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Progrès récents dans la spectroscopie infra-rouge  
à la transformée de Fourier(IRTf).

### RECENT ADVANCES IN THE FTIR SPECTROSCOPY OF KAOLINITE

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RECENT ADVANCES  
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FTIR SPECTROSCOPY  
OF KAOLINITE

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The multiplexing advantage of Fourier-transform spectrometers has enabled excellent signal-to-noise ratios to be obtained with various low throughput sampling methods, such as diffuse reflection (DR) and photoacoustic spectroscopy.

These FTIR techniques are known as DRIFT and FTIR-PAS, respectively.

Because they involve little or no sample preparation, there is minimal risk of sample distortion. This is an important consideration in infrared studies of solids, such as coal and the clay minerals.

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This particular study is directed towards kaolinite, a 1:1 dioctahedral phyllosilicate of composition  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , which is commonly associated with Alberta coal deposits.

Both DRIFT and FTIR-PAS results for kaolinite are discussed.

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For ready comparison, the PAS spectra are shown in blue and the DRIFT spectra in black.

Diffuse Reflection arises from penetration of the incident radiation into the sample, followed by partial absorption and multiple scattering at the boundaries of individual particles, according to

$$I_d = I_o \exp(-\mathcal{E} d)$$

where  $I_d$  = intensity of diffuse radiation

$I_o$  = incident intensity

$\mathcal{E}$  = molar extinction coefficient

$d$  = mean penetration depth.

DRIFT spectra are most frequently analysed in terms of Kubelka-Munk (K-M) theory. The K-M or remission function  $f(R)$  is given by:

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s}$$

where  $R$  = measured reflectance

$k$  = absorption coefficient

$s$  = scattering coefficient.

This yields an optical spectrum resembling the true absorption spectrum of the sample.

The operating conditions for the mid-infrared DRIFT experiments were:

- Harrick Praying-Mantis Reflectance attachment
- Globar source
- KBr/Ge beamsplitter
- Liquid N<sub>2</sub>- cooled MCT detector
- Samples dispersed in KBr (~0.7% by wt.)

The DRIFT sample spectra were ratioed against a single-beam reference spectrum of KBr.

