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## Mid-Infrared Spectroscopic Observations of the Moon

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## I. MOON AND PLANETS

## Mid-infrared spectroscopic observations of the Moon

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[Plate 9]

## 1. INTRODUCTION

Now that space probes have actually landed on the Moon, and man is soon to follow, one might suppose that the need for the development of lunar remote sensing techniques is past. Exactly the opposite is true. It must be remembered that no nation is financially able to support exploration of more than a very small percentage of the total surface area of the moon. Small areas immediately adjacent to a landing site will, of course, be explored in detail. Hopefully, there will be a few traverses made to discover the degree of lateral inhomogeneity of the surface materials. Realistically, however, we must plan on extending this 'ground truth' information to cover the entire lunar surface by remote means. In fact, remote sensing techniques will be employed prior to much of the detailed lunar surface exploration in order to define areas of maximum interest.

The mid-infrared region of the spectrum is a wavelength region which possesses a high potential usefulness for remote sensing, because the molecular vibration spectra in this region are directly interpretable in terms of molecular composition. It is the purpose of this paper to examine this potential, review the theoretical justification for use of this wavelength region, describe laboratory studies of possible lunar surface materials, and present the data so far obtained from the moon itself.

## 2. THEORETICAL BACKGROUND

The infrared spectrum of the Moon is a special case in molecular spectroscopy, i.e. one in which the target apparently consists of a relatively cold, particulate, inorganic surface from which, because of relative energy considerations, essentially only the emission spectrum is available.

In order to understand how and why characteristic information is contained in the emission spectrum one must first discuss the absorption and reflexion processes. This is because, for solid materials, a simply stated relation exists between the emission and reflexion spectrum.

The source of radiation from any solid material is the large number of excited electronic, atomic and molecular oscillators. At a given temperature, the spectrum of the emitted energy consists essentially of a continuum, rather than of discrete lines or bands, because of the close spacings of the energy levels of these oscillators. The emitted radiation actually

results from the acceleration of electrical charges within the material. Because of the complexity of the interactions of these charges in the solid body, it is virtually impossible to apply electromagnetic theory directly to explain variations in the spectral emissivity. Instead, thermodynamical considerations are usually applied.

The energy leaving a surface of a thermally excited material is the sum of a great number of components, and will depend very greatly on the condition of the surface. For a partially transmitting substance, the energy will arise from various depths within the material and be transmitted through, or reflected by, the surface. McMahon (1950, 1951), by simultaneously accounting for the absorption and emission from within each elemental volume, and also considering the imprisoning effects of reflexion from the interior surfaces, arrives at the following relation:

$$E_{(\lambda, \tau)} = \frac{(1 - R_{(\lambda, \tau)}) (1 - T_{(\lambda, \tau)})}{(1 - R_{(\lambda, \tau)}) T_{(\lambda, \tau)}}, \quad (1)$$

where  $E_{(\lambda, \tau)}$ ,  $R_{(\lambda, \tau)}$  and  $T_{(\lambda, \tau)}$  refer to the spectral emissivity, reflectivity and transmissivity, all at temperature  $\tau$ . For an opaque material where  $T_{(\lambda, \tau)} = 0$ , this expression reduces to Kirchhoff's law in its common form:

$$E_{(\lambda, \tau)} = [1 - R_{(\lambda, \tau)}], \quad (2)$$

which is valid for smooth surfaces. For the purposes of the present discussion, we assume that Kirchhoff's law in the form given above, holds for all surfaces.

The absorption process will be discussed before we consider reflexion, because in this way we can best illustrate why information characteristic of bulk composition is available in all three types of spectra (absorption, reflexion, emission).

Electromagnetic theory, based on the Maxwell relations and the wave equation, indicates that the propagation of an electromagnetic wave through a material can be characterized by specifying two quantities of the material. These are  $k$ , the absorption index, and  $n$ , the refractive index, and are commonly referred to as the optical constants of the material.

Both  $k$  and  $n$  are dependent on wavelength, but in different ways. The absorption index provides a measure of how much energy is absorbed from the light wave; it involves the excitation of harmonic oscillators to higher quantized energy levels. In regions where the wave frequency approaches a bound harmonic oscillator resonant frequency,  $k$  varies rapidly with wavelength,  $\lambda$ .

When  $n$  varies with wavelength, the medium is said to display dispersive effects, i.e. the wave packet spreads as the light wave traverses the material. The index of refraction depends upon the degree of polarization (a function of the physical location of effective charges) within the medium. Hence,  $n$  changes whenever there is a displacement of molecular dipolar, ionic, or electronic charges. Rapid variation of  $n$  with  $\lambda$  is called anomalous dispersion.

When the light wave frequency is of the same magnitude as a harmonic oscillator resonant frequency, two conditions prevail: the maximum energy can be absorbed by the oscillator, and there is a maximum charge displacement. Thus, absorption bands are always accompanied by anomalous dispersion. A plot of  $n$  against  $\lambda$  in these regions will produce a typical N-shaped curve.

In dealing with condensed dispersive media, such as most inorganic solids, the theory indicates that it is necessary to consider a complex index of refraction, defined as

$$n' = n(1 - ik).$$

This is shown to vary with wavelength,  $\lambda$ , or frequency,  $\nu$ , as

$$n'^2 - 1 = \frac{4\pi N e^2 n_e}{M} [(\nu_0^2 - \nu^2) + i\beta\nu]^{-1}, \quad (3)$$

where  $N$  denotes the number of molecular oscillators per unit volume,  $e$  is the electronic charge,  $n_e$  is the number of effective charges per molecule,  $M$  is the reduced mass associated with the motion of the charges and  $\beta$  is the damping term, or the transition probability. The imaginary part of  $n'^2 - 1$  is given by  $n^2 k$ , and has a maximum at frequency  $\nu = \nu_0$ , where there is also a maximum value for the polarizability  $\rho_0$ . The polarizability is given by

$$\rho_0 = \frac{e^2 n_e}{M} \frac{1}{\nu_0 \beta}. \quad (4)$$

The maximum value of  $n^2 k$  therefore locates the exact frequency of the resonance for a condensed medium.

In making a measurement of transmission against wavelength, i.e. recording a transmission spectrum, the following relation holds:

$$\frac{I_x}{I_0} = \frac{n^2}{1 + k^2} e^{-\alpha d}, \quad (5)$$

where  $I_0$  is the incident flux,  $I_x$  is the transmitted flux,  $d$  is the thickness of the sample and  $\alpha$  is given by

$$\alpha = 4\pi n k \nu \quad (\text{if } \nu \text{ is in cm}^{-1}), \quad (6)$$

and is known as the absorption coefficient. Thus, the experimentally observed absorption coefficient,  $\alpha$ , is proportional to  $n k$  rather than  $n^2 k$ , which is, as we have stated above, what locates the exact resonance frequencies. To locate the exact resonance frequencies from a transmittance spectrum, corrections must therefore be applied.

We have said that rapid variations in  $k$  result from the excitation of bound harmonic oscillators. To illustrate that the information in the infrared spectrum is characteristic of composition, we will therefore briefly discuss molecular vibrations.

All molecules, and molecular assemblages are continually executing a seemingly random vibrational motion, i.e. a motion in which the interatomic distances and bond angles are periodically changing, without altering the position of the centre of mass. Analyses reveals that this motion is, in fact, the superposition of a number of relatively simple motions known as the normal vibrational modes, each of which occurs with a fixed frequency and, when excited, will usually result in a change in both  $k$  and  $n$ , and in the appearance of a specific band in the infrared spectrum.

The number and type of these normal modes which can occur in a given molecule are dependent upon three fundamental properties of the material, which completely and uniquely define it. These are: (1) the chemical constitution, i.e. the number and type of atoms of which the substance is composed; (2) the spatial geometry of the equilibrium positions of these atoms relative to each other; and (3) the potential field, or the strengths of the interatomic forces (representative of the interatomic bonds and angles) which are operative in the molecule. Because a molecule is restricted to existing in definite discrete

energy levels of vibration, radiation is only absorbed or emitted by a molecule when it undergoes a transition from one of these energy states to another. The amounts of energy either required to cause, or which result from, such transitions correspond to the infrared region of the electromagnetic spectrum.

The ease with which bands in a spectrum can be identified from the theoretical predictions decreases with the increasing size and decreasing symmetry of the particular molecule.

When the molecule exists in the liquid or solid state, interatomic interactions usually have significant effects and exact definition of the normal modes becomes extremely difficult. This is true even in crystals where the surroundings of a molecular unit have a fixed and well-defined configuration. As the crystal structure becomes more random and ill-defined, it is necessary to rely more on empirical methods, and the interpretation of the spectra must be done by inference and analogy. While exact interpretation becomes increasingly difficult, the infrared spectra of materials still provide information concerning chemical constitution in the form of 'fingerprint' spectra, in which bands indicative of 'functional group' vibrations appear.

Inorganic solids are often quite highly absorbing in the mid-infrared, so that preparation of samples sufficiently thin to transmit radiation is difficult. In such cases it is more common to obtain spectral information by reflectance measurements.

Reflexion from a smooth or mirror surface results from the combined effect of  $n$  and  $k$ , and the intensity of reflected energy at a particular wavelength is given by the Fresnel equation. Because we are concerned here with situations in which the index of refraction is complex, the amplitudes  $A_i$ , and  $A_r$ , of the incident and reflected beams, respectively, are related by the expression

$$A_r = \frac{A_i[n(1-ik) - 1]}{[n(1-ik) + 1]} \quad (\text{for perpendicular incidence}). \quad (7)$$

When this is multiplied by its complex conjugate, the expression for the reflected intensity results:

$$R_s = \frac{(n-1)^2 + n^2k^2}{(n+1)^2 + n^2k^2}. \quad (8)$$

It can be seen that the reflectivity is high when  $n$  is greatly different from unity, or when  $k$  is high. For oblique angles of incidence, the reflectance depends upon the state of polarization of the incident beam, which produces complicated expressions for the total reflectance.

For a given vibrational transition, the resulting band in the reflexion spectrum is shifted to longer wavelengths from its position in the transmission spectrum. This is because, as  $k$  passes through a maximum,  $n$  follows the typical N-shaped curve, and the combined effect of  $n$  and  $k$  is to both broaden and distort the band. There are several ways in which a reflexion spectrum can be transformed to yield a curve equivalent to the transmission spectrum. The most convenient of these is by use of the Kramers–Kronig or Robinson–Price analysis (see Hunt *et al.* 1964*c*).

We have so far been concerned only with smooth surfaces, and hence with specular or bidirectional reflectance. When a surface is rough, or particulate, the reflectance contains a diffuse component. This diffusely reflecting component comes about because of the penetration of part of the incident radiation into the sample. Part of this radiation is



returned to the surface after partial absorption and multiple reflexion and scattering at the boundaries of individual particles. No general theory currently exists which gives a valid quantitative description of the diffuse component.

In materials which selectively absorb radiant energy (i.e. non-grey or non-black bodies), complications arise because the spectral intensity distribution changes differently for the specular and diffuse parts of the reflected radiation. As will be seen, this leads to a situation in which the two components are effectively opposing each other in the region of an absorption band.

Generally, theories which describe diffuse reflectance do so in terms of an absorption coefficient,  $k$ , and a scattering coefficient,  $s$ . In the most completely developed of these theories, due to Kubelka (1948) and Munk, the absorption coefficient  $k$  bears the same significance as that usually employed in spectroscopic transmission techniques, where it is called  $\alpha$ . However,  $s$ , the scattering coefficient, is more difficult to specify in a general way, is usually assumed to be wavelength independent, and must be specified for each particular case.

The Kabelka–Munk theory yields two formulae of considerable practical importance. They express the transmission and reflectance of a diffusely reflecting layer of thickness  $d$ . The transmission,  $T$ , is given by

$$T = \frac{4\beta}{(1+\beta)^2 e^{\alpha d} - (1-\beta)^2 e^{-\alpha d}}, \quad (9)$$

where  $\beta$  is defined as 
$$\beta = \left[ \frac{\alpha}{\alpha + 2s} \right], \quad (10)$$

and where  $\alpha$ , the absorption coefficient, is as defined previously.

