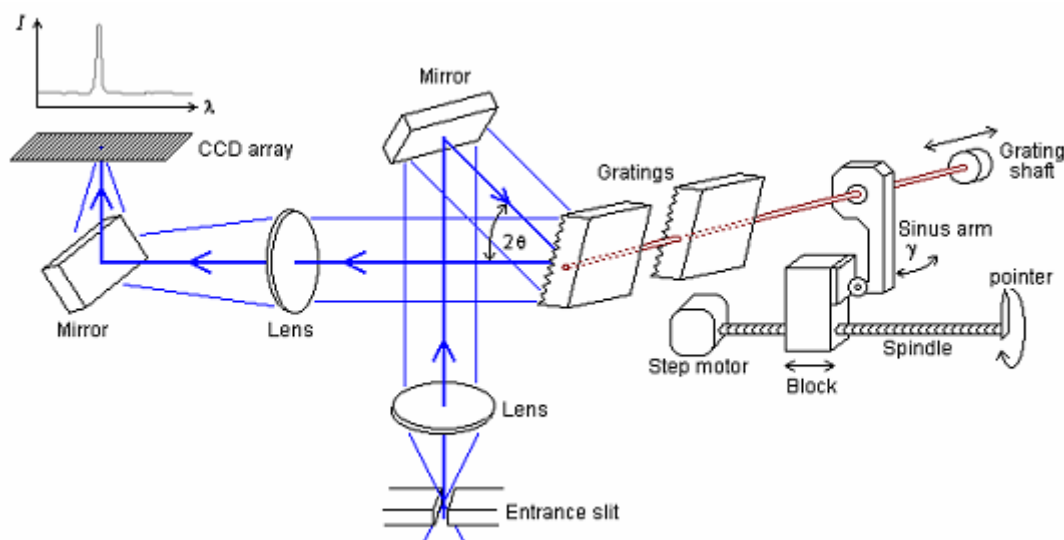

Figure 1. Sketch of the DILOR-HORIBA "LabRam" spectrometer, integrated in the DILOR XY-system. The essentials of the mechanical and optical connections between slit, grating, CCD and sinus arm are shown. The first part of the Raman scattering process, involving light collection, Rayleigh filtering with a notch filter and focusing, is not shown.

2.2 The RENISHAW "Raman System 1000" Type

This kind of spectrometer type was delivered by Renishaw, Plc., Great Britain. The spectrometer has a single grating (with 1800 grooves/mm), as shown in Fig. 2. The grating sits on a geared tooth wheel that is connected *via* a turning spindle driven by a stepping motor controlled by the computer. The collected, filtered and focused Raman light passes from the slit through a lens to the grating and further on to the CCD detector (384 x 576 pixels). The focal length of the spectrometer was 80 mm and a slit width of 0.1 mm was used. As the stepping motor revolves the spindle, the grating is

tilted, thereby shifting the peak of a line on the CCD. Two R1000 instruments were examined (in short called R1 and R2).
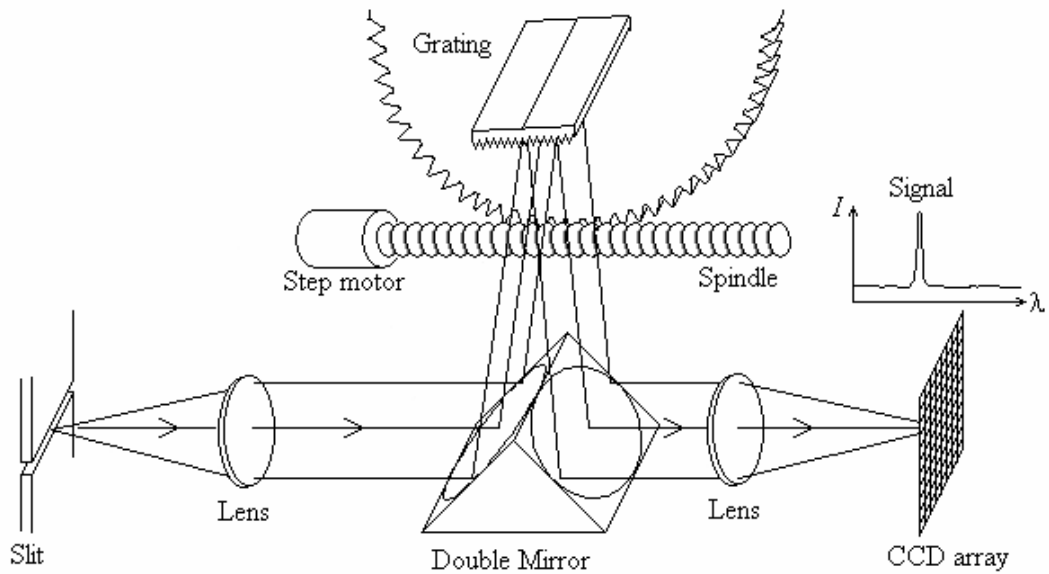

Figure 2. Sketch of the RENISHAW "Raman System 1000" spectrometer. The essentials of the mechanical and optical connections between slit, grating, CCD and sinus arm are shown, but the first part of the Raman scattering process, prior to the entrance slit, has been left out.

When comparing Figs. 1 and 2 it is obvious that the most essential part of these sinus drives is the moving mechanism; that is the rotating spindle controlling the tilt of the grating and thus controlling which wavelengths reach which part of the CCD.

3. Diffraction Physics of the Sinus Arm Drive

As well known, the diffraction of light by a grating (both ruled and holographic) can be expressed by the Eq. (2):

$$\sin \alpha + \sin \beta = kn\lambda \qquad\qquad (2)$$

where λ is the wavelength, k is the order of diffraction, n is the number of grooves per unit length, α and β are the normal angles of incident and diffracted light, respectively, as shown in Fig. 3.
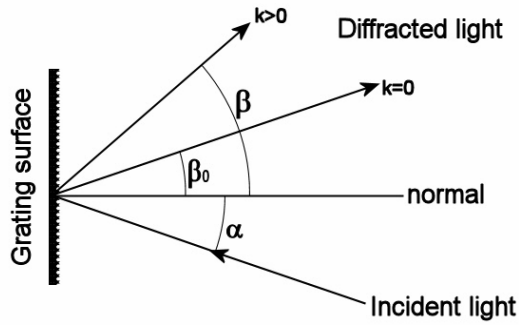
Figure 3: Diffraction of monochromatic light.