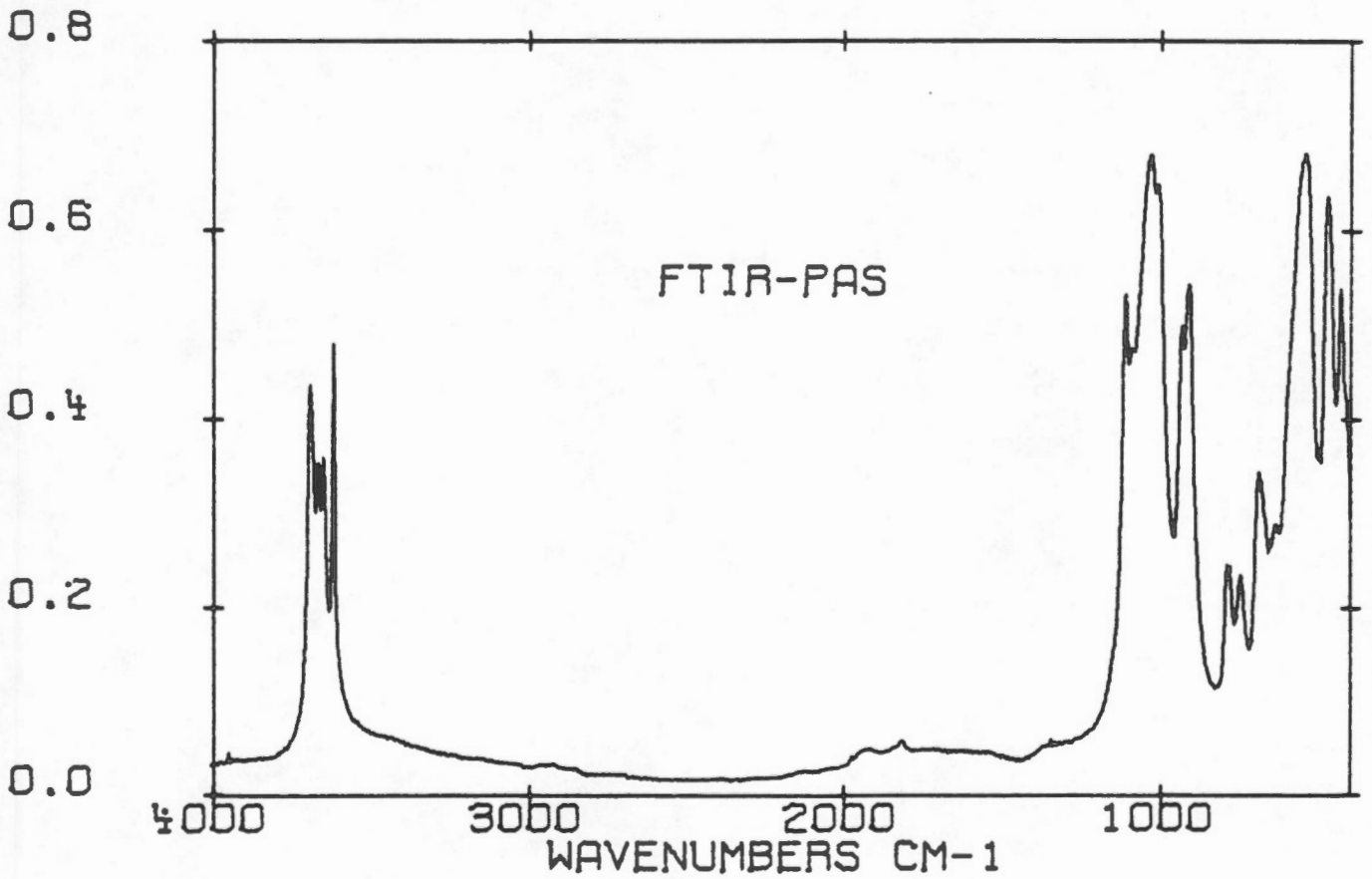
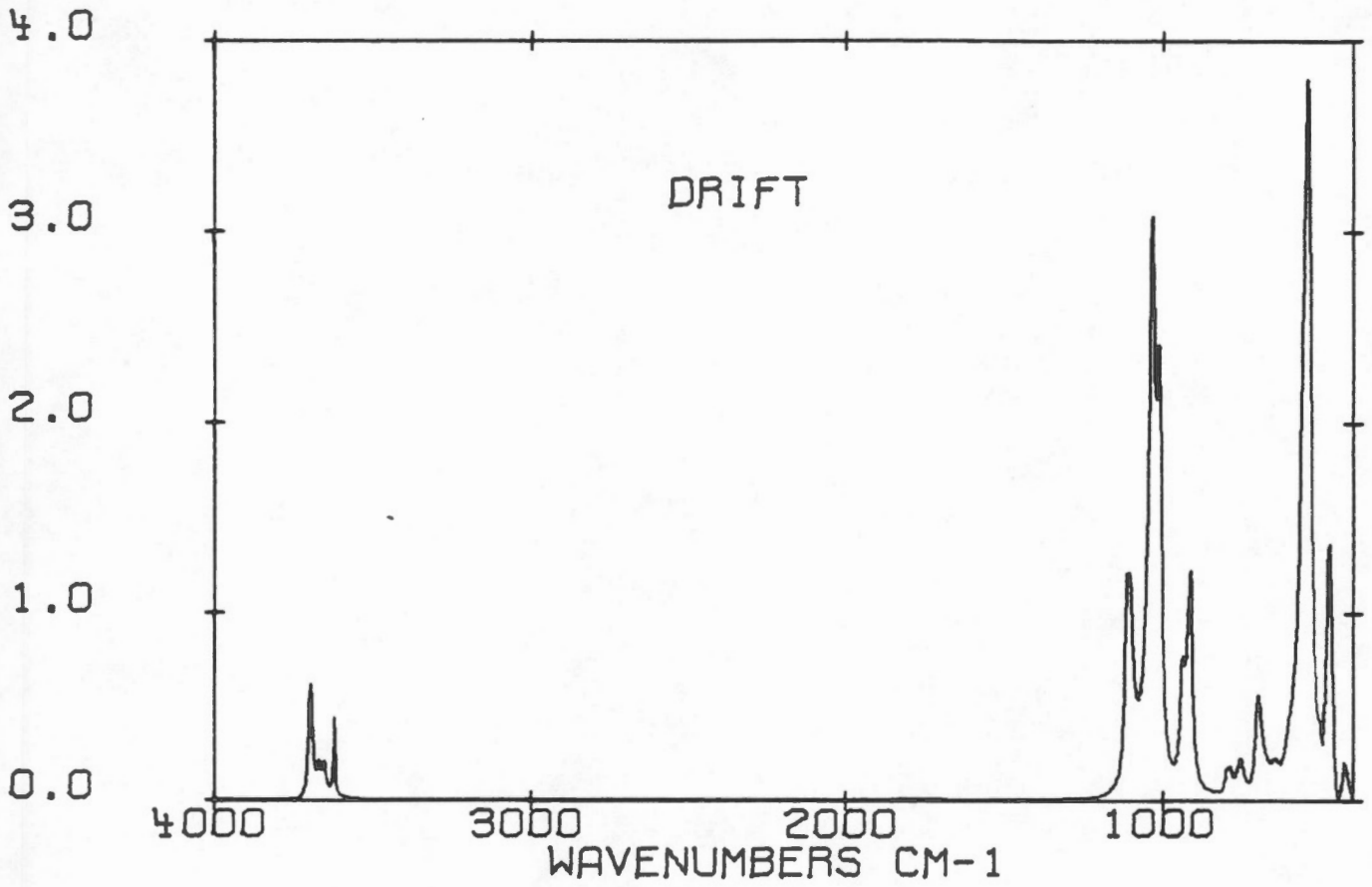
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The corresponding PAS spectra were recorded on the neat sample with a PARC 6003 photoacoustic cell.

Two mirror velocities of 0.059 and 0.070 cm/sec were routinely used. These yield modulation frequencies spanning 0.94 to 11.2 kHz for the infrared spectral range 400-4000 cm<sup>-1</sup>.

Source normalization was performed with a single-beam reference spectrum of carbon lampblack measured at the same mirror velocity.

# MID-INFRARED SPECTRA OF KAOLINITE





In FTIR-PAS, the sample is placed in a sealed cell containing an inert gas and a highly sensitive microphone.

