Adsorption of 2,2′-Bipyridyl onto Sepiolite, Attapulgite and Smectite Group Clay Minerals from Anatolia: The FT-IR and FT-Raman Spectra of Surface and Intercalated Species

SEVIM AKYÜZ*
Physics Department, Instanbul University, Science Faculty, Vezneciler 34459, Istanbul, Türkiye

TANIL AKYÜZ
Atomic Energy Agency, Çekmece Nuclear Research and Training Center, P.K.1, Havaalani, Istanbul, Türkiye

and

J. ERIC D. DAVIES
Environmental Science Division, Lancaster University, LA1 4YQ, Lancaster, Great Britain

Abstract. The adsorption of 2,2′-bipyridyl by natural sepiolite, attapulgite, hectorite, saponite and natural and ion exchanged (Mn, Fe, Co, Ni, Cu, Zn or Sn) bentonites has been investigated by FT-IR and FT-Raman spectroscopy. Spectroscopic results indicate that most of the adsorbed molecules are coordinated to either exchangeable cations (in the case of smectite group clays) or Lewis acidic centres (in the case of sepiolite and attapulgite) as bidentate ligands. The formation of monoanionic surface species has also been detected, to a relatively small extent. No physisorbed surface species has been observed. XRD patterns and UV-visible spectra of the samples are also recorded for additional information.

Key words: FT-IR spectroscopy, FT-Raman spectroscopy, clays, sepiolite, attapulgite, hectorite, saponite, bentonite, adsorption, 2,2′-bipyridyl.

1. Introduction

Many organic substances can intercalate into the interlamellar space of smectite group clays, such as bentonite, saponite and hectorite [1]. Generally the fixation of these compounds is due to their interaction with exchangeable cations, which balance the deficit of charge of the silicate layers. This type of interlayer adsorption into smectites involving 2,2′-bipyridyl has already been the subject of several investigations [2–8]. Although there are some IR spectroscopic studies on the adsorption of 2,2′-bipyridyl on some smectite group clay minerals and alkaline-

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* Author for correspondence.

earth oxides [4,5,7,9], to our knowledge no Raman spectroscopic study has been published in the literature.

Sepiolite and attapulgite (palygorskite) are composed of trimorphic layers arranged in ribbons which are joined through oxygen ions [10,11]. The tetrahedral sheets are continuous but the apices of SiO_4 tetrahedra in adjacent ribbons point in opposite directions, giving rise to a corrugated surface with open channels running parallel to the ribbons. Attapulgite has a smaller trimophic unit than sepiolite; it consequently has smaller channel widths. They both have the ability of selectivity sorbing polar and non-polar molecules on the external surfaces and in some cases (for small polar molecules) inside the channels [12].

In our previous study [13] the adsorption of 4,4'-bipyridyl by sepiolite and smectite group clay minerals was investigated using FT-IR and FT-Raman spectroscopy. Raman spectroscopic investigation has been found to be very useful in shedding light on the host–guest interactions, since it enables one to analyse clearly the 1100–950 and 600–400 cm^{-1} regions of the spectra of adsorbed molecules, regions which are obscured in the IR spectrum by the host vibrational modes of aluminosilicates.

In this study we wish to extend our previous study [13] to 2,2'-bipyridyl adsorption by clays. Since several unusual physicochemical properties of transition metal 2,2'-bipyridyl complexes adsorbed onto smectite surfaces have recently been reported [3] it is interesting to analyse the interactions of adsorbed 2,2'-bipyridyl molecules by clays from Anatolia, by using vibrational spectroscopy.

2. Experimental

Natural sepiolite, attapulgite and saponite samples were obtained from Mihalliccik-Eskisehir and bentonite and hectorite samples were obtained from the Cankiri region of Anatolia (Turkey). The samples were identified by XRD, DTA, IR and chemical analyses. The hectorite sample was found to have carbonate (calcite and $MgCO_3$) impurity. The chemical analyses of the clays were given in our previous paper [13], except for attapulgite, the results being: 60.9%, SiO_2; 10.4%, Al_2O_3; 10.3% MgO; 3.5% $\sum(Fe_2O_3 + FeO)$; 1.9% CaO; 0.8% K_2O; 0.8% P_2O_5; 0.5% TiO_2; 0.1% S; 0.05% Na_2O; 0.05% MnO and 10.45% loss on ignition. The chemical analyses of the smectite group clay minerals indicated a cation exchange capacity (CEC) of 70 meq/100g for hectorite and 110 meq/100g for saponite. The CEC of the homoionic Mn, Fe, Co, Ni, Cu, Zn and Sn bentonites are: 74; 120; 110; 107; 111; 92 and 62 meq/100g of clay, respectively. The variation in the CEC values of the homoionic bentonites is probably due to the presence of impurities. The mean CEC value of Wyoming bentonite (SWy-1) is known to be 76.4 [14]. The influence of H^+ and impurities on the CEC values of clays cannot be neglected.

2,2'-Bipyridyl treated samples were prepared either by immersing air-dried clays in an n-hexane solution of 2,2'-bipyridyl (B.D.H.) in sealed bottles at room temperature for two days or by solid-solid reactions between clays and bipyridyl,

analogous to that of Co-montmorillonite and bipyridyl [4]. The products were washed with n-hexane several times to remove excess bipyridyl. 2,2′-Bipyridyl treated Co-bentonite is yellowish brown, Fe and Sn-bentonites are dark pink and Cu-bentonite is blue. The other clays do not alter in colour after being treated with bipyridyl. Chemical analyses [8] indicated that the amounts of bipyridyl adsorbed or intercalated onto sepiolite and bentonite are 0.7 and 0.9 mmol/g, respectively.

