

Vibrational Spectroscopic Investigation of 2,2'-Bipyridine Adsorbed on Loughlinite from Aqueous Suspensions

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The adsorption of 2,2'-bipyridine onto loughlinite (Na-sepiolite) has been investigated by FT-IR and micro-Raman spectroscopy. Spectroscopic results indicate the formation of monoanionic surface species. Most of the adsorbed molecules are incorporated in the channels of the clay structure and coordinated to Lewis acidic centers directly or indirectly through water molecules.

Key Words: Clays, Infrared and Raman spectra, 2,2'-Bipyridine, Loughlinite, Sepiolite, Vibrational frequencies.

INTRODUCTION

Bipyridines are of interest in connection with their applications as the basis of the herbicides¹, to obtain new biologically active materials² and to detect heavy metals in solution³ and in medicine⁴. 2,2'-Bipyridine (2,2'-bipy) complexes have great potential for solar energy conversion and energy storage^{5,6}. It has applications in the field of luminescence, photonics and electrochemistry^{7,8}. IR spectra of 2,2'-bipy⁹ and resonance Raman spectra and normal modes of the neutral molecule and its anion radical have been reported¹⁰. 2,2'-Bipyridine is also an interesting molecule for surface coordination studies. Since it has different binding modes (monodentate or bidentate) and in principle the molecule may assume different conformations (*via* rotation of the C-C bond, connected the two pyridine rings) when adsorbed on a surface. Adsorption of 2,2'-bipy at Au(III) electrode/ electrode interface has been investigated by Hoon-Khosla *et al.*¹¹, using FTIR spectroscopy along with *ab initio* Hartree-Fock calculations. They concluded that 2,2'-bipy molecules coordinated to the surface of gold atoms assume a *cis*- or nearly *cis*-conformation. Interaction of 2,2'-bipy with sepiolite were also investigated^{12,13}. In our former work we have investigated adsorption of 2,2'-bipy onto sepiolite, palygorskite and bentonites by using FTIR and FT-Raman spectroscopies. In the case of sepiolite, most of the adsorbed 2,2'-bipy molecules were found to coordinate surface hydroxyls and formation of anionic surface species were also found but relatively small extent¹². On the other hand, Sabah and Cevik¹³ were investigated interaction of 2,2'-bipy with sepiolite by bottle adsorption and IR spectroscopic techniques. They proposed that 2,2'-bipy molecules were not only adsorbed onto the external surface of sepiolite but were also incorporated in its channels¹³.

Loughlinite is a scarce mineral and known as natural Na-sepiolite¹⁴. It belongs to phyllosilicates class of clay minerals and has a chemical formula $\text{Na}_2\text{Mg}_3\text{Si}_6\text{O}_{16}\cdot 8\text{H}_2\text{O}$. Structurally it consists of blocks and channels extending in the c-axis direction. It has ability of selectively sorbing molecules on the external surfaces and inside the channels, resembling sepiolite and palygorskite. Among the phyllosilicates class of clay minerals, loughlinite has been the least studied¹⁵⁻¹⁷. Up to our best of knowledge no vibrational spectroscopic study has been reported on adsorption of 2,2'-bipy onto loughlinite.

EXPERIMENTAL

The natural loughlinite sample was obtained from Mihalicic-Eskisehir region of Anatolia (Turkey). Loughlinite can be distinguishable from sepiolite by XRD reflections¹⁷. Loughlinite has d(110) reflection at 12.9 Å, whereas sepiolite has 12.3 Å. The investigated loughlinite sample, firstly was ground to a fine powder of < 0.5 µm particle size and then was analyzed by X-ray diffraction, differential thermal analysis and IR spectroscopy for purity. The chemical composition of loughlinite was given in our previous paper¹⁶. 2,2'-Bipyridine was reagent grade (Fluka) and was used as received. 2,2'-Bipyridine treated loughlinite was prepared by immersing clay in aqueous solution of 2,2'-bipy in a sealed bottle at room temperature for 2 d. Clay organic suspension was centrifuged at 7000 g for 10 min. The product was then kept in a desiccator to dry.

The IR spectra (4000-400 cm^{-1}) of self-supporting films, prepared according to Madejova¹⁸ or KBr discs of samples were recorded on a Jasco 300E FT-IR spectrometer (2 cm^{-1} resolution) based on averaging 200 sample and 30 background scans. Micro Raman spectrum was recorded on a Jasco NRS 3100 spectrometer. Sample show high fluorescence peculiarity. Spectral manipulations such as baseline adjustment, band fitting and obtaining second derivative were performed using GRAMS/AI Thermo Galactic software. Band fitting was done using Lorentzian or Voigt function and fitting was undertaken until reproducible results were obtained with squared correlations of $r^2 \sim 0.9998$. The second derivatives of the spectra were obtained by using Sav-Golay function.