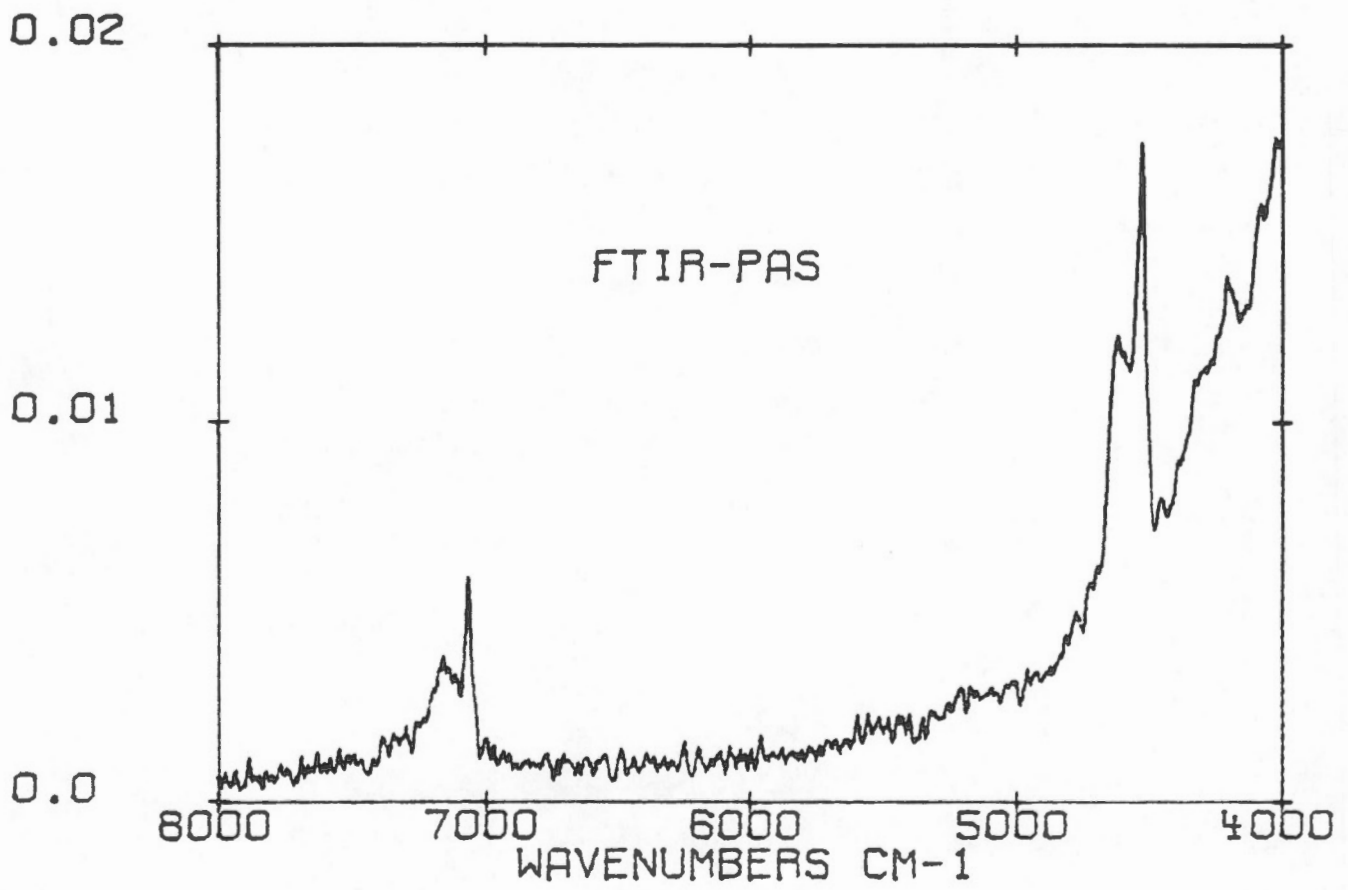
The incident radiation is modulated by the interferometer so that absorption by the sample gives rise to a periodic heating and cooling of the adjacent gas layer.

The information on the sample absorption is thus transmitted through the gas as a pressure wave of the same frequency as the modulated radiation, and is detected by the microphone.

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The infrared spectra presented here were recorded on an evacuable Bruker model IFS 113V FTIR spectrometer at a nominal resolution of 4  $\text{cm}^{-1}$ .

# NEAR-INFRARED SPECTRUM OF KAOLINITE



This near-infrared PAS spectrum of kaolinite represents one of the first examples of the FTIR-PAS technique applied to the near-infrared region.

This was accomplished by using a tungsten-halogen source,  $\text{CaF}_2$  /Si beamsplitter, and a very slow interferometer mirror velocity of 0.032 cm/sec.

The peaks at  $\sim 4600$   $\text{cm}^{-1}$  are combination bands of the fundamental O-H stretching ( $\sim 3600$   $\text{cm}^{-1}$ ) and Si-O stretching ( $\sim 1000$   $\text{cm}^{-1}$ ) modes, while the low intensity features at  $\sim 7200$   $\text{cm}^{-1}$  correspond to the first overtone of the O-H stretching vibrations.

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Valuable information concerning the nature of intermolecular bonding in the interlamellar space of layer silicates can be derived from near-infrared spectra.

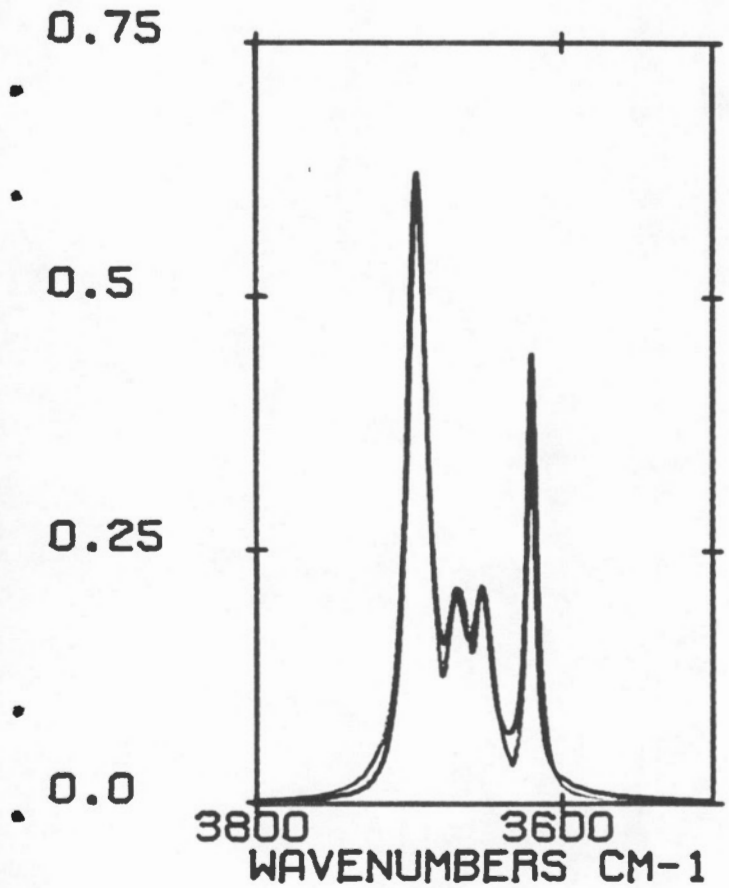
Although DR spectroscopy has been commonly employed for this purpose, FTIR-PAS has some unique advantages, including no physical disruption of the sample and the capability of surface and depth profiling studies.