To analyse e. g. the DILOR-HORIBA "LabRam" spectrometer, we consider Fig. 1 in detail. The angles α and β (shown in Fig. 3) can be expressed in terms of two other angles γ and θ_0 (shown in Fig. 1). Assume that

$$\alpha = \gamma + \theta_0 \quad \text{and} \quad \beta = \gamma - \theta_0. \tag{3}$$

The boundary condition of zero-order reflection occurs for $\gamma = 0$ (i. e. no diffraction; the grating works as a mirror). We then have $|\theta_0| = |\alpha| = |\beta|$. Also,

$$\gamma = \tfrac{1}{2}(\alpha + \beta) \quad \text{and} \quad \theta_0 = \tfrac{1}{2}(\alpha - \beta) \tag{4}$$

The wavelength dependence on the tilt angle of the grating (the setting) can then be expressed as Eq. (5):

$$\lambda = \frac{\sin\alpha + \sin\beta}{kn} = \frac{2\sin\dfrac{\alpha+\beta}{2} * \cos\dfrac{\alpha-\beta}{2}}{kn} = \frac{2\sin\gamma * \cos\theta_0}{kn} \tag{5}$$

Since θ_0 and n are fixed (e. g. for the DILOR-HORIBA "LabRam" instrument, $n = 150$ or 600 grooves/mm and $2\theta_0 = 24^\circ$), λ is proportional to $\sin\gamma$ for each order of diffraction $k > 0$. This is the reason for the name of the sinus drive.

4. Principles of Operation

After mounting and physical alignment of each grating of the spectrometer (this is usually done by the manufacturer), calibration of the grating and data acquisition system remains. As modern spectrometers are computer controlled, the calibration is mainly the matter of programming this control. Later on, when spectra having calibration errors are obtained, it is rather difficult for a non-expert (common user) to determine the reason: The errors might be due to mechanical problems (e. g. mirror or grating tilt errors may be sending light beams to wrong parts of the CCD), or due to errors in the computation of the data (e. g. caused by erroneous parameter settings in the computer program, which ultimately controls both things).

The design and quality of the sinus drive and the computer thus may influence the precision of the obtained spectrum. Depending on the tilt of the grating, light of a certain wavelength is sent to a certain part of the CCD array and detected as charge in the appropriate pixel. The wavenumber (or wavelength) must however be correctly calculated by the computer. If the parameters for the CCD signal processing algorithm are erroneously set, poor wavelength calibration results. The interpretation of the pixel data gets biased - even if the grating is correctly calibrated and the wavelengths of the incoming light is hitting the right pixels. For these reasons the order in which to correct the appropriate software parameters is of importance.

As described previously, sources of light with well-known lines must be used to calibrate a Raman spectrometer: It can be lines from e.g. a neon or mercury lamp, or gas laser plasma lines, giving absolute calibration, or Raman scattering from suitable, well-documented substances, e. g. cyclohexane, etc. This last method has the advantage that the frequency of the laser line does not influence the Raman shift calibration.

Following the manual [43] for calibrating the DILOR-HORIBA "LabRam" spectrometer, the first step is to put the 0th order grating reflection at the centre of the CCD array. The grating is turned to the position of specular reflection (i. e. $\alpha = \beta = \theta_0$, $\gamma = 0$), where all wavelengths of light emerging from the slit should become focused on the same spot of the CCD array. A variable parameter (called *ZeroSpectro* in the LABSPEC software [43]) is adjusted iteratively in the software to tilt the grating (via the zeroing of the step motor) until the focused spot is well positioned at the centre of the CCD. When a satisfactory starting point for the grating tilt has been obtained in this way, another software parameter (called *KoeffSpectro*) is adjusted, linking the movement of the stepping motor to the wavelength of the diffracted light. The parameter in principle tells the computer how much the wavelength changes for each step of the motor. The higher the value, the larger the shift in wavelength calculated predicted per step. Changing *KoeffSpectro* to a higher value will therefore cause the computer to assume fewer steps (and consequently a smaller turning of the grating) to reach a selected diffracted wavelength. Hence the entire spectrum will be observed with shifted spectral peaks. Also two software coefficients concerning the display of the spectrum onto the computer screen need to be calibrated. These coefficients depend of optical parameters of the system, such as grating dispersion and spectrometer focal length. As these characteristics will be constant in a thermostat room, there is normally no need to adjust these values after the initial calibration done by the manufacturer.

The RENISHAW "Raman System 1000" software (based on the GRAMS/386™ software packet) similarly allows settings of analogous calibration parameters [44].

To view a specific part of a spectrum, the grating has to be set to a certain angle. This is done by asking the computer to move the grating stepwise to a position specified by the wavelength (or

wavenumber) of the light hitting the central pixel on the CCD. This is referred to as the CCD **central position**, in the following abbreviated to **CP**.

5. Examination of Reproducibility and Calibration

Extensive examination of the DILOR-HORIBA spectrometer was started because apparent inconsistencies were found in its sinus drive system. We wanted to discover the reason for this and therefore needed to obtain a basic understanding of the instrument: the influence of the software parameters, forward vs. backward scanning, shift between the two gratings (manipulation of the shaft shown on Fig.1) and temperature variations of the room. As the basis for our examination, the known [2], [45], [46] line spectrum of neon in the range 540-967 nm was chosen, like previously in other reports on wavelength calibrations [7], [8], [9], [10], [18], [22]. The results obtained for the 600 grooves/mm grating here serve as an example of our results. Positions of the lines imaged onto the CCD of the spectrograph were determined by visual interpolation between pixels with an accuracy of about 0.1 - 0.2 pixel. The image of each spectral line typically extends a few pixels, providing the useable sample spectrum data for interpolation.

To a start it was found that the spectrum of a neon lamp, obtained with the 600 grooves/mm grating tilted to have the CCD central position at 660 nm (**CP** = 660 nm), could be reproduced with excellent accuracy (± 1 pixel for all accessible lines), at room temperature. This was true over long periods of time (several weeks) and independent of the grating tilt history. That is, similar spectra with identical peak frequencies resulted for e.g. **CP** = 660 nm at all times. This satisfactory result was independent of whether prior tilt scanning has been forward (i. e. towards the red) in large wavelength-jumps, or forwards in several small jumps (moving the grating 0.5 nm at a time), or whether the position was reached after a backward jump towards the blue. During backwards scanning the grating is automatically moved beyond the desired position by half a spindle revolution and then forward so as to successfully eliminate any backlash in the moving parts. The backlash problem has been discussed in e.g. ref. [9].

Careful exchange of gratings (from 600 to 150 grooves/mm or backwards) typically caused displacements of peak values by on the order of 1-1.5 pixels (a few wavenumbers). Similar *small* shifts in position were observed when moving other integrated mirrors of the DILOR XY spectrometer system forth and back. After such mechanical manipulation it is thus recommended to re-calibrate the zero tilt position.