RESULTS AND DISCUSSION

The molecular model of 2,2'-bipy is given in Fig. 1. The natural 2,2'-bipy and its anion radical may display various possible forms characterized by the torsion angle θ between the two pyridine rings. In solid state, 2,2'-bipy is in *trans*-coplanar configuration¹⁹ ($\theta = 180^\circ$) (C_{2h} symmetry), however in complexes, it usually assumes a coplanar or nearly coplanar *cis*-conformation^{20,21} ($\theta = 0^\circ$) (C_{2v} symmetry).

Loughlinite is a green clay stone, but it became pink coloured after being treated with 2,2'-bipy. In order to elucidate the interaction mechanism of 2,2'-bipy with the clay framework, we carefully investigate the IR and Raman spectra of adsorbed 2,2'-bipy, in comparison with those of solid 2,2'-bipy^{12,22}, radical anion of 2,2'-bipy^{10,23-26} and 2,2'-bipy complexes^{22,27}.

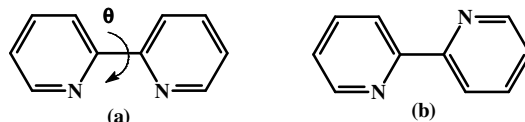


Fig. 1. Molecular model of 2,2'-bipyridine molecule, in *cis*-(C_{2v} symmetry) (a) and in *trans*- (C_{2h} symmetry) (b) configurations

The FT-IR spectra of 2,2'-bipy treated loughlinitite and un-treated loughlinitite are given in Fig. 2. 1750-1250 cm^{-1} region of the FTIR spectrum of 2,2'-bipy treated loughlinitite is given in Fig. 3, in comparison to that of un-treated loughlinitite. The micro-Raman spectrum of the 1700-800 cm^{-1} region of 2,2'-bipy treated loughlinitite is given in Fig. 4. The vibrational spectroscopic results are tabulated in Table-1 together with the appropriate literature data. The IR and Raman results indicates that, although solid 2,2'-bipy is in *trans*-conformation adsorbed 2,2'-bipy is in *cis*-conformation. When vibrational spectra of 2,2'-bipy adsorbed onto loughlinitite are compared to those of the solid 2,2'-bipy¹² and 2,2'-bipy complexes²⁷ (Table-1) it is found that most of the vibrational bands show all the characteristics of coordinated 2,2'-bipy; namely certain modes of adsorbed 2,2'-bipy have upward shifts in frequency, compared to those of free bipy. The IR spectroscopic studies of adsorption of pyridine and pyridine derivatives on clays and oxide surfaces indicated that certain modes of the aromatic molecule, particularly the ring modes around 1600-1400 cm^{-1} were very sensitive to the adsorption sites²⁸⁻³². They increase in value upon coordination of the lone pair on nitrogen atom to Lewis acidic sites or to surface hydroxyls. This is what we observed in the vibrational spectra of 2,2'-bipy treated loughlinitite. Analogous shifts upon bidentate coordination to a metal were also predicted by quantum chemical calculations²² on Zn halide 2,2'-bipy complexes. The ring modes around 1600-1400 cm^{-1} and ring breathing mode, around 994 cm^{-1} were found to be most sensitive modes to coordination. The coordination sensitive ring stretching modes of 2,2'-bipy are observed *ca.* 1589 vs. (Ra), 1578 vs. (IR), 1482 (Ra) cm^{-1} and 994 vs. (Ra)(ring breathing) in the vibrational spectra of solid 2,2'-bipy, whereas the corresponding modes are observed at 1600, 1597, 1485 and 1023 cm^{-1} , respectively, in the vibrational spectrum of 2,2'-bipy treated loughlinitite $\{\Delta(v_{\text{ads}} - v_{\text{solid}}) = 11, 19, 3 \text{ and } 29 \text{ cm}^{-1}$, respectively}. These modes were observed at 1606, 1598, 1491 and 1030 cm^{-1} , respectively in the IR spectrum of ZnCl_2 (2,2'-bipy) complex²² $\{\Delta(v_{\text{complex}} - v_{\text{solid}}) = 17, 20, 9 \text{ and } 36 \text{ cm}^{-1}$, respectively}. Investigation of the vibrational spectra 2,2'-bipy treated loughlinitite, also revealed the presence of anionic surface species. The intensities of the 2,2'-bipy radical anion bands, however, are found to be much weaker in comparison to those of coordinated 2,2'-bipy. Based on the vibrational spectra, it is proposed that most of the adsorbed 2,2'-bipy molecules are coordinated to Lewis acidic sites of loughlinitite as bidentate ligands. It is also proposed bidentate coordination because no splitting of the coordination sensitive modes has been observed. Unidentate coordination would result in two bands, one with a wave-number quite close to the free molecule and the other with an upward shift. The results show that both bipyridine rings are affected by coordination.

