

Infrared and Raman Spectroscopy

Methods and Applications

Edited by Bernhard Schrader

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D. Bougeard, M. Buback, A. Cao,
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A. Röseler, H. Schnöckel, B. Schrader, H. W. Schrötter,
M. Spiekermann, E. Taillandier, H. Willner



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Preface

Infrared spectroscopy is now nearly 100 years old, Raman spectroscopy more than 60. These methods provide us with complementary images of molecular vibrations: Vibrations which modulate the molecular dipole moment are visible in the infrared spectrum, while those which modulate the polarizability appear in the Raman spectrum. Other vibrations may be forbidden, 'silent', in both spectra. It is therefore appropriate to evaluate infrared and Raman spectra jointly. Ideally, both techniques should be available in a well-equipped analytical laboratory. However, infrared and Raman spectroscopy have developed separately. Infrared spectroscopy became the 'work-horse' of vibrational spectroscopy in industrial analytical laboratories as well as in research institutes, whereas Raman spectroscopy up until recently was essentially restricted to academic purposes.

This is due to the fact that fluorescence of impurities may completely mask a Raman spectrum if it is excited, as usual before 1986, in the visible range of the spectrum. Since the quantum yield of fluorescence exceeds that of the Raman effect by a factor of about one million, traces of fluorescent compounds – ubiquitous impurities like stop cock grease, the 'whitening dyes' (blancophores) of many detergents, or the products of photochemical or oxidation processes or of the pyrolysis of pure samples – may preclude the observation of Raman spectra which are excited by radiation in the visible (VIS) or ultraviolet (UV) region. However, most of these fluorescent compounds do not show electronic absorption bands in the near infrared (NIR) region. Therefore, in a Raman spectrum which is excited by radiation in the NIR, fluorescence should not appear. During the late 1980s it was demonstrated (Hirschfeld and Chase, 1986) that most samples afford undisturbed Raman spectra excited with the radiation of a neodymium doped yttrium aluminum garnet (Nd:YAG) laser at a wavelength of 1064 nm.

Thus, Raman spectroscopy as well as infrared spectroscopy can now be applied – either individually or in combination – to most problems where they appear useful.

This book intends to supply the basic information necessary to apply the methods of vibrational spectroscopy, to design experimental procedures, to perform and evaluate experiments. It does not intend to provide a market survey of the instruments which are available at present, because such information would very soon be outdated. However, the general principles of the instruments and their accessories, which remain valid, are discussed. Details concerning sample preparation and the recording of the spectra, which is the subject of introductory courses, are assumed to be known. Special procedures which are described in monographs, such as Fourier transformation or chemometric methods, are also not exhaustively described. This book has been written for graduate students as well as for experienced scientists who intend to update their knowledge.

After a short outline of the early history of infrared and Raman spectroscopy (Section 1), a general survey is given of different aspects of vibrational spectroscopy (Section 2). This survey is sufficient for readers who intend to get an impression of the fundamentals of vibrational spectroscopy. It serves as a common basis for subsequent chapters, which describe special experimental features, the theory, and applicational details: Section 3, Tools for infrared and Raman Spectroscopy; Section 4, Vibrational spectroscopy of different classes and states of compounds; Section 5, Evaluation procedures, and Section 6, Special techniques and applications.

In order to provide comprehensive and up-to-date information, several specialists of vibrational spectroscopy have contributed chapters dealing with their particular fields. The editor did not make considerable effort to force the authors to use exactly the same nomenclature. The nomenclature used by different authors reflects the common usage in the pertinent literature of the individual fields. There are typical but established differences in the nomenclature used by chemists and physicists – chemists prefer to think in terms of molecules and their properties, whereas physicists like to concentrate on phenomena and formalisms. However, the IUPAC and IUPAP rules as well as the SI units are obeyed wherever suitable and possible. The literature citations of all chapters are collected in a common section at the end of this book, arranged according to the name-date system (Ebel and Bliefert, 1990).

