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Recent advances in analytical infrared spectroscopy

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Infrared spectroscopy is the most generally applicable of all characterization tools for qualitative analysis, but it is perhaps one of the most difficult to exploit to its full potential. Recent developments in instrumentation allow spectra to be obtained under difficult conditions of low sample transmission, low concentration, spectral overlap and rapid spectral change: these developments include Fourier transform infrared spectroscopy, ratio-recording dispersive spectrometers, photovoltaic and photoconductive detectors, and computer manipulation of spectra. Simpler spectrometers with fixed or variable frequency filters are particularly suitable for commercial and industrial applications, and tunable infrared lasers are potentially powerful tools for detecting and measuring atmospheric contaminants. Recognition of spectra, even with computer searching of data banks, remains a challenge, and human pattern recognition and intelligence are still essential tools in the fields of minerals, and inorganic and biological materials. There is now an urgent need for detailed monographs on specific groups of compounds to give potential users readier access to sound correlations of spectra and structure.

INTRODUCTION

Infrared spectroscopy is undoubtedly the most widely applicable tool for qualitative identification of a chemical species, but it is perhaps also one of the most difficult to exploit to its full potential. Its breadth of application is remarkable, covering gases, liquids, crystalline and amorphous solids, solid-state defects, surface structures, and surface-adsorbed species. Only symmetrical diatomic gases at modest pressure fail to respond to an infrared probe. As a tool for qualitative analysis, infrared spectroscopy is unrivalled in its ability to reveal unexpected components and to provide clues to their nature. As a tool for quantitative analysis of mixtures, however, infrared spectroscopy can only be safely applied where the range of components is strictly defined.

Difficulties in the application of infrared spectrometry have been of three kinds: instrumental, interpretative and manipulative. The first, instrumental, delayed its general use for over 20 years after its potential was first demonstrated by Coblentz in the early 1900s, but the last 10 years have seen an extraordinary diversification of spectrometers, lasers and detection systems that have expanded the range of applications of infrared spectroscopy into outer space and to other equally challenging problems of the Earth's surface. Difficulties in the interpretation of the spectra obtained lie in the highly empirical nature of infrared spectra, their often unique discriminating power, the problem of distinguishing physical and chemical effects in spectra, and the confusions arising from unsuspected impurities. These problems can make the interpretation of novel spectra a research project, rather than an unambiguously informative probe. Nevertheless the promise of identification by computer searching of spectral libraries is now being realized at least within restricted fields of substances. In other fields, such as mineral spectroscopy, I shall argue that only the steady accumulation of detailed research monographs on specific mineral families will allow the full benefits of infrared study to be derived. The third difficulty, manipulative, is the problem of presenting the sample in a form appropriate to the instrument. This is a constant challenge to the ingenuity of the spectroscopist, but it will not be reviewed here as there have been no revolutionary developments in the handling of solids, liquids and gases.

McDonald (1980), in the most recent of his invaluable two-yearly reviews of analytical infrared spectrometry, reported that nearly 1% (over 8000) of the citations in the Chemical Abstracts Search data base covering 1978–9 were pertinent to infrared spectrometry, and even after ruthless pruning he listed 800. In spite of its wide coverage, his review is therefore highly selective and strongly coloured by his own special interests: this is still more true of the present short survey of the field, which will deal briefly with instrumental developments and applications of particular interest to me.

