Quality-Control and Process-Monitoring
by
Vibrational Spectroscopy

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Introduction

Over the last years vibrational spectroscopy has – based on new instrumental developments and in combination with chemometric evaluation procedures - developed to an indispensable tool for academic research and industrial quality control in a wide field of applications ranging from chemistry to agriculture and from life sciences to environmental analysis. In this communication a condensed overview on the physical principles and some instrumental aspects of mid-infrared (MIR), near-infrared (NIR) and Raman spectroscopy will be discussed and the advantages and disadvantages of the individual techniques will be outlined with reference to their implementation as industrial routine tools. For more detailed information on the theory and instrumentation of these spectroscopic techniques the interested reader is referred to the literature.¹⁻⁴

While mid-infrared spectroscopy has been a well-established research tool and structure elucidation technique in the academic as well as industrial environment over many decades, Raman spectroscopy was restricted for a long time primarily to academic research and has gained a broader industrial recognition only in combination with the Fourier-Transform technique and NIR-laser excitation in the late eighties. Just recently dispersive Raman spectroscopy with charge-coupled device (CCD) detection is undergoing a further renaissance with reference to process-control applications.²⁻⁴ On the other hand, NIR spectroscopy has been used only occasionally since the early fifties for industrial problem solving, later on more frequently in the field of agriculture, but a real break-through as quality- and process-control tool occurred only within the last decade since the introduction of efficient chemometric evaluation techniques and the development of light-fiber coupled probes. In actual fact, despite the lack of comparable specific spectral information, NIR spectroscopy is quickly overtaking Raman and primarily mid-infrared spectroscopy as a process-monitoring technique.⁴ The main reason is the much easier sample presentation and the possibility to separate the sample measuring position and the spectrometer by light fibers over distances of several hundred meters. Although similar arguments hold for Raman spectroscopy, the restriction to only small sample volumes, comparatively low sensitivity, interference by fluorescence and safety arguments are still limiting its industrial application on a real broad scale.
Basic Principles

Although the three spectroscopic techniques are very different in several aspects, their basic physical origin is the same: absorption bands in the MIR, NIR and Raman spectra of chemical compounds can be observed as a consequence of molecular vibrations.

![Diagram of Raman, Mid-IR, and Near-IR spectroscopy](image)

**Figure 1.** Characteristic vibrational transitions, wavenumber regions and principal physical differences between MIR, NIR and Raman spectroscopy.

Considering the simple diatomic oscillator of Fig.1, the vibrational frequency $\nu$ (based on a harmonic oscillator approximation) can be correlated with molecular parameters by:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{\mu}}$$  \hspace{1cm} (1)

where the force constant $f$ reflects the strength of the bond between $m$ and $M$ and the reduced mass $\mu$ is given by:

$$\mu = \frac{mM}{m + M}$$  \hspace{1cm} (2)
Thus, the vibrational frequencies are very sensitive to the structure of the investigated compound and this is the basis for the wide-spread application of MIR (and less frequently) Raman spectroscopy for structure elucidation.

Furthermore, due to the different excitation conditions of MIR, NIR and Raman spectroscopy (Fig.2), the relationships between the absorption intensities and the addressed functionalities of the molecules under examination vary significantly.

![Excitation conditions and structural specificities of the different vibrational spectroscopic techniques.](image)

Figure 2. Excitation conditions and structural specificities of the different vibrational spectroscopic techniques.

These specific features lead to extremely different responses of the same molecular vibration to the applied technique. Based on the model of an anharmonic oscillator, Figs.1 and 2 summarize the potential energy (V) transitions, excitation conditions and the most important qualitative aspects of the three spectroscopic techniques. The principal difference between the three techniques is, that Raman spectroscopy is a scattering technique whereas mid- and near-infrared spectroscopy are absorption techniques. Thus, whereas scanning MIR and NIR spectrometers operate with a polychromatic source from which the sample absorbs specific frequencies corresponding to its molecular vibrational transitions (mostly fundamental vibrations for the MIR and overtone or combination vibrations for the NIR), in Raman spectroscopy the sample is irradiated with monochromatic laser light whose frequency may vary from the visible (VIS) to the NIR region. This radiation excites the molecule to a virtual energy state which is far above the vibrational levels of this anharmonic oscillator for a VIS laser and in the range of high overtones for NIR laser excitation (see also Fig.5). From this
excited energy level the molecule may return back to the ground state by elastic scattering thereby emitting the Rayleigh line which has the same frequency as the excitation line and does not contain information in terms of the molecular vibration (this case is not shown). If it returns only to the first excited vibrational level by inelastic scattering, the emitted Raman line (so-called Stokes line) has a lower frequency and the frequency difference to the excitation line corresponds to the vibrational energy of the MIR absorption. Also not shown is the case of the anti-Stokes line, where the starting level is the first excited vibrational state and the molecule returns to the ground state by inelastic scattering, thereby emitting a Raman line of higher frequency (here too, the frequency difference to the excitation line corresponds to the vibrational energy of the MIR absorption) but of lower intensity compared to the Stokes line, due to the lower population probability of the excited state (law of Boltzmann). Commonly, the Stokes lines are used for practical Raman spectroscopy and refer to the same vibrational transitions as MIR spectroscopy. One of the limiting factors for the application of the Raman technique, however, becomes evident by comparing the intensities of the source and the scattered radiation:

\[ I_{\text{Raman}} \approx 10^{-4} I_{\text{Rayleigh}} \approx 10^{-8} I_{\text{source}} \]  

(3)

As shown in Fig.1, Raman and MIR spectroscopy cover approximately the same wavenumber region with the Raman technique extending down to lower wavenumbers (ca. 50 cm\(^{-1}\)) due to instrumental reasons (primarily because of the MIR detector cut-off). In some cases, this additional frequency range is valuable, since it often contains absorptions of lattice modes of molecular crystals which may be very characteristic for a specific polymorph.

Another important relation for the comparison of VIS- versus NIR-Raman spectroscopy, is the dependence of the scattered Raman intensity \( I_{\text{Raman}} \) on the fourth power of the excitation frequency \( \nu_{\text{exc}} \):

\[ I_{\text{Raman}} \approx \nu_{\text{exc}}^4 \]  

(4)

The consequences of this relationship with reference to the application of VIS- or NIR-Raman spectroscopy for an individual problem will be outlined below.

NIR spectroscopy covers the wavenumber range adjacent to the MIR and extends up to the VIS region. NIR absorptions are based on overtone and combination vibrations of the investigated molecule and due to their lower transition probabilities, the intensities usually decrease by a factor of 10-100 for each step from the fundamental to the next overtone.\(^3\) Thus, the intensities of absorption bands successively decrease from the MIR to the visible region, thereby allowing an adjustment of the sample thickness (from millimeters up to centimeters), depending on the rank of the overtone. This is a characteristic difference to MIR and Raman spectra, where the intensities of the fundamentals vary irregularly over the whole frequency range and depend exclusively on the excitation conditions of the individual molecular vibrations. Thus, for a Raman band to occur, a change of the polarizability \( \alpha \) (the ease to shift electrons) has to take place during the variation of the vibrational coordinate \( q \). Alternatively, the occurrence of an MIR band requires a change of the dipole moment \( \mu \) during the vibration under consideration. These different excitation conditions lead to the complementarity of the Raman and MIR technique as structural elucidation tools, because Raman spectroscopy predominantly focuses on vibrations of homonuclear functionalities (e.g. C=C, C-C, S-S) whereas the most intense MIR absorptions can be traced back to polar groups.
(e.g. C-F, Si-O, C=O and C-O). In a simplified form, NIR spectroscopy requires – additionally to the dipole moment change – a large mechanical anharmonicity of the vibrating atoms (see Fig. 2).\(^5\) This becomes evident from the analysis of the NIR spectra of a large variety of compounds, where the overtone and combination bands of CH, OH and NH functionalities dominate the spectrum whereas the corresponding overtones of the most intense MIR fundamental absorptions are rarely represented. One reason for this phenomenon is certainly the fact, that most of the X-H fundamentals absorb at wavenumbers > 2000 cm\(^{-1}\) so that their first overtones appear already in the NIR frequency range. The polar groups leading to the most intense fundamental absorptions in the MIR on the other hand, absorb usually at wavenumbers < 2000 cm\(^{-1}\), so that their first (and sometimes higher) overtones still occur in the MIR region. Due to the intensity loss for each step from the fundamental to the next overtone, the absorption intensities of these functionalities have become negligible by the time they occur in the NIR range. Thus, for the production of low-attenuation polymer optical fibers for the VIS and NIR region, for example, the C-H functionalities of poly(methylmethacrylate) are replaced by C-F groups\(^5\), although these functionalities are among the most intense MIR absorbers.