The diffuse reflectance  $R_d$  is given by

$$R_d = \frac{(1-\beta^2)(e^{\alpha d} - e^{-\alpha d})}{(1+\beta)^2 e^{\alpha d} - (1-\beta)^2 e^{-\alpha d}}. \quad (11)$$

For an optically thick sample  $d \rightarrow \infty$  (which leads to  $T = 0$ ),  $R_d$  becomes

$$R_d = \frac{1-\beta}{1+\beta} = \frac{1 - [\alpha/(\alpha + 2s)]^{\frac{1}{2}}}{1 + [\alpha/(\alpha + 2s)]^{\frac{1}{2}}}. \quad (12)$$

Considering the expression (equation (8)) given earlier for the specular component of reflectance, it can be seen that, in the limiting case of no transparency,  $\alpha \rightarrow \infty$ , so  $k \rightarrow \infty$ , and consequently  $R_s \rightarrow 1$ , which is the maximum value for  $R_s$ , indicating complete reflexion. In the other limiting case of complete transparency, even though  $d \rightarrow \infty$ , as  $\alpha \rightarrow 0$ ,  $k \rightarrow 0$  and  $R_s \rightarrow (n-1)^2/(n+1)^2$ .  $R_s$  is then, obviously, always less than 1 for real materials. For the type of materials we are concerned with here,  $n$  is typically about 1.5, which gives values of about 0.1 for  $R_s$ .

However, from expression (12) for the diffuse component of reflexion, it can be seen that as  $\alpha \rightarrow \infty$ ,  $R_d \rightarrow 0$ ; but where  $\alpha \rightarrow 0$ ,  $R_d \rightarrow 1$ . We can therefore see that these two components of the total reflectance  $R_T = (R_s + R_d)$  have opposing dependencies on the value of  $\alpha$ , which is of critical importance to the evaluation of molecular vibration spectra as a remote sensing tool.

Characterizing information is available in a spectrum only when it shows detectable, relatively rapid changes in  $\alpha$  with changing wavelength,  $\lambda$ . If we consider a completely specularly reflecting sample,  $R_T = R_S$ , which is approximated by an optically polished surface of the material, the spectrum would show high relative intensities where  $\alpha$  has high values, and low relative intensities where  $\alpha$  has low values. But just the opposite is true for a completely diffuse reflector.

Roughening or grinding a sample to smaller and smaller particle sizes will decrease the specular component and increase the diffuse component of the reflexion. The general effect on the appearance of the spectrum is to decrease the over-all intensity (we are assuming that the observations are all made at the specular angle, by which we mean the angle of maximum reflexion for the polished surface), and to lower the relative intensity in the region where the material absorbs highly, but to raise the relative intensity everywhere outside these regions. The result then is a decrease in spectral contrast.

The above discussion is considerably simplified. There are many factors which determine the changes which occur in the spectrum of a material as it is progressively reduced from a polished surface to smaller and smaller particle sizes. The relationship between the particle size and the wavelength, the manner in which the surface is packed, the crystal habit, and the degree of homogeneity all introduce particular effects. The fact that the reflexion and absorption maxima and minima for the same resonance frequency are slightly offset in wavelength, and the fact that multiple reflexions from the same material tends to sharpen a spectral band lead to distortion of the appearance of features in the spectrum of a given material.

Despite these complicating effects, which tend to dilute the characterizing information, whatever information remains should be sufficient to allow the type of material to be categorized into basic or acidic rock types, if not specifically identified.

Kirchhoff's law holds sufficiently well, even in the case of finely powdered materials, for the emission spectrum to be directly correlated with the reflexion spectrum. Consequently, it follows from the above discussion that roughening or grinding a sample will reduce the spectral contrast in its emission spectrum as well as in its reflexion spectrum. As shown by Surveyor experiments, the lunar surface materials consist largely of fine particles, suggesting that characterizing spectral information may be difficult to detect, particularly after attenuation by the earth's atmosphere. Yet, laboratory studies show that spectral content is not entirely lost from the emission of even very fine powders. Thus, it appears very likely that compositional information is available in the infrared emission from the Moon. When one considers how difficult it is to obtain a perfect black body, it seems most unlikely, despite the fact that the Moon is a difficult target, that no compositional information is available in its infrared spectrum.

### 3. LABORATORY STUDIES

#### (a) *Historical summary*

Numerous bibliographies have been assembled which deal with infrared spectroscopic studies in general, and several of these include a limited number of references to work performed on solid materials and minerals (Bauleke 1953; Brown *et al.* 1954; Crowley

1959; Blau, Miles & Ashman 1958). Only one, by Lyon (1962), deals specifically with minerals and related materials. In this excellent bibliography he lists some 440 references which deal with the absorption, reflexion and emission spectra of minerals and solid materials, and includes references to papers discussing pertinent spectroscopic techniques for obtaining such spectra. The bibliography covers all work done on such materials from Coblenz's classical investigations and resultant cataloguing in the early part of the century, to 1962. As this work indicates, apart from Coblenz's investigations, the majority of research on the infrared spectra of minerals and rocks has been done since 1950, with the most significant initial contributions being made by McMahan (1950, 1951), Simon & McMahan (1953), and Gardon (1956). The vast majority of these investigations were performed for very specific purposes largely unrelated to our interest here, except in so far as they initially located the regions where characterizing data exists, and defined the types of information available from infrared studies of solid materials. These studies range from exploratory investigations, in which techniques known to be extremely powerful in elucidating the molecular structure of gases and liquids are applied to solids, to very sophisticated experimental and theoretical investigations of the molecular structure of solids. Most of these studies are characterized by a lack of restriction, in the sense that the most appropriate technique was selected from all those available, and the samples used were carefully selected, characterized and prepared to optimize the quality and quantity of data acquired. The present discussion of laboratory studies is limited to those which can be specifically applied to our purposes—i.e. those dealing with the spectral content of possible lunar surface materials with surface conditions which may be considered to be lunar. These studies have typically been performed by investigators specifically interested in the problems of remote compositional sensing of terrestrial or extraterrestrial surfaces, and they amount, in essence, to feasibility studies. Their first concern was to determine where the spectral information is located, how much is there, and how diagnostic it is. Their second was to determine how the spectral information is modified by degradation of the surface, or how the amount of information depends on particle size. We will consider these problems separately here, and also the problem of compositionally heterogeneous samples.

(b) *Location of spectral information*

The location of absorption and reflexion bands of many of the materials of interest are already defined by the early studies listed in the bibliographies. However, of the more recent investigations, by far the most comprehensive series of studies were carried out by Lyon and his co-workers (1963, 1965 *a, b*), and the results have been collected in two volumes constituting a final report to N.A.S.A. evaluating the use of infrared spectrophotometry for compositional analyses of lunar and planetary soils. While it is beyond the scope of this article to consider in detail the content of this work, some of the more pertinent aspects will be briefly presented.

In part I of the report, Lyon (1963) studied the absorption spectra of some 370 rock and mineral samples and performed 80 reflexion measurements. He has listed the position of the spectral peaks in absorption for various minerals and rocks, concentrating in the 8 to 25  $\mu\text{m}$  range. Figure 1 shows a comparison of the absorption spectra of a group of acidic



and basic rocks, and figure 2 shows the spectral changes which occur in proceeding through a series of plagioclase feldspar tektosilicates with increasing amounts of anorthite. These two figures clearly indicate the extent to which the infrared absorption spectra of minerals are diagnostic, and are representative of the care and organization with which his work was performed. In part II, which primarily deals with rough and powdered samples,

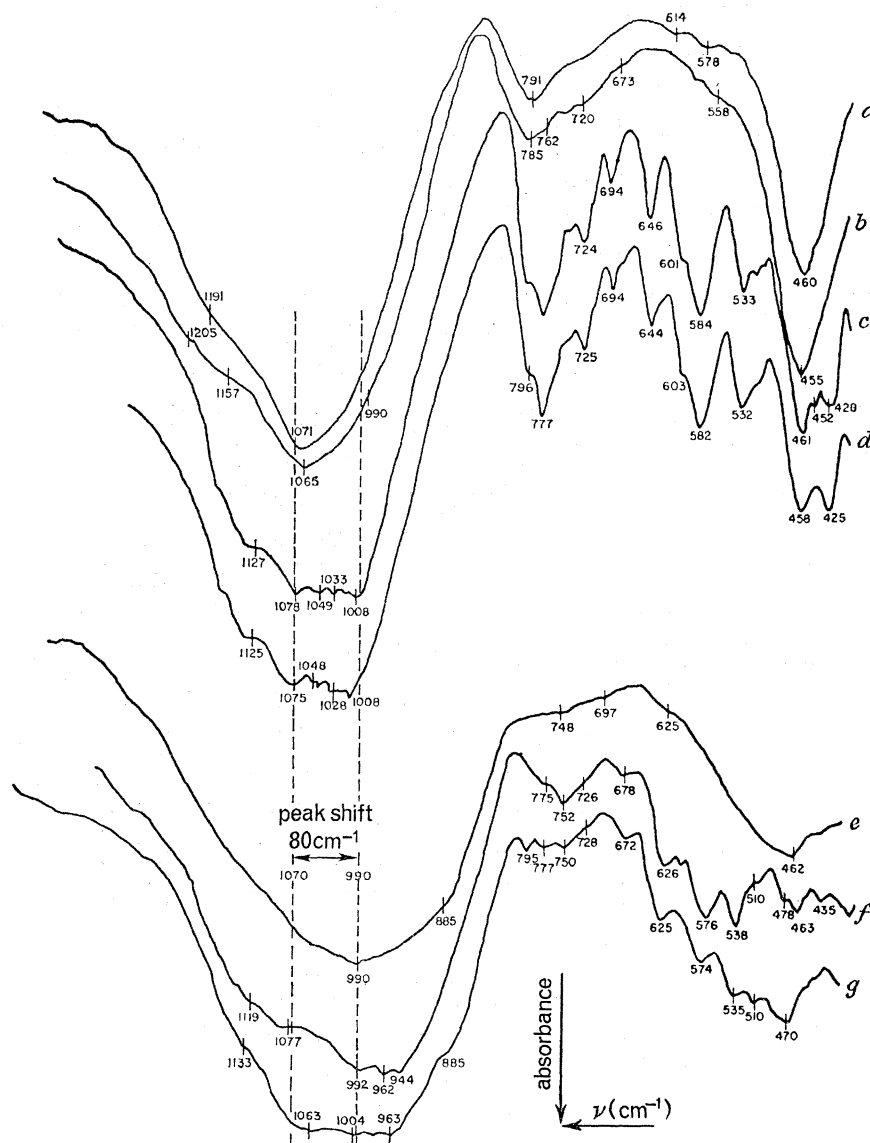


FIGURE 1. Absorption spectra of a group of acid rocks (upper four curves) and a group of basic rocks (lower three curves). The curves are displaced vertically. Dashed vertical lines show peak shift associated with composition. To convert wave-numbers ( $\text{cm}^{-1}$ ) to wavelengths ( $\mu\text{m}$ ):  $\mu\text{m} = 10^4/\text{cm}^{-1}$ . *a*, Katman ash; *b*, obsidian; *c*, *d*, granite; *e*, basalt; *f*, gabbro; *g*, diabase. (From Lyon 1963.)

Lyon (1965*b*) presents 40 absorption, 38 reflexion and 256 emission spectra. A set of 29 representative rock samples are investigated, for which all three types of spectra are presented together for each sample after normalization. Examination of these spectra, of

which figure 3 is typical, illustrates the differences to be expected by using the different techniques on the same sample.