The FT-IR spectra of KBr discs of samples were recorded on a Nicolet 510 spectrometer. The FT-Raman spectra were recorded on a Bruker IFS 66 FT-Raman instrument using 1.06 μm excitation from a Nd:YAG laser. Five hundred scans were accumulated at 4 cm^{-1} resolution using a laser power of 100 mW. No spectra could be obtained using visible 488.0 and 514.5 nm excitation due to strong fluorescence.

The XRD patterns of the products were obtained on a Jeol JDX 19C diffractometer using CuK$_\alpha$ radiation. Diffuse reflectance UV-visible absorption spectra were recorded on a Unicam spectrometer.

3. Results and Discussion

Only Co, Fe, Sn and Cu-bentonites became coloured after being treated with 2,2′-bipyridyl. The UV-visible spectra of these clays were recorded and two bands were observed around 310 and 530 nm in the case of bipyridyl treated Fe and Sn-bentonites and around 308 and 660 nm in the case of bipyridyl treated Cu-bentonite. In the electronic absorption spectrum of the Fe(bipy)$_3$(ClO$_4$)$_2$ complex in aqueous solution, Berger and McMillin observed [15] two broad bands around 350 nm and 520 nm and assigned them to metal to ligand charge-transfer bands $(d \rightarrow \pi^*)$. Our result for Fe-treated bentonite is in accord with Berger and McMillin's finding.

The XRD patterns of 2,2′-bipyridyl treated hectorite, saponite, natural and Fe, Cu and Zn-bentonites were also recorded and basal spacings of 18.1, 18.0, 18.2, 18.2, 18.5 and 18.2 Å respectively were observed. The basal spacing of the untreated clays were found to be around 12 Å. Ogawa et al. [4] found the basal spacings of 2,2′-bipyridyl treated Na, Ca and Co montmorillonites to be around 18 Å, similar to the value found by Traynor et al. [2] for the basal spacings of 2,2′-bipyridyl treated ion-exchanged hectorites. Based on the XRD results, these authors [2,4] concluded that the complex ions [M(bipy)$_3$]$^{n+}$ were intercalated at a monolayer coverage with their 3-fold axis perpendicular to the silicate sheets. Our XRD results are comparable with the previous findings [2,4].

In the solid state the 2,2′-bipyridyl molecule is in the *trans* coplanar configuration [16], thus belonging to the molecular C_{2h} point group; however the *cis* form occurs on formation of complexes with metal ions.

The vibrational bands of adsorbed 2,2′-bipyridyl are assigned in comparison to those of the free molecule [17], the IR [18–20] and resonance Raman spectra [15,20] of bipyridyl complexes, the IR spectra of species adsorbed on montmorillonite [5] and on alkaline earth oxides [9] and finally with those of the bipyridyl anion (2,2′-

TABLE I. Vibrational wavenumbers (cm^{-1}) of microcrystalline 2,2′-bipyridyl (bipy) and its adsorbed surface species on sepiolite and attapulgite

Assignment [17]		bipy this study		bipy on M[a] [5]	bipy[-] [21]	bipy[-] on MgO [9]	bipy on Sepiolite		bipy on Attapulgite
		IR	R	IR	IR	IR	IR	R	IR
νring	Ag	–	1589 vs	–	1597 w	–	1601 m	1601 vs	–
					1585 m				
νring	Bu	1578 vs	–	1595 s	1570 vs	1570 sh	1599 sh	–	1599 w
νring	Ag	–	1572 vs	–	–	1533 w	1582 w	1578s	1584 sh
							1534* w		1539* vw
νring	Bu	1558 vs	–	–			1569 m		1564 m
					1490 vs	1488 s	1498* m	–	1492* w
νring + δ(CH)	Ag	–	1482 ms	–	–	–	1492 sh	1492 m	–
νring + δ(CH)	Bu	1451 vs	–	1480 m	1460 w	–	1478 m	–	1476 m
				1470 m			1463* m		1459* m
νring + δ(CH)	Ag	–	1447 s	–	–	–	–	1451 m	–
νring + δ(CH)	Bu	1415 vs	–	1438 m	1415 s	1417 s	1437 s	1433 vw	1438 s
				1422 sh			1423 w		1423 m
overtone or combination		1311 vw	–	1310 vw	–	–	1314 w	1311 sh	1313 sh
νring	Ag	–	1301 s	–	1277 vs	1278 s	–	1305 s	–
								1277* w	
νring	Bu	1269 vw	–	–	1208 vw	1215 w	–	–	–
δ(CH)	Bu	1249 m	–	–	1162 w	–	–	1156* w	–
δ(CH)	Ag	–	1237 s	–	–	–	–	1236 w	–
δ(CH)	Ag	–	1146 w	–	–	–	–	–	–
δ(CH)	Bu	1139 vw	–	–	–	–	–	–	–
δ(CH)	Ag	–	1094 vw	–	–	–	–	–	–
δ(CH)	Bu	1083 m	–	–	–	–	–	1080 vw	–
νring + δring	Bu	1064 w	–	–	–	–	–	–	–
νring + δring	Ag	–	1045 m	–	–	–	–	1056 w	–
δring	Bu	1039 s	–	–	–	–	–	–	–
ring breath	Ag	–	994 vs	–	–	–	–	1006 s	–
ring breath	Bu	992 ms	–	–	954 m	958 vs	–	–	–
γ(CH)	Bg	–	814 vw	–	–	–	–	–	–
δring	Ag	–	764 m	–	764 m	–	–	766 w	–
γ(CH)	Au	756 vs	–	760 s	745 w	–	757 s	–	762 ms
γ(CH)	Au	740 m	–	–	713 vs	–	741 w	–	741 w
δring	Bu	652 m	–	–	681 m	–	–	–	652 vw
δring	Bu	618 m	–	–	621 vw	–	–	–	–
δring	Ag	–	614 m	–	646 w	–	–	623 w	–
γring	Bg	–	357	–	–	–	–	357 vw	–
ring–ring str.	Ag	–	331	–	–	–	–	331 vw	–
γring	Bg	–	234	–	–	–	–	234 vw	–
ring scissoring	Bu	[161][b]	–	–	–	–	–	162 vw	–

vs = very strong; s = strong; ms = medium strong; m = medium; w = weak; vw = very weak

[a] M = montmorillonite

[b] Taken from Ref. 17.