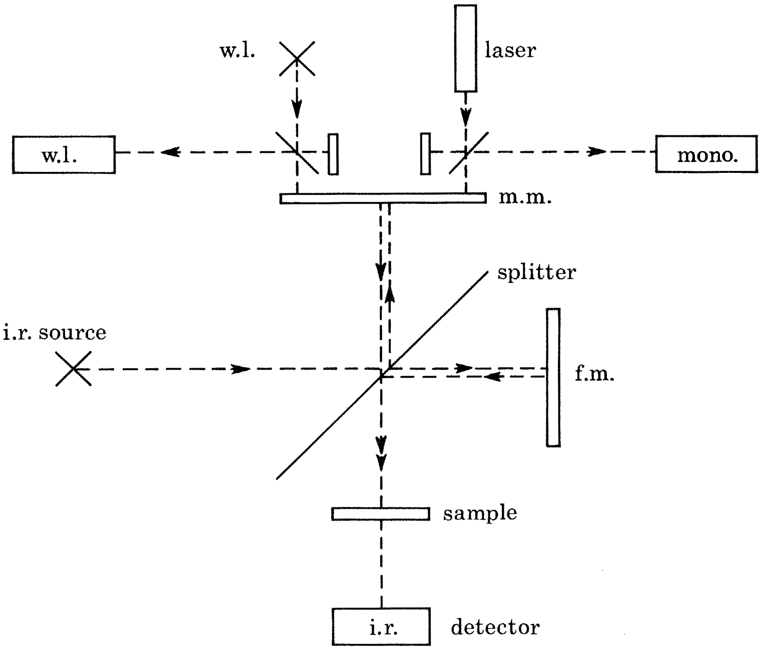

Figure 1. Schematic diagram of a Michelson interferometer. Radiation from the i.r. source is divided by a beam splitter between fixed (f.m.) and moving (m.m.) mirrors, then recombined to pass through the sample and fall on the detector. Interference between the two beams modulates the energy reaching the detector as the moving mirror moves over a short distance around zero path difference. Subsidiary interferometers use a monochromatic source to monitor the mirror movement, and a white light source to trigger data collection reproducibly for multiple mirror scans. Reproduced from Durig (1980), with permission.

DEVELOPMENTS IN INSTRUMENTATION

Interferometers versus dispersive spectrometers

The Michelson Fourier transform infrared (F.t.i.r.) spectrometer has grown to maturity within the last 10 years, and is now competing directly with dispersive spectrometers at the top end of the price range for mid-infrared general purpose applications. The present situation, which has by no means stabilized, was well reviewed at a recent Nato Advanced Study Institute (Durig 1980). The interferometer offers many unique advantages because of its high sensitivity, high speed of accumulating spectra, high resolving power, frequency reproducibility, and absence of stray light. It operates by recording the interference pattern generated by combining beams reflected from two plane mirrors (figure 1), one of which is moved over a path-length that determines the resolution of the instrument. A monochromatic source generates a simple cosine wave intensity variation at the detector as the mirror moves (figure 2 *a*), and a two-line or three-line source generates two or three superimposed cosine interference patterns (figure 2 *b*, *c*) whose components are no longer visually recognizable. A continuous source generates a pattern that is a superposition of waves corresponding to all the frequencies emitted, and the resolution of this complex pattern into its component waves is achieved by a Fourier transformation, performed on a dedicated computer.