What however did cause an *appreciable* effect was the selection of another angle of rotation for the sinus arm spindle (another **CP**). Three typical obtained spectra are shown in Fig. 4, corresponding to different selected **CP** values. The only difference between the spectra ought to be the shifted spectral window, without any displacement of the line positions. The found peak wavenumber values of a suitable neon line, truly at 540.05616 nm (value in air [2], [21], [22], [27], [45], [46], [47], [48], as others given here) are indicated in Fig. 4. As seen the line position, determined by interpolation assuming a Gaussian line shape, varied from about 540.01 to 540.20 nm. Careful examination showed that other peaks of the upper spectrum occurred at wavelengths about 0.10 nm shorter than the corresponding peaks of the middle spectrum, and at about 0.19 nm shorter than those of the bottom spectrum. The errors of the upper, middle and lower spectra relative to the standard value were about -0.05, +0.05 and +0.14 nm, respectively. Other recordings behaved similarly, with displacements depending on the actual **CP** setting, as shown in Fig. 5. Appreciable magnitudes of correction (up to ~0.6 nm or ~6 cm^{-1}) were sometimes needed.
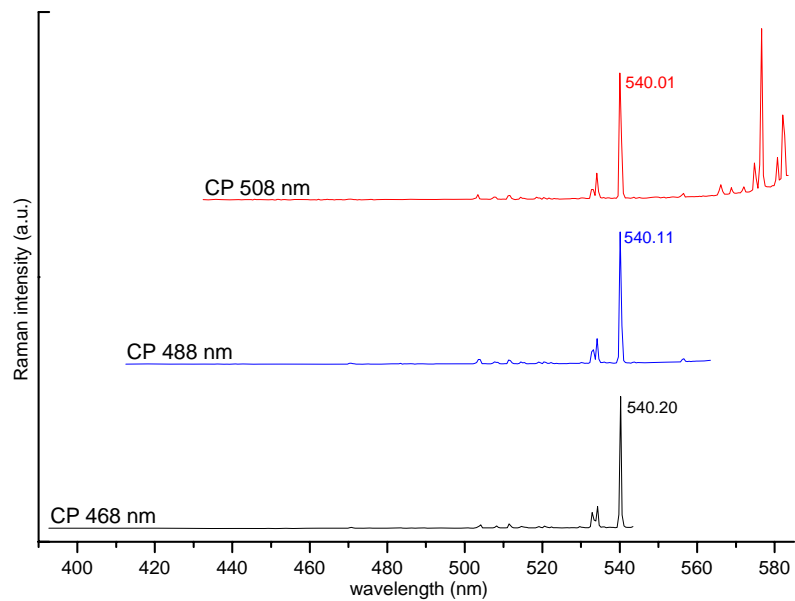
Figure 4: Line spectra obtained for a neon lamp at three selected **CP** settings of the CCD central position for the DILOR-HORIBA "LabRam" (DH1) instrument. Wavelengths obtained for the 540.05616 nm line [2], [21], [22], [27], [45], [46], [47], [48] are indicated.
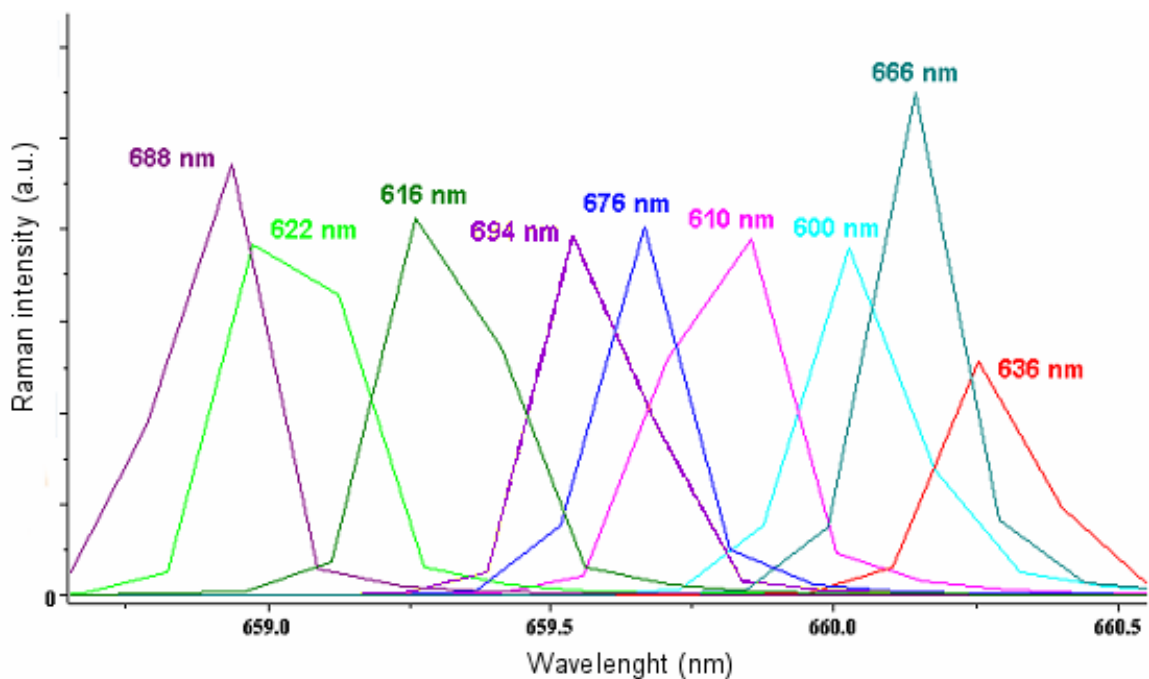

Figure 5:   Expanded view of obtained spectra of the neon line at 659.89529 nm [2], [21], [22], [27], [45], [46], [47], [48] (659.89526 nm was given by Vickers [11]) in dependence of the setting of the **CP** (i. e. revolution of the sinus arm spindle) for the DILOR-HORIBA "LabRam" instrument (DH1). **CP** settings are indicated for each curve.