TABLE-1
 VIBRATIONAL WAVENUMBERS OF SOLID 2,2'-bipy¹², 2,2'-bipy RADICAL ANION²⁶,
 RUTHENIUM COMPLEX, ADSORBED ON SEPIOLITE¹² AND ON LOUGHLINITE

Assignment	2,2'-bipy ¹²		2,2'-bipy ⁻ (anion)		[Ru(bpy) ₃] ²⁺	2,2'-bipy on sepiolite ¹²		2,2'-bipy on loughlinite (this study)	
	IR	Ra	IR ²⁶	RRa ²⁴	IR ²⁷	IR	Ra	IR	Ra
$\nu_{\text{ring}} A_g$	-	1589vs	1597w, 1585m		1610	1601m	1601vs	1600m, 1585*sh	
$\nu_{\text{ring}} B_u$	1578vs	-	1570vs		1602	1599sh	-	1598sh	-
$\nu_{\text{ring}} + \delta(\text{CH}) A_g$	-	1572vs	-	1568	1567	1582w	1578s	1576sh	-
$\nu_{\text{ring}} B_u$	1558vs	-	1490vs		-	1569, 1498*m		1563w	1562m, 1504*sh
$\nu_{\text{ring}} + \delta(\text{CH}) A_g$	-	1482m	-	1492	1492	1492sh	1492m	1491*vw	1485vs
$\nu_{\text{ring}} + \delta(\text{CH}) B_u$	1451vs	-	1460w		-	1478m	-	1473w	-
$\delta(\text{CH}) A_g$	-	1446s	-	1469	1464	1463*m	1451m	1458	1465*sh
$\nu_{\text{ring}} + \delta(\text{CH}) B_u$	1415vs	-	1415s		1444	1437s	1433vw	1437m	1429w
$\delta(\text{CH}) + \delta_{\text{i,r}} A_g$	-	1309s	-	-	1322	-	1311sh	1314w	1315s
$\nu_{\text{i,r}} + \delta(\text{CH}) A_g$	-	1301	-	1338	1312	-	1305s	-	1303sh
$\nu_{\text{ring}} B_u$	1269vw	-	1208vw		1278	-	-	-	1272m
$\delta(\text{CH}) B_u$	1249m	-	1162w		1269	-	-	-	1253w
$\delta(\text{CH}) A_g$	-	1237s	1277vs		1277	-	1277*w, 1234w	-	-
$\delta(\text{CH}) A_g$	-	1146w	-	1140	1178	-	1156*w	1175**	1170s
$\delta(\text{CH}) B_u$	1139vw	-	-	-	1161	-	-	-	1146m
$\delta(\text{CH}) A_g$	-	1094vw	-	1082	1114	-	-	-	1104m
$\delta(\text{CH}) B_u$	1083m	-	-	-	-	-	1080vw	-	1083m
$\nu_{\text{ring}} + \delta_{\text{ring}} B_u$	1064w	-	-	-	1067	-	-	-	-
$\nu_{\text{ring}} + \delta_{\text{ring}} A_g$	-	1045m	-	1010	-	-	1056w	1059**	1060m
$\delta_{\text{ring}} B_u$	1039s	-	-	-	-	-	-	-	-
Ring breath A_g	-	994vs	-	971	1028	-	1006s	-	1023ms
Ring breath B_u	992m	-	954m		1025	-	-	-	947*w
$\gamma(\text{CH}) B_u$	-	814vw	-	-	-	-	-	-	823m

*2,2'-bipy radical anion bands. **Obtained by band component analysis.

