1
Introduction

This book discusses the experimental technique known as photoacoustic (PA) infrared spectroscopy. Research and applications in this field have enjoyed more or less continual development since its emergence over 30 years ago: a substantial body of literature – comprising more than one thousand publications – on PA infrared spectra exists today. The present work attempts to review and synthesize this literature, a principal objective being to summarize the current status of the technique. Recent advances in this field are also described. The assembled information will allow spectroscopists and researchers in specific disciplines to determine whether the method is appropriate for their needs.

PA infrared spectroscopy can be viewed from several perspectives. For example, it can be regarded as one of a large number of photoacoustic and photothermal (PT) methods used by physicists, chemists, and other researchers to characterize condensed matter and gases. It should be noted that both optical and thermophysical properties of materials can be investigated by these methods. From this viewpoint, PA infrared spectroscopy is a specialization within a much broader field, made possible by the development and application of transducers and optical instrumentation that operate in the infrared region of the electromagnetic spectrum. Of course some might suggest that this (obviously valid) interpretation tends to ascribe a secondary status to PA infrared spectroscopy.

Vibrational (infrared and Raman) spectroscopists[1)] will almost certainly approach PA infrared spectroscopy in a different way. For these scientists, PA detection of infrared spectra can be described as an enabling technology, significantly increasing the number and type of samples for which viable data can be obtained. The reader will soon recognize that the viewpoint of the infrared spectroscopist is adopted in this book. In fact PA detection of infrared absorption spectra, using modern equipment and radiation sources, offers several well-known advantages. The most important of these are the following:

- Minimal sample preparation is required.
- The technique is suitable for opaque materials.
- Depth profiling can be effected for inhomogeneous or layered solids.
- PA spectroscopy is nondestructive (the sample is not consumed).

1) The author of this text is included in this group.

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It is not an exaggeration to assert that these characteristics are critical in many circumstances: for example, samples exhibiting various problematic characteristics may be encountered in industrial laboratories on a daily basis. These include, but are not limited to, viscous liquids, semisolids, and dispersions; metal powders, carbonaceous solids, and granular materials; polymers and layered solids with physical structures or chemical compositions that may be altered by grinding. Traditional infrared sample preparation methods are often inappropriate or have deleterious effects on these substances. Hence the minimization of sample preparation in PA infrared spectroscopy can be considered its most important attribute. Examination of the scientific literature confirms that the majority of spectroscopists using this technique implicitly agree with this statement. The use of PA infrared spectroscopy for the characterization of problematic, even 'intractable', samples is discussed throughout this book.

Notwithstanding these statements, the capacity for PA depth profiling is an almost equally important feature: this experimental technique has been utilized extensively to study layered polymers, adsorption on substrates, and surface oxidation of hydrocarbon fuels or other species. Thus the PA spectroscopist also possesses the capability for analysis of surface and subsurface layers (in this context, 'surface' implies depths on the order of micrometers, while 'subsurface' regions extend tens of micrometers), a goal that surely can be said to be the dream of many chemists and physicists.

PA spectroscopy – frequently referred to by the acronym PAS – is sometimes described as an 'unconventional' infrared technique. The very significant number of publications in the primary scientific literature reporting research-quality PA spectra belie this somewhat pejorative description. It is hoped that the present account adequately demonstrates the wide-ranging applicability of the technique and makes a convincing argument for its increased future use.

1.1 Single- and Multiple-Wavelength PA Spectroscopies

PA spectroscopy can be divided into two broad categories. The first can be described as single-wavelength spectroscopy, since only one wavelength of light impinges on the sample of interest. Signal generation in a gas-microphone cell can be used to illustrate this technique. Three steps can be identified. First, modulated radiation from a laser or other suitable source impinges on the condensed-phase sample; second, the absorbed radiation is converted to heat by radiationless processes; and third, the heat generated within the sample is transferred to its cooler surroundings. Periodic heating of the boundary layer of carrier gas adjacent to the warm surface creates a pressure (acoustic) wave that is detected by the transducer (microphone). This experiment can be extended to include measurement of wavelength (wavenumber) dependence of optical absorption by systematically changing the wavelength of the incident radiation to build up a PA spectrum. Sequential observation of PA signals can be effected by selecting different lines from a

multiple-wavelength laser or by use of an optical filter, such as a grating monochromator, in conjunction with broad-band radiation. These techniques were used to obtain PA infrared spectra by several research groups, particularly in the 1970s and early 1980s when PA spectroscopy enjoyed a rapid increase in popularity. Currently, multi-line gas (CO_2 and CO) and solid-state mid- and near-infrared lasers are used for specific PA applications, an important example being trace gas detection. This implementation of single-wavelength PA infrared spectroscopy is discussed in later chapters.