These observations lead us to carry out extended series of measurements, to reveal the cause and nature of these errors. The spectra of several neon peaks were studied as a function of the **CP** setting. For each line the "spectral window" was moved in steps of 1 nm, from the lowest to the highest possible **CP** setting allowing the line to be observed. E.g. the 659.89529 nm line [2], [21], [22], [27], [45], [46], [47], [48] could be observed for **CP** settings from 596 to 738 nm. For each **CP** setting the position of the line was determined as precisely as possible by interpolation between pixels. The measured positions were then compared to the "true" line value and the correction difference calculated. A typical result is shown in Fig. 6, giving wavenumber unit corrections. Deviations expressed in the wavelength nm unit had similar patterns.
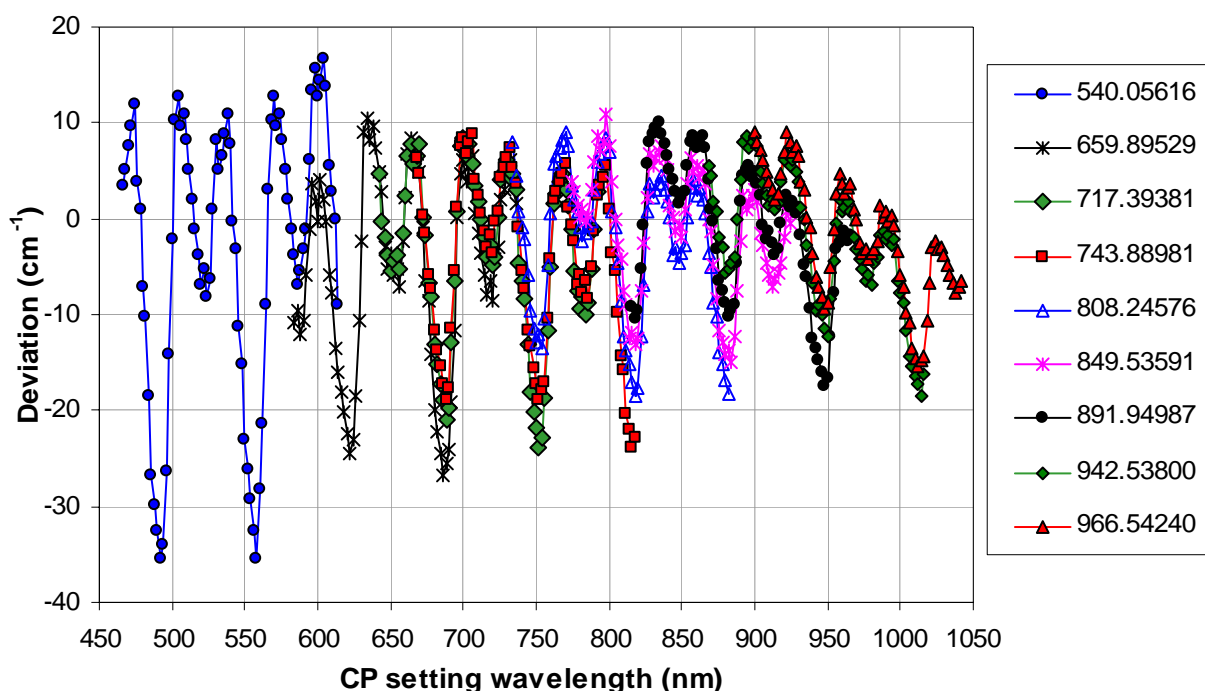

Figure 6: Deviation in wavenumber (cm^{-1} from true value of neon line positions in air given in nm) obtained at 20 ^{o}C as a function of selected sinus arm rotation for the DILOR-HORIBA "LabRam"-instrument (DH1). The line positions were taken from the literature [2], [22], [27], [45], [46], [47], [48]; slightly different values were given by some authors (659.89526 nm [11] , 808.24581 nm [21] , 849.53598 nm [21] and 891.95007 nm [21]).

By inspection of Fig. 6, an obvious repetitive pattern in the peak displacement is seen. In the overlaps between the spectral windows of the chosen neon lines we found the values to agree in a satisfactory way, see e.g. values near 600 and 800 nm. It was obvious that the spectrometer had a high reproducibility, but a very bad linearity, which meant that a sensitive calibration must be applied, depending on the **CP**. Without correction, errors ranging from –35 to + 15 cm^{-1} or from –1.2 to +0.8 nm were seen.

The measurements were repeated weekly for a long time and the reproducibility of any given measurement proved to be quite stable, with variations of just one pixel (or in few cases two). The overall picture remained the same.

We also tried other similar type Raman instruments that we had access to. The same kind of behaviour was seen on the two RENISHAW instruments, see Fig. 7. However only two waves were seen. They proved to be related to the turning of the spindle.
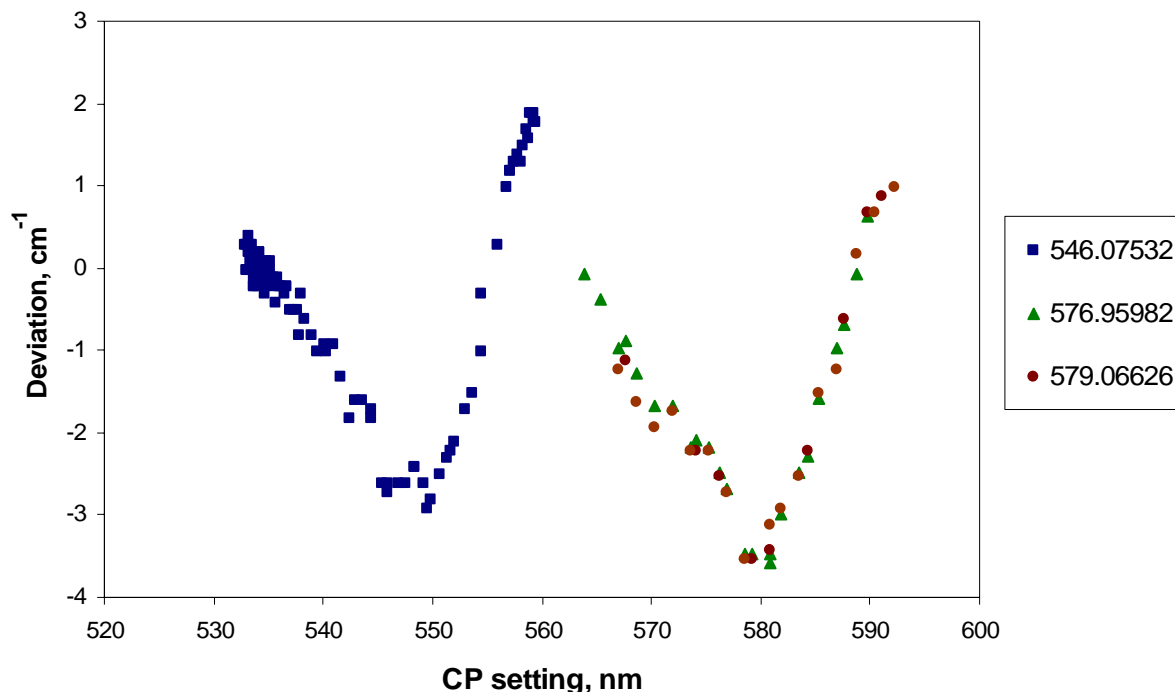

Figure 7:   Deviation in wavenumber (cm^{-1}) from true value of mercury line positions given in nm in air [22], [47], [49] at 20 ^{o}C, as a function of selected setting obtained for a RENISHAW 1000-instrument (R1) in prof. M. H. Brooker's laboratory in Memorial University, St. Johns, Canada (R1). Similar results were seen for another RENISHAW 1000-instrument (R2) at Risø National Laboratory., Roskilde, Denmark.

The Renishaw company has included into their instrumental concept a patented recording mode where the grating is moved during the measurement, so as to sweep the spectrum over the CCD-area during integration. We have tried this so-called continuous scanning procedure and found the resolution of the bands be much reduced. This is understandable when one has the deviation behaviour shown in Fig. 7: the quality of the spectra suffer from lack of precision of the wavenumber scale and a broadening occurs.