* Indicates 2,2′-bipyridyl mono anion (bipy)[-] bands.

ν; δ; γ; indicates in-plane stretching, in-plane bending and out-of-plane bending modes, respectively.

bipyridyl[-]) [21], in order to characterize the species formed upon adsorption. The results are tabulated in Tables I and II together with the appropriate literature data.

3.1. BIPYRIDYL ADSORPTION ON SEPIOLITE AND ATTAPULGITE

Sepiolite and attapulgite are fibrous clay minerals, in contrast to the layered structure of smectites: they are consequently not expandable. However, both have
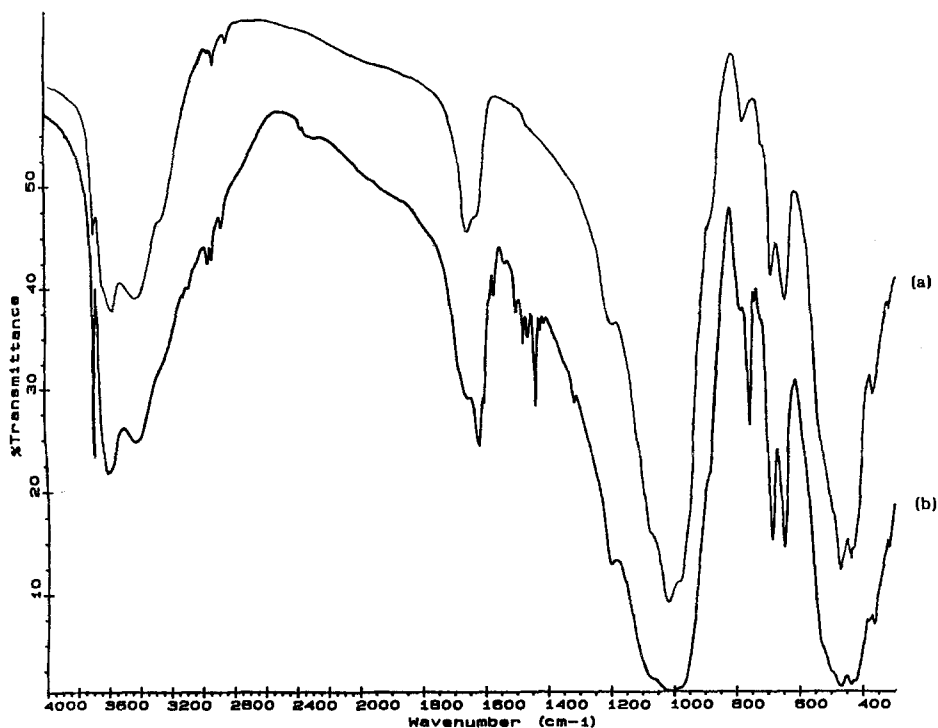
Fig. 1.   Infrared spectra of (a) sepiolite and (b) 2,2'-bipyridyl treated sepiolite.

sorption active centers [12]. The IR and Raman spectra of natural and bipyridyl treated sepiolite are given in Figures 1 and 2, whereas the IR spectra of natural and treated attapulgite are given in Figure 3. Sepiolite is found to adsorb much more 2,2'-bipyridyl than attapulgite, which is consistent with the slight difference in their structures: in sepiolite the channel width is larger than in attapulgite and the specific surface area of the former mineral is higher than that of the latter [12].