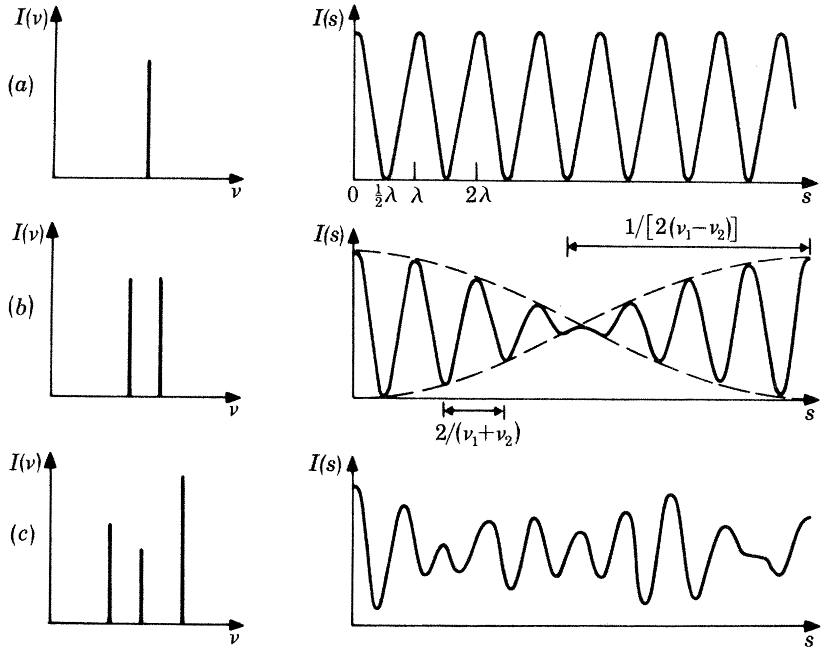

FIGURE 2. A monochromatic source produces a simple cosine interference pattern (*a*), whose period corresponds to a change in path difference of one wavelength. Two-line and three-line sources, (*b*) and (*c*), produce two or three superimposed cosine patterns, which reinforce each other at zero path difference. Fourier transformation of the interferogram regenerates the source spectrum.

The advantages of the interferometer have been classified as follows.

1. The energy throughput, or Jacquinot's advantage: an interferometer transmits a higher proportion of the source energy to the detector because the entrance and exit apertures are circular, of constant dimensions for a given resolution band width, and can be matched exactly to the detector aperture. In contrast, the slit aperture of a dispersive instrument is generally poorly matched to the detector aperture.

2. The multiplexing, or Fellgett's advantage: since an interferometer measures a combination of all frequencies at once, the detector noise levels, categorized by a standard deviation of σ and a variance σ^2, can be distributed among all n frequency elements being measured, so the variance attributable to any one is σ^2/n, and the standard deviation is $\sigma/\sqrt{n}$. There is therefore a theoretical improvement in signal:noise ratio of $\sqrt{n}$ for an interferometer. This factor is 42 for a spectrum over 4000–400 cm^{-1} at 2 cm^{-1} resolution. Alternatively, for the same signal:noise ratio, there is a time advantage of 1800.

3. The frequency accuracy, or Connes advantage: because the motion of the interferometer mirror is monitored by the interference pattern generated by a laser, the frequencies measured are directly related to the laser wavelength. This gives a high reproducibility of sampling the interferogram, which allows the summation of successive interferograms with little spectral degradation. It also provides Fourier-transformed spectra in the form of digitized intensity data at defined frequencies, directly comparable with other spectra on the same instrument.

4. Computational advantages: F.t.i.r. instruments necessarily incorporate a computer to undertake the Fourier transformation. The same computer can then serve to store and manipulate the digital spectral data obtained, allowing spectral subtraction, signal averaging, curve smoothing, computer matching with a data base, or quantitative analysis of components with a high redundancy by matching over the whole spectral range. On a monochromator, digitizing and computational facilities are extra costs, and digitizing an analogue output can probably never achieve the long-term frequency accuracy of an interferometer.