In practice to obtain the best possible spectra with either the RENISHAW 1000 or the DILOR-HORIBA "LabRam" instrument, the gratings should not be moved, and a calibration should be done each time to get a precise wavenumber scale.

6. Discussion of Reasons for CP Setting Errors

Ideally, the graphs in Figs. 6 and 7 should be lines near zero, but as mentioned we found disturbances of a repetitive nature. For Fig. 6, the deviations varied periodically from approximately +0.8 to −1.3 nm, equalling a total shift of 14 pixels from lowest to highest neon line shift. The deviations were suspected to be caused by imperfections in the motor, its internal gear wheels, the spindle, its mounting, the pitch of the screw thread, and the transfer of the movement to the sinus arm (Fig. 1), in total resulting

in a non-uniform tilting movement of the grating in response to different settings. In Fig. 7, most probably the errors are due to a gear wheel in the stepping motor.

For easy watching of the rotation, a pointer was placed on the end of the spindle of the DILOR-HORIBA "LabRam"-instrument (DH1). The neon lamp offers easily identifiable spectral lines in the range from approximately 500 to 900 nm. About 7 revolutions of the spindle could be characterised with this source. In Fig. 6, the repetitive length (e.g. from a local minimum to the next local one) clearly proved to correspond precisely to one turn of the sinus drive spindle. Thus an imperfection of the sinus drive spindle caused displacements of the recorded spectra. The tendency was that the peak positions differed up to 2.1 nm, corresponding to up to 50 cm^{-1} in the blue and 17 cm^{-1} in the red end of the spectrum. The precision specified by the manufacturer, "better than 2 pixels", was clearly unreachable.

In order to correlate the displacement of spectra with the assumed irregularities on the spindle, a physical measurement of the spindle was made. When a scan was made from 0 nm (**CP**) to 1562.5 nm (**CP**), the spindle was observed to rotate exactly 24 times. The mirror block moved 3.0 cm during this scanning, resulting in a turning of the grating sinus arm by 28.6 degrees. It follows from this that 1 revolution caused a 1.25 mm movement of the block and a $\Delta\lambda$ of 65.1 nm. Scanning errors of 1-2 nm thus may be caused by displacement imperfections of the block on the order of 20-40 μm.

The RENISHAW system allowed only about two revolutions to be easily measured, but similar problems occurred, as shown in Fig. 7, though not so large. The distance between the two local minima corresponded exactly to one third revolution of the spindle.

Another sinus drive of the DILOR-HORIBA "LabRam"-instrument (modification DH2) was subsequently installed to improve the instrument.

When analysing the calibration of this DH2 spectrometer, a new kind of behaviour showed up. When plotted against **CP,** the wavy deviation curves have not disappeared but their amplitudes have decreased to about 15 cm^{-1} and importantly they now did not overlap well. As an example, the error curves for two neon lines are plotted versus the **CP** in Fig. 8. It is seen that the curves show quite the same patterns.

When trying to find a reason we noted that the pattern seemed to depend on the pixel number, i. e. the overlap is now depending on the position on the CCD. If the deviation curves are plotted versus the pixel number much more uniform curves are obtained, see Fig. 9, in which four different error curves for neon lines are plotted versus the pixel number. It is seen that the curves show quite the same patterns, although perhaps shifted.

As our first guess, the reason for these errors might be a non-linearity in the position of the pixels on the CCD. The presence of such placing errors has been discussed by Vickers et al. [14] who have found errors on the order of 0.4 μm for their nominally 22 μm wide pixels. Our whole CCD is 2500 μm long and corresponding to about 150 nm in Fig 8. An error of 0.4 μm would then give a wavelength shift amplitude on the order of 150 x 0.4 / 2500 nm = 0.024 nm. This error is more than 10 times too small to account for the behaviour in our instrument.

