

INFRARED ANALYSIS OF THE ORIENTATION OF PYRIDINE MOLECULES IN CLAY COMPLEXES

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ABSTRACT

INFRARED spectroscopy affords a useful method for the determination of the orientation of molecules sorbed on layer silicates. The orientation of the molecules can be inferred from the observed dichroism of specific absorption bands. Examples of the analysis are illustrated in three complexes with pyridine. One flat and one vertical orientation are observed for the ionic form dependent on layer charge. A different vertical orientation is observed for the neutral molecule. The interpretation of the infrared absorption analysis is confirmed by X-ray diffraction.

INTRODUCTION

STRUCTURAL analyses of clay-organic complexes have suffered from the limitation imposed by the nature of the material, which precludes the collection of sufficient data to give the required resolution. In most cases, the orientation of the organic molecules has been inferred from X-ray diffraction observation of layer spacings and the molecular dimensions. These complexes, in which the molecules adopt generally a single orientation, will show anisotropic absorption of the radiation and are susceptible to analysis by an optical method.

In order that a vibrational mode of the molecule should interact with infrared radiation, it is necessary that a change in dipole moment occurs during the vibration. The direction of these oscillating dipoles with respect to the molecular axis is a result of the symmetry of the molecule and the symmetry type of the vibration involved. In the gas and liquid states, the molecules are randomly oriented and all the active vibrations will give rise to absorption, but when the molecules are oriented in space, as in a crystal, the efficiency of the absorption is a function of the angle between the direction of the oscillating dipole and the electric vector of the radiation. Therefore, if the symmetry species of the vibrational modes associated with the observed frequencies has been previously established, it is possible to determine the orientation of the molecules by observing the dichroism of the absorption bands.

A simple case will be that of an aggregate consisting of planar molecules oriented parallel to each other. In this case, only the in-plane vibrations are excited by radiation normal to the molecular plane, whereas absorption by out-of-plane vibrations will appear only for inclined incidence and will increase in intensity as the inclination angle increases.

It should be noted that the symmetry of the molecule in the condensed state may be different from that of the free molecule, and also that coupling of vibrations between different molecules can occur. For these reasons, caution must be exercised in the interpretation of dichroism measurements and the results must be substantiated, if possible, by other techniques. Furthermore, the value of dichroism measurements is affected by several factors such as the "imperfection" of the orientation, so that the information may be of a qualitative nature.

RESULTS

In this paper, examples are presented of the analysis for complexes of montmorillonite (Wyoming) and vermiculite (Llano) with pyridine. Two kinds of complexes were prepared with montmorillonite: (a) by sorbing neutral pyridine molecules on the Na saturated form, and (b) by introducing the pyridine as a cation. In the case of the Llano vermiculite only the ionic form complex could be prepared by successively exchanging the natural Mg^{2+} ions with Na^+ , propyl-ammonium, and finally, pyridinium ions. In each case, films were prepared so that the silicate layers were in a strongly preferred orientation in the plane of the film. Infrared spectra were obtained for normal and inclined incidence and only those bands whose assignment is unequivocal and are in regions free of silicate absorptions have been selected for observation.

The infrared spectrum of pyridine has been studied extensively and the assignment of most of the observed bands is well established (Kline and Turkevich, 1944; Corsin, Fox, and Lord, 1953). The molecule is planar and possesses a twofold axis (z) and two vertical planes of symmetry (xz , yz) (Fig. 1). The molecule is thus of point group C_{2v} . According to the character table of this point group, the vibrations are classified in the following classes (Herzberg, 1945):

- (1) Symmetry class A_1 , with dipole changes parallel to the principal axis C_2 (z axis),
- (2) Symmetry class A_2 , which are infrared inactive,
- (3) Symmetry class B_1 , having dipole changes along the x axis, and
- (4) Symmetry class B_2 , with dipole changes parallel to the y axis.

Classes A_1 and B_1 are in-plane vibrations while class B_2 is an out-of-plane vibration.