Comparison of the FTIR-PAS and DRIFT spectra of kaolinite shows significant differences. The following explanations, which are commonly invoked, have been systematically checked and discounted:

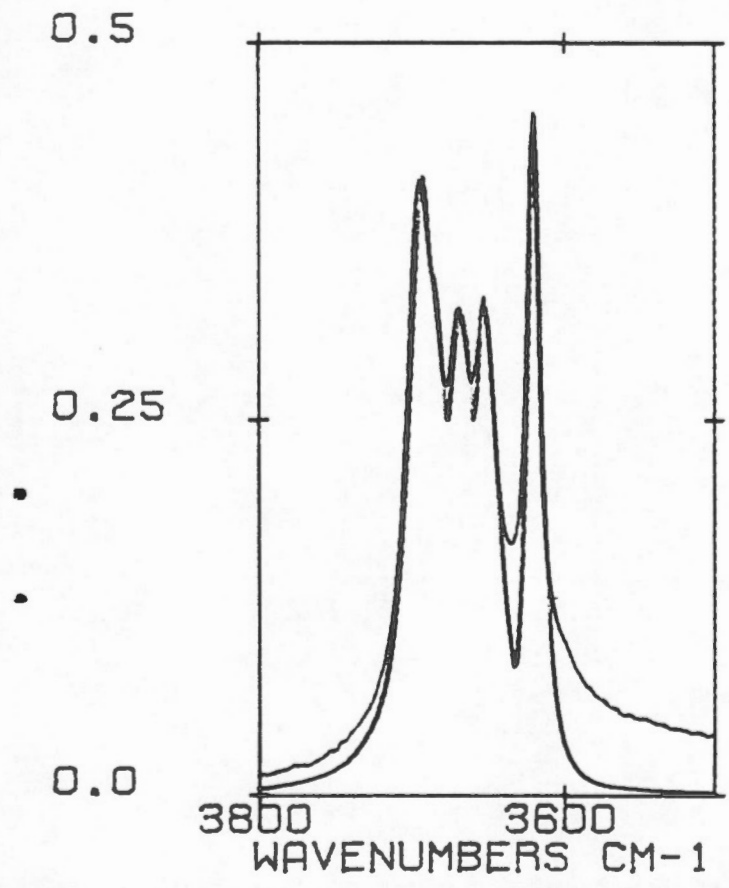
1. Specular reflection effects - PAS spectra of kaolinite diluted in KBr were nearly identical, in relative intensity, to those of the neat sample.
2. Optical saturation - PAS spectra recorded at very high mirror velocities (0.665 cm/sec) showed little difference with respect to those at lower mirror velocities.
3. Particle size effects - PAS and DRIFT spectra were recorded for several kaolinite samples of various particle sizes and no apparent size-dependence was noted.
4. Dependence of sampling depth on infrared modulation frequency - the relative band intensities did not increase with decreasing wavenumber in the PAS compared with the DRIFT spectra, as predicted by theory.

Thus, some other factors, not yet understood, are responsible for the observed differences in the FTIR-PAS and DRIFT spectra. The next few figures illustrate the precise nature of these differences.