The superposition of many different overtone and combination bands in the NIR region causes a very low structural selectivity for NIR spectra compared to the Raman and MIR ana
gla where many fundamentals can usually be observed in isolated positions. Nevertheless, also NIR spectra should be assigned as detailed as possible with reference to their molecular origin,\(^6\) thereby allowing a more effective application for research purposes and combination with chemometric evaluation procedures. For the assignment of overtones and combination bands to their fundamentals it is recommendable to use the wavenumber notation instead of the wide-spread wavelength (nm or \(\mu\) m) scale. It should be mentioned, however, that the wavenumber positions of the overtones deviate with increasing multiplicity from the exact multiples of their fundamentals due to the anharmonicity of the vibrations.\(^3,5,6\)

\[
\begin{align*}
\text{RAMAN} & \quad l_{\text{Raman}} = c \\
\text{MID-INFRARED} & \quad \log \frac{I_0}{I} = A = a \cdot b \cdot c \\
\text{NEAR-INFRARED} & \quad \text{NO SAMPLE PREPARATION} \\
& \quad \text{SAMPLE PREPARATION REQUIRED (EXCEPT ATR)} \\
& \quad \text{NO SAMPLE PREPARATION}
\end{align*}
\]

Figure 3. Quantitative and sample preparation aspects of Raman, mid-infrared and near-infrared spectroscopy.
As far as the quantitative evaluation of vibrational spectra is concerned (Fig.3), MIR and NIR spectroscopy follow Beer’s law whereas the Raman intensity $I_{\text{Raman}}$ is directly proportional to the concentration of the compound to be determined. To avoid compensation problems, in most cases quantitative Raman spectroscopy is performed with an internal standard band in the vicinity of the analytical absorption.

An important issue for the implementation of a technique as an industrial routine tool is the sample preparation required for this technique. In this respect it can be seen from Fig.3, that Raman and NIR spectroscopy have considerable advantages over MIR spectroscopy, which usually requires individual sample preparation steps before data acquisition. Only the technique of attenuated total reflection (ATR)$^7$ circumvents time-consuming sampling procedures for MIR spectroscopy.

**Instrumentation**

Figure 4 summarizes the present state of the most frequently used monochromator/detection principles for the different scanning spectroscopies.

![Figure 4](image)

Figure 4. The current monochromator/detection principles of scanning MIR, NIR and Raman spectrometers.

As mentioned above, in Raman spectroscopy two techniques are presently in current use:
--- excitation by a VIS-laser combined with monochromatization of the scattered radiation by a holographic grating and simultaneous detection of the dispersed, narrow frequency ranges by a charge-coupled device (CCD) detector
--- NIR-laser excitation and measurement in a Fourier-Transform (FT) spectrometer.

Both alternatives establish only compromises and the choice of the applied technique depends on the individual problem.

**Figure 5.** Fluorescence and scattering efficiency in NIR- and VIS-Raman spectroscopy.

In Fig.5 the trends of the main limiting factors – fluorescence and low scattering efficiency - have been outlined with reference to the two excitation mechanisms. If a molecule is irradiated with visible radiation, it may be excited to an energy level of the next-higher electronic state. Return to the ground state or an excited vibrational level of the original electronic state can easily proceed via fluorescence as shown in Fig.5. Thus, for a large proportion of samples, irradiation with visible light causes strong fluorescence by additives or impurities (or by the sample itself) which will superimpose and in many cases „inundate“ the Raman spectrum of the sample. A number of time-consuming approaches have been proposed to circumvent the problem, including prior purification or „burning out“ the fluorescence. These approaches have at best been only partially successful. Additionally, highly coloured samples may absorb the Raman photons thereby preventing them from reaching the detector and leading to thermal degradation of the investigated material. The use of an NIR laser excitation confers a number of advantages on a Raman system. Both fluorescence and self-absorption of the Raman signal are very much reduced and due to the lower energy of the excitation radiation thermal degradation is also less of a problem. However, these advantages
are partly neutralized by the disadvantages of using a low-frequency laser as source. The NIR laser (Nd:YAG, 1064nm) Raman technique is obviously less sensitive due to the $\nu^4$-dependence of the scattering efficiency (see also Fig.5). Thus, a shift of the excitation line from the VIS region (e.g. Ar-ion laser, 488 nm/20492 cm$^{-1}$) to the NIR region (1064 nm/9398 cm$^{-1}$) reduces the scattering intensity within the relative Raman region from 0 to 4000 cm$^{-1}$ for factors between 23 and 87, respectively. As shown in Fig.4, however, NIR-Raman spectroscopy is performed on FT-spectrometers and the sensitivity loss can be quite efficiently compensated by accumulation of multiple scans. As a valuable compromise to suppress fluorescence and at the same time retain an acceptable scattering efficiency, excitation with a diode laser at 785 nm (12739 cm$^{-1}$) is increasingly used.