The spectral range chosen by Lyon has been extended to longer wave-lengths by such workers as Duke & Stephens (1964), and by Tarte (1962, 1963), where absorption studies of specific groups of materials have been carried out to investigate spectral variations in

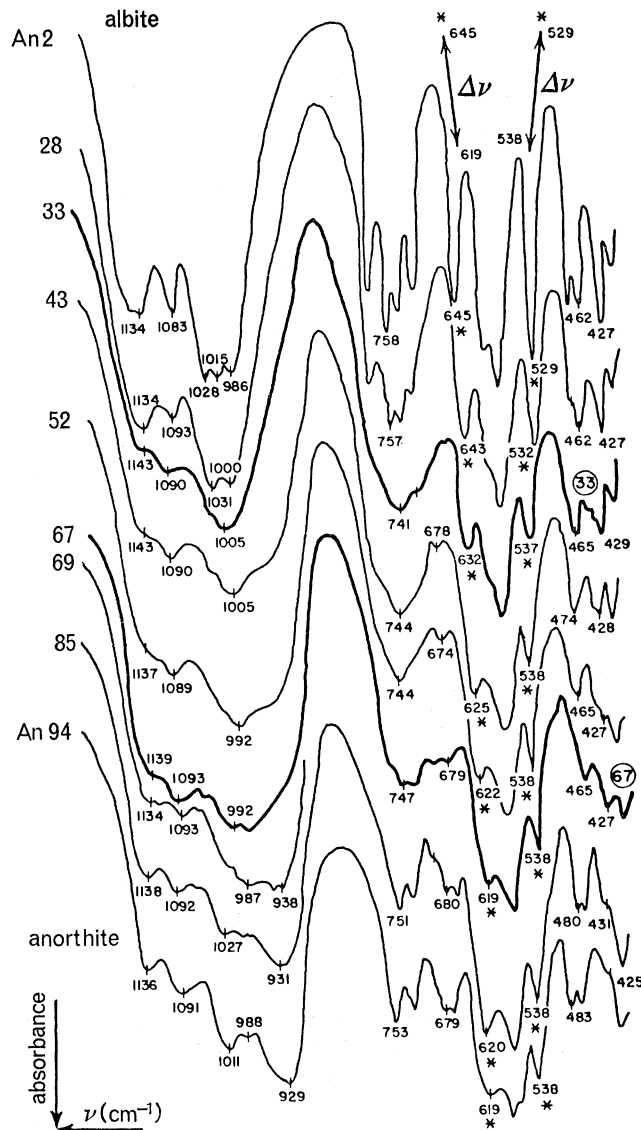


FIGURE 2. Absorption spectra of plagioclase feldspar tektosilicates showing spectral changes with increasing amounts of anorthite (An). (From Lyon 1963.)

homologous series by preparing known isomorphous compounds. These studies indicate that, while the high-frequency range is characterized by specific patterns of the  $\text{SiO}_4$  tetrahedron, at lower frequencies the spectrum is more affected by the nature of the cation. More pertinent work for our purposes has been performed in this low frequency region (from 15 to  $200 \mu\text{m}$ ) by Aronson and his co-workers (1966*a*), who have investigated the region for the specific purpose of lunar and planetary exploration, using reflexion techniques. Figure 4 shows his reflexion spectra for some olivines.

While the vast majority of this type work has been carried out in great detail on various silicate minerals and rocks, comparable information is available for many non-silicate materials also. An example of this work is that done by Hunt, Wisherd & Bonham (1950), Miller & Wilkins (1952), and Adler & Kerr (1962, 1963). The characterizing bands for some non-silicate minerals are shown in figure 5.

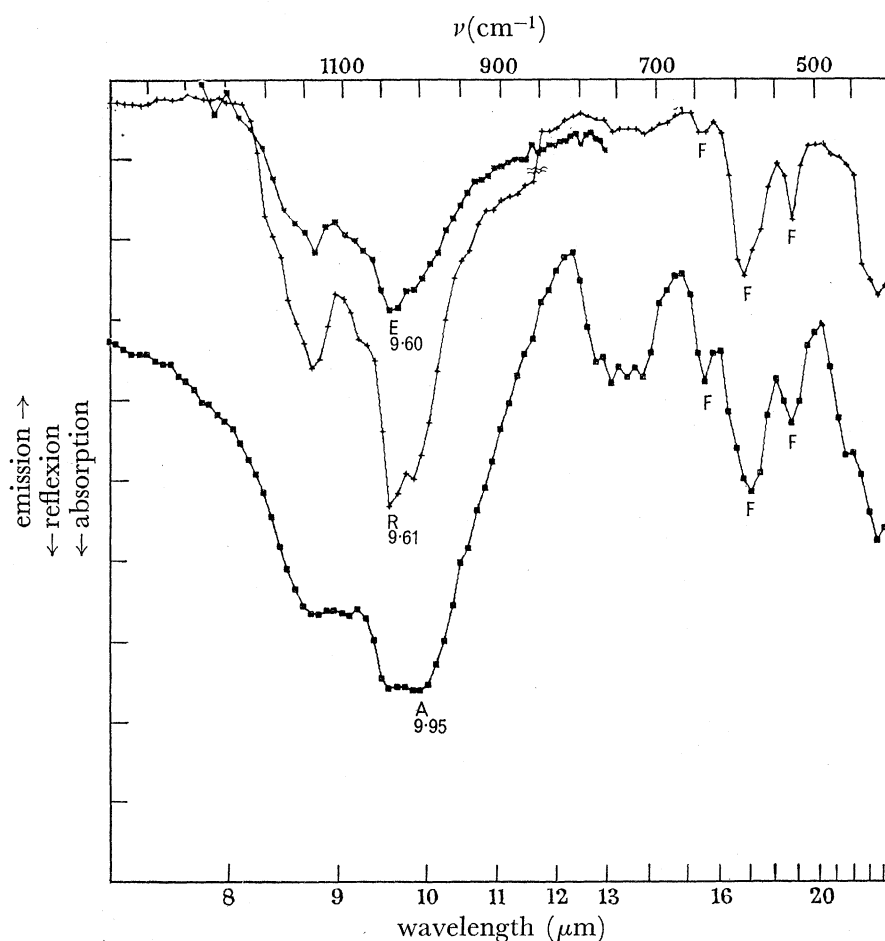


FIGURE 3. Absorption (A), reflexion (R) and emission (E) spectra of quartz syenite. (From Lyon 1965 *b*.)

(c) *Modification of spectrum by surface condition*

From the above discussion it is obvious that, provided a suitable sample can be prepared—i.e. one sufficiently thin for transmission studies, or one sufficiently smooth for reflexion and emission investigations, compositionally diagnostic information is readily available from the infrared spectra of rocks and minerals. However, because here the concern is with obtaining data from a remote source which can in no way be prepared or altered, it is necessary to consider how spectra obtained under optimal sampling conditions are modified by roughening the surface of polished samples, or by reducing the particle size of particulate samples. This problem has received a great deal of attention, both experimentally and theoretically, because of its utmost importance to any study of the feasibility of

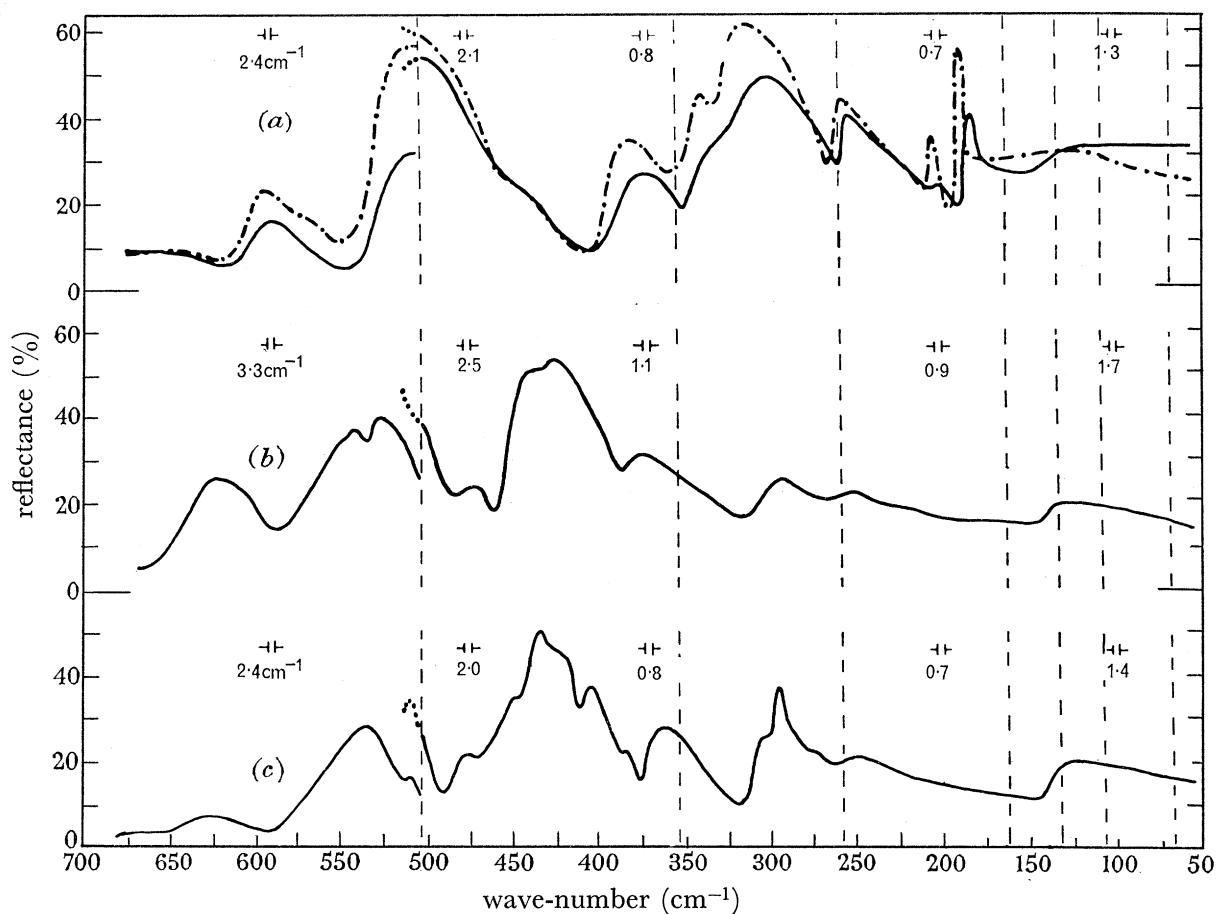


FIGURE 4. Far infrared reflectance spectra of olivines (polished surfaces,  $45^\circ$  incidence). The experimental slit widths are indicated. (From Aronson *et al.* 1967.) (a) Fayalite, —, room temperature, ----,  $77^\circ\text{K}$ ; (b) Fo 70: Fa 30, room temperature; (c) 'Pure' forsterite, room temperature.

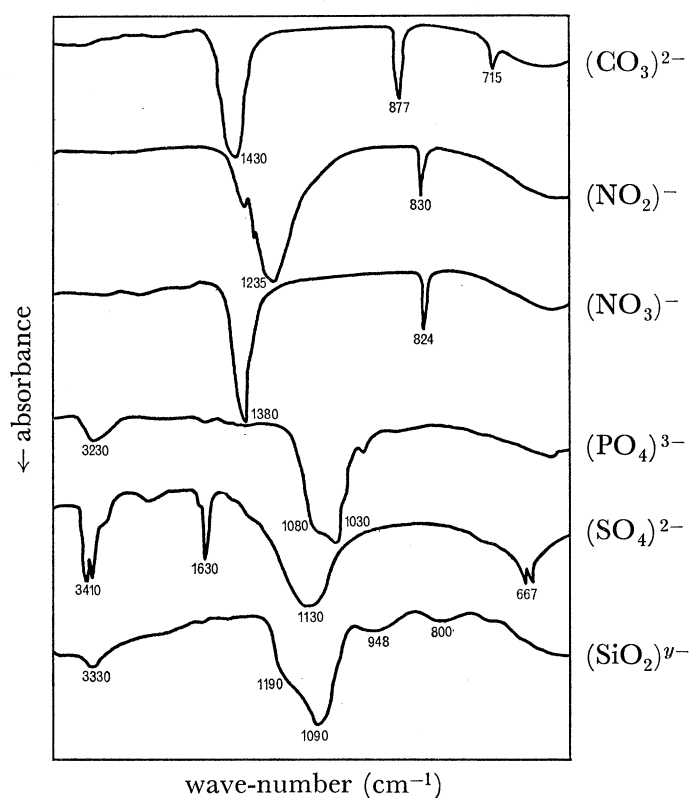


FIGURE 5. Absorption spectra of inorganic anions. (From Lyon 1963.)



obtaining compositional information from the infrared emission of lunar and planetary surfaces.

The amount of spectral information available from a spectrum is referred to in terms of 'spectral contrast', which Lyon (1965*b*) defines as follows: 'A spectrum which has one or more peaks that diverge markedly from the average level of the remainder of the curve is said to have spectral contrast.' Lyon proceeds to use the difference between the minimum and maximum values of a feature, or the average of the maxima on either side of the feature, to indicate the amount of spectral contrast. Aronson *et al.* (1967) define the spectral contrast as the ratio of the maximum of the spectrum outside the peak to the peak value.