When the vibrational spectra of bipyridyl adsorbed by sepiolite and attapulgite are compared to those of the free molecule [17] and bipyridyl complexes [15, 18–20] (see Table I), it is found that most of the vibrational bands show all the characteristics of coordinated bipyridyl; namely, certain modes of adsorbed bipyridyl have upward shifts in frequency, compared to those of the free molecule. Analogous shifts were observed in the complexes of pyridine and pyridine derivatives and explained by coupling with metal–ligand vibrational frequencies [13, 23–25]. It is noteworthy that we also observed coincidences in some of the IR and Raman vibrational modes of bipyridyl in sepiolite, indicating that the adsorbed molecules are in a *cis*-conformation, consistent with the conformation in bipyridyl complexes [26].
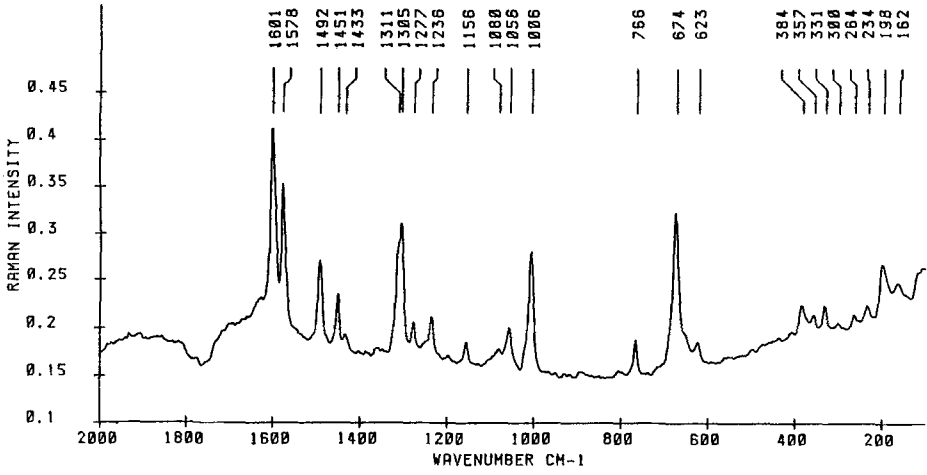
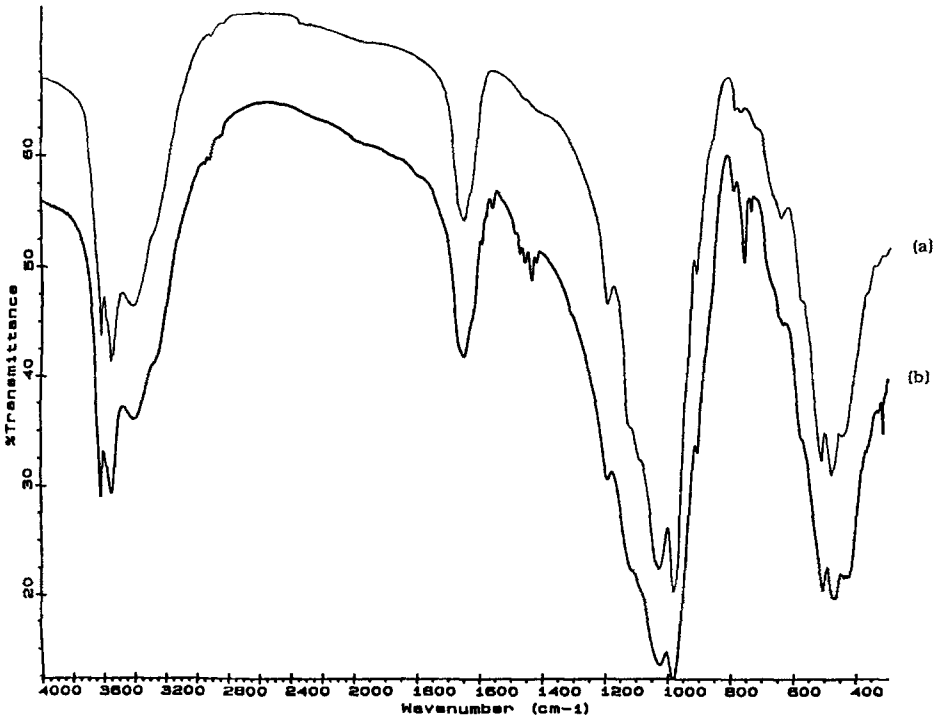Fig. 2. Raman spectrum of 2,2'-bipyridyl treated sepiolite.

Fig. 3. Infrared spectra of (a) attapulgite and (b) 2,2'-bipyridyl treated attapulgite.

In addition to some of the ring stretching modes of pyridine and its derivatives ($1500-1600$ cm^{-1}), the ring breathing mode is known to be very sensitive to coordination of pyridine rings via σ donation from nitrogens. These coordinate in a chelating fashion and the increases in frequency depends on the coordination strength [13, 23–25]. Ring breathing modes are observed at 992 cm^{-1} (IR) and 994 cm^{-1} (Ra) in the vibrational spectra of microcrystalline 2,2'-bipyridyl (C_{2h}). Unfortunately, the $950-1000$ cm^{-1} region is obscured by the mineral framework vibrational modes [ν(Si–O)] in the IR spectra of clays (Figure 1); however, in the Raman spectrum of 2,2'-bipyridyl treated sepiolite the ring breathing mode in-phase component has clearly been observed as a strong band at 1006 cm^{-1} [$\Delta(\nu_{ads} - \nu_{crys}) = 12$ cm^{-1}] (Figure 2). The out-of-phase component of this mode was observed at 1018 cm^{-1} in the IR spectrum of the Co(bipy)$_3$Cl$_2$ complex [18] (see Table II). We have also observed upward shifts up to 18 cm^{-1} in the coordination sensitive ring stretching modes of bipyridyl adsorbed onto both sepiolite and attapulgite, in comparison to those of the free molecule (see Table I), similar to those of Mbipy$_3$Cl$_2$ complexes [18]. Thus the vibrational wavenumbers of bipyridyl adsorbed onto sepiolite and attapulgite are found to be closer to those of the coordinated molecule than of the free molecule. On the ohter hand the vibrational spectra of 2,2'-bipyridyl treated sepiolite and attapulgite showed some adsorption bands which were not attributable to either 2,2'-bipyridyl or the clay structure, which are indicated in Table I with asterisks. These bands, however, are found to be close to those of the 2,2'-bipyridyl anion (2,2'-bipy$^-$) [9,21]. The intensity of these bands is found to be much weaker in comparison to those of coordinated bipyridyl.

Based on the vibrational spectra, we propose that most of the adsorbed bipyridyl molecules are coordinated to Lewis acidic sites of sepiolite and attapulgite as bidentate ligands. We propose bidentate coordination because we do not observe splittings of the coordination sensitive ring modes. Unidentate coordination of 2,2'-bipyridyl would result in two bands, one with a wavenumber quite close to the free molecule and the other with an upward shift. Our results show that both rings are affected by coordination. On the other hand it is worth mentioning that we also observed some intensity and frequency changes in the OH group stretching bands of surface hydroxyls (Si–OH) of the bipyridyl treated sepiolite. But these bands are found to be less affected by adsorption of bipyridyl in the case of attapulgite, probably because the surface Si–OH groups in attapulgite appear to be less abundant than in sepiolite [12]. Therefore H bonding interaction of adsorbed bipyridyl with the surface hydroxyls through the lone pairs of both nitrogens as bidentate ligands, cannot be excluded in the case of sepiolite. The OH group vibrational modes of sepiolite and attapulgite are given in Table III.