# O-H STRETCHING REGION OF KAOLINITE

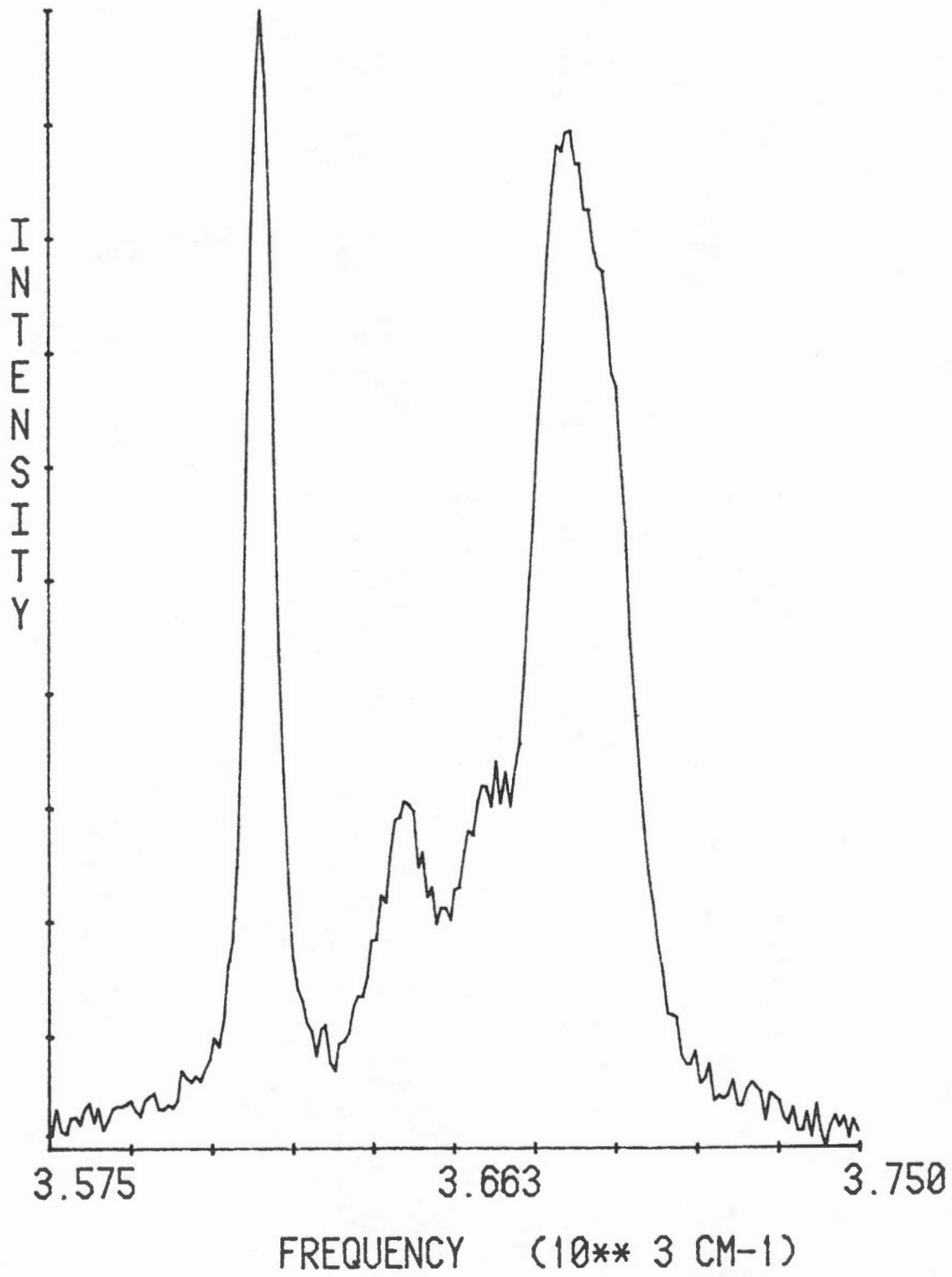


- OBSERVED DRIFT SPECTRUM
- THEORY (4 BANDS)

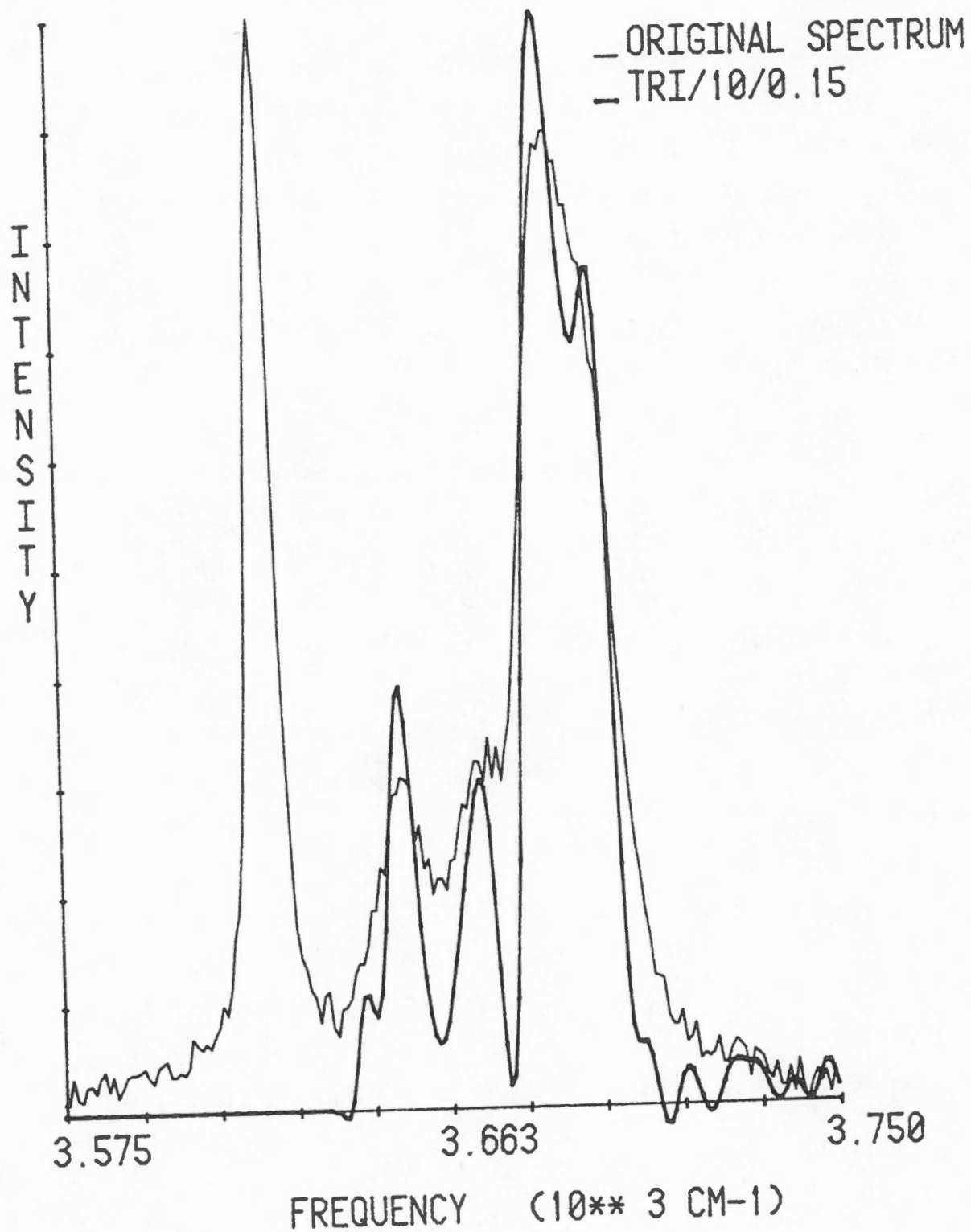


- OBSERVED PAS SPECTRUM
- THEORY (5 BANDS)

KAOLINITE OH RAMAN SPECTRUM



# DECONVOLUTION OF INNER-SURFACE OH BANDS



The preceding figures show the O-H stretching region of kaolinite, as observed in the DRIFT, FTIR-PAS and Raman spectra.

Computer modelling of the infrared spectra showed that 4 Lorentzian bands located at 3695, 3668, 3652, and 3620  $\text{cm}^{-1}$ , of relative intensity 71:34:34:100 adequately simulated the K-M plot, whereas 5 Lorentzian bands at 3693, 3687, 3668, 3652, and 3620  $\text{cm}^{-1}$  of relative intensity 91:77:71:72:100 were required to reproduce the FTIR-PAS features in this region.