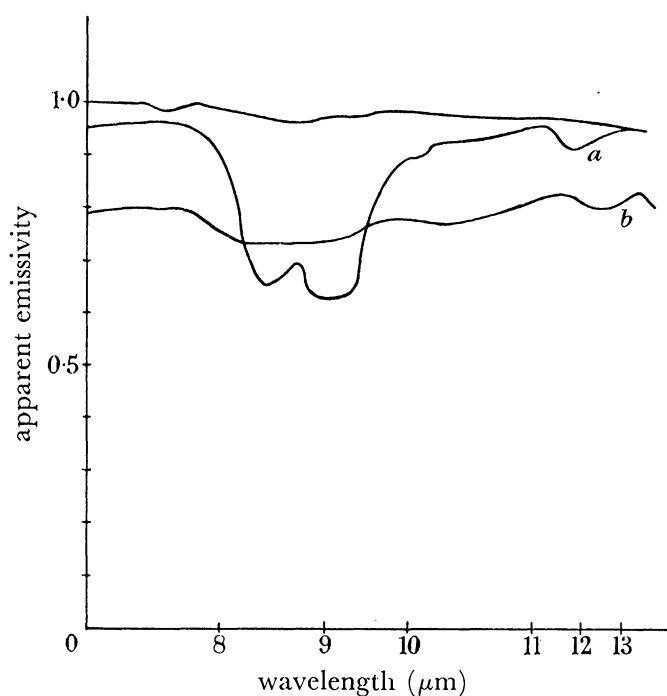


FIGURE 6. Apparent spectral emissivity of quartz as a function of grain size. Uppermost curve is that of a black body. Curve (*a*) illustrates the spectral emission of quartz particles 50 to 100  $\mu\text{m}$  in diameter. The strong emission band at 9  $\mu\text{m}$  is greatly reduced in curve (*b*), which illustrates the spectral emission quartz particles 1 to 2  $\mu\text{m}$  in diameter. (From Van Tassel & Simon 1964.)

A more satisfactory working definition of spectral contrast must include both the difference and the ratio of the maximum and minimum values, as well as specification of the width of the feature, the absolute or relative intensity, the signal to noise of the system necessary to detect it, and specification as to the type of spectrum being measured—i.e. emission, reflexion or transmission.

In one of the first specific feasibility studies, Van Tassel & Simon (1964) examined the spectral emission of a series of minerals selected as possible lunar surface materials as shown in figure 6, they found that the amount of spectral information was greatly diminished for very fine (1–2  $\mu\text{m}$ ) grain sizes. They concluded that the feasibility of compositionally mapping the lunar surface is a function of the particle size which exists there.

Lyon (1965 *b*) performed a series of experimental investigations, using both emission and reflexion techniques, to determine in general the effects introduced into the spectra by departures from optically smooth surfaces. He concluded that rock types can be identified if spectral contrast is evident, and that the degree of surface roughness, physical discontinuities and the particle size have very significant effects on the amount of spectral contrast. He pointed out that serious problems are only introduced when the particle size is reduced below 50 to 100  $\mu\text{m}$ , but that, while this results in reduced contrast, it in no way causes wavelength shifts sufficient to cause identificational confusion.

Aronson *et al.* (1967) have considered in detail the amount of spectral information available from fine particulate material. On the basis of reflectance measurements they concluded that the main requirement for observing spectral contrast in such samples is the capability of achieving a sufficiently large signal to noise ratio. Aronson & McLinden (1966) and Aronson, Emslie & McLinden (1966) demonstrated that by increasing their signal/noise ratio, the spectral information available from powdered fayalite is essentially the same as that obtained from a polished surface.

The general conclusion that may be drawn from this work is that the spectral contrast of the fundamental molecular vibrational bands (sometimes referred to as the reststrahlen features) is greatly decreased in going from polished to roughened surfaces, and is further decreased as the sample is ground to finer and finer particle size. As explained in the previous section, this appears to be due to the competing behaviour of the specular and diffuse components of the total reflectance or emission. Hovis & Callahan (1966) studied the total reflectance spectra of igneous rocks and minerals, and note for dunite an exception to this general observation. In this case, as the particle size is reduced from 1 to 2 mm down to 0.1 to 0.25 mm they reported an increase in reflectance of the reststrahlen features rather than a decrease. They ascribe this as possibly being due to a selective filtering effect.

For most materials, the positions of the minima in the emission spectrum do not appear to shift when the particle size is decreased. This is because the shifts are usually small, the spectral contrast is diminished, and the bands are broadened. However, in quartz-containing minerals Conel (1965) reported that there does appear to be a definite shift in the position of the minima with decreasing particle size because of very strong contributions from the reststrahlen features of quartz. Hovis & Callahan (1966) reported the appearance of a new feature in the spectrum of many materials (quartz, granite, dunite and tuffs) which in some cases continued to be enhanced while the original features continued to be diminished as the particle size was reduced. They concluded that this effect is not due to selective filtering but do not offer an explanation for its appearance.

(*d*) *Effect of mixtures of minerals*

It is necessary to examine the ways in which the spectral features of the various components mix in the composite spectrum if one is to study natural materials. Several authors have investigated the spectral information available from a compositionally heterogeneous surface. If the minerals are spatially separated, either as distinct rocks or as large grains in a single rock, the individual reflectances or emittances should add linearly with weighting factors proportional to their respective areas. Lyon (1965 *b*) has demonstrated that this

simple rule is applicable in emission. Using a piece of quartz and a piece of dunitite, he found that the emission spectrum obtained is the sum of the two components and that this is also true for sand-sized particles. Hovis & Callahan (1966) likewise have demonstrated that this appears to be true for mixtures of relatively large particle sizes in total reflexion measurements. Aronson *et al.* (1967) have considered in more detail the mixing of several minerals, and concluded that if the facets of the individual components of the mixture are large compared with the wavelength, then the linear mixing rule is adequate. However, for the case where the grains of the different components are very small, such a simple mixing rule is not adequate. They developed a mixing rule applicable to this latter case based on the Lorentz–Lorenz relation.

(e) *Other spectroscopic techniques*

Other means than conventional dispersive spectroscopic techniques have been used in attempts to obtain compositional information from the Moon. Petit & Nicholson (1930), for example, used what amounted to filter, or band pass, radiometry by using a piece of fluorite and a piece of glass as filters in their study of lunar emission. Hunt (1966) developed another type of filter technique, which he called spectrum matching. The technique was demonstrated both in the laboratory and in making observations of the Moon by Hunt, Salisbury & Reed (1967).

It is when a remote, energy limited, emitting surface is to be observed through a relatively rapidly changing attenuator and/or from a moving observation point, that the advantages of extremely rapid data acquisition afforded by the spectrum matching technique are best utilized.

The technique, as used in the laboratory was illustrated by using an infrared camera which scans an  $X$ – $Y$  raster in a focal plane, and, using a liquid helium cooled, copper-doped germanium detector, permits the output to be displayed on film and on an oscilloscope. This instrument is described by Rehnberg, Yoder & Hunt (1967). Figure 7, plate 9, displays the results. Figure 7*a* is a photograph in the visible of the samples tested, with the sample area outlined. The samples were resting on a sheet of aluminium foil, which is visible through the transparent quartz. The upper surfaces of the other samples are seen. In all cases, the infrared radiation sampled was emitted from the upper surfaces.

Each of the remaining five images is composed of a raster of instantaneous processed signals (in the sense that they are the collected radiance from a small surface area which has been reflected from either a mirror or a reststrahlen plate) received from the targets chopped against the emission from a black body source. Figure 7*b* was generated by reflecting the target radiance from a plane mirror, and so is essentially a relative radiance image. In figure 7*c* to *f* the emissions from the samples were processed by reflexion from reststrahlen plates of quartz, olivine, albite and tremolite respectively. A spectrum match between a reststrahlen plate and one of the samples should be indicated by a minimal signal—i.e. darkest shade of grey in figure 7*c* to *f*.

From a consideration of figure 7*c* to *f* one sees that the information obtainable from some reststrahlen plates (such as quartz, tremolite and olivine) is more clearly definitive than from others (such as albite), even though a perfect spectrum match for one sample



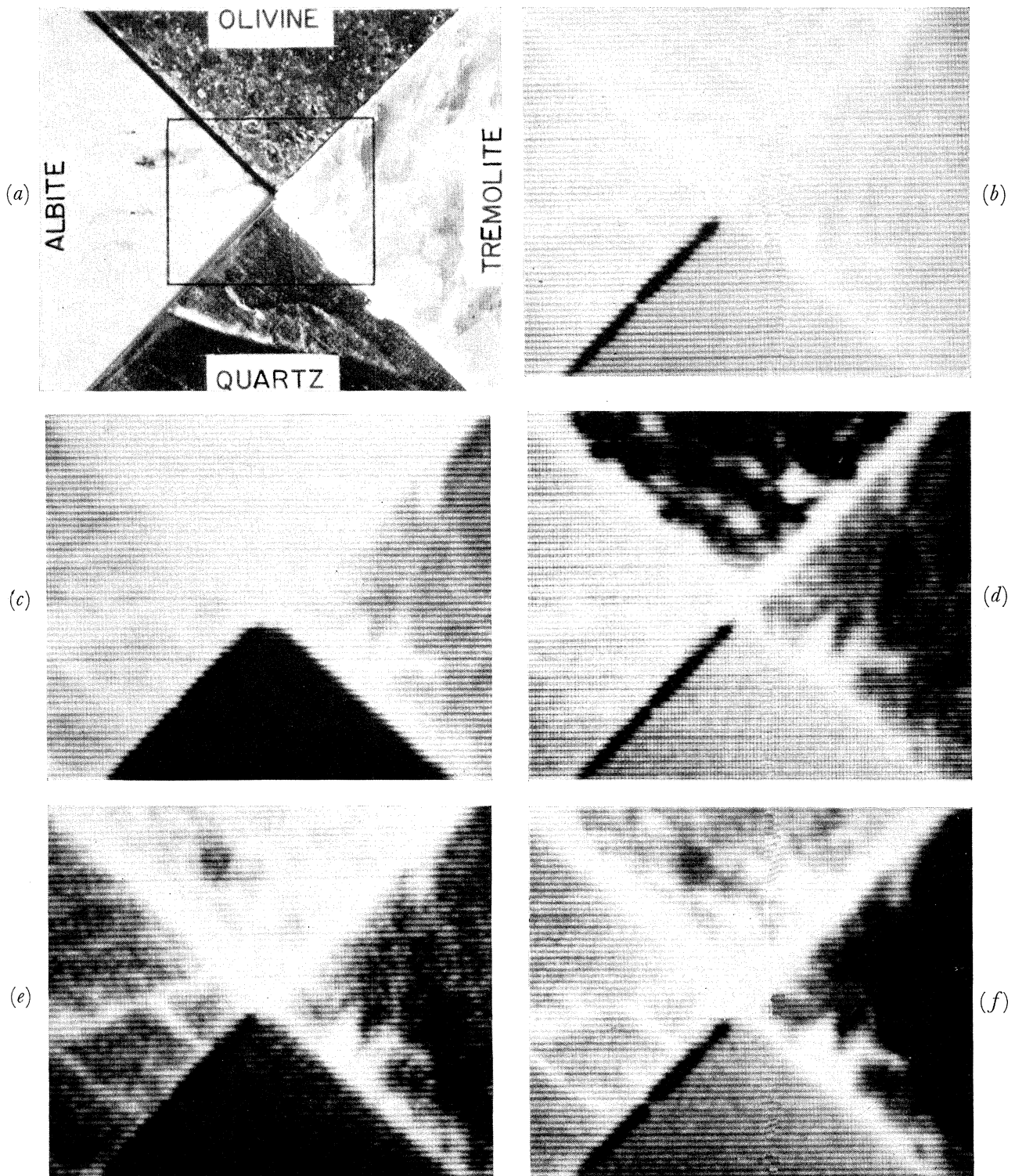


FIGURE 7. Illustration of the feasibility of the spectrum matching technique. Samples of quartz, olivine, albite, and tremolite, shown in visible photograph *a*, are scanned with an infrared imaging device to produce pictures *b*, *c*, *d*, *e* and *f*. Picture *b* was produced after the infrared emission of the samples was reflected from a mirror, and pictures *c*, *d*, *e* and *f* were produced using the following reststrahlen plates in place of the mirror: (*c*) quartz; (*d*) olivine; (*e*) albite; (*f*) tremolite. (From Hunt *et al.* 1967.)



MATHEMATICAL,  
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& ENGINEERING  
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THE ROYAL  
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has been achieved in each case. The albite case (7e) is included to illustrate the effects produced by using a poor reststrahlen material. Despite the use of a poor reststrahlen material, however, given the four pictures produced using all four reststrahlen plates, one has no difficulty in identifying the four samples in terms of their relative likeness to the particular reststrahlen material.

Hunt (1966) emphasizes that spectrum matching is a technique of comparisons, involving comparisons of the relative magnitudes of the signals obtained when the emission of one target is reflected from a series of different reststrahlen materials, and/or when the emissions from a series of targets are reflected from one reststrahlen material. The technique is most useful in the rapid detection of compositional differences among a series of targets, and the general nature of such differences (i.e. acidic or basic rocks), rather than in the specific identification of the composition of a given target. The latter involves all the problems of identification encountered in conventional spectroscopy.