This book has emerged from manuscripts prepared for advanced courses on vibrational spectroscopy, for lectures, and for encyclopedic articles. I would like to thank all authors for dedicating their spare time to this work and to express my gratitude to all who helped me organize the manuscript, especially Frau Anne Tamburrano, who typed large parts of the manuscript and produced the bibliography and the index. My wife Christa helped me prepare draft manuscripts and to organize the whole book. Mrs. Barbara Hoeksema did a great job to remove Germanisms and to improve the English. Heinz Sprünken has drawn many figures, Elke Manzel has recorded several spectra. Many colleagues, especially Prof. Dr. Wolfgang Kiefer, Prof. Dr. Heinz W. Schrötter, Dr. Goran Baranović, Dr. Gabor Keresztury, Dr. David Moore, and his wife, Viera gave important advice for improving the text. Dr. Steffen Pauly, VCH Publishers, helped considerably to produce a consistent book.

I would like to invite the readers of this book to give comments and recommendations which could improve it.

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Essen, Spring 1994

Bernhard Schrader

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1 Early history of vibrational spectroscopy*

Around 60 B. C., T. Lucretius Carus wrote:

Forsitan et rosea sol alte lampade lucens possideat multum caecis fervoribus ignem circum se, nullo qui sit fulgore notatus, aestiferum ut tantum radiorum exaugeat ictum.

(Perhaps the sun, shining with a high rosy torch, is surrounded by more fire with invisible heat, which is not recognized by its glare, thus amplifying the heat-transferring power of the rays (citation from Nonnenmacher, 1961)).

Mariotte in 1686 noticed that heat emerging from a fireplace can be focused by a mirror but does not pass through a glass plate. This observation was confirmed by Scheele in 1781. Herschel decomposed the radiation of the Sun with a prism. Using mercury thermometers with blackened bulbs, Herschel in 1800 showed that there is invisible but heat-transporting radiation beyond the red end of the solar spectrum. Most of the components of present infrared spectrometers were already described during the nineteenth century (Jones, 1981): thermopiles made of antimony/bismuth junctions which employ the thermoelectric effect, discovered by Seebeck (1823), were produced by Nobili (1830). Melloni (1833) discovered the transparency of sodium chloride for infrared radiation. He used it to construct the first mid-infrared spectrometer (Melloni, 1835). Ångström (1868) determined the exact wavelengths of the Fraunhofer lines in the solar spectrum by using diffraction gratings – which had already been made and used by Fraunhofer himself in 1821 – with up to 10000 lines per inch (about 4000 lines per cm)! Bell (1881) constructed the photophone, the photoacoustic detector. Langley (1881) invented the bolometer and, using his own IR spectrometer, already detected sulfur dioxide in the atmosphere of Pittsburgh (personal communication of E.K. Plyler, cited by Jones, 1981). Langley also described (1883) the 'window' in the spectrum of atmospheric water vapor between 8 and 12 μm . Using a combined grating and prism spectrometer, Langley (1884) was able to determine the refractive index of sodium chloride to about 5 μm . He thus made it possible to calibrate the wavelength scale of infrared prism spectrometers. Michelson introduced the two-beam interferometer in 1890.

The first spectra of molecular vibrations were observed in 1881 by Abney and Festing. They prepared photographic emulsions, which were sensitive in the near infrared region

* Chapter 1 is contributed by B. Schrader, Essen

up to 1200 nm, and photographed the absorption spectra of 48 organic liquids with path lengths up to 60 cm by using 3 1/2 prisms, mostly in a double pass arrangement. "When we find a body having a band at 0.74 μm and another beginning at 0.907 μm and ending at 0.942 μm , we may be pretty sure that we have an ethyl radical present. In the aromatic group the critical line is at wavelength $\lambda = 0.867 \mu\text{m}$. If that line be connected with a band we feel certain that some derivative of benzene is present...". "It seems highly probable by this delicate mode of analysis that the hypothetical position of any hydrogen which is replaced can be identified ..., a point of prime importance to organic chemistry". – Abney and Festing knew that these bands are associated with the hydrogen in the molecule, but they did not know that they were observing the overtones and combinations of normal vibrations of C–H, N–H, and O–H bonds.