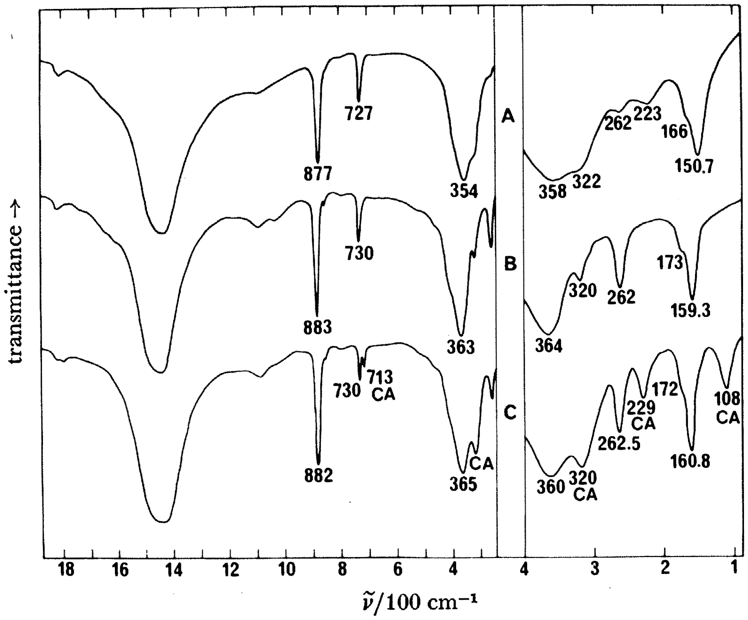

FIGURE 3. Spectrum B corresponds to nearly pure dolomite, $CaMg(CO_3)_2$, and spectrum A to a mineral, ankerite, in which 50 % of the Mg in dolomite is replaced by Fe^{II}. In spectrum C, corresponding to a calcite–dolomite mixture, calcite bands are labelled CA. The most distinctive features in the spectra appear in the range 100–400 cm^{-1} (Farmer & Warne 1978).

In practice, F.t.i.r. spectrometers undoubtedly do achieve markedly better signal:noise ratios than diffraction instruments, although optical imperfections and the poor characteristics of the triglycine sulphate pyroelectric detectors commonly fitted for wide frequency coverage do limit this improvement to well below the theoretical value. On the other hand, a fast-scanning interferometer can make more efficient use of photoconductive and photovoltaic detectors than can diffractometers, and instruments so equipped are capable of astonishing speed and sensitivity. For example, Bertie, in Durig (1980), has presented a very acceptable infrared spectrum over 4000–400 cm^{-1} recorded through a 0.25 mm aperture in 10 min with a mercury cadmium telluride detector. This corresponds to a detection limit for most samples of around 50 ng (assuming that the manipulative problems can be solved) or satisfactory spectra from opaque samples transmitting only 0.5 % of the radiation. By using a beam condenser, spectra can be obtained of sub-nanogram samples within a 30 μm aperture.

The high speed of spectral accumulation (about 1 s for a single scan of 4000–400 cm^{-1}), and the sensitivity in low-energy situations have greatly broadened the field of infrared spectroscopy. The speed of acquisition of spectra permits applications to rapidly changing samples (kinetic studies, gas chromatograph eluates, evolved gases in thermal decomposition) (Hirschfeld 1980; Lephardt & Fenner 1981). The sensitivity to low energy levels favours its use for atmospheric analysis either by emission or by absorption over long path lengths (Herget & Brasher 1980; Niki *et al.* 1980), for opaque samples such as carbon-filled polymers (Siesler 1980) and the pellets with large surface area used in surface studies, and for such techniques as attenuated total reflexion and diffuse reflectance, which often dissipate much of the incident energy. Photoacoustic detection, which determines directly the energy absorbed by a sample by its heating effect on the surrounding air, is possible only on F.t.i.r. instruments. This technique is inefficient but highly tolerant of sample form (Vidrine 1980; Rockley 1980). The most spectacular application of F.t.i.r. to low-energy sources is probably its use to provide high-resolution spectra of planetary atmospheres (Wynn-Williams & Cruikshank 1981). Many of the unique features of F.t.i.r. spectroscopy still await full exploitation (Hirschfeld 1978).