#### 4. GROUND-BASED STUDIES

Ground-based observations of the mid-infrared emission from the lunar surface provide many distinct advantages over observations made from balloons, rockets and spacecraft. These are the ability to achieve very high spatial resolution on the target, accurate tracking capability and the comparatively great convenience afforded by the flexibility in choice, use, ease of adjustment and modification of instrumentation during an observing period. However, such observations suffer from one extremely serious disadvantage, and that is the severe attenuation of data caused by the presence of an unpredictably variable and time-dependent absorbing, scattering and emitting atmosphere. Correctly accounting for and removing the effects of the atmospheric attenuation from the data presents the most intractable problem in any ground-based observational programme. It is interesting that each recent investigator has attempted to eliminate troublesome atmospheric variability by different methods.

##### (a) *Ground-based spectroscopic studies*

The first dispersed infrared spectra of the Moon in the 8 to 14  $\mu\text{m}$  atmospheric window were recorded by Langley and Very (Langley 1884) between 1884 and 1887 at the Allegheny Observatory. Following Nichol's (1897) discovery of the quartz reststrahlen bands beyond 8  $\mu\text{m}$ , Coblenz (1906) pointed out that various other common minerals behaved similarly, and suggested that the Moon may reflect solar energy in the 8 to 14  $\mu\text{m}$  range and thus have introduced an error in Langley's estimated lunar temperature. Very (1906) calculated that, even if the lunar surface were completely reflecting, the contribution of solar reflected energy would be less than 1 %, thereby establishing that the vast majority of energy leaving the Moon in this 8 to 14  $\mu\text{m}$  wavelength range is emitted energy from the hot lunar surface.

Pettit & Nicholson (1930) confirmed Very's conclusion in 1930, but became concerned about the possibility that lunar surface materials with strong reflexion bands could be lowering the emissivity in the wavelength region under observation. They therefore made the first attempt to determine whether spectral data was contained in the emission,

essentially by filter radiometry, using fluorite and a glass screen. They concluded that the emissivity from the lunar surface is unity, and that, for all practical purposes, it is unaffected by any silica content. They do not state, however, that silicates are not present on the surface, but rather that, if they are present, they exist in some finely divided form-like sand, or that they are porous like pumice. These negative results apparently discouraged any additional attempts to determine the composition of the lunar surface by infrared spectroscopy until the 1960's, although many dispersed spectra of the Moon were recorded in the interim for other purposes.

Adel (1946) recorded spectra of the Moon in the early 1940's using the whole width of the lunar disk as a target. In this early work he was primarily concerned with defining the atmospheric windows available for spectroscopic work, pointing out the presence of a micro-window at  $6.3\ \mu\text{m}$ , a major window from 8 to  $14\ \mu\text{m}$  and a lesser window from 16 to  $24\ \mu\text{m}$  (Adel & Lampland 1940).

While other investigators recorded dispersed lunar infrared spectra throughout the next 20 years, all were recorded for purposes other than examining the Moon itself, usually either as an assumed blackbody source for studying atmospheric transmission, or as a reference source for making other astronomical observations, such as those made by Sinton & Strong (1960) of Mars and Venus.

By 1960 investigators began again to be interested in obtaining compositional data from the Moon because of the increasing interest in space exploration, and the possibility of placing a man on the Moon. Murray (1961), for example, considered the possible mineralogical significance of lunar and planetary infrared radiation, suggesting that compositional information could be acquired from it.

Several laboratory investigations of the infrared spectroscopic behaviour of possible lunar surface materials provided data amounting to feasibility studies for obtaining compositional information from the infrared emission of the Moon. The most useful of these studies are those which were specifically directed toward obtaining information which could be applied to lunar studies, and have been discussed in the preceding section.

Hunt & Salisbury (1964*a*) made the first dispersed spectral observations of the lunar surface with the specific objective of discovering, by direct observation, whether compositional data was available and detectable in the mid-infrared. Our aim was not to attempt to determine the overall or absolute composition of the lunar surface, but to investigate whether or not differences in spectral behaviour existed between different features and areas on the Moon. Burns & Lyon (1964) had concluded from their extensive laboratory studies that no specific data of this type were obtainable from ground-based observations in the 8 to  $14\ \mu\text{m}$  region, because of the general atmospheric attenuation and, in particular, because of the presence of the intense ozone absorption band at  $9.64\ \mu\text{m}$ . In view of this conclusion, we initially elected to explore the 16 to  $24\ \mu\text{m}$  window, where the atmospheric attenuation is entirely due to water vapour. Data are expected in this window because the differences between the emission spectra of silicate rocks and minerals in the  $20\ \mu\text{m}$  region, due to the O–Si–O bending modes, are as characteristic as those obtained near  $10\ \mu\text{m}$ , due to the Si–O stretching modes.

Using a modified Perkin–Elmer 98 spectrometer with a KBr prism and a Golay detector on the 42 in. reflecting telescope at Lowell Observatory, we detected a difference in

spectral behaviour indicative of a compositional difference between Serenitatis and Copernicus. The data on which this preliminary result was based were collected on only one night, when transmission through the window was exceptionally good. Although spectra from the four areas investigated were recorded sequentially, and as close together in time as possible, the size of the statistical sample was small in terms of the variations that we subsequently found to exist in atmospheric properties. Subsequent attempts during 1964 to repeat these observations were frustrated by the inability to achieve satisfactory transmission through the 16 to 24  $\mu\text{m}$  window corresponding with assigned telescope time. At these times (Hunt & Salisbury 1964*b*), we used the same instrumentation to record spectra in the 8 to 14  $\mu\text{m}$  region where, because we were using a prism more suitable for the longer wavelength region, quite poor spectral resolution was achieved.

On several clear nights we recorded more than 70 spectra, concentrating on Copernicus and the Serenitatis and Haemus Mountains areas. The only possible differences they indicated in the 8 to 14  $\mu\text{m}$  spectra were among Serenitatis, Kepler and the Haemus Mts. A high level of confidence was not placed on the existence of these differences, because the magnitude of the discrepancies lay within the limits of variability of the atmosphere, and they were not sufficiently reproducibly obtained.

In discussing these data (Hunt & Salisbury 1964*b*), we presented a thorough discussion of the problems of ground-based spectroscopic observations of the Moon, including problems introduced by the presence of the atmosphere and fluctuations in it, by temperature differences on the Moon, and by differences in particle size and surface roughness. We also demonstrated the possibility of distinguishing genuine compositional differences from spurious effects caused by these factors. We concluded that the length of time between reaching the same point in sequential spectra from different areas, which was approximately 3 min, was much too long, and suggested that the short-term atmospheric fluctuations, especially with the low resolution we were using, could not be satisfactorily accounted for with such delay intervals.

It is possibly of interest to report an attempt made by us in 1965 to eliminate this time lag between recording spectra, by directly recording a difference spectrum between two lunar features. To do this we mounted a Perkin-Elmer Model 521 spectrophotometer on the Perkins 72 in. telescope (then a 69 in.) at Lowell Observatory. The source compartment was replaced with an optical system which allowed the energy from one lunar feature to traverse the sample beam, while the energy from another feature traversed the reference beam. This system did not prove to be satisfactory because: (1) of the extreme accuracy with which the emission intensities had to be balanced at some wavelength selected as a reference point; (2) the total amount of energy arriving at the thermocouple detector was generally small because of the high resolution of the grating instrument; and (3) because the instrument operates on the optical null principal, and the very low-energy levels in both beams, encountered when intense atmospheric absorption bands were scanned, resulted in pen drifting.

In view of these difficulties, single-beam spectra were recorded, referencing the energy from the lunar feature against an electronic test signal, which could be accurately controlled from a supplementary test signal source. Again we felt that the time lag of 3 min necessary to spectrally scan each target allowed too much variation in the atmospheric



attenuation to confidently identify compositional differences. In order to overcome the effects of atmospheric variations, one further experiment was performed, which essentially amounted to two-filter radiometry, with the use of the P.E. 521. Two narrow wavelength bands, one at  $11.43\ \mu\text{m}$  and one at  $9.22\ \mu\text{m}$  were selected, and the emission from a particular feature were repeatedly and alternately detected through these two bands. The emission through each band was observed for approximately  $1\frac{1}{2}$  min before changing wavelengths, so that the magnitude of the atmospheric changes occurring at a particular wavelength were also monitored. Each feature studied was observed in this way for about 10 min before a new feature was selected. Data were collected from features in this way on the nights of 15 to 19 February 1965, but the variations in these data due to atmospheric effects convinced us that a much more rapid method must be developed to detect differences in composition. We therefore proceeded to develop the spectrum matching technique.

The spectrum matching technique has the advantage of allowing very rapid comparison of spectral information from different target areas. Observations by means of this technique were made by Hunt, Salisbury & Reed (1967) during the late winter of 1965 with the 69 in. Perkins telescope at Lowell Observatory. Reflexion plates of quartz and olivine were used, not because we believe that the Moon is composed of olivine or quartz, but because the reststrahlen bands of these minerals fall in the atmospheric windows on either side of the ozone absorption band. Spots 70 km in diameter were sampled on the lunar surface.

An illustration of the procedure used, and an example of the way in which the data were collected, is shown in figure 8, which also serves to illustrate exactly what has been plotted in figure 9. The difference in the magnitudes of the signal levels recorded from Copernicus and the target area when their emission was reflected from the quartz reststrahlen plate is referred to as the 'quartz spread', and is so indicated in figure 8 together with ' $x$ -axis'. These 'quartz spread' values are plotted along the abscissa of figure 9. It is an indication of the radiance difference between Copernicus and the target. The value of the difference between the adjusted signals received when the emission from a given target is reflected in turn from the olivine and quartz reststrahlen plates is referred to as the 'olivine minus quartz' value, and is indicated as such in figure 8 together with ' $y$ -axis'. It is this quantity which is plotted on the ordinate of figure 9, and the magnitude of its value is indicative of whether a difference in composition, and/or surface condition, exist between that feature and Copernicus.

The results of preliminary measurements made on the nights of 13, 14 and 15 April 1965 are shown in figure 9 and have had the effects due to the instrument function removed. Continuous curves are drawn through sets of data points obtained from the Moon, and each set of points for a particular feature is enclosed in a box. The curves are of the shape shown because of the changing temperature of the features relative to the reference point, Copernicus, which is also changing in temperature due to movement of the subsolar point across the lunar disk during the lunar day.

Because of this temperature effect, a difference in the 'olivine minus quartz' value for features separated along the  $x$ -axis are not in themselves meaningful. However, direct comparisons can be made between features in the same position on the  $x$ -axis. A lunar

calibration curve was constructed by assuming that the central highlands are homogeneous in composition and particle size and by then examining different areas within the Central Highlands at progressively higher latitudes (and hence lower temperatures). The curve in the central block of figure 9 was constructed in this way, and its consistency with laboratory calibration curves suggests that it is the result of a valid assumption. Nevertheless, in interpreting the data it must be borne in mind that data points separated along the  $x$ -axis must be compared with caution.

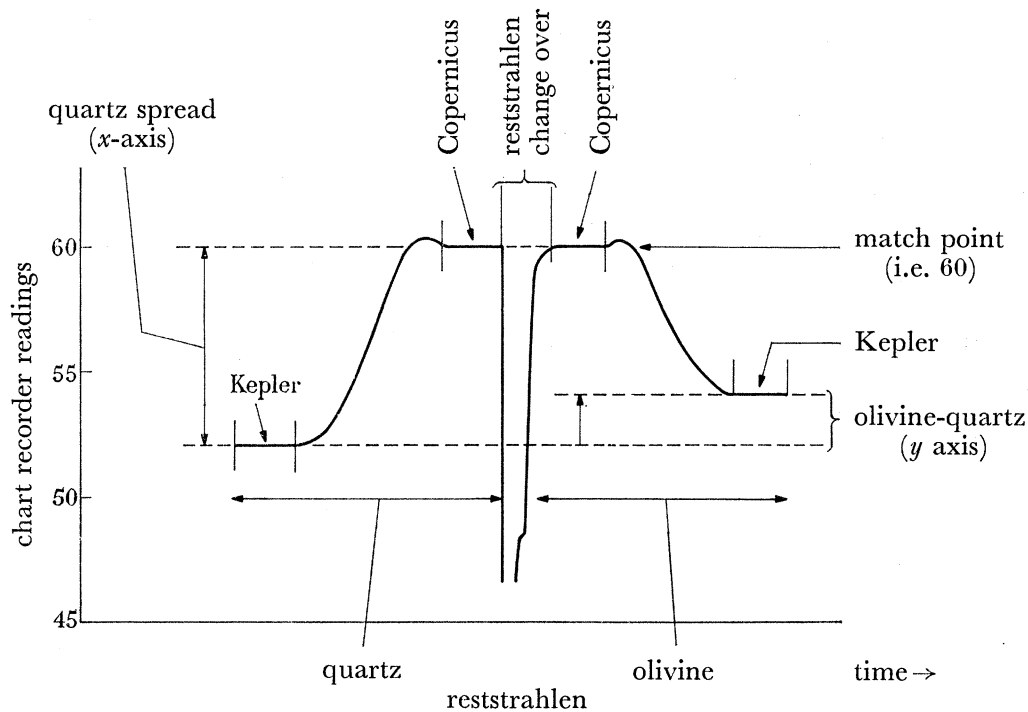


FIGURE 8. Illustration of the manner in which lunar measurements were obtained on the feature Kepler. Data obtained by this procedure are explained in the text and plotted in figure 9. (From Hunt *et al.* 1967.)