We suspect that the errors are due to a combination of deficiencies in the software and the drive.
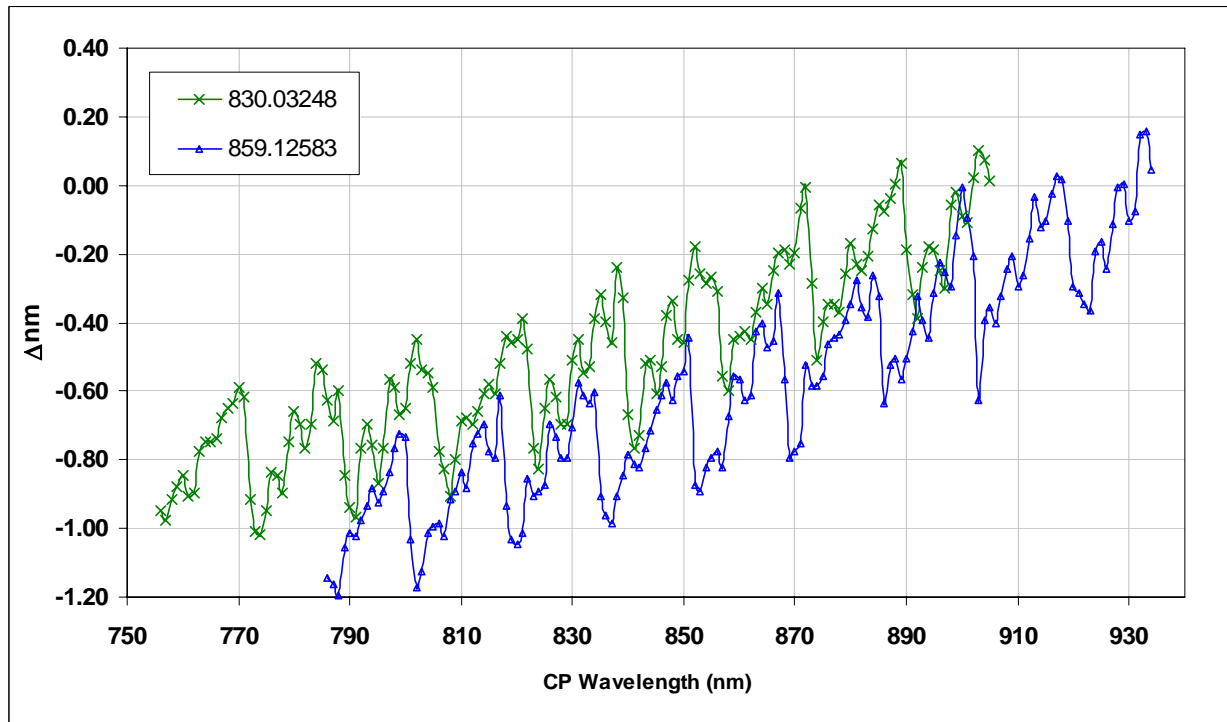
Figure 8: Deviation curves obtained in nm (from true value of neon line positions given) for two different neon lines given in nm, plotted as a function of selected sinus arm rotation for the DILOR-HORIBA "LabRam"-instrument (DH2), versus the **CP** at 20 $^{\circ}$C. It is seen that the curves are not straight lines and not near zero, as one would like.
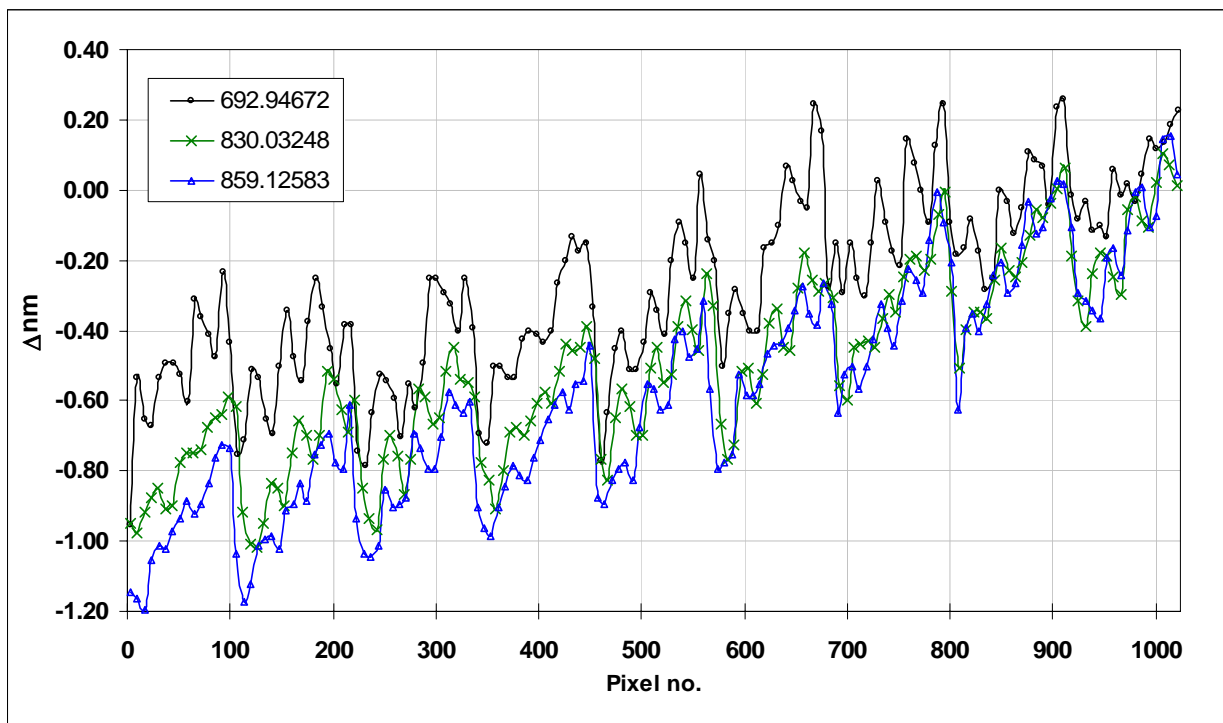

Figure 9: Deviation curves obtained in nm (from true values of four different neon line positions given in nm) for the DILOR-HORIBA "LabRam"-instrument (DH2), plotted as a function of pixel number at 20 $^{\circ}$C for different **CP** settings. It is seen that the patterns of the curves overlap when plotted in this way.

7. Temperature Effects

It is well known that temperature has an influence on the accuracy in spectroscopy. Ito et al [50] have described a thermal box that improved their Raman spectral reproducibility significantly when keeping the temperature of their instrument within 0.1 ⁰C. During our work with DH1 and DH2 it was found of interest to study the peak displacements as a result of temperature variations in the room. At moderate (± 0.5 degrees) variations around 22 ⁰C the errors were between 1-2 pixels. Deliberate raising of the temperature in the laboratory caused a more significant, almost linear change in the calibration curves as seen in Fig. 10. The pattern is largely preserved from one series to the next, but a large shift of the entire graph is seen. The zero order parameter *ZeroSpectro* was not changed between series.

Mestari et al. [23] have found for their direct mode DILOR-HORIBA instrument that the calibration shifted minus 0.2-0.3 cm^{-1} per degree of heating. Similar values have been given in other references [19]. From Fig. 10 it is obvious that our instrument is more temperature sensitive, as we find a calibration shift of approximately minus 1.6 cm^{-1} pr. degree of heating.
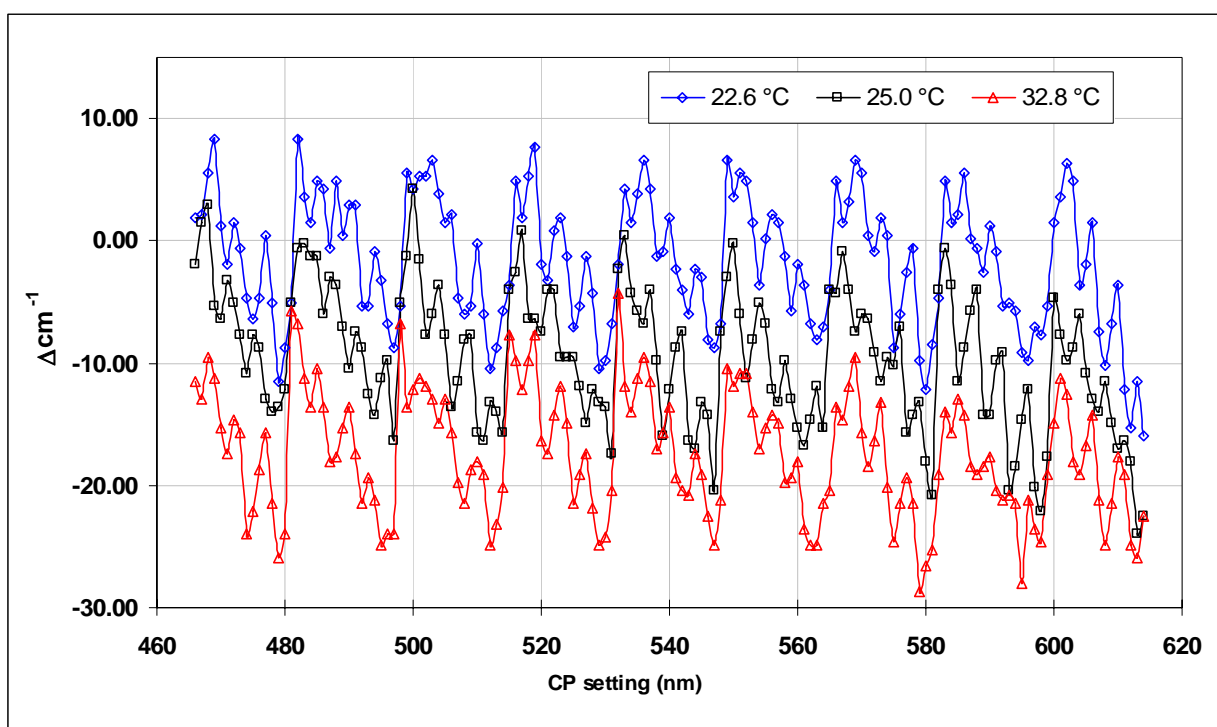

Figure 10: The effect of temperature on the calibration for the DILOR-HORIBA "LabRam"-instrument (DH2). Calibration based on the neon line at 540.05616 nm (air).