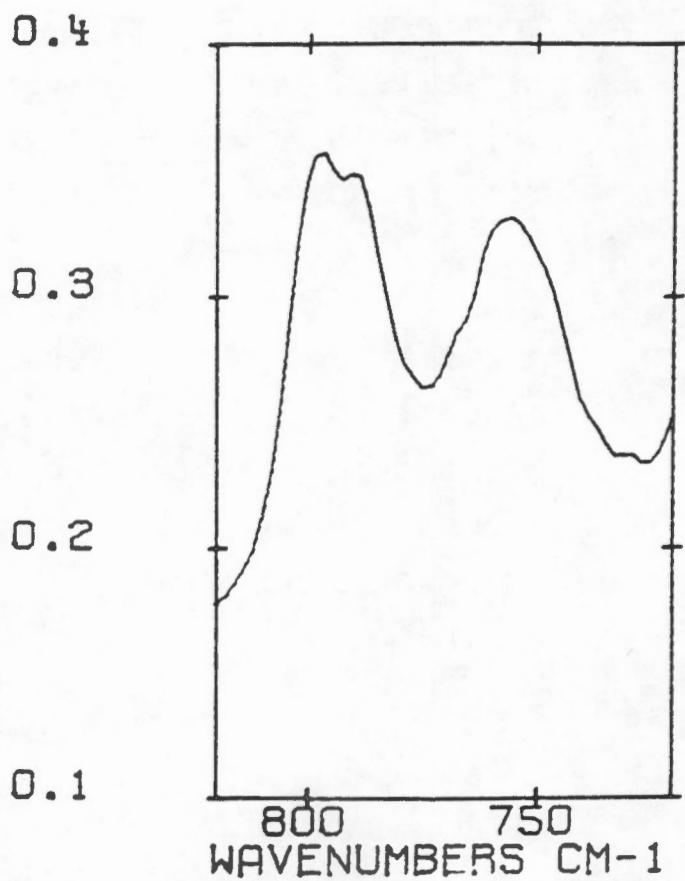
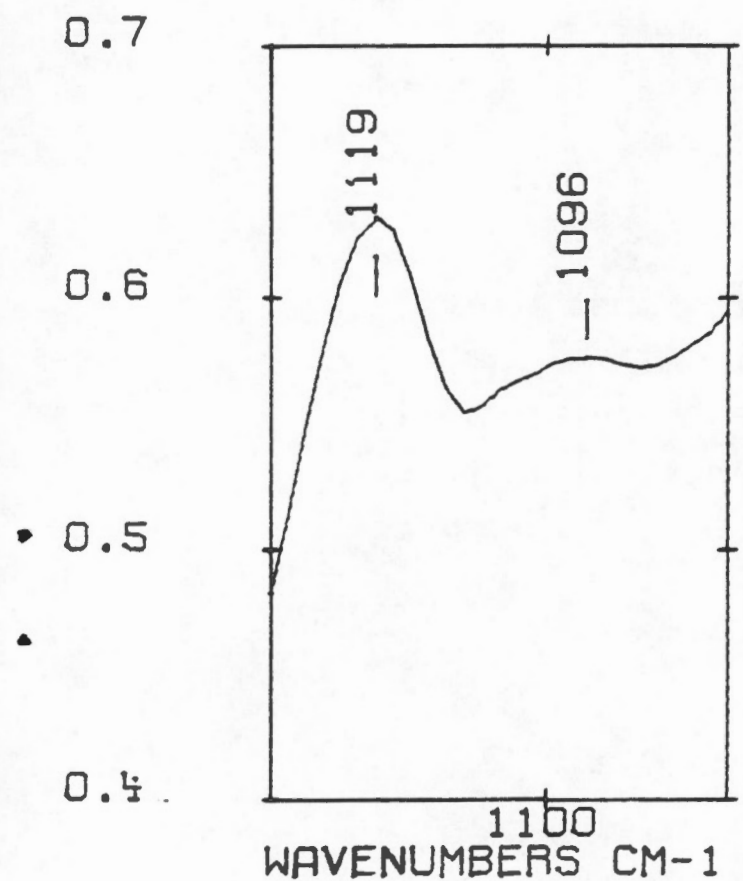
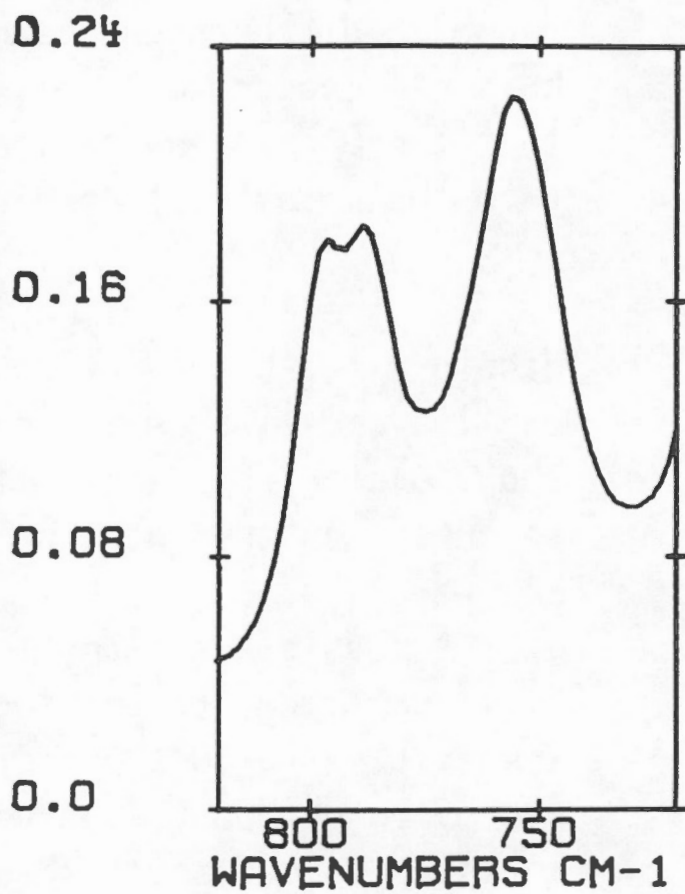
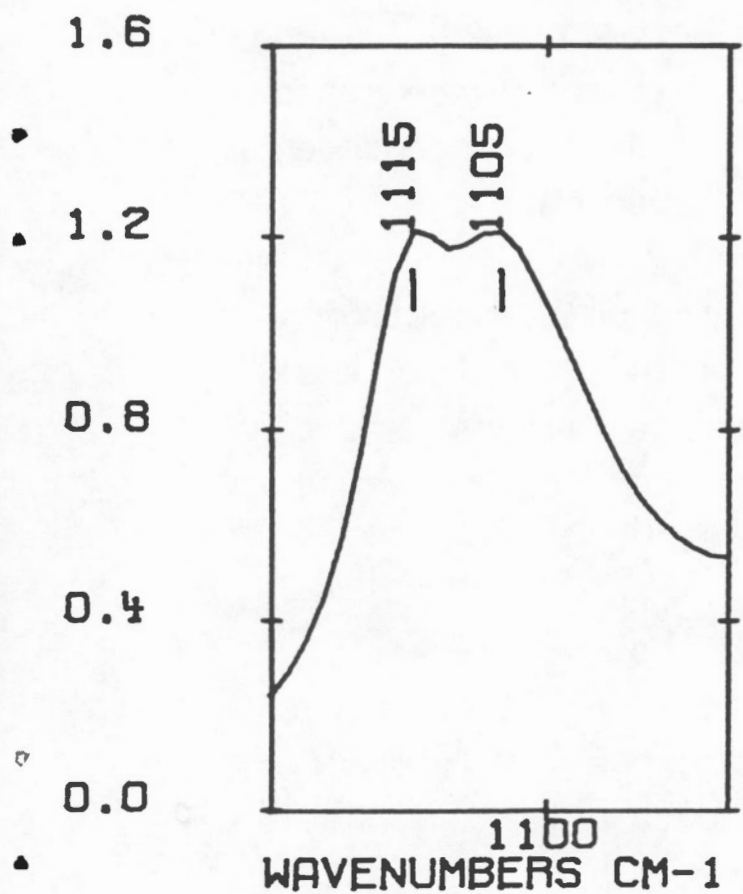
The PAS results are in good agreement with the Raman findings which indicate the presence of 5 peaks at 3695, 3684, 3669, 3651, and 3620  $\text{cm}^{-1}$ .