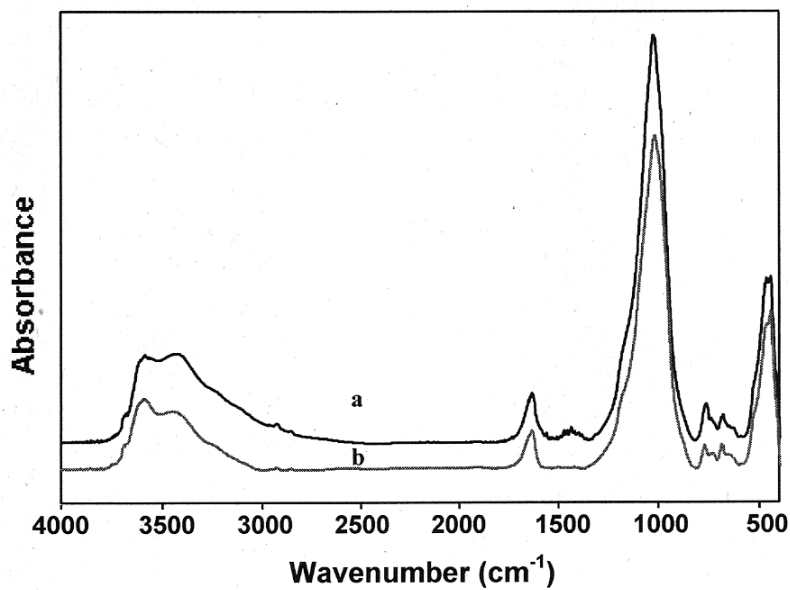


Fig. 2. FT-IR spectra of 2,2'-bipy treated loughlinite (a) and starting loughlinite (b)

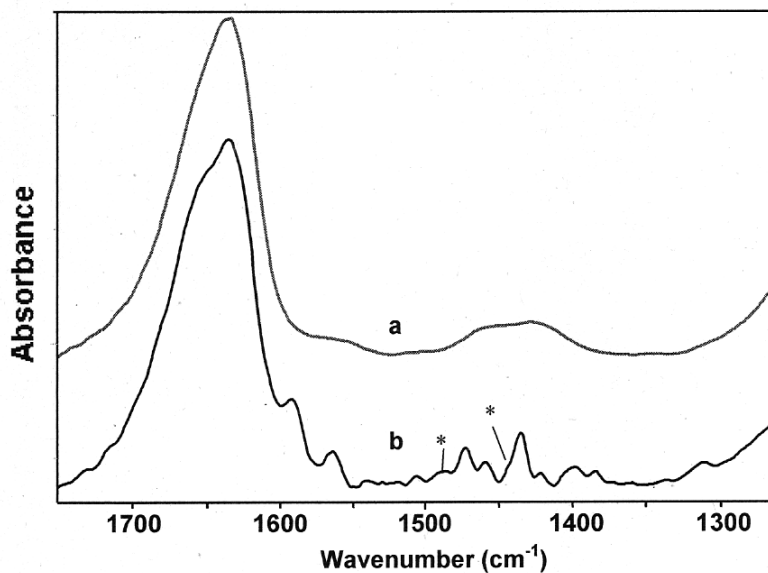


Fig. 3. 1750-1250 cm⁻¹ region of the FT-IR spectra of starting loughlinite (a) and 2,2'-bipy treated loughlinite (b), 2,2'-bipy radical anion bands are indicated with asterisks