Ångström (1889, 1890) recorded the absorptions of carbon monoxide, carbon dioxide, carbon disulphide, methane, benzene, and others in the wavelength range up to 8 μm , using a rock-salt prism spectrometer with lenses and a bolometer. Around the same time, Julius (1892) obtained the infrared spectra of some 20 organic compounds up to a wavelength of 10 μm in a cell with rock salt windows and at a sample thickness of about 0.2 mm. "He found that all compounds containing the methyl, CH_3 group had an absorption band at 3.45 μm ." He arrived at the conclusion "that the absorption of heat waves is due to intramolecular movements; in other words, the internal structure, i.e., the grouping of the atoms in the chemical molecule, determines the character of the absorption. He found that the chemical atom lost its identity in a compound; i.e., the effect is not 'additive', so that one can not foretell the absorption spectrum of the compound from a knowledge of the spectra of the constituent elements" (Coblentz, 1905). Using a KCl prism, Rubens and Aschkinass (1898) observed the emission and absorption spectra of CO_2 and water vapor up to 20 μm .

In 1905, Coblentz published an atlas containing absorption spectra of 120 organic compounds, as well as emission and reflection spectra (e.g., of the Moon) in the range up to 15 μm . He recorded these spectra during a two-year post-doctoral project, using instruments he built in the course of his graduate research program. He clearly described the differences between the absorption spectra of o-, m- and p-xylene, by having absorption bands at 13.6, 12.9, and 12.66 μm respectively. "In some compounds there is evidence that certain bands, e.g., the 3.43 μm band, are due to a definite group of atoms, e.g. the CH_3 -groups in the chain compounds and terpenes; in other compounds the evidence is just as strongly in favor of the manner of bonding of the atoms, e.g., the methylene hydrocarbons of the petroleum distillates; still other compounds, e.g., benzene and its derivatives, *especially phenyl mustard oil*, in which we have the *characteristic vibration of the mustard oils superposed upon the vibration of the benzene nucleus*, show that both the groups of atoms and their manner of bonding with other atoms, as well as the kind of atom have a great influence upon the absorption curve" (Coblentz, 1905). He observed that different isomers give rise to different spectra, and that there are also characteristic vibrations of the CH_2 or CH_3 , NH_2 , C_6H_6 , NO_2 , OH, and NCS groups.

Unfortunately, the importance of this work, published by a physicist, and its consequences was not acknowledged by chemists. It was not until the Second World War that this new method began to find broad acceptance.

In the laboratories of BASF (Badische Anilin- and Soda-Fabrik) at Ludwigshafen, the importance of infrared spectroscopy for industrial purposes was realized as early as the 1930's. The first IR instrument with a modulated beam was built by Lehrer in 1937 and modified to a double beam instrument with optical compensation in 1942. Luft described the first non-dispersive infrared analyzer in 1943. He used the gas to be analyzed as absorber in a photo-acoustic detector cell. Thus, the instrument was sensitive only to this gas. He also provided a survey of early industrial applications of infrared spectroscopy (Luft, 1947).

Based on the servo techniques developed during the Second World War automatically recording infrared spectrometers were introduced to the market in the United States. Especially the Perkin-Elmer Model 21 stimulated the application of infrared spectrometry worldwide. In 1957, some 100 Model 21 spectrometers were sold along with about 300 of the low-cost Model 137, Infracord.

During the 1960s further improvements made infrared spectroscopy a very useful tool used worldwide in the analytical routine laboratory as well as in many fields of science. Grating spectrometers replaced the prism instruments due to their larger optical conductance (which is explained in Sec. 3 of this book). The even larger optical conductance of interferometers could be employed after computers became available in the laboratory and algorithms which made Fourier transformation of interferograms into spectra a routine. The computers which became a necessary component of the spectrometers made new powerful methods of evaluation possible, such as spectral subtraction and library search.

The Raman effect also allows the observation of vibrational spectra; it provides information which complements that obtained by IR spectroscopy. This effect had been repeatedly predicted. Lommel (1878) described certain anomalies of fluorescence, the color of which is dependent on the nature of the sample and the frequency of the exciting radiation, with the necessity of bands with the frequency $\nu \pm \omega$, if a damped anharmonic oscillator of the frequency ω is irradiated with light of the frequency ν . Smekal (1923), Kramers and Heisenberg (1925), Schrödinger (1926), and Dirac (1927) predicted the Raman effect by applying quantum mechanics to molecules. Raman was looking for the optical analogue of the Compton effect, when, on February 7, 1928, his co-workers Krishnan and Venkateswaran observed 'modified scattering' of sunlight, which Raman identified as Kramers-Heisenberg effect. A short paper describing 'A New Type of Secondary Radiation' by Raman and Krishnan was cabled to Nature on February 16th, 1928. Other papers followed (Raman et al., 1928).