The prominent shoulder at 3687  $\text{cm}^{-1}$  in the PAS spectrum has not been previously reported in infrared studies. These results indicate that weakly infrared-active modes may be more readily observed in the PAS spectrum.

It should also be noted that the relative absorption intensity of the 3620  $\text{cm}^{-1}$  to the 3694  $\text{cm}^{-1}$  band, which is frequently used as a measure of the crystallinity of a particular kaolinite sample, must be referenced to the infrared sampling method used.



COMPARISON OF DRIFT AND FTIR-PAS SPECTRA  
OF INTERNATIONAL KAOLINITE



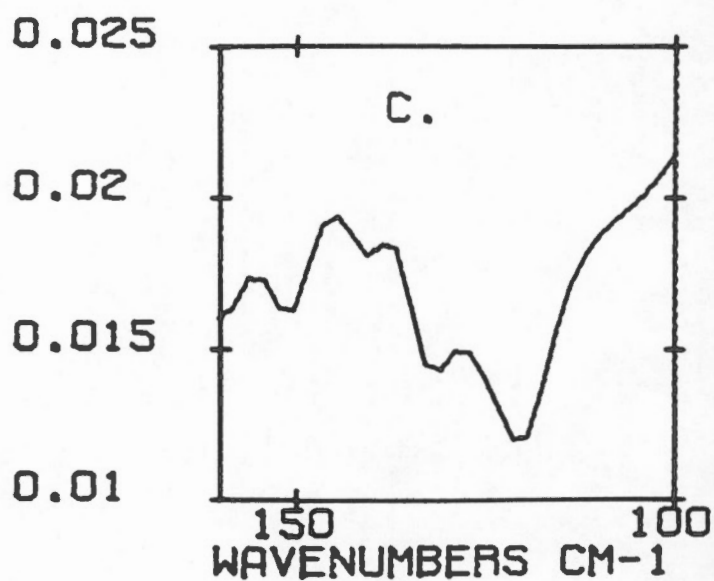
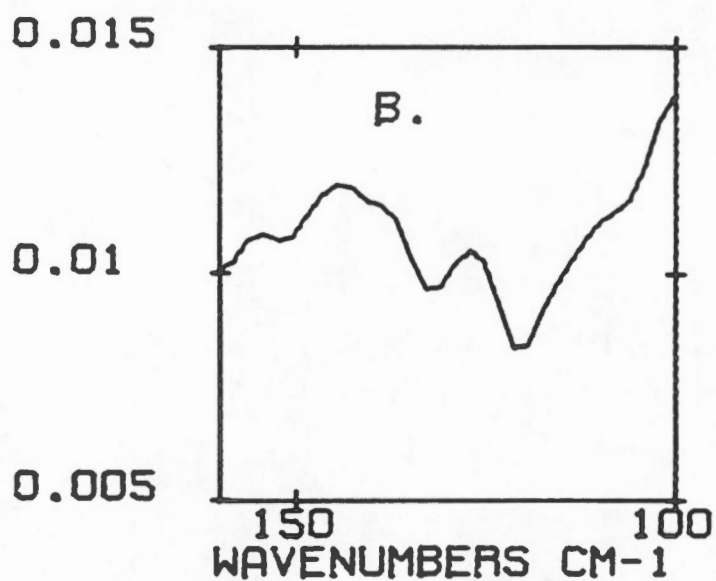
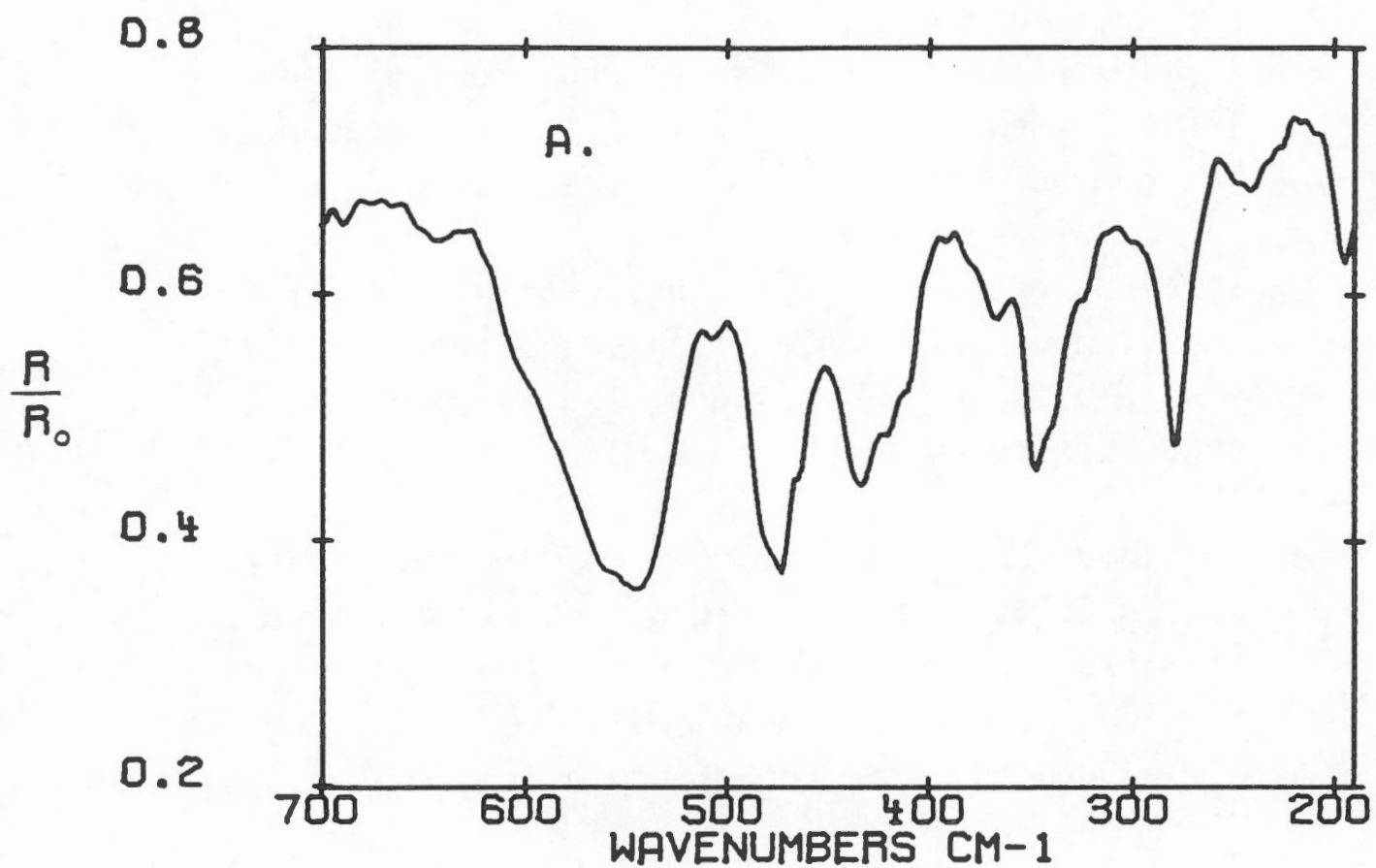
These figures present further examples of the dramatic differences observed between the DRIFT and FTIR-PAS spectra of kaolinite. It should be noted that the DRIFT results are in closest correspondence with the reported transmission spectra.

In the  $1100\text{ cm}^{-1}$  region, the DRIFT spectrum displays two bands, of approximately equal intensity at  $1115$  and  $1105\text{ cm}^{-1}$ , whereas the FTIR-PAS spectrum shows a single peak at  $1119\text{ cm}^{-1}$  and a low, broad feature, centered at  $\sim 1096\text{ cm}^{-1}$ .

A possible explanation is that the peak at  $\sim 1117\text{ cm}^{-1}$ , due to the in-plane Si-O vibration, is insensitive to particle size whereas the lower frequency band, due to the perpendicular Si-O vibration intensifies and shifts  $\sim 10\text{ cm}^{-1}$  to