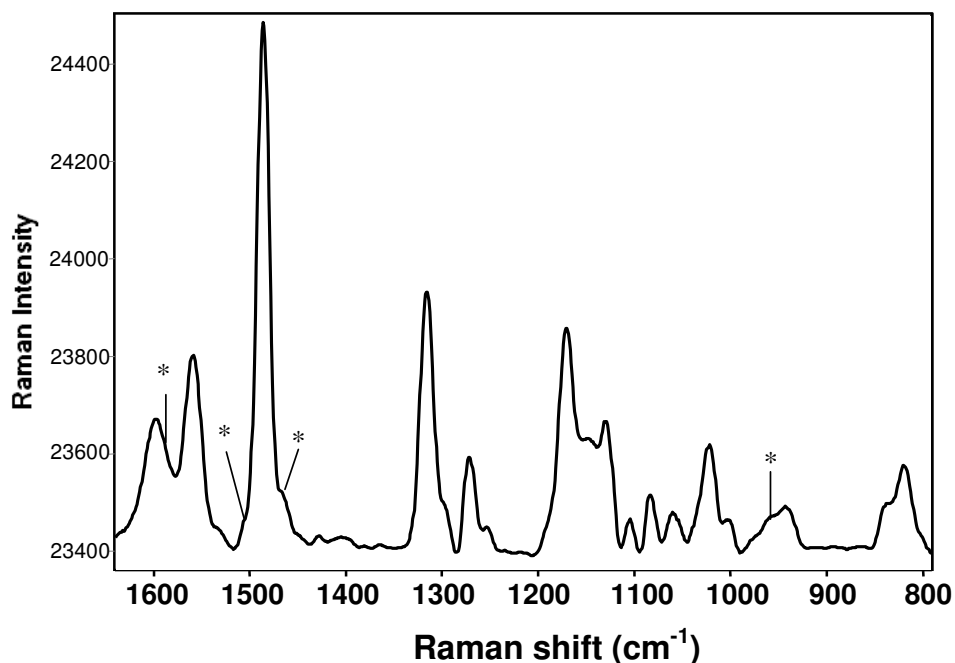


Fig. 4. 1700-800 cm^{-1} region of the micro-Raman spectrum of 2,2'-bipy treated loughlinite. 2,2'-Bipy radical anion bands are indicated with asterisks

Adsorption of 2,2'-bipy affected the Si-O stretching vibrations of the clay framework. Fig. 5 represents Si-O stretching region of the FT-IR spectrum of 2,2'-bipy treated loughlinite, in comparison with that of un-treated loughlinite. The band component analyses of the FT-IR spectra of un-treated loughlinite and 2,2'-bipy treated loughlinite are given in Figs. 6 and 7, respectively. The Si-O stretching bands are observed at 1181, 1066, 1019, 984 and 958 cm^{-1} in the IR spectrum of the untreated loughlinite, whereas, the corresponding bands are observed at 1175 ($\Delta = \nu_{\text{treated}} - \nu_{\text{untreated}} = -6 \text{ cm}^{-1}$), 1076 ($\Delta = +10 \text{ cm}^{-1}$), 1022 ($\Delta = +3 \text{ cm}^{-1}$), 982 ($\Delta = -2 \text{ cm}^{-1}$) and 952 cm^{-1} ($\Delta = -6 \text{ cm}^{-1}$) in the IR spectrum of 2,2'-bipy treated loughlinite. The SiO stretching vibrations are known to be significantly affected by changes in swelling and orientation of the clay platelets³³. The results indicate that adsorbed 2,2'-bipy molecules are incorporated in the channels of the clay structure and coordinated to Lewis acidic centers directly or indirectly through water molecules.

Conclusion

The comparison of the IR and Raman spectra of the adsorbed 2,2'-bipy, with those of free 2,2'-bipy, 2,2'-bipy monoanion and coordinated 2,2'-bipy, offered data on the nature and characteristics of the formed clay-organic complexes. The vibrational spectroscopic results indicated the presence of two different types of surface species *i.e.* chemisorbed neutral molecules and chemisorbed monoanions. Concentration

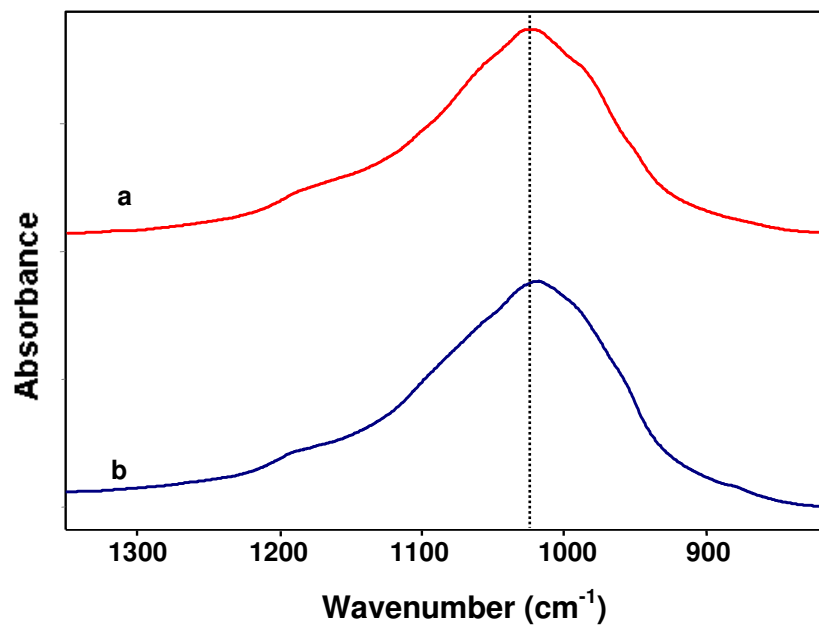


Fig. 5. 1350-800 cm⁻¹ region of the FT-IR spectra of 2,2'-bipy treated loughlinite (a) and starting loughlinite (b)