We also propose that the generation of the 2,2'-bipyridyl anion takes place via an electron transfer process from the surface to the organic molecule. However, this spectroscopic study indicated that the concentration of the negative species must be comparatively very low.

TABLE II

Vibrational wavenumbers of 2,2′-bipyridyl (bipy) adsorbed on smectite group clays and of the cobalt tris-bipyridyl complex $Co(bipy)_3Cl_2$

Column groups: **Bipy this study** (IR, R); **Co(bipy)₃Cl₂ [14]** (IR); **Bipy adsorbed on ion exchanged bentonites** (Mn-, Fe-, Co-, Ni-, Cu-, Zn-, Sn-); **Bipy adsorbed on natural clays** (Bentonite, Hectorite, Saponite).

Bipy IR	Bipy R	Co(bipy)₃Cl₂[14] IR	Mn- IR	Fe- IR	Fe- R	Co- IR	Co- R	Ni- IR	Ni- R	Cu- IR	Cu- R	Zn- IR	Zn- R	Sn- IR	Sn- R	Bentonite IR	Hectorite IR	Hectorite R	Saponite IR
–	1589 vs	1650 sh	1603 sh	1606 ms	1602 s	1604 ms	1601 s	1601 sh	–	1607 sh	1607 s	1605 sh	1605 s	1606 ms	–	1609 sh	–	1589 s	1607 sh
1578 vs	–	1600 vs	1597 s	1599 s	–	1599 s	–	1600 s	–	1601 vs	–	1598 s	–	1587 s	–	1598 s	–	–	1599 s
–	–	–	1581 w	1589 ms	–	1583 w	–	1583 m	–	1582 m	–	–	–	–	–	–	–	–	–
1558 vs	1572 vs	1570	1575 w	–	1573 m	–	–	–	1574 vw	–	1572 m	1578 m	1574 m	–	1574 m	1577 vw	1575 vw	1569 m	1578 vw
–	–	–	1564 m	1564 m / 1532* m	1566 vw	1565 m	1567 m	1567 m	–	1566 m	–	1568 m	–	1561 m / 1531* s	–	1566 m / 1533* m	1565 m	–	1566 m / 1531* m
–	1482 ms	1490	1492 ms	1493 m	1493 m	1493 m	1493 m	1494 m	–	1494 m	1500 m	1494 ms	–	1493 sh	–	1492 m	–	1485 m	1493 ms
1451 vs	–	1470 vs	1475 ms	1475 ms	1475 vw	1475 ms	–	1475 s	–	1475 s	–	1477 s	–	1473 s	–	1476 ms	1472 m	–	1477 s
–	–	–	1456 m	1459 ms	1461 vw	1459 m	–	1456 sh	–	1455 sh	–	1457 sh	–	1459 s	–	1458 m	1456 sh	–	1459 m
1415 vs	1447 s	1442 vs	1441 s	1441 s	1436 w	1444 s	1437 w	1445 vs	–	1445 s	–	1444 s	–	1438 s	–	1440 s	1436 m	1447 vw	1441 s
–	–	–	1422 w	1422 w	1420 vw	1422 w	–	1422 w	–	1422 w	1419 vw	1422 w	–	1422 w	–	1423 m	1421 w	–	1422 m
1311 vw	1301 s	1312 vs	1315 w	1314 m	1315 s	1315 w	1313 ms	1315 w	–	1315 w	1322 s	1316 m	–	1311 vw	1315 ms	1315 vw	1312 m	1308 ms	1316 m
–	–	–	–	1320 sh	1273* w	–	–	–	–	–	–	–	–	1323 m / 1273* w	–	–	–	1276* w	–
1269 vw	–	–	–	–	–	–	1263 w	–	–	–	1266 w	–	–	–	–	–	–	–	–
1249 m	1237 s	1249	–	–	1248 vw	1245 sh	–	–	–	–	–	–	–	–	1247 vw	–	–	1251 vw	–
–	–	–	–	–	1159* vw	–	1165* vw	–	–	–	1161* vw	–	–	–	–	–	–	1155* w	–
–	1094 vw	–	–	–	1109 vw	–	–	–	–	–	–	–	–	–	–	–	–	–	–
1064 w	–	1062	–	–	1065 w	–	1064 w	–	–	–	1062 vw	–	–	–	–	–	–	1062 w	–
–	–	–	–	–	1034 m	–	–	–	–	–	1040 m	–	–	–	1035 m	–	–	–	–
–	–	1018 vs	–	–	1023 m / 1016 m	–	1024 ms	–	–	–	–	–	–	–	1014 ms	–	–	1020 sh	–
992 ms	994 vs	–	–	–	997 w	–	–	–	–	–	–	–	–	–	–	–	–	1001 s	–
–	814 vw	–	–	–	804 vw	–	–	–	–	–	–	–	–	–	–	–	–	812 vw	–
756 vs	764 vw	(778 vs / 765 sh)	765 ms	762 ms	766 m	765 ms	765 w	765 ms	–	765 ms	769 w	769 ms	–	–	765 w / 761 ms	758 ms	762 ms	764 m / 762 ms	–
740 m	–	737 vs	738 m	741 w	–	738 m	–	738 m	–	735 m	–	738 m	–	741 sh	–	741 w	742 w	–	741 m
652 m	–	651	650 w	653 sh	641* w	651 w	649 w	653 sh	–	651 sh	–	652 w	–	–	–	654 sh	653 m	–	653 w
618 m	–	630 v	628 vw	630 sh	–	631 sh / 620 sh	632 vw	–	–	621 sh	–	–	–	630 sh	–	–	–	–	–
–	614 m	–	–	–	614 vw	–	–	–	–	–	–	–	–	–	–	–	616 vw	–	–

* Indicates 2,2′-bipyridyl mono anion bands (bipy‾).