In France, Rocard (1928) immediately attributed this novel effect to optical modulation by the oscillating molecule. Cabannes (1928) described the new effect as 'optical beating' and predicted the existence of pure rotational Raman scattering in anisotropic molecules. In the Soviet Union, Landsberg and Mandelstam (1928) published their results on the light scattering of quartz, describing lines which differed from those expected by Debye's theory. They explained this phenomenon as inelastic scattering of light quanta.

In the United States, Wood (1928) realized that he had already recorded Raman lines on his photographic plates when he investigated resonance fluorescence. He introduced the term 'anti Stokes' for scattered light, whose quanta have a higher energy than those of the exciting light (see Sec. 2.4).

Since Raman was the first to publish a spectrum of scattered light containing frequency-shifted lines, he received the Nobel prize for physics on December 11, 1930, "for his work on the 'diffusion' of light and for the discovery of the effect which bears his name."

As mentioned above, the basic theory of the Raman effect was developed before its discovery. However, at this time numerical calculations of the intensity of Raman lines were impossible, because these require information on all eigenstates of a scattering system. Placzek (1934) introduced a 'semi-classical' approach in the form of his polarizability theory. This provided a basis for many other theoretical and experimental studies. Physicists and chemists worldwide realized the importance of the Raman effect as a tool for qualitative and quantitative analysis and for the determination of structure.

It soon became apparent that the Raman effect was "not a substitute for infrared spectroscopy", which in the thirties was a much more difficult technique than Raman spectroscopy, but a "complement to be evaluated in connection with infrared spectroscopy" (Schaefer and Matossi, 1930). Kohlrausch (1931, 1938, 1943) in particular explored the relation between Raman spectra and molecular structures. However, until about 1950, Raman spectroscopy was applied more often than IR spectroscopy and it was only rarely that the two types of spectra were jointly evaluated. The reverse became true after 1950, when automatically recording infrared spectrometers were introduced to the market. Infrared spectroscopy found its place in routine analysis.

The most important stimulus to the development of Raman spectroscopy has been the laser, invented by Maiman in 1960. During a short period the mercury arcs were replaced by these really monochromatic and most powerful light sources. At the same time the photographic plates were replaced by photomultipliers, and scanning grating spectrometers replaced the prism spectrographs. Also, the introduction of double and triple monochromators, an elaborate sample technique (Kiefer, 1977), and later of diode arrays and charge-coupled devices (CCDs) contributed considerably to the development of Raman spectroscopy. This is also true of 'non-classical' Raman effects, utilizing resonance and non-linear phenomena. Nevertheless, the main obstacle to an application as routine method of analytical chemistry could not be removed until the late 1980's: the fluorescence of the impurities which are found in most 'real life' samples. Excited by radiation in the visible (or UV) region of the spectrum it is by orders of magnitude stronger than the Raman effect. In addition, the technical developments which have improved the quality of the spectra and the convenience of recording them, however, are somewhat compromised by the higher price of the instruments. As a result, the scope of these instruments has remained much the same, and the number of Raman spectrometers in use has been still only a small fraction of the number of infrared spectrometers.

There is a real chance of a breakthrough of Raman spectroscopy in routine analytics. Excitation of Raman spectra by near-infrared radiation and recording with interferometers, followed by the Fourier transformation of the interferogram into a spectrum – the so-called NIR-FT-Raman technique – has made it possible to obtain Raman spectra of most samples uninhibited by fluorescence. In addition, the introduction of dispersive spectrometers with multi-channel detectors and the development of several varieties of Raman spectroscopy has made it possible to combine infrared and Raman spectroscopy whenever this appears to be advantageous.

The following chapters describe the most important work in the different fields. Comprehensive reviews of the history of vibrational spectroscopy have been published by Jones (1981, 1985). Möller and Rothschild (1971) have compiled a complete bibliography of far-infrared spectroscopy covering the period between 1892 and 1969. Reviews of the history of the Raman effect have been published by Brandmüller and Kiefer (1978) and by Long (1988).

