1. INTRODUCTION

In textbook descriptions of chemical sensors, almost invariably a chemical sensor is described as a combination of a (dumb) transducer and a (smart) recognition layer. The reason for this is that most transducers, while (reasonably) sensitive, have limited analyte specificity. This is in particular true for non-optical, e.g. mass-sensitive or electrochemical systems, but also many optical transducers are as such incapable of distinguishing between different substances. Consequently, to build sensors operational in multi-component environments, such transducers must be combined with physico-chemical, chemical or biochemical recognition systems providing the required analyte specificity. Although advancements have been made in this field over the last years, selective layers are frequently not (yet) up to the demands set by industrial or environmental applications, in particular when operated over prolonged periods of time. Another significant obstacle are cross-sensitivities that may interfere with the analytical accuracy. Together, these limitations restrict the real-world applicability of many otherwise promising chemical sensors.

To reduce the dependence on potentially error-prone recognition systems, the use of smart transducers with possibly high intrinsic analyte specificity would be an obvious escape route. This leads directly to spectroscopic sensors. With spectroscopic transducers, the signal measured is a, more or less specific, spectral “fingerprint” rather than a change of some non-specific parameter like adsorbed mass or refractive index. Hence, it is possible to realise directly measuring sensors, capable of working either entirely independent of recognition systems or in combination with comparatively simple layers, e.g. for trace component enrichment. The degree of achievable specificity is very much dependent on the chosen wavelength range. While generally moderate in the electron excitation domain (UV/VIS), analyte
selectivity increases significantly when entering the range of vibrational spectroscopy. The two common vibrational spectroscopic methods, Infrared (IR) and Raman spectroscopy, both have proven their worth as substance-specific, reliable transducer principles for chemical sensing. Together, IR and Raman allow quantitative and qualitative detection of practically any molecule consisting of more than one atom. Thus, it is possible to detect almost any substance, in solid, liquid or gaseous form using vibrational spectroscopic sensors, even labile compounds and transient intermediates. As an added bonus, the individual spectral signatures of different compounds allow to simultaneously detect and quantify multiple analytes with one sensor, giving IR and Raman transducers a key advantage over sensors with pure mono-analyte capability.

Recent advances in instrumentation range from novel (laser) sources and highly compact spectrometers over waveguide technology to sensitive detectors and detector arrays. This, in combination with the progress in electronics, computer technology and chemometrics, makes it possible to realise compact, robust vibrational spectroscopic sensor devices that are capable of reliable real-world operation. A point that also has to be taken into account, at least when aiming at commercialisation, is the price. Vibrational spectroscopic systems are usually more expensive than most other transducers. Hence, it depends very much on the application whether it makes sense to implement IR or Raman sensors or if less powerful but cheaper alternatives could be used.

2. FUNDAMENTALS OF VIBRATIONAL SPECTROSCOPY

Vibrational spectroscopy measures and evaluates the characteristic energy transitions between vibrational or vibrational-rotational states of molecules and crystals. The measurements provide information about nature, amount and interactions of the molecules present in the probed substances. Different methods and measurement principles have been developed to record this vibrational information, amongst which IR and Raman spectroscopy are the most prominent. The following focuses on these two techniques, the corresponding instrumentation and selected applications.

As this chapter aims at explaining the basics, operational principles, advantages and pitfalls of vibrational spectroscopic sensors, some topics have been simplified or omitted altogether, especially when involving abstract theoretical or complex mathematical models. The same applies to methods having no direct impact on sensor applications. For a deeper introduction into theory, instrumentation and related experimental methods, comprehensive surveys can be found in any good textbook on vibrational spectroscopy or instrumental analytical chemistry.1-4