TABLE III. OH group vibrations of natural and 2,2'-bipyridyl treated sepiolite and attapulgite in the IR spectra

Assignment [9]	Sepiolite		Assignment [18]	Attapulgite	
	Natural	bipy treated		Natural	bipy treated
ν(OH) SiOH	3719 m sh	–	ν(OH) SiOH	3689 w sh	–
ν(OH) Mg$_3$OH	3688 s	3682 vs			
ν(OH) dioctahedral sys.	3636 sh	–	ν(OH) Al$_2$-OH ν(OH) (Al,Fe^{2+})-OH (Al,Mg)-OH (Fe^{3+},Mg)-OH	3616 s 3686 sh	3618 vs 3585 sh
ν(OH) coordinated water	3566 vs	3589 s br	ν(OH) coordinated water	3549 s	3550 s
ν(OH)	3407 s br	3406 s br	ν(OH)	3415 s br	3401 m br
Zeolitic water	3272 sh	3240 sh	zeolitic water	3279 sh	3280 sh
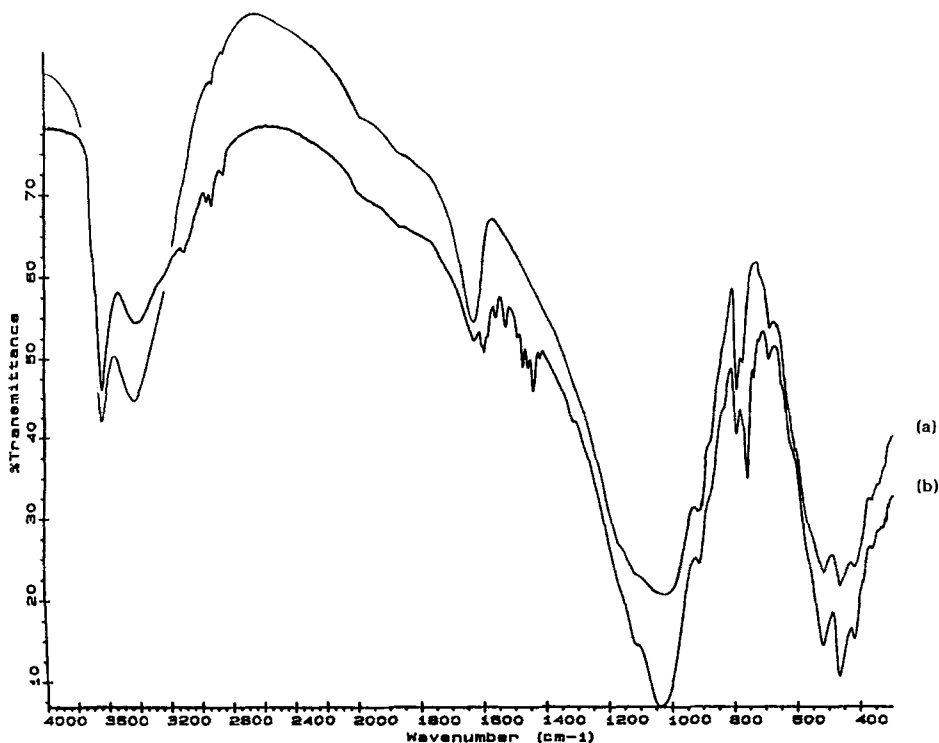
Fig. 4.   Infrared spectra of (a) Fe-bentonite and (b) 2,2'-bipyridyl treated Fe-bentonite.