The infrared spectrum of pyridine sorbed on Na-montmorillonite is modified only slightly with respect to that of the liquid state. Absorptions have been observed at 703, 748, 1217, 1443, 1492, 1596 cm^{-1} , and others

around 3000 cm^{-1} . In Fig. 2 are represented the changes in intensity of the selected bands for two different inclinations of the film. Of these bands the 703 and 748 cm^{-1} correspond to out-of-plane vibrations of symmetry class B_2 , the 1443 band has been assigned to a vibration of symmetry class B_1 , and the 1490 cm^{-1} band to a vibration of symmetry class A_1 . Only the 1443 cm^{-1} band (dipole moment change parallel to the x axis) shows a significant increase with the incident angle, indicating a disposition of the molecules

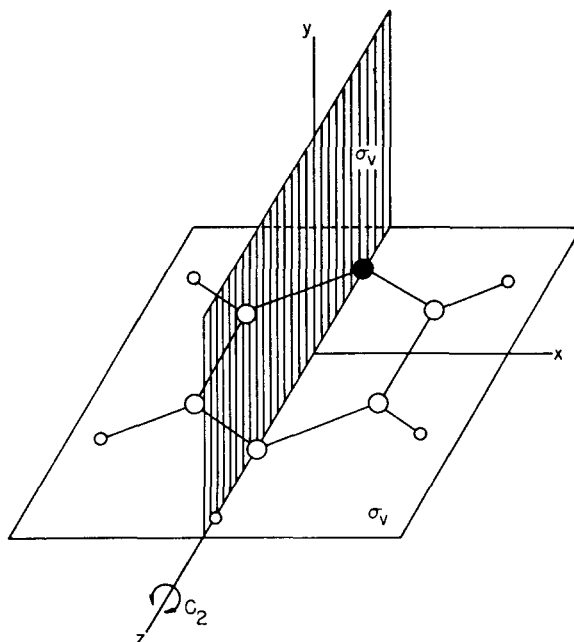


FIG. 1. Symmetry elements of the molecule of pyridine, point group C_{2v} .

with their planes essentially perpendicular to the silicate layers and with the principal axis (C_2) parallel to the layers. This orientation is illustrated by the diagram in the upper part of Fig. 2.

The infrared spectrum of the pyridinium ion, which also belongs to the point group C_{2v} , is different from that of the pyridine, giving the basis for the differentiation between these two species in adsorption studies (Parry, 1963; Swoboda and Kunze, 1966). Bands have been observed at 677 , 748 , 1340 , 1492 , 1550 , 1625 , 1640 cm^{-1} , and several others above 3000 cm^{-1} , in the pyridinium-montmorillonite complex. The position of the bands coincides with those reported previously for the pyridinium ion by other authors (Cook, 1961; Gill, Nuttall, Scaife, and Sharp, 1961).

Although the assignment of the bands for the pyridinium ion is not so well established, it is logical to assign the 677 and 748 cm^{-1} bands to out-of-plane

vibrations and those between 1400 and 1700 cm^{-1} to in-plane vibrations or combination modes.

In Fig. 3 are represented the selected absorption bands of the pyridinium ion adsorbed on montmorillonite for two inclinations of the film. Only the 677 and 748 cm^{-1} bands (out-of-plane vibrations, symmetry class B_2) with dipole moment changes perpendicular to the molecule plane, show significant increase in intensity with the angle of incidence. This result indicates that the pyridinium ions are oriented with their planes parallel to the silicate sheets.