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2 General survey of vibrational spectroscopy*

Molecules consist of atoms which have a certain mass and which are connected by elastic bonds. As a result, they can perform periodic motions, they have *vibrational degrees of freedom*: All motions of the atoms in a molecule relative to each other are a superposition of so-called *normal vibrations*, in which all atoms are vibrating with the same phase and *normal frequency*. Their amplitudes are described by a *normal coordinate*. Polyatomic molecules with n atoms possess $3n - 6$ normal vibrations (linear ones have $3n - 5$ normal vibrations), which define their *vibrational spectra*. These spectra depend on the masses of the atoms, their geometrical arrangement, and the strength of their chemical bonds. Molecular aggregates such as crystals or complexes behave like 'super molecules' in which the vibrations of the individual components are coupled. In a first approximation the normal vibrations are not coupled, they do not interact. However, the elasticity of bonds does not strictly follow Hooke's law. Therefore overtones and combinations of normal vibrations appear.

Infrared and Raman spectrometers are the most important tools for observing vibrational spectra. Depending on the nature of the vibration, which is determined by the symmetry of the molecule, vibrations may be *active* or *forbidden* in the infrared or Raman spectrum. The following characteristics are most relevant to the application of vibrational spectra throughout chemistry and physics. They are to be explained and illustrated in detail in the subsequent chapters:

1. Vibrational spectroscopy involves different methods, the most important of which are infrared (IR) and Raman spectroscopy.
2. The IR and Raman spectra of two molecules are different, if these molecules have different constitutions, isotopic distributions, configurations, conformations or if their environments are different for whatever reason. This also includes the infrared or Raman optical activity of enantiomers.
3. Definite substances can be identified by their IR and Raman spectra, interpreted like fingerprints.
4. The spectra show certain bands, i.e., *characteristic vibrations*, which are typical of particular groups of atoms and which are defined by definite ranges of frequencies **and** intensities in the IR *and* the Raman spectra. These may be employed for the elucidation of the molecular structure.
5. Molecular structures may also be derived from the spectra by employing model calculations.

* Chapter 2 is contributed by B. Schrader, Essen

6. The intensities of the bands in the spectrum of a mixture are usually proportional to the concentrations of the individual components. It is thus possible to determine the concentration of one substance or to carry out a multi-component analysis.
7. Vibrational spectra of substances in any state can be recorded; the spectra of one substance in different phases are similar, but they differ with respect to the activity and intensity of vibrations, their frequency, the half width, and the fine structure of the bands.
8. IR and Raman spectra can usually be recorded non-destructively. After the spectra have been recorded, the sample can be recovered and used for other purposes. Raman spectra can be recorded from samples in a closed ampoule.
9. The recording and evaluation of IR and Raman spectra may be automatized. The spectra may be obtained *on-line* and in *real time*.
10. The time needed to record a vibrational spectrum is of the order of seconds to minutes or, with special equipment, may even be less.

2.1 Molecular vibrations

Each atom has three *degrees of freedom*: it can move independently along each of the axes of a Cartesian coordinate system. If n atoms constitute a molecule, there are $3n$ degrees of motional freedom. Three of these degrees – the translational ones – involve moving of all atoms simultaneously in the same direction parallel to the axes of a Cartesian coordinate system. Another three degrees of freedom also do not change the distance between atoms, they describe rotations, e.g., about the principal axes of the inertial ellipsoid of the molecule. The remaining $3n - 6$ degrees are motions which change the distances between atoms: the lengths of the chemical bonds and the angles between them. Since these bonds are elastic, periodic motions occur. All vibrations of an idealized molecule result from superposition of $3n - 6$ non interacting normal vibrations.

The simplest model of a vibrating molecule describes an atom bound to a very large mass by a weightless spring (Fig. 2.1-1 a). The force F which is necessary to move the

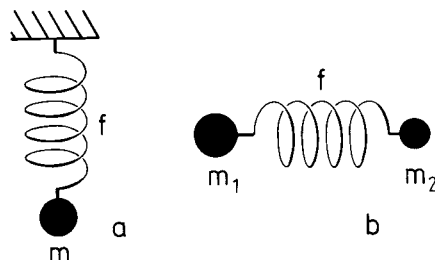


Figure 2.1-1 Models of a harmonic oscillator, **a** mass m on a spring with the force constant f , **b** two masses, m_1 and m_2 , connected by a spring with the same force constant.