higher frequency when the particle size is decreased by grinding with KBr. Arguing against this proposal is the fact that this effect was not observed in PAS spectra of kaolinite samples of various particle sizes or diluted in KBr.

The right-hand figures show that the relative intensity pattern for the peaks at  $797$ ,  $789$ , and  $756\text{ cm}^{-1}$  in the DRIFT spectrum are effectively reversed in the FTIR-PAS spectrum. This behavior is contrary to that predicted by the theory of Rosencwaig and Gersho.

# FAR-INFRARED SPECTRA OF KAOLINITE



These far-infrared spectra of kaolinite demonstrate the excellent quality of far-infrared data that can be obtained with the DRIFT technique.

A Hg arc source, DTGS detector with polyethylene window and various thickness mylar beamsplitters (3.5, 6 and 12  $\mu\text{m}$ ) were used to cover the range 700-100  $\text{cm}^{-1}$ .

Above 200  $\text{cm}^{-1}$ , the spectra were measured for samples diluted in powdered polyethylene (PE) and normalized against a PE reference spectrum. For very low frequencies, neat kaolinite was used and ratioed against a mirror standard.

The lower figures, from left to right, are of International kaolinite and of Georgia kaolinite, type 121-S. The upper figure is of International kaolinite.

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As a final note, preliminary results in our laboratory show great promise in extending the FTIR-PAS technique to the far-infrared region by using polyethylene as a window material.