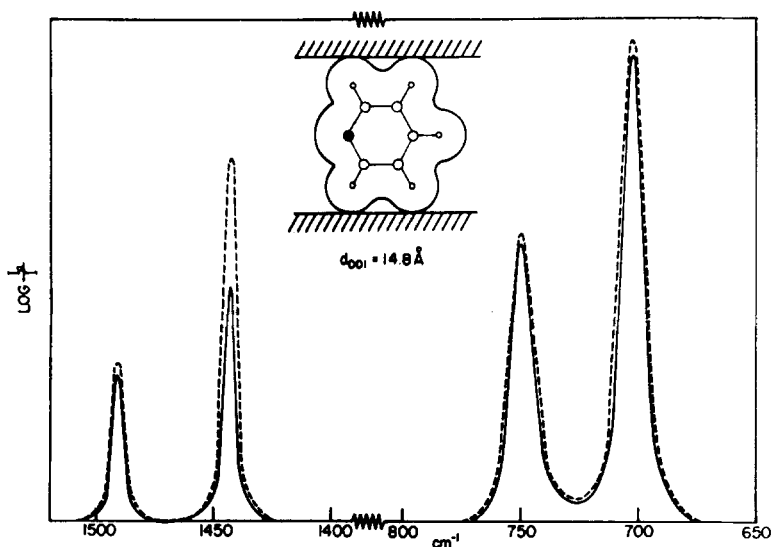


FIG. 2. Selected infrared absorption of pyridine sorbed on Na-montmorillonite for two angles of incidence: — 0° and --- 40° . The upper diagram illustrates the orientation of the molecules in the interlayer region, consistent with the observed directional dependence of the 1443 cm^{-1} band (vibration of symmetry class B_1 , with dipole changes in the plane of the ring and perpendicular to the twofold symmetry axis). The measured basal spacing is indicated.

The orientations arrived at by infrared spectroscopy agree with those inferred by Greene-Kelly (1955) from X-ray spacing measurement and one-dimensional Fourier synthesis. They also confirm Greene-Kelly's analysis (1963) of the change of birefringence in prepared oriented aggregates of pyridine-montmorillonite complexes. The basal spacings of our complexes coincide with those reported by this author. The Na-montmorillonite-pyridinium gives a spacing of 14.8 Å (8 orders observed) while the montmorillonite-pyridinium gives a spacing of 12.5 Å (6 orders observed).

The pyridinium-vermiculite complex shows absorption bands at about the same positions as those of the montmorillonite complex. The four selected

bands have maxima at 680, 757, 1491, and 1543 cm^{-1} . Only the 1491 cm^{-1} band increases significantly in intensity with inclination of the film (Fig. 4). This band, which is present at the same frequency as in pyridine, must have the same origin and has been assigned (Cook, 1961) to a vibration of symmetry class A_1 , with dipole moment change along the principal axis (C_2). This result indicates that the pyridinium ions sorbed in the Llano vermiculite adopt a vertical orientation with the N-H groups directed to the silicate layer and, therefore, are differently oriented from those previously found in montmorillonite.

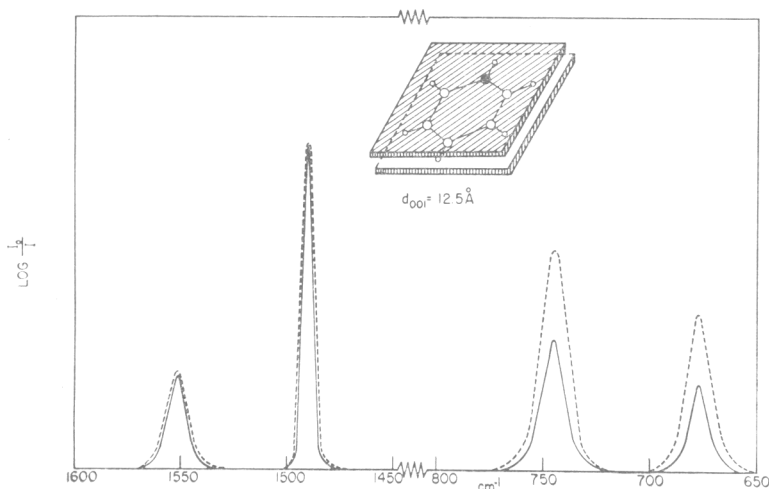


FIG. 3. Infrared absorption bands of pyridinium ion sorbed on montmorillonite for two angles of incidence (—0° and ---40°) showing the directional dependence of the features at 677 and 748 cm^{-1} (out-of-plane vibration, symmetry class B_2). The orientation of the pyridinium ions is illustrated.

This new, alternative orientation of the pyridinium ion must be a consequence of differences in the available space due to the higher layer charge of the vermiculite. For the Wyoming montmorillonite the area per exchange site is approximately 70 \AA^2 . Since the projected area of the pyridinium ion in the flat position is of the order of 40 \AA^2 , there is sufficient space available for this orientation. The Llano vermiculite has an exchange capacity approaching the level of two charges per a - b unit per layer level. The equivalent surface per exchange site is about 24 \AA^2 and can only accommodate the ion in a vertical position. In this orientation the projected area of the pyridinium ion is also $\sim 24 \text{\AA}^2$.