8. "Golden Values of CP"

As seen in Fig. 6 and 7, certain **CP** settings in some situations gave zero or small deviations. We name these the "Golden **CP** Values" of zero deviation. In other words, it may be possible to choose to work with certain **CP** values, that at a fixed temperature result in small or negligible errors. Each "Golden Value" must however be determined carefully because the slopes of the deviation curves can be very steep. For our instruments this procedure yielded a number of golden **CP** settings which could be routinely used when scanning the spectrometers, and which minimised

the influence from the spindle imperfections. Clearly temperature stability of the room is essential. As seen from Fig. 10, the golden values for e.g. a temperature of 23 ^{o}C are not good any more at 25 ^{o}C or other temperatures.

9. Solution to the Problems

As the use of the spectrometer in this way gets restricted to a finite number of wavelength values, the system loses some of it's dynamics. On the long view it will be preferable to install a more precise spindle so as to diminish this problem and to solve eventual other errors.

Until then, another solution would be in the controlling software to implement a possibility for the user to model the imperfections so as to automatically take the deviations into account. The method described herein would be suited to provide the basis for such a model.

10. Conclusion

A procedure has been found which allows the evaluation of mechanical imperfections (e.g. in the spindle), that influence the performance of dispersive Raman spectrometers with moving gratings. A method (to use pre-selected 'Golden Values' of **CP** settings) is suggested that allows one to obtain reliable spectra with minimal errors.

The accuracy of the wavelength determination seems to be limited by some property of the instrumentation that we do not fully understand.

Since we have examined only few Raman spectrometer systems, it would be imprudent to assume that other instruments will perform exactly like those in this study. We have however described a procedure that might be used to examine the performance.

Acknowledgements

References

[1]   Sharma, S. K.; Pandya, N.; Muenow, D. W., "*Calibration of a Multichannel Micro-Raman Spectrograph with Plasma Lines of Argon and Krypton Ion Lasers*", Microbeam Anal. **1988,** *23*, 171-174.

[2]   Hamaguchi, H.-O., "*Calibrating Multichannel Raman Spectrometers"*, Appl. Spec. Reviews **1988,** *24(1&2)*, 137-174.

[3]   Lindrum, M.; Nickel, B., "*Wavelength Calibration of Optical Multichannel Detectors in Combination with Single- and Double-Grating Monochromators* ", Appl. Spectrosc. **1989,** *43(8),* 1427-1431.

[4]   Knoll, P.; Singer, R.; Kiefer, W. "*Improving Spectroscopic Techniques by a Scanning Multichannel Method",* Appl. Spectrosc. **1990,** *44(5),* 776-782.

[5]   Deckert, V.; Kiefer, W., "*Scanning Multichannel Technique for Improved Spectrochemical Measurements with a CCD Camera and its Application to Raman Spectroscopy",* Appl. Spectrosc. **1992,** *46(2),* 322-328.

[6]   Shen, C.; Vickers T. J.; Mann, C. K., "*Abscissa Error Detection and Correction in Raman Spectroscopy*", Appl. Spectrosc. **1992,** *46(5),* 772-777.

[7]   Wollman S. T.; Bohn, P. W. "Evaluation of Polynomial Fitting Functions for Use with CCD Arrays in Raman Spectroscopy", Appl. Spectrosc. **1993,** *47(1),* 125-126.

[8]   Tseng, C.-H.; Ford, J. F.; Mann, C. K.; Vickers, T. J. "*Wavelength Calibration of a Multichannel Spectrometer*", Appl. Spectrosc. **1993,** *47(11),* 1808-1813.

[9]   Carter, D. A.; Pemberton, J. E., "*Frequency/Wavelength Calibration of Multipurpose Multichannel Raman Spectrometers. Part I: Instrumental Factors Affecting Precision*", Appl. Spectrosc. **1995,** *49(11),* 1550-1560.

[10]   Carter, D. A.; Thompson, W. R.; Taylor, C. E.; Pemberton, J. E., "*Frequency/ Wavelength Calibration of Multipurpose Multichannel Raman Spectrometers. Part II: Calibration Fit Considerations and Calibration Standards*", Appl. Spectrosc. **1995,** *49(11),* 1561-1576.

[11]   Vickers, T. J.; Rosen C. A.; Mann, C. K., "*Compact Raman Spectrometers: Data Handling Methods*", Appl. Spectrosc. **1996,** *50(8),* 1074-1081.

[12]   McCreery, R. L., "*Instrumentation for Dispersive Raman Spectroscopy*", in "*Modern Techniques in Raman Spectroscopy*", Editor: Laserna, J. J., J. Wiley & Sons, New York, **1996,** 41-72.

[13]   Fountain III, A. W.; Vickers, T. J., Mann, C. K., "*Factors that Affect the Accuracy of Raman Shift Measurements on Multichannel Spectrometers*", Appl. Spectrosc. **1998,** *52(3),* 462-468.

[14]   Vickers, T. J.; Mann, C. K., "*Raman Shift Calibration of a Compact Multichannel Spectrometer*", Appl. Spectrosc. **1999,** *53(12),* 1617-1622.

[15]   Carrabba, M. M. "*Wavenumber Standards for Raman Spectroscopy*", in "*Handbook of Vibrational Spectroscopy*", Ed. Chalmers, J. M. and Griffiths, P. R., J. Wiley & Sons, Ltd. **2002**, Vol. *1,* 912-919.

[16]   Brunsgaard Hansen, S.; Berg, R. W.; Stenby, E. H.; "*Upgrade of a Raman Spectrometer*", Appl. Spectrosc. Reviews **2004**, *39(3),* 385-397.

[17]   "*Standard Guide for Raman Shift Standards for Spectrometer Calibration*", in Annual book of ASTM Standards, E1840, Vol. 03.06, ASTM, W. Conshohocken, Philadelphia, PA 19428, **1996**, pages 859-867.

[18]   Tedesco, J. M.; Davis, K. L., "*Calibration of dispersive Raman process analyzers*", Proceedings Paper presented at the SPIE Conference on Online Chemical Process Monitoring with Advanced Techniques, Boston, Massachusetts, Nov. **1998**, SPIE vol. 3537, 0277-786X, **1999**, p. 200-212.