Dispersive instruments are, however, by no means absolete. At the bottom of the range, they are now remarkably cheap and effective while at the top of the range, digitized spectra can be stored, stray light has been greatly reduced, and ratio-recording has increased the precision of low transmission measurements. Such instruments allow satisfactory spectral subtraction with liquid or solid samples. Diffraction instruments also give rapid access to limited regions of spectra, and they can cover the range from 4000 to 200 cm^{-1} in a single scan. This last feature is crucial for mineral and inorganic spectra, as their most distinctive features often lie below 400 cm^{-1} (figure 3), which is the general limit of interferometers imposed by the KBr-supported germanium beam-splitter used in the 4000–400 cm^{-1} region. Polyester beam-splitters come into use at lower frequencies, but the interchange of beam-splitters is not yet a trivial operation. Moreover, the usual 200 cm^{-1} limit of commercial grating instruments matches well the limit imposed by the widely used and highly convenient KBr pressed-disc technique of sample preparation, as the discs transmit to about 230 cm^{-1}. Thus a different sample preparation technique (e.g. polyethylene discs) becomes essential below 230 cm^{-1}, and this is a convenient point to change instruments if spectra are required in the far infrared.

Infrared laser spectrometers

Perhaps both interferometers and grating instruments will finally be displaced by tunable laser spectrometers, but that time appears some way off as yet. Tunable diode lasers of different compositions can now cover almost any point in the range 4000–400 cm^{-1}. These lasers can be rapidly tuned over a range of 1 cm^{-1} by electrical means, and this range can be varied over some 200–300 cm^{-1} by controlling temperature or some other external variable. They are particularly suitable for atmospheric analysis (Hinckley 1976), because their narrow line width can pick out one interference-free rotation–vibration line of the target molecule. Their use also permits a very sensitive detection technique called optical heterodyning. Mixing two adjacent laser frequencies at the surface of a photodiode generates a difference frequency, which can be detected by microwave techniques: by this means atmospheric gases can be remotely detected by measuring the laser radiation scattered back to the source by atmospheric dust or distant landscape features. This technique is also applied in studying the infrared emission of astronomical features (Wynn-Williams & Cruikshank 1981).

The high intrinsic brightness of diode lasers allows measurements at absorbances greater than 10. This makes them suitable for process control applications on solid or liquid product flow lines, and for accurate absorbance measurements. Photoacoustic detection with lasers is said to have the highest sensitivity of any technique of localized gas monitoring.

Filter spectrometers

Where high resolution is unnecessary, infrared filters provide an inexpensive solution with high energy throughput, simple optics and the robustness necessary for on-line analyses in industrial situations (Frant & LaButti 1980). Industrial gas analysers have been incorporated into laboratory instruments, for example to give rapid routine determination of carbon, sulphur and water in minerals after liberation of the oxides by ignition (Bouvier & Abbey 1980). Wedge filters are the basis of highly sensitive monochromators covering the 4000–600 $\mathrm{cm^{-1}}$ region: these have been adapted to atmospheric analysis in cells with long path lengths, and incorporated into instruments that can give the spectra of microscopic specimens.

A commercially important and rather surprising application of filters is in the quality control of grains and other foodstuffs, by using diffuse reflectance in the near infrared. The near infrared is a complex region in which mainly combination frequencies and overtones of proton vibrations occur, and diffuse reflectance is a technique that has not been popular with spectroscopists because of the low-contrast spectra usually obtained. It has been shown, however, that empirical computerized combinations, positive and negative, of the reflected energy at 6–20 filter-selected frequencies can give excellent results for moisture, protein, fat and carbohydrate contents of milled seed, grain, or other vegetable products, provided that different standard curves are prepared for each closely defined type of product. More surprisingly, calibration curves for non-chemical qualities can be validated, including digestibility, malting quality or feeding acceptability. Clearly, these non-chemical qualities must be some function of the chemical components that do contribute to the near infrared spectrum. But their successful prediction raises doubt about what is being measured even when a satisfactory calibration curve is obtained for such chemical components as free amino acids or fibre content.

Although the final analytical procedure is extremely rapid and suitable for unskilled operators, the validation of the procedure requires several hundred samples analysed by standard methods, covering the whole range of physical and chemical variation likely to be encountered in the product to be analysed (Starr *et al.* 1981). The successes already achieved by this technique in several unlikely applications have led to unreasonable expectations of its applicability to any and every plant constituent, no matter how minor. Such hopes must suffer more disappointments than successes.