The differences recorded between features in the figure allowed certain conclusions to be drawn, which are: (a) features which lie along any one curve have approximately the same value for  $R_{s(\lambda)}P_{s(\lambda)}$  where  $R_{s(\lambda)}$  is the reflectivity and  $P_{s(\lambda)}$  is a factor accounting for the surface roughness; (b) the  $R_{s(\lambda)}P_{s(\lambda)}$  values for features which lie on different curves are different, but it is not possible to say whether these are compositional differences or particle size (spectral contrast) differences with the use of just two reststrahlen materials; and (c) these differences are very small for the features so far examined on the Moon in this way, indicating a general condition of low spectral information content for lunar surface materials in the wavelength regions corresponding to the atmospheric window.

The second modern investigator to attempt to measure lunar emission spectra was Murcay (1965). In contrast with the technique of Hunt & Salisbury, who sought to make more and more rapid spectral measurements in order to avoid the deleterious effects of atmospheric variability, Murcay used spectral measurements made through different air masses to extrapolate to zero atmospheric absorption.

Murcay (1965) made spectral observations of the lunar radiation from 8 to  $10.4\ \mu\text{m}$  with a carefully calibrated small littrow-type NaCl prism spectrometer, using a Reeder thermocouple detector. It required about 3 min to record a spectrum. This instrument was mounted at the Newtonian focus of a 12 in.,  $f/8$  telescope which was located at a site at 11500 ft. on Squaw Mountain (40 miles west of Denver, Colorado). Observations were made near full Moon in September and October 1964 with the objective of determining the absolute emissivity of the lunar surface.

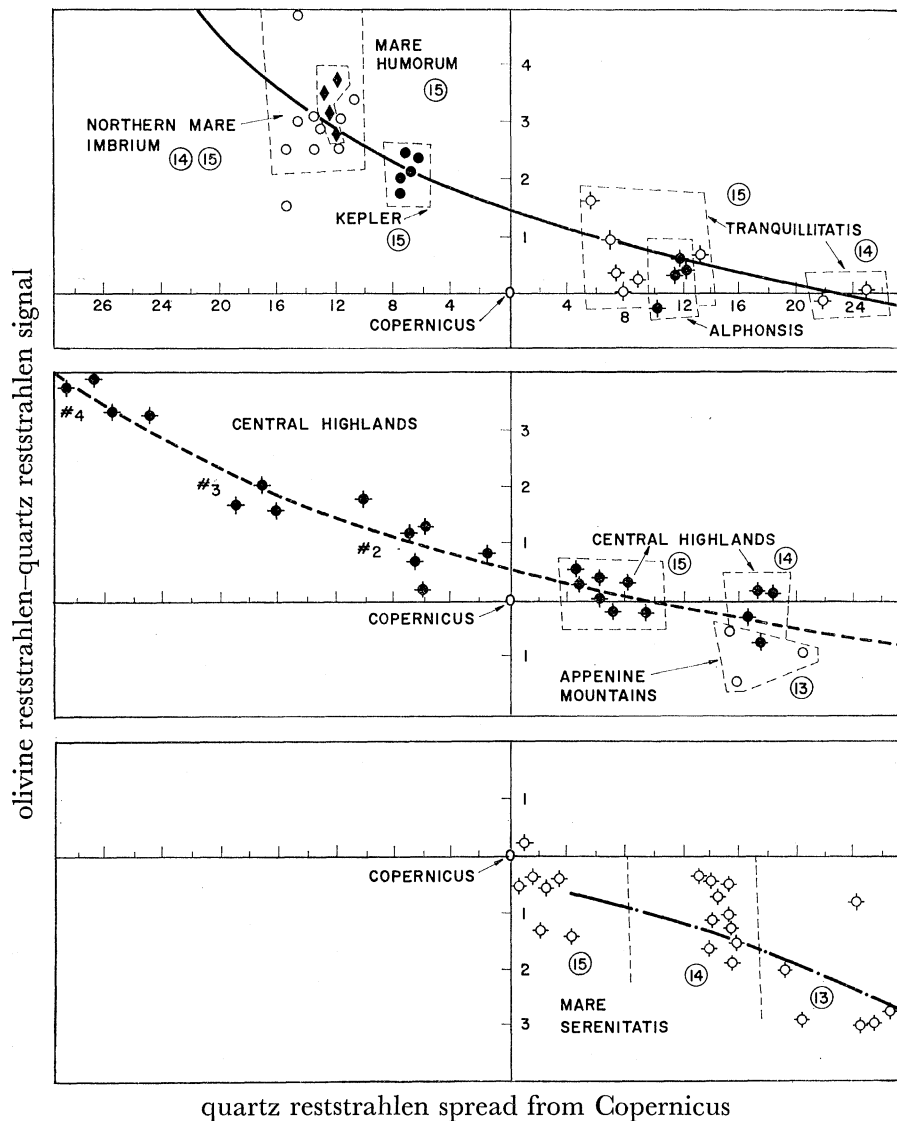


FIGURE 9. Data obtained from various features on the Moon are plotted in terms of the difference in signal level for the quartz reststrahlen between the feature and Copernicus ( $x$ -axis), and in terms of the difference in signal level between the quartz and olivine reststrahlens for each feature ( $y$ -axis). The curves are drawn in each block to indicate the trend of the data due to temperature differences alone. In the central block all measurements were made in the Central Highlands, those on the left from different areas, those on the right from the same area. The upper and lower blocks show the reststrahlen behaviour of other areas that appear to differ in their spectral emission from that of the Central Highlands. The numbers indicate the data in March 1965 on which each group of data prints was acquired. (From Hunt *et al.* 1967.)

Despite the fact that changes in the air mass through which he viewed varied from 0.90 to 5.2 standard air masses, the change in radiance outside the  $9.6\ \mu\text{m}$  ozone band were found to be small. In making corrections for the water-vapour absorption, he found that the values for transmission derived by Adel & Lampland (1940), by comparison with Yates & Taylor's (1960) values, or by extrapolation according to the square root law, all yielded values within 1 or 2%. His observations were made over a strip extending  $\pm 30^\circ$  in latitude on the Moon, and the radiance values he obtained were corrected to an equivalent radiance at the subsolar point by assuming a  $\cos \theta$  distribution and integrating over the  $\pm 30^\circ$  spread in latitude. Murcra concluded from this work that the data definitely indicated that the emission from the lunar surface deviates significantly from black body radiation, and his final emissivity values are shown in table 1. Murcra's results are in disagreement with those obtained at balloon altitudes by Van Tassel (1966), but are in agreement with those later obtained by a more sophisticated balloon-borne experiment conducted by the University of Denver (including Murcra) and us. These results will be described in §5.

TABLE 1. EMISSIVITY OF LUNAR SURFACE ASSUMING  
120 °C SURFACE TEMPERATURE (MURCRA 1965)

wavelength ( $\mu\text{m}$ )	$\Sigma$	wavelength ( $\mu\text{m}$ )	$\Sigma$
8.3	0.95	9.0	0.95
8.4	0.97	10.0	0.89
8.5	0.98	10.1	0.93
8.6	0.96	10.2	0.91
8.7	0.96	10.3	0.91
8.8	0.95	10.4	0.92
8.9	0.97		

The third modern investigator to attempt to measure lunar emission spectra using a ground-based telescope was Goetz (1967). Rather than attempt to make measurements more rapidly than the atmosphere can change, or extrapolate his measurements to zero atmosphere, Goetz depended primarily upon sophisticated data reduction techniques to statistically reduce atmospheric effects. He recorded a total of 794 spectra from 22 lunar positions on 43 nights during 1966, using a modified Ebert-Fastie Grating spectrometer with a liquid-hydrogen cooled mercury-doped germanium detector. The spectrometer was mounted at the  $f/16$  focus of a 24 in. reflecting telescope at Mount Wilson. Each spectrum recorded from 8 to  $13\ \mu\text{m}$  required 7 min to obtain. Goetz adopted a differential two-beam recording method, basically the same as that used by Westphal, Murray & Martz (1963), in which the signal from the lunar target is referenced against the signal from the adjacent sky. Five hundred and fifty-nine of these spectra were carefully analysed for differences in emissivity which would be diagnostic of compositional differences.

This was done by forming the quotient, rather than the difference, of pairs of spectra from each area, in order to remove the basic atmospheric transmission components. Long wavelength period trends, present because of temperature differences between targets and slow changes in the intervening air masses, were removed by fitting the quotient curves,  $Q(\lambda) = W_1(\lambda)/W_2(\lambda)$  (where  $W_1(\lambda)$  and  $W_2(\lambda)$  are flux densities in a wavelength interval

$\Delta\lambda$  arriving at the detector) to a second-order polynomial  $P(\lambda) = a\lambda^2 + b\lambda + c$ , and the data were then presented as residuals, defined as

$$r = \frac{Q(\lambda) - P(\lambda)}{P(\lambda)}.$$

The average residuals for each area were then compared as shown in figure 10. On the basis of this work, Goetz concludes that, of the twenty-two features he investigated, which included all major types of lunar surface features, only two features, Plato and Mare Humorum showed definite, consistent spectral differences from the rest, and that these differences are similar to each other and occur at the short wavelength end of the spectrum between 8.2 and 8.4  $\mu\text{m}$ . He does additionally point out that two other features, Copernicus and Tycho, show a lower emissivity between 8.4 and 9  $\mu\text{m}$ , but not consistently.

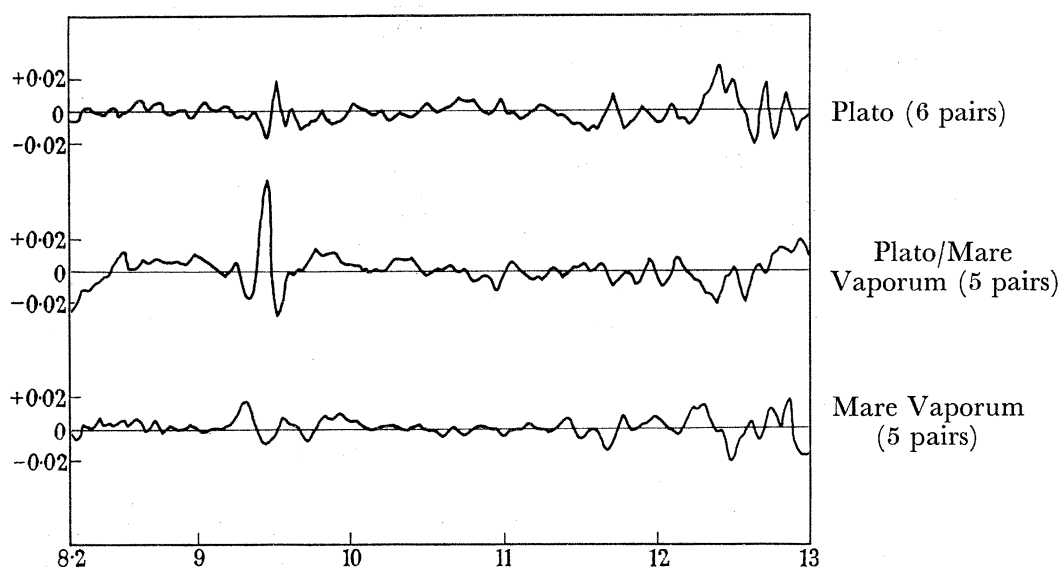


FIGURE 10. Average residuals for different lunar areas, and comparison of these residuals. Note spectral difference in the Plato/Copernicus and Plato/Tycho comparisons between 8.2 and 8.4  $\mu\text{m}$ . (From Goetz 1967.)