The pyridinium-vermiculite complex exhibits a well-defined layer periodicity of 13.8 \AA . In Fig. 5 is represented the result of one-dimensional Fourier synthesis from 17 orders of X-ray diffraction intensities observed from a single crystal prepared by the same procedure which yielded the film for infrared

analysis. The interlayer region includes two maxima for planes at 6.0 and 7.8 Å from the origin. The complex conforms closely to a stoichiometric content of two pyridinium ions per a - b unit per layer level. Relative areas under the several incompletely resolved electron density maxima are near to appropriate atomic number sums for the model assumed, and the resolution of 1.8 Å between the interlayer peaks is appropriate for an aromatic ring as located by a diffraction data sequence which resolves projected distances greater than 1 Å but not less than 1 Å.

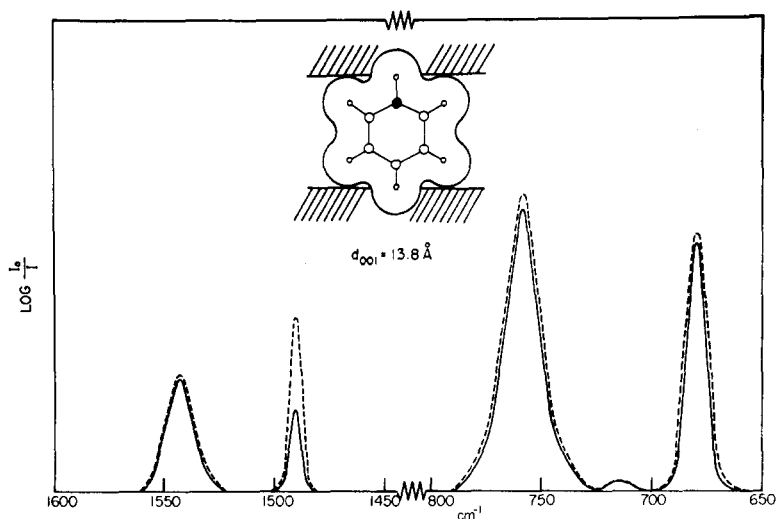


FIG. 4. Infrared absorption bands of pyridinium ion sorbed on vermiculite at two incidence angles (—0° and ---40°), showing the directional dependence of the 1491 cm^{-1} feature (vibration of symmetry class A_1 with dipole changes along the C_2 axis). The orientation illustrated is consistent with the measured basal spacing (13.8 Å).

The thickness of the ion in a vertical position ~ 7 Å, could not be accommodated in the measured interlayer clearance which is only about 4.6 Å (13.8 - 9.2), but the NH group and the CH group in para position can be seated on one side and the other in the open hexagonal (trigonal) surface oxygen arrangements of the silicate skeleton, as illustrated in the diagram included in Fig. 4. The van der Waals clearance required for the ortho and meta hydrogen is also about 4.6 Å.

Both the infrared and the X-ray data allow the possibility of a slight tilting of the aromatic ring. Some tilt is apparently necessary to accommodate the neutral pyridine molecule in the 14.8 Å montmorillonite complex. A comparable slight tilt also could conceivably be required for three-dimensional accommodation of these pyridinium ions. Work is in progress to elucidate this point through the analysis of three-dimensional data.

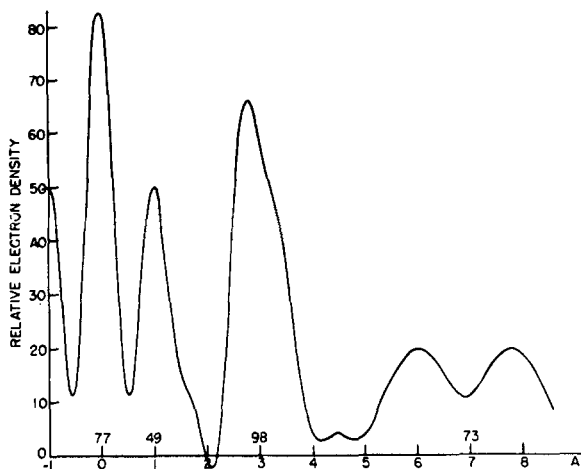


FIG. 5. One-dimensional Fourier synthesis from the 001 sequence of the pyridinium-vermiculite complex. Numerals denote the relative areas under the major partially resolved peaks.

ACKNOWLEDGMENTS

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