THE CHALLENGE OF INTERPRETATION AND RECOGNITION

In the previous section it was pointed out that developments in techniques and instrumentation have opened up many new fields of application, and have greatly facilitated many of the old; for further details, the two-yearly reviews of McDonald should be consulted. In this section, however, I shall consider briefly the other major hurdle in applied infrared spectroscopy, the problem of recognizing the spectra obtained. Although the identification of unknowns from their infrared spectra is usually considered a suitable undergraduate exercise, it is in fact a very difficult problem and one that has made the infrared spectroscopist unwilling to move far outside the field of small organic molecules with spectra rich in narrow absorption bands. Even here, the larger industrial laboratories are turning to computer searching rather than human intelligence either to identify completely one of a limited number of possible compounds, or to indicate the chemical nature of a less closely defined product (Hirschfeld 1980). Such computer searching facilities are particularly necessary in g.c.–i.r.–mass spectrometry, which may handle 1000 single compounds in one working shift. Searching a wide data base is, however, a costly and lengthy process, and the limited information stored can give only a list of possibilities, which may itself be excessively long.

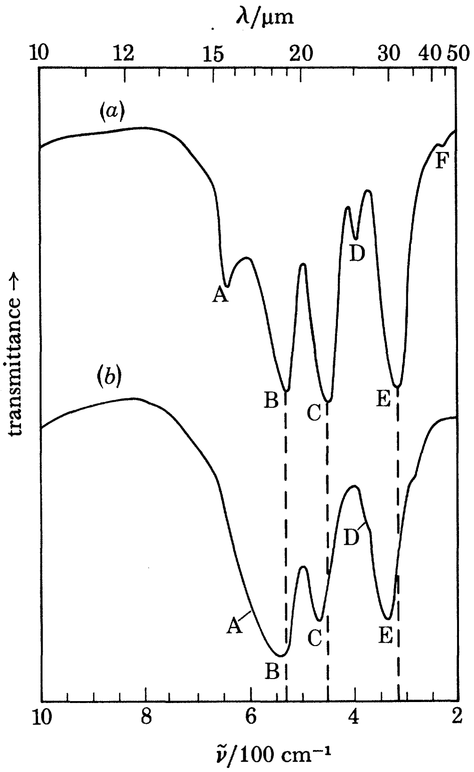

FIGURE 4. Differences between the spectrum of a platy form of haematite ((*a*), kidney ore) and that of an equidimensional form ((*b*), specularite) are due solely to particle shape. Vibrations perpendicular to the plates (A and D in spectrum (*a*)) are shifted to higher frequencies and vibrations parallel to the plates (B, C and E) to lower frequencies, compared with the corresponding vibrations in spectrum (*b*) (Wilson *et al.* (1981); figure adapted from Estep-Barnes (1977)).

In view of these difficulties in the traditional field of small-molecule spectroscopy, it can be understood why there has been a marked reluctance to develop the use of infrared spectroscopy for the characterization of natural materials, both mineral and biological, with all their complexity and their often apparently rather featureless spectra. To take mineral spectra as an example, we find here quite a variety of intimidating difficulties. The theoretical basis of crystal spectra involves novel features, such as long-range and short-range dipole coupling effects, not present in small-molecule theory. As a consequence of these dipole interactions, the effect of physical factors, such as particle shape, can be greater than that of chemical structure (figure 4). Each mineral species covers a range of compositions, and even tolerates some latitude in structure. It is not surprising, therefore, that in the initial stages of the study of a group of minerals by infrared spectroscopy the information flow is entirely negative: the spectra raise problems rather than solve them.