Goetz's technique of obtaining residuals through the use of fitted polynomials is a powerful tool for the detection of short wavelength period (features less than 2  $\mu\text{m}$  wide) differences in the emission spectra of different areas. He detected no such differences in the 8.2–13  $\mu\text{m}$  region between Serenitatis and Tranquilitatis, indicating that the short wavelength period differences between the emission from the two areas is less than 0.5%, despite the differences that Hunt, Salisbury & Reed (1967) detected with the spectrum matching technique.

#### (b) Discussion

It is readily apparent from all the ground-based telescopic observations that have been made that the amount of spectral information in the atmospherically attenuated infrared emission from the Moon, at least in the 8 to 14  $\mu\text{m}$  window, is small. The three different



approaches tried by modern investigators to detect what information there is, have each been primarily concerned with the variable attenuation of the atmosphere. As described in the preceding section, each investigator or group of investigators has obtained different results. Because of the differences in their respective approaches to the problem, it is difficult to compare these results. An attempt, however, is made to do so.

The absolute spectrum obtained by Murcay (1965) stands alone in ground-based studies, because the two other investigations consisted of relative measurements. The agreement of Murcay's data with the latest spectrum obtained from balloon altitudes indicates, however, that these results are probably correct.

Hunt *et al.* (1964*a, b*, 1967) have, like Goetz (1967), attempted to make relative measurements of the differences in spectral emission between different areas on the Moon. We place limited confidence in our early spectroscopic measurements, primarily because of the slowness of the spectral scan with respect to the frequency of atmospheric fluctuations, and because of the relatively limited amount of data collected on a statistical basis. We believe, however, that the differences ultimately found with the more rapid spectrum matching technique are real—i.e. they are due to differences in the emission spectra, whether due to genuine compositional or particle size differences, of the lunar surface materials, rather than to some source of random or systematic error. The differences that we find between Serenitatis and Tranquilitatis are not, however, mirrored in the results of Goetz (1967). In view of the latest balloon results, it would appear that this is probably due in part to the difference in wavelength region studied—i.e. we used a germanium long pass filter, which passes radiation of  $\lambda > 7 \mu\text{m}$ . Despite atmospheric attenuation, our results may reflect the presence of the  $7 \mu\text{m}$  band shown in the latest balloon spectra. In addition Goetz's technique of data reduction is dependent upon the width of the features in the spectrum. While very sensitive in the detection of short wavelength period differences (narrow bands) in the emission spectra of different areas, it is relatively insensitive to long wavelength period differences (wide bands). Thus, whereas his detection limit may be a signal difference of 0.2 % for  $0.2 \mu\text{m}$  wide bands, broader bands, which are characteristic of many natural rock materials, and particularly of heterogeneous mixtures, would have higher detection limits. If this spectral information lay partly in the ozone band, and if the signal level did not rise again within Goetz's wavelength range, even relatively large differences (of the order of 20 %) could go undetected. The latest balloon results indicate that just this sort of spectral information may be present in lunar emission.

##### 5. BALLOON-BORNE STUDIES

Considering the difficulties posed by atmospheric attenuation of ground-based spectra, it is hardly surprising that spectroscopic observations have been made at balloon altitudes above most of the atmosphere. It is unfortunate, however, that these have been so few. At the time of this writing there have been just two successful attempts to obtain lunar mid-infrared spectral data from balloon altitudes. These spectra, although few in number, are the clearest indication of the potential of mid-infrared spectroscopy for remote sensing of lunar composition, because the ambiguities introduced by atmospheric attenuation are at a minimum.

Both balloon-borne spectroscopic experiments were carried out as part of the A.F.C.R.L. programme, using a 24 in. (61 cm) aperture,  $f/10$ , Cassegrain telescope system that can automatically acquire and track the Moon during a balloon flight. The primary and secondary mirrors are gold-coated beryllium. The infrared energy from the telescope is reflected into the spectrometer by a gold-coated beam splitter. A portion of the visible energy is passed by the beam splitter into a camera system, which photographically records the area of the Moon under observation and the wander of the pointing system. The entire telescope system was designed and built under the direction of Dr A. Howell of Tufts University.

The first successful balloon-borne spectroscopic experiment was performed at an altitude of 31.7 km on 5 February 1966, using a spectrometer designed and built by R. A. Van Tassel (1966). The spectrometer was constructed from the standard optical components of a Perkin-Elmer Model 98 monochromator, using a Littrow mount and a  $60^\circ$  potassium bromide prism. The wavelength range observed was 8.7 to  $22\ \mu\text{m}$ , a Reeder thermocouple detector being used. The area on the Moon observed was a  $400 \times 250$  km strip in the Central Highlands between the craters Abulfeda and Sacrobosco.

Unfortunately, the telescope system tracked the Moon just long enough for two lunar spectra to be obtained, during a part of the slit programme when the slits were relatively wide open (1.8 mm). Thus, the spectral resolution is only 8%. In addition, the lunar radiation was not chopped against a constant temperature black body reference during the flight, but rather against the blackened back of the chopper blade. Thus, despite the close resemblance of these spectra to the emission of a black body in the laboratory (see figure 11), these results were considered very preliminary.

A more sophisticated spectrometer was constructed for a second flight of the balloon system on 25 March 1967 as a cooperative project between the University of Denver and A.F.C.R.L. The spectrometer was constructed under the direction of Dr D. Murcay of Denver University, who also directed the initial data reduction. Unlike the first balloon-borne instrument, this spectrometer referenced the lunar radiation against the emission from a constant temperature black body source, and included a second black body source which could be inserted in the sample beam for calibration purposes. Spectra were produced by means of an O.C.L.I. circular variable wedge filter, having a 2% spectral resolution, and a liquid-helium cooled, copper-doped germanium detector. The wavelength range selected was from 5 to  $13.6\ \mu\text{m}$ , because we had predicted the presence of non-silicates on the lunar surface that would have bands in the 5 to  $8\ \mu\text{m}$  region (Salisbury, Smalley & Ronca 1965).

During the flight, the telescope system again experienced pointing difficulties, but two good spectra of a single region on the Moon were obtained from an altitude of 28.4 km. The spot size under observation and the wander area of the pointer (estimated from eleven photographs taken immediately after the spectra were obtained) are shown in figure 12. These spectra are shown in figure 13.

It is apparent from figure 13 that lunar emission, at least from the area under observation, differs significantly from that of a black body. The relative emissivity between 5 and  $6\ \mu\text{m}$  is shown as greater than 1.0 owing to the presence of reflected solar, as well as emitted lunar radiation. The relatively low emissivity from 10 to  $13.6\ \mu\text{m}$  is consistent

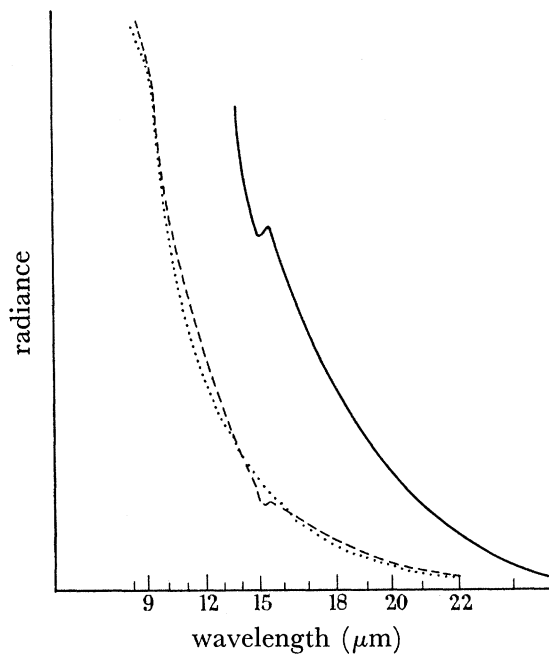


FIGURE 11. Spectrum of an area in the lunar Central Highlands obtained by the automatic balloon-borne system on 5 February 1966. The  $15\ \mu\text{m}$  band is due to  $\text{CO}_2$  in the atmosphere above the balloon. (From Van Tassel 1966.) ---, lunar spectrum; ····, black body spectrum; —, lunar spectrum (gain  $\times 4$ ).

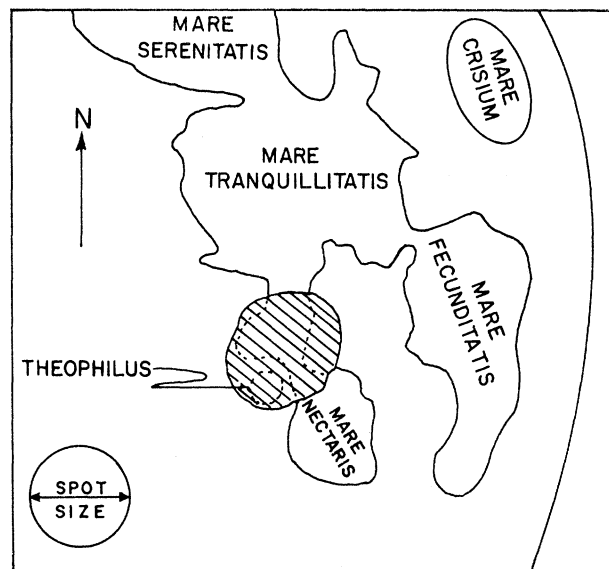


FIGURE 12. The area under observation was  $180\ \text{sec arc}$  in diameter. Pointing errors caused the spectral data to be collected from an area slightly larger, which is shown cross hatched.

with the ground-based results of Murcray (1965). It must be due, at least in part, to the composite temperature of the surface being observed. The band centred at  $7\ \mu\text{m}$  and the abrupt change in slope of the curve at  $8.5\ \mu\text{m}$  both appear, however, to be due to spectral features in lunar emission. If these bands are, in fact, real, the  $7\ \mu\text{m}$  band is probably due

to carbonates, nitrates, or some other sublimate type of material, and is consistent with the ground-based results of Goetz (1967). The probable band between 8.5 and 9.5  $\mu\text{m}$  may be due to silicates, and would indicate the presence of acidic, rather than basic, rocks on the lunar surface. This is not to say that the lunar crust is acidic. It may well be that, like the sublimate, the materials producing this band are entirely superficial, or local, or both.

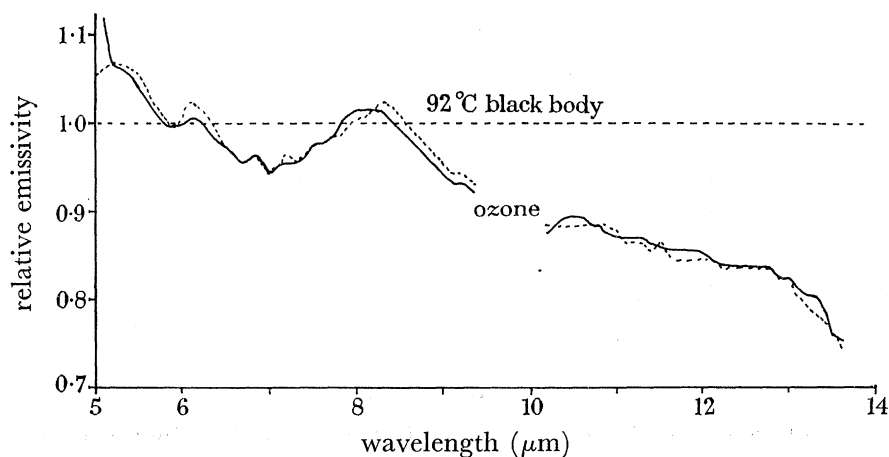


FIGURE 13. Two lunar emission spectra from the region around the crater Theophilus. Using the radiance values obtained, the emissivity of the moon compared to that of a blackbody at 92 °C has been calculated.

Additional flights of the balloon system are planned in order to confirm these spectra, as well as to obtain spectra from other areas on the moon. The telescope can be pre-programmed to point at five different areas on each flight, offering the potential of mapping the relatively large scale variations in lunar spectral emission within 12 to 18 months. The observational spot size can ultimately be reduced to obtain more detailed information.

## 6. ROCKET-BORNE STUDIES

At even the highest balloon altitudes there remain small amounts of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and other gases which prevent the acquisition of unattenuated spectral data from the Moon. Consequently, we have pursued another cooperative research programme with scientists of American Science and Engineering, Inc., to obtain lunar emission spectra from an Aerobee rocket.

The rocket-borne spectrometer was designed and constructed under the direction of Dr L. Sodickson, of A.S.E., who is also responsible for data reduction.