The second category is multiple-wavelength (multiplex) PA spectroscopy, as practiced with Fourier Transform infrared (FT-IR) spectrometers. Most readers already know, of course, that these spectrometers have attained very wide acceptance in analytical, research, and teaching laboratories during the last four decades. In the present context, the most important attribute of an FT-IR spectrometer is its capability for simultaneous measurements at a range of wavelengths; spectral coverage is determined mainly by the optical characteristics of the beamsplitter, the window material in the sample accessory, and the detector. An optical detector is not required in conventional PA FT-IR spectroscopy, and the accessible wavelength interval depends only on the beamsplitter and the window fitted on the gas-microphone cell. This technique has been used extensively for about three decades and is the source of the majority of the literature discussed in this book. Signal generation in the PA FT-IR experiment can be described in terms similar to those in the previous paragraph. Modulation is provided by the moving mirror in the interferometer or by use of an external device such as a chopper. This is discussed in more detail in Chapter 3.

1.2 Scope

As noted in the previous section, PA infrared spectroscopy has long been practiced with lasers, scanning monochromators, and FT-IR spectrometers. Indeed, the ongoing use of many types of instrumentation in PA spectroscopy demonstrates the breadth of the field. Although many workers today naturally associate infrared spectroscopy with FT-IR spectrometers, it should be emphasized at the outset that PA FT-IR spectroscopy is, in fact, a specialization within the broader discipline of PA infrared spectroscopy. This book adopts the wider definition of the field and examines a number of relevant PA infrared techniques from both historical and modern perspectives.

Spectroscopists are well aware that definitions of wavelength regions tend to differ for reasons that may be either historical, technological, or a combination of the two. Near-, mid-, and far-infrared PA spectroscopies are discussed in this book. Unless otherwise stated, these regions are demarcated as follows: near-infrared, 4000–12 500 cm^{-1} (wavelengths 2.5–0.8 μm); mid-infrared, 400–4000 cm^{-1} (25–2.5 μm); and far-infrared, 50–400 cm^{-1} (200–25 μm). It should be noted that this division of the electromagnetic spectrum, although not uncommon, is somewhat

arbitrary; for example, the low-wavenumber limit given for the far-infrared region is based on the few published PA far-infrared spectra rather than more conventional far-infrared limits that encompass lower wavenumbers and longer wavelengths.

1.3 Other Sources of Information

Many review articles and conference proceedings dealing with PA spectroscopy have been published during the last three decades. Some literature reviews provide an overview of PA methods and emphasize work at shorter wavelengths (ultraviolet and visible) that is not discussed in this book. Mid-infrared PA spectroscopy receives very limited attention in most of these articles; some, however, discuss near-infrared spectroscopy and are therefore relevant to specific sections of this text. The early work of Adams (1982) is a typical example. Similarly, Vargas and Miranda (1988) published a detailed summary of PA and PT techniques that contains a short section on PA spectroscopy in the near- and mid-infrared regions. Further references discuss PA spectroscopy and its relationship to PA and PT methods (Pao, 1977; Rosencwaig, 1978, 1980; Tam, 1986; Almond and Patel, 1996).

Initial work in mid-infrared PA spectroscopy was summarized by Vidrine (1982) and Graham, Grim, and Fateley (1985). McClelland (1983) discussed several aspects of signal generation and instrumentation in an important survey of PA spectroscopy that emphasized the infrared region. The latter article is considered to be authoritative and continues to be cited by many practitioners who utilize PA infrared spectroscopy. Numerical methods, specifically phase correction and signal averaging, were discussed a few years later by the present author (Michaelian, 1990).

Two research groups made major contributions to the advancement of PA infrared spectroscopy and should be particularly noted with regard to review publications. R. A. Palmer of Duke University, together with many students and other collaborators, published extensively on research topics including PA infrared spectra of polymers, the role and significance of the PA phase, and the development of step-scan FT-IR PA spectroscopy. Consistent with this research effort, a review on PA spectroscopy of polymers by Dittmar, Palmer, and Carter (1994) contains a useful summary of the history and principles of PA infrared spectroscopy. Numerous other publications by this research group are referred to in later chapters.

Similarly, J. F. McClelland and co-workers at Iowa State University made a very considerable contribution to PA infrared spectroscopy during the last three decades. These investigators have a substantive history in instrumentation that culminated in the successful manufacture of commercial sample accessories for FT-IR spectrometers. McClelland and his colleagues published several detailed review articles, including a summary of the PA FT-IR technique that discusses

signal generation and demonstrates a series of qualitative and quantitative applications (McClelland *et al.*, 1992). Other reviews discussed sample handling in PA FT-IR spectroscopy (McClelland *et al.*, 1993) and the implementation of PA spectroscopy with step-scan and rapid-scan spectrometers (McClelland *et al.*, 1998). PA FT-IR spectroscopy was reviewed in Volume 2 of *Handbook of Vibrational Spectroscopy* (McClelland, Jones, and Bajic, 2002) with particular reference to signal generation, instrumentation and sampling. These publications will be of considerable use to investigators who require an introduction to PA infrared spectroscopy.

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