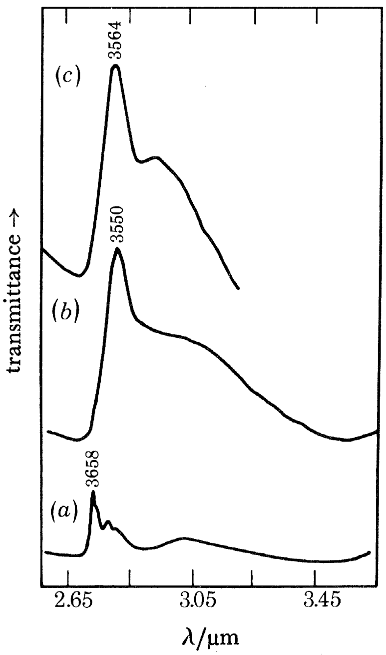

FIGURE 5. In fresh biotite (*a*), most of the hydroxyl groups are associated with three divalent cations, either Mg or Fe^{II}. In iron-rich biotites, oxidation results in ejection of part of the Fe^{III} formed from the biotite structure, and the resulting Fe_2^{III} OH groupings give a strong band near 3550 cm^{-1} in oxidized biotites (*b*) and vermiculites (*c*).

Against these discouraging obstacles, however, must be placed the many advantages to be gained once a satisfactory interpretation of the spectra has been achieved. The technique is rapid, and economical of sample. It is applicable to both crystalline and non-crystalline compounds, whereas the traditional identification tool, X-ray diffraction, is applicable to crystalline minerals only. As the spectra are determined by bond forces and bond geometry, they give immediate information on, or at least clues to, the chemical structure of unknowns, and allow further chemical information to be drawn from the effects of chemical and physical treatments on the spectra of the products. Finally, some of the difficulties in interpreting spectra arise from the fact that the information provided is sometimes unique, and no assistance in solving the problem is available from other more traditional investigational tools. The solution of such a problem then provides a completely new insight into mineral chemistry.

As an example, it may be noted that infrared spectroscopy provides evidence from OH stretching frequencies for a variety of vacant sites within the octahedral sheet of biotite micas, but no other technique can assist in the identification of the environment of the various types of hydroxyl group seen. This problem is far from fully solved, but the ability to recognize vacant sites has allowed infrared spectroscopy (figure 5) to establish the surprising ease with which ferric ions are ejected from the octahedral sheet of biotites under oxidizing conditions at ambient temperatures (Farmer *et al.* 1971). The use of infrared spectroscopy to characterize amorphous materials has shown that hydrous precipitated silica-aluminas have very different chemical structures (figure 6) according to whether they form above or below pH 5.5 (Farmer *et al.* 1979). The investigation of the hydroxyaluminium silicate species formed in acid solution has led to the synthesis of a novel tubular inorganic structure, a synthesis guided by infrared spectroscopy (Farmer & Fraser 1979). This in turn has thrown new light on the mechanism of formation of podzols, the classic highly differentiated soil type that covers much of northern Europe, Asia and Canada (Farmer *et al.* 1980). The ability of infrared spectroscopy to probe surface structures and surface reactions has given unique information on the surfaces and reactions of layer silicate clays and hydrous oxides under ambient conditions (Farmer 1971). Detailed information is now available, for the first time, on the surface structure at the solid–aqueous interface of a naturally occurring iron hydroxide (figure 7), goethite, thus constructing a bridge between detailed chemical structure and colloid theory (Parfitt *et al.* 1976). The crystalline regularity of this surface, formed in aqueous solution, was a surprise to many colloid theorists.