The A.S.E./A.F.C.R.L. Aerobee rocket payload consisted of an all-reflective Cassegrainian telescope which focused infrared radiation on thermistor bolometer detectors through an O.C.L.I. circular variable wedge filter. The focal length of the telescope was 45 in. The spectral range covered was 3.8 to 14  $\mu\text{m}$  with 2% resolution. The energy collected by a 5 by 10 in. rectangular primary mirror was divided into two separate beams by a split secondary mirror and focused on two detectors. Both beams were chopped



between a 10 minute of arc field of view on the lunar disk and a reference 115 °C blackbody cavity carried in the instrument. The fields of view of the two detectors were nearly coincident, being separated by about 1.5 minutes of arc.

The telescope, detectors and all associated electronics were contained in an 8 × 12 × 30 in. package which was mounted in the nose cone of an Aerobee rocket. During flight the nose cone was counter-rotated against the main body of the rocket. The instrument package was then pivoted out of the stationary nose cone to point at the Moon, using a lunar pointing system designed and constructed under the direction of Dr F. C. Wilshusen of the University of Colorado. Error signals for the servo system were generated with auxiliary optics and visible photo detectors boresighted with the telescope. The data were telemetered to the ground.

The rocket was launched from Fort Churchill on 26 November 1966. The pointing system acquired the Moon, and pointed at its centre to within  $\pm 4$  min arc. Useful data were obtained over 200 s, in which time 50 spectral scans were obtained for each detector. Unfortunately, due to yawing of the rocket during flight, and the dynamic characteristics of the pointing control, the centre of the instrument field of view performed an approximately elliptical motion across a portion of the lunar disk at a rate of ten cycles per spectral scan. The field of view remained within the lunar disk at all times. Composite spectra of selected areas of the Moon have been constructed by sampling many spectra during the time intervals in each when certain areas were viewed. Assembling the composite spectra has involved a lengthy and difficult data reduction process. The spectra are presently being analysed for consistency during different portions of the flight, for departures from blackbody emission, and for comparison with the spectral emission from selected rock samples. As a result, they are not available for presentation at this time.

## 7. SUMMARY

The need for remote sensing techniques has not decreased with the presence of spacecraft on the lunar surface. On the contrary, such techniques are badly needed to extend the 'ground-truth' information to unexplored regions of the lunar surface, as well as to identify anomalous areas that are sufficiently interesting to merit manned exploration.

Theoretical and laboratory studies have shown that the features in mid-infrared molecular-vibration spectra can be used to characterize the mineralogical composition of rocks, and that this information is present in the emission spectrum of a rock surface. These studies also show that as the surface of a rock is roughened or ground to a fine particle size, the spectral contrast of its emission spectrum is reduced, but not eliminated. In the light of these results, one would expect that characterizing spectral information would be difficult, but not impossible, to detect in lunar infrared emission.

Efforts have been made to detect lunar emission spectra from the ground, balloons and rockets, as summarized in table 2. Ground-based studies are made very difficult by atmospheric attenuation, and each modern investigator has attempted to eliminate atmospheric effects in a different manner. As a result of such differences in technique, as well as in the wavelength regions studied, early observations appeared to be ambiguous or in disagreement.

The first modern observation of lunar infrared spectra was made by Hunt & Salisbury (1964*a*) in the 16 to 24  $\mu\text{m}$  spectral region. We found a relatively large difference between the spectral emission from different lunar features, but were unable to satisfactorily repeat these measurements because of the unavailability of the 16–24  $\mu\text{m}$  atmospheric window in terms of transparency.

TABLE 2. RECENT MEASUREMENTS OF LUNAR SPECTRAL EMISSION

date	type	investigators	wavelength ( $\mu\text{m}$ )	areal resolution	spectral resolution ( $\mu\text{m}$ )	detector
1964	ground-based	Hunt & Salisbury	16–24	50 $\times$ 290 sec arc strip	< 0.4	Golay cell
1964	ground-based	Hunt & Salisbury	8–14	50 $\times$ 290 sec arc strip	$\sim$ 0.7	Golay cell
1965	ground-based	Hunt & Salisbury	8–14	25 $\times$ 250 sec arc strip	0.08	thermocouple
1965	ground-based	Hunt & Salisbury	spectrum matching	50 sec arc spot	n/a	Golay cell
1965	ground-based	Murcra	8.2–10.4	ca. 1000 sec arc strip	< 0.2	thermocouple
1966	ground-based	Goetz	8.2–13.0	20, 30, 40 sec arc spots	0.08	Hg/Ge (liq. H <sub>2</sub> cooled)
1966	balloon-borne	Van Tassel	8.7–22	150 $\times$ 250 sec arc strip	$\sim$ 0.7	thermocouple
1966	rocket-borne	ASE–AFCRL	5–13.6	10 min arc spot	0.2	thermistor
1967	balloon-borne	Denver–AFCRL	5–13.6	180 sec arc spot	0.2	Cu/Ge (liq. He cooled)

Hunt & Salisbury (1964*b*), Hunt *et al.* (1967) and Goetz (1967) have also sought to detect differences in spectral emission from different lunar features through the 8 to 14  $\mu\text{m}$  atmospheric window. Unfortunately, this wavelength region appears to display only very small (up to 2%) differences in spectral emission between different lunar features. Hunt *et al.* (1967) and Goetz (1967) detected such differences, but their results appear to conflict. This conflict may well be due to the differences in their techniques and wavelengths of observation. In particular, it may be noted that Hunt *et al.* (1967) utilized a 7  $\mu\text{m}$  long pass filter, and did not use a short pass filter, thus admitting a relatively small, but perhaps critical, amount of energy in spectral regions not studied by Goetz (1967)—i.e. at 7 to 8.2 and 16 to 24  $\mu\text{m}$ .

Murcra (1965) sought to determine the total emissivity of the Moon, rather than to detect differences in emissivity from place to place. He found that the apparent emissivity of a large area on the lunar surface was up to 11% below unit emissivity at the long wavelength end of his 8.2 to 10.4  $\mu\text{m}$  observation range. This relatively large deviation in apparent emissivity came as a surprise to others in the field, because of the very small differences in emissivity between different areas in this spectral region found by ground-based experiments, and because of the lack of any significant deviation from black body behaviour indicated by the first balloon-borne experiment (Van Tassel 1966).

At this rather confusing juncture, the March 1967 University of Denver–A.F.C.R.L. balloon-borne experiment obtained two spectra of the region around Theophilus that are particularly illuminating. They show an emission band at 7  $\mu\text{m}$  that is consistent with the

presence of sublimates, such as carbonates or nitrates, on the lunar surface. The  $7\ \mu\text{m}$  band might be the source of spectral information that produced the apparent conflict in the results of Hunt *et al.* (1967) and Goetz (1967), because of the difference in the wavelength regions they observed. They also show a less well-defined band at  $9\ \mu\text{m}$  that is consistent with the presence of acidic silicates, as well as a deviation from blackbody behaviour in the vicinity of  $10\ \mu\text{m}$  of the same magnitude as that detected by Murcray (1965). Because the probable  $9\ \mu\text{m}$  band is partially obscured by atmospheric ozone absorption, and because the emissivity does not rise again at longer wavelengths to clearly define an emission band, this spectral feature would be very difficult for Goetz (1967) to detect. These balloon-borne spectra must, of course, be substantiated by later observations before they can be given full credence, but it is encouraging that they serve to confirm the ground-based studies performed so far, and to explain apparent inconsistencies in the results of different workers.

It would clearly be of interest to obtain lunar emission spectra completely outside the Earth's atmosphere to better elucidate the  $9\ \mu\text{m}$  band, which is at least partially obscured by atmospheric ozone absorption, even at balloon altitudes. To date there has been only one successful rocket flight to obtain such spectra, and the data from this experiment are plagued by the effects of pointing errors. We hope to be able to remove these errors in time, and that more sophisticated space experiments will ultimately be performed.

In the meantime, it appears that complementary balloon-borne and ground-based experiments offer the best near-term method for determining the composition of the lunar surface materials, and for mapping the variations in composition over the near-earth face of the Moon. The research performed thus far has been, for the most part, of a preliminary nature. It has, however, served to demonstrate the great potential of mid-infrared spectroscopy as a remote sensing tool.

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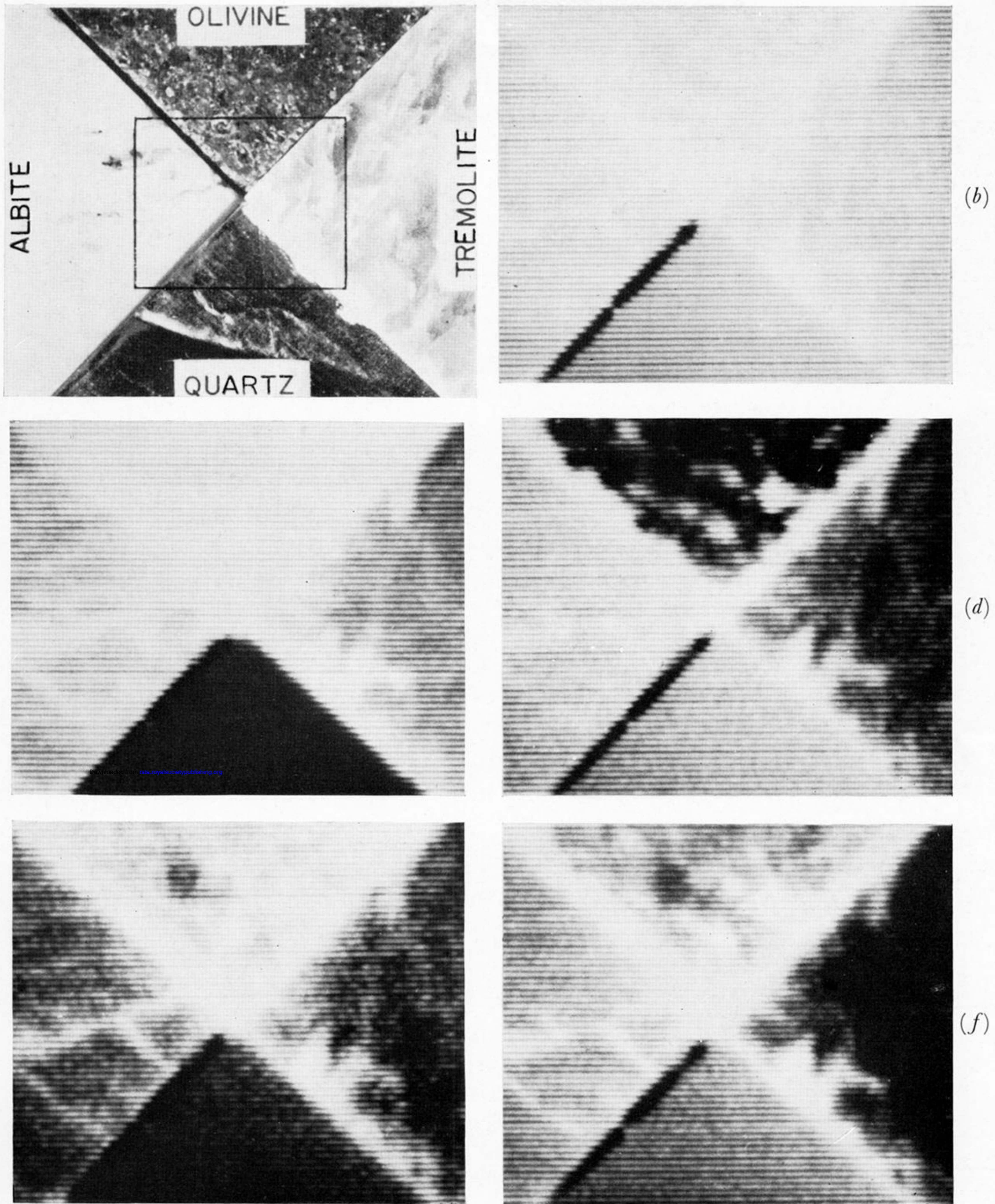


FIGURE 7. Illustration of the feasibility of the spectrum matching technique. Samples of quartz, olivine, albite, and tremolite, shown in visible photograph *a*, are scanned with an infrared imaging device to produce pictures *b*, *c*, *d*, *e* and *f*. Picture *b* was produced after the infrared emission of the samples was reflected from a mirror, and pictures *c*, *d*, *e* and *f* were produced using the following reststrahlen plates in place of the mirror: (*c*) quartz; (*d*) olivine; (*e*) albite; (*f*) tremolite. (From Hunt *et al.* 1967.)