As far as MIR spectroscopy is concerned, today almost exclusively FT-based instruments are in routine use (Fig.4). Besides the optical principle of the Michelson interferometer also polarization interferometers based on a stationary and a moving MIR-transparent (KBr) wedge have been integrated in scanning spectrometers. Contrary to Raman and MIR spectroscopy, scanning NIR spectroscopy offers the largest multiplicity of monochromator principles. Thus, apart from different designs with moving parts, such as grating instruments and FT-spectrometers with Michelson and polarization interferometers (with NIR-transparent quartz wedges) two fast-scanning approaches with no moving parts are available: diode-array systems and acousto-optic tunable filters. In this context it should be mentioned that miniaturization has certainly progressed most significantly for NIR spectroscopy. A similar trend is also observable for VIS-Raman CCD spectrometers.

**Process-Monitoring**

In Fig.6 the most important aspects for the implementation of the individual spectroscopies as process-monitoring tools are addressed.

<table>
<thead>
<tr>
<th>RAMAN</th>
<th>MID-INFRARED / ATR</th>
<th>NEAR-INFRARED</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMALL SAMPLE VOLUME ($\mu l$) OR SAMPLE THICKNESS ($\mu m$)</td>
<td>LIMITED</td>
<td>LARGE SAMPLE THICKNESS (UP TO cm)</td>
</tr>
<tr>
<td>LIGHT-FIBER OPTICS (&gt; 100m)</td>
<td>LIGHT-FIBER OPTICS (&gt; 100m)</td>
<td>TRANSMISSION TRANSFLECTION DIFFUSE-REFLECTION PROBES</td>
</tr>
<tr>
<td>AT-LINE / IN-LINE PROBES</td>
<td>ATR-PROBES</td>
<td></td>
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</tbody>
</table>

Figure 6. Experimental prerequisites of the different spectroscopic techniques for their implementation as process-monitoring tool.
The very small representative sample volume or thickness in Raman and MIR/ATR spectroscopy may certainly lead to problems if special care is not taken to avoid the formation of a stationary layer on the reactor window or on the ATR crystal. In this respect, NIR spectroscopy is the method of choice in view of the comparatively large sample volume/thickness involved in these measurements. The ability, to separate the spectrometer from the point of sampling is certainly a great advantage for Raman and NIR spectroscopy. Although light-fibers based on ZrF$_4$ and AgCl are also available for MIR spectroscopy, it should be mentioned that cost, attenuation properties$^3$ and mechanical/optical stability are still inferior compared to the well-established quartz fibers. Specific probes are available for all three techniques. Especially NIR spectroscopy offers a wide range of in-line and at-line transmission and diffuse-reflection probes designed for the measurements of liquids and solids. Large differences can also be identified with respect to the ability of measuring aqueous solutions. Water is an extremely strong absorber in the MIR and also a strong NIR absorber thereby limiting the available wavenumber regions in both techniques. In contrast, it is a weak Raman scatterer and it is recommended to consider Raman spectroscopy as an analytical tool for aqueous solutions. Care has to be taken, however, with the NIR-Raman FT-technique (1064nm), because due to the absorption of the water overtone vibration the Raman spectrum may be modified relative to the VIS-laser excited Raman spectrum.$^9$

Adding up the specific advantages and disadvantages of the individual techniques, NIR spectroscopy is certainly the most flexible alternative in terms of a process-monitoring tool.

**Conclusion**

Over the last years MIR, NIR and Raman spectroscopy have been further developed to a point where each technique can be considered a candidate for industrial quality-control and process-monitoring applications. The basic theory, the presently available instrumentation and the various advantages and disadvantages of the different methods have been shortly summarized in this article and it is hoped, that it may serve its purpose to assist in the final decision for the appropriate analytical or process-monitoring instrumentation.

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**References**