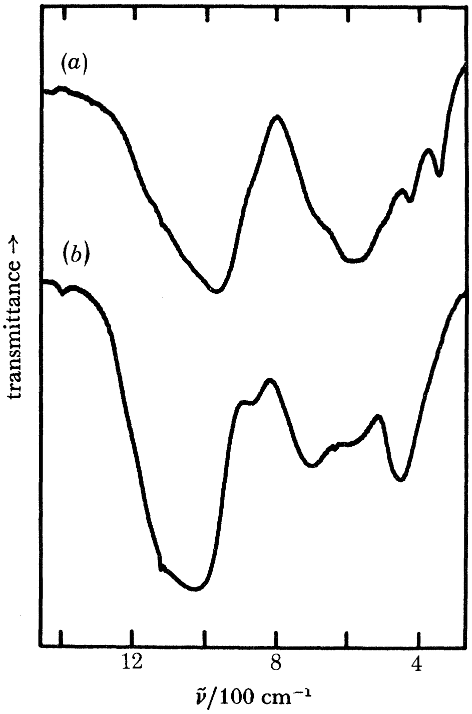

FIGURE 6. Infrared spectra clearly distinguished silica–alumina sols and gels formed in dilute acid solution (proto-imogolite, (*a*)) from those formed in alkaline solution (hydrous feldspathoids, (*b*)). The former contain only 6-coordinated Al and orthosilicate groups, whereas the latter contain a condensed tetrahedral network incorporating 4-coordinated Al and Si.

The application of infrared spectroscopy to biological polymers can be as rewarding as its application to minerals. A recent Nato conference on the infrared and Raman spectroscopy of biological molecules (Theophanides 1979) showed a preponderance of Raman applications, which reflects the relative simplicity of the technique and its ability to probe structures in solution. On the other hand, successful applications of infrared spectroscopy to recognizing unexpected carbohydrate and polyphosphate components of fungal cell walls (Bacon *et al.* 1968, 1969; Jones *et al.* 1968) indicate that the technique has considerable potential, as yet little used, for the empirical identification of biological polymers. In this field, difference F.t.i.r. spectroscopy has shown promise in distinguishing closely related polysaccharides (Seymour *et al.* 1980).

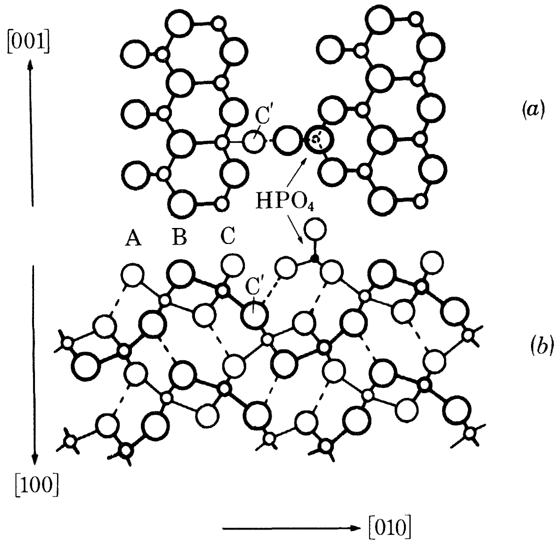

FIGURE 7. (*a*) Plan and (*b*) section of the goethite surface. Infrared spectra show three sharp absorption bands from surface OH, corresponding to the three types labelled A, B and C in the diagram. The A-type hydroxyl groups can be completely replaced by bridging HPO_4 groups as shown. The sharpness of the absorption bands from surface species indicates a regular quasi-crystalline surface structure.

It is a feature of the applications to mineral and biological chemistry discussed above that they have arisen from close interaction and collaboration between specialists in the fields concerned and spectroscopists committed to the practical use of their speciality as an investigative tool. Such studies are widely distributed in the scientific literature in both pure and applied journals, and are not easily accessible to new entrants to the fields who wish to make use of infrared spectroscopy, as is obvious from the naïve and mistaken interpretations of spectra that appear too often in the literature. Although the first monograph surveying the whole field of the infrared spectra of minerals (Farmer 1974) does give access to the published literature, it does not contain enough actual spectra to be a satisfactory laboratory handbook. The urgent need now is for detailed monographs covering more restricted areas of application, to make what has been and will be achieved readily available for immediate use. We look forward to the day when the equivalents of the Hummel/Scholl (1969, 1973) compilation of polymer spectra are available in the fields of inorganic and biological materials.

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