[19]   Davies, K. L.; Tedesco, J. M.; Shaver, J., "*Advances in Fiber Optic Raman Instrumentation*", Proceedings Paper presented at the SPIE Conference on Biomedical Applications of Raman Spectroscopy, San Jose, California, Jan. **1999**, SPIE vol. 3608, 0277-786X, **1999**, p. 148-156.

[20]   Pelletier, M. J., "*Effects of Temperature on Cyclohexane Raman Bands*", Appl. Spectrosc. **1999**, *53(9)*, 1087-1096.

[21]   Crosswhite, H. M., "*The Iron-Neon Hollow-Cathode Spectrum*", J. Res. of Natl. Bur. Stand., Sec. A (Physics and Chemistry), **1975**, *79A (no.1)*, 17-69.

[22]   Kim, S. B.; Hammaker, R. M.; Fateley, W. G., *Calibrating Raman Spectrometers Using a Neon Lamp*, Appl. Spectrosc. **1986**, *40(3)*, 412-415.

[23]   Mestari, A.; Gaufrès R.; Huguet, P., "*Behaviour of the Calibration of a Raman Spectrometer with Temperature Changes*", J. Raman Spectrosc. **1997**, *28*, 785-789.

[24]   Hendra, P. J.; Loader, E. J., "*The routine frequency calibration of He/Ne laser excited Raman spectrophotometers*", Chem. & Ind. **1968**, 718-719.

[25]   Craig, N. C.; Levin, I. W., "*Calibrating Raman Spectrometers with Plasma Lines from the Argon Ion Laser*", Appl. Spectrosc. **1979,** *33(5)*, 475-476.

[26]   Julien, C.; Hirlimann, C., "*Calibration of a Raman Spectrometer Using the Kr+ Laser Plasma Lines*", J. Raman Spectrosc. **1980,** *9(1)*, 62-66.

[27]   Striganov, A. R.; Sventitskii N. S., "*Tables of Spectral Lines of Neutral and Ionised Atoms*", IFI/Plenum Data Corp., New York, 2nd edition, **1968**.

[28]   Stommen, D. P.; Nakamoto, K., *Laboratory Raman Spectroscopy*, J. Wiley & Sons, New York, **1984**.

[29]   Ferraro, J. R.; Nakamoto, K., "*Introductory Raman Spectroscopy*", Academic Press, Inc., New York, **1994**, 113-118.

[30]   McCreery, R. L., "*Calibration and validation*", Chapter 10 in "*Raman Spectroscopy for Chemical Analysis*", Chemical Analysis, **2000,** *157*, Wiley-Interscience, 251-291.

[31]   Smith, E.; Dent, G., "*Calibration*", section 5.8 in "*Modern Raman Spectroscopy, a Practical Approach*", J. Wiley & sons, New York, **2005**,.51-53.

[32]   Mann, C. K.; Vickers, T. J., "I*nstrument to Instrument Transfer of Raman Spectra*", Appl. Spectrosc. **1999,** *53(7)*, 856-861.

[33]   Fountain III, A. W.; Mann C. K.; Vickers, T. J., "*Routine Wavenumber Calibration of an FT-Raman Spectrometer*", Appl. Spectrosc. **1995**, *49(7)*, 1048-1053.

[34]   http://www.chemistry.ohio-state.edu/~rmccreer/freqcorr/shift.html

[35] Lepla, K. C.; Horlick, G., "*Data Processing Techniques for improved Spectrochemical Measurements with Photodiode Array Spectrometers*", Appl. Spectrosc. **1990,** *44(8)*, 1259-1269.

[36] Sadler, D. A.; Littlejohn, D.; Riley, R.; Perkins, C. V., "Improvements in Spectral Line shape Reproduction from Spectrographs with CCD detection", Appl. Spectrosc. **1996,** *50(4)*, 504-510.

[37] Fryling, M.; Frank, C. J.; McCreery, R. L., "*Intensity Calibration and Sensitivity Comparisons for CCD/Raman Spectrometers*", Appl. Spectrosc. **1993,** *47(12)*, 1965-1974.

[38] Ray, K. G.; McCreery, R. L., "*Simplified Calibration of Instrument Response Function for Raman Spectrometers Based on Luminescent Intensity Standards*", Appl. Spectrosc. **1997,** *51(1)*, 108-116.

[39] Frost, K. J.; McCreery, R. L., "*Calibration of Raman Spectrometer Instrument Response Function with Luminescent Standards. An Update*", Appl. Spectrosc. **1998,** *52(12)*, 1614-1618.

[40] Jones, J. P.; Wambles, Jr., R. E.; Mann, C. K.; Vickers, T. J., "*Effect on Noise of Intensity-Axis Correction of Spectra Recorded with Charge-Coupled Device Detectors*", Appl. Spectrosc. **2002,** *56(5)*, 564-569.

[41] Brooker, M.H.; Nielsen, O. Faurskov; Praestgaard, E. *"Assessment of correction procedures for reduction of Raman spectra"*, J. Raman Spectrosc., **1988**, *19(2)*, 71-78.

[42] Murphy, W.F.; Brooker, M.H.; Faurskov Nielsen, O.; Praestgaard, E.; Bertie, J.E.: *"Further assessment of reduction procedures for Raman spectra."* J. Raman Spectrosc., **1989,** *20(10)*, 695-699.

[43] ISA, Dilor-JobinYvon-Spex, *User Manual for XY Modular Laser Raman Spectrometer*, 244 ter rue des Bois Blancs, 59000 Lille, France (**1997**).

[44] RENISHAW plc, Instruction Manual, Raman Calibration Source, M-9800-0216-01,Old Town, Wotton-Under-Edge, Gloucestershire GL127DW UK.

[45] Burns, K.; Adams, K. B.; Longwell, J. "*Interference Measurements in the spectra of Neon and Natural Mercury*", J. Opt. Soc. Am. **1950,** *40*, 339-344.

[46] Burns, K.; Adams, K. B., "*Interference Measurements in the spectrum of Argon I*", J. Opt. Soc. Am. **1953,** *43(11)*, 1020-1024.

[47] Kaufman, V.; Edlén, B. "*Reference Wavelengths From Atomic Spectra in the Range 15 Å to 25000 Å*", J. Phys. Chem. Ref. Data **1974**, *3(4)*, 825-895.

[48] Phelps III, F. M., *MIT Wavelength Tables* (The MIT Press, Cambridge, Massachusetts, **1982**), Vol. 2, Wavelengths by Element.

[49] Strey, G., "*Calculation of the Raman shift in Vacuum*", Spectrochim. Acta, **1969,** *25A*, 163-167.

[50] Ito, K.; Kato, T.; Ona, T., "*Improvement of reproducibility for quantitative analysis of real samples by NIR FT-Raman spectroscopy using a thermal box*", J. Raman Spectrosc. **2001**, *32*, 389-394.