3.2. BIPYRIDYL ADSORPTION ON SMECTITES

The intercalation of 2,2'-bipyridyl within smectite group clay minerals has been shown by X-ray diffraction to result in an increase in the interlayer spacings, as mentioned previously.
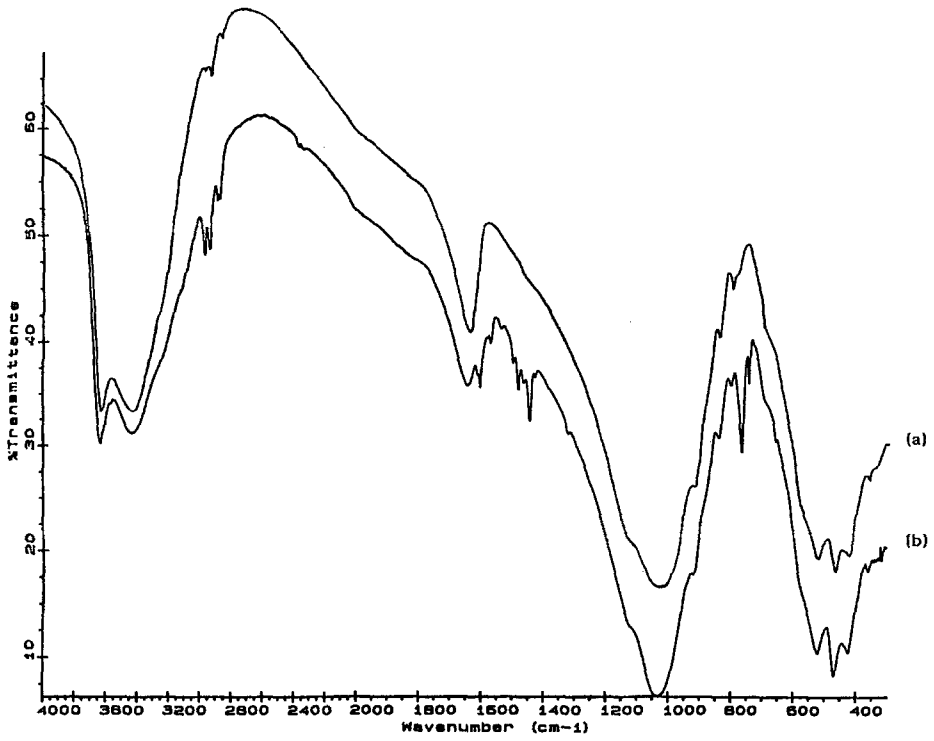
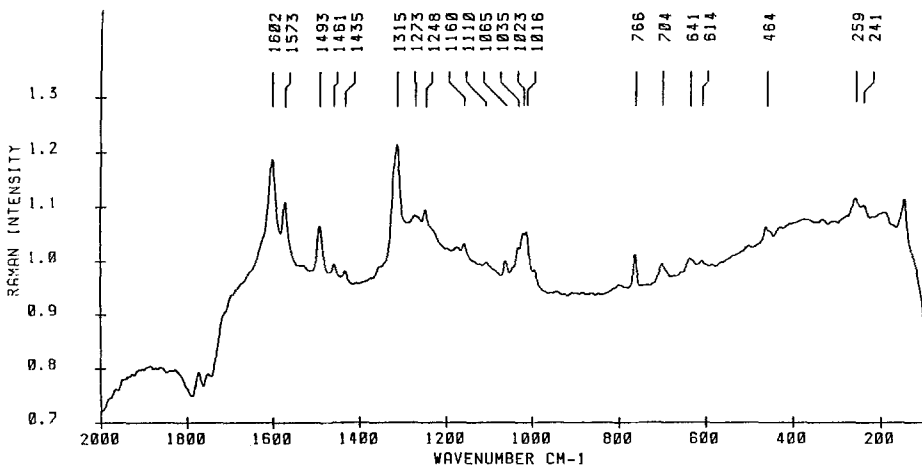Fig. 5.   Infrared spectra of (a) saponite and (b) 2,2′-bipyridyl treated saponite.

Fig. 6.   Raman spectrum of 2,2′-bipyridyl treated Fe-bentonite.
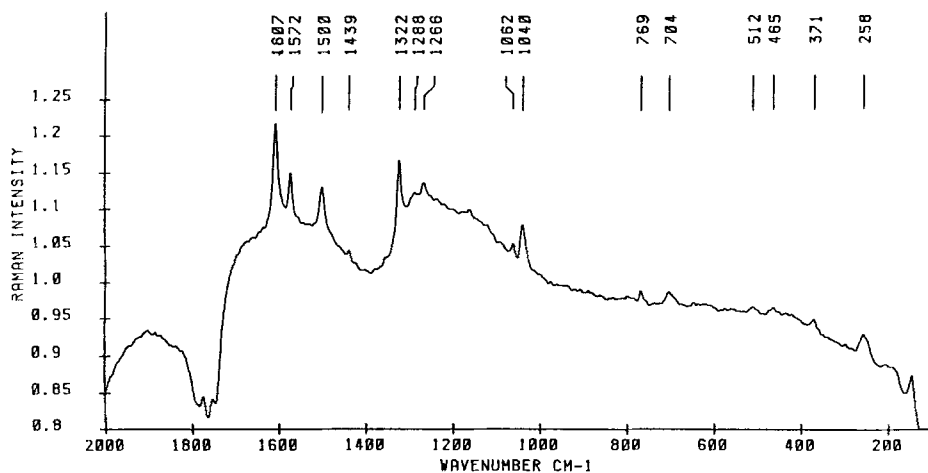
Fig. 7.   Raman spectrum of 2,2'-bipyridyl treated Cu-bentonite.
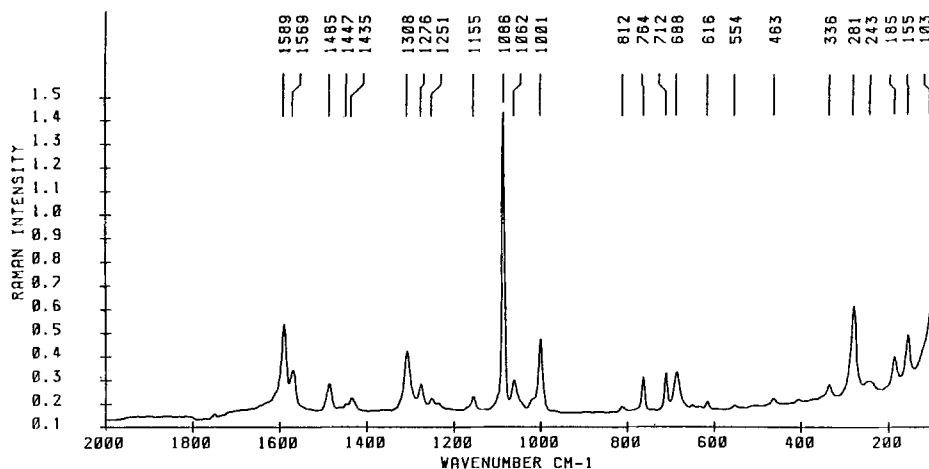

Fig. 8.   Raman spectrum of 2,2'-bipyridyl treated hectorite.