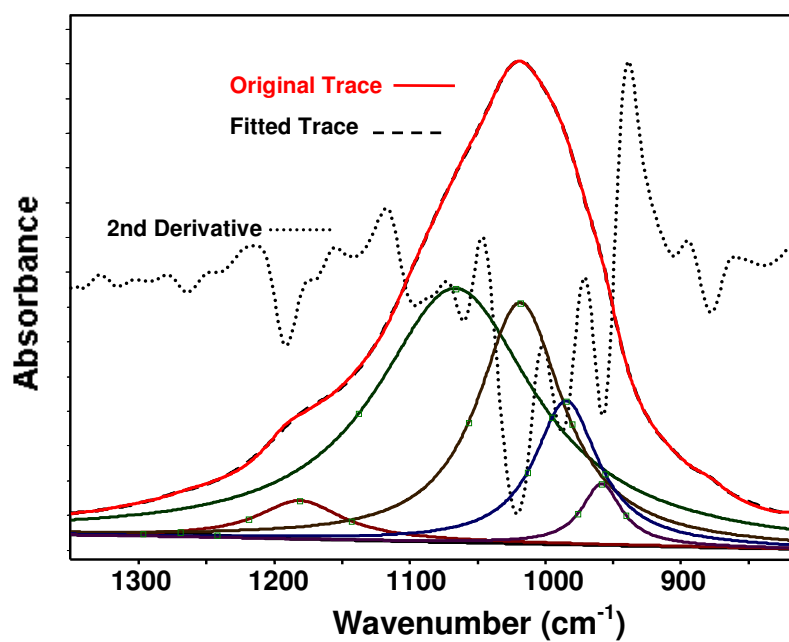


Fig. 6. Band component analysis of the 1350-850 cm⁻¹ region of the FT-IR spectrum of untreated loughlinite. 1181, 1066, 1019, 984 and 958 cm⁻¹ bands are revealed

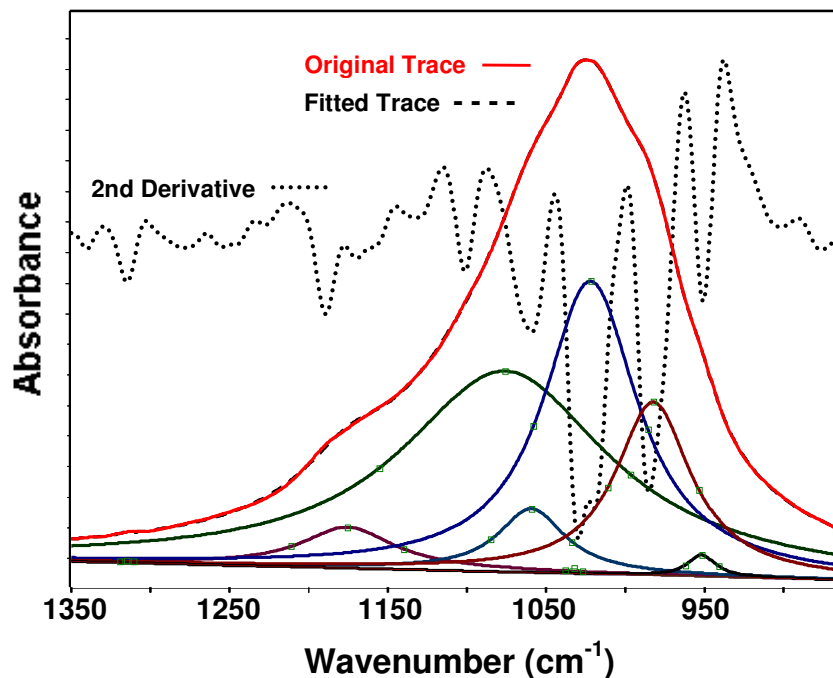


Fig. 7. Band component analysis of the 1350-850 cm^{-1} region of the FT-IR spectrum of 2,2'-bipy treated loughlinitite. 1175, 1076, 1022, 982 and 952 cm^{-1} bands belong to Si-O stretching modes of loughlinitite structure and, 1059 cm^{-1} band belong to adsorbed 2,2'-bipy are revealed

of 2,2'-bipy monoanions, however, is found to be very small in comparison to the coordinated molecules. Most of the adsorbed molecules are incorporated in the channels of the clay structure and coordinated to Lewis acidic centers directly or indirectly through water molecules.

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