The vibrational bands of bipyridyl adsorbed on the smectite group clay minerals studied are given in Table II together with those of Co(2,2'-bipy)$_3$ Cl$_2$ and our values for the free molecule. The IR spectra of bipyridyl treated Fe-bentonite and saponite are shown in Figures 4 and 5 as examples of smectites and the FT-Raman spectra of bipyridyl treated Fe and Cu-bentonite, and hectorite are given in Figures 6–8.

The vibrational wavenumbers of bipyridyl adsorbed on the smectite group clays are found to be closer to those of the tris-complexes of 2,2'-bipyridyl [18], than the free molecule, similar to the results obtained for fibrous clays. The generation of the 2,2'-bipyridyl anion on ion-exchanged clays is found to be much less than on

natural clays (natural bentonite, hectorite and saponite), indicating that in the case of ion-exchanged clays, the adsorbed bipyridyl molecules have a distinct tendency to form chelates with transition metal ions, rather than being in interaction with silicate layers.

In the case of smectite group clays, although we observe some splittings in the coordination sensitive modes of adsorbed bipyridyl, none of the components are found close to those of the free molecule. Therefore these splittings must occur due to the coordination of bipyridyl to different strength cations.

4. Conclusions

The combination of the IR and Raman spectroscopic study with XRD analysis can contribute to the better understanding of the structure and behaviour of clay-organic complexes. The use of an FT-Raman spectrometer enables the Raman spectra of the clay samples to be obtained which are found to be very informative to monitor the surface species formed on clays.

The vibrational spectroscopic study of 2,2'-bipyridyl treated clays studied indicated that two different types of surface species are generated: chemisorbed neutral molecules and chemisorbed monoanions. The concentration of organic anions is found to be very small in comparison to the coordinated molecules. 2,2'-Bipyridyl molecules adsorbed on attapulgite are coordinated to Lewis acidic centers, whereas on sepiolite both coordination to Lewis acidic centers and H-bond formation to surface hydroxyls through both nitrogen lone pairs are monitored. The bipyridyl molecules intercalated into smectite type clay minerals are found to form tris-bipyridyl complexes with exchangeable cations. As the spectroscopic results indicate that *both* rings of bipyridyl are affected bidentate coordination is proposed for all chemisorbed species.

Acknowledgements

References

1. B.K.G. Theng: *The Chemistry of Clay-Organic Reactions*, Adam Hilger, London (1974).
2. S.M.F. Traynor, M.M. Mortland, and T.J. Pinnavia: *Clays Clay Minerals* **26**, 318 (1978).
3. A. Yamagishi: *J. Coord. Chem.* **16**, 131 (1987).
4. M. Ogawa, T. Hashizume, K. Kuroda, and C. Kato: *Inorg. Chem.* **30**, 584 (1991).
5. F.J. Berry, M.H.B. Hayes, and S.L. Jones: *Inorg. Chim. Acta* **178**, 203 (1990).
6. R. Greene-Kelly: *Trans. Faraday Soc.*, 412 (1955).
7. R. Chester and H. Elderfield: *Chem. Geol.* **7**, 97 (1971).
8. E.A. Ferreiro, S.G. De Bussetti, and A.K. Helmy: *Z. Pfanzenernaehr. Bodenkd.* **146**, 369 (1983). *Chem. Abstr.* **99**, 44008g (1983).

9. S. Coluccia, A.C. Guglielminotti, and C. Morterra: *J. Chem. Soc. Faraday Trans.* **75**, 2188 (1979).
10. K. Brauner and A. Preisinger: *Tschermaks Min. Petr. Mitt.* **6**, 120 (1956).
11. W.F. Bradley: *Am. Mineral.* **25**, 405 (1940).
12. J.M. Serratosa: *Proceedings of International Clay Conference*, 1978, (eds. M.M. Mortland and V.C. Farmer), p. 99, Elsevier, Amsterdam (1979).
13. S. Akyüz, T. Akyüz, and J.E.D. Davies: *J. Incl. Phenom.* **15**, 105 (1993).
14. B. van Olphen and J.J. Fripiat (Eds.): *Data Handbook for Clay Materials and Other Non-Metallic Minerals*, Pergamon Press, N.Y. (1979).
15. R.M. Berger and D.R. McMillin: *Inorg. Chim. Acta* **177**, 65 (1990).
16. L.L. Merrit and E.D. Schroeder: *Acta Crystallogr.* **9**, 1982 (1956).
17. N. Neto, M.M. Miranda, L. Angeloni, and E. Castellucci: *Spectrochim. Acta* **39A**, 97 (1983).
18. R.G. Inskeep: *J. Inorg. Nucl. Chem.* **24**, 763 (1962).
19. L. Arnaudet, R. Bougon, B. Ban, P. Charpin, J. Isabey, M. Lance, M. Nierlich, and J. Vigner: *Can. J. Chem.* **68**, 507 (1990).
20. P.K. Mallick, G.D. Danzer, D.P. Strommen, and J.R. Kincaid: *J. Phys. Chem.* **92**, 5628 (1988).
21. E. Koning and E. Lindner: *Spectrochim. Acta* **28A**, 1393 (1972).
22. C. Serna, G.E. Van Scoyoc, and J.L. Ahrichs: *Am. Mineral.* **62**, 784 (1977).
23. S. Akyüz, A.B. Dempster, R.L. Morehouse, and S. Suzuki: *J. Mol. Struct.* **17**, 105 (1973).
24. S. Suzuki and W.J. Orville-Thomas: *J. Mol. Struct.* **37**, 321 (1977).
25. S. Akyüz, T. Akyüz, and J.E.D. Davies: *J. Mol. Struct.* **265**, 85 (1992).
26. M. Kim and K. Itoh: *J. Phys. Chem.* **91**, 126 (1987).