A Vibrational Spectroscopic Study of the Adsorption of 4,4′-Bipyridyl by Sepiolite and Smectite Group Clay Minerals from Anatolia (Turkey)

SEVIM AKYÜZ*
Department of Physics, Faculty of Science, Istanbul University, Vezneciler, 34459 Istanbul, Turkey

TANIL AKYÜZ
*Turkish Atomic Energy Agency, Cekmece Nuclear Research & Training Centre,
PO Box 1, Havalimani, Istanbul, Turkey*

and

J. ERIC D. DAVIES
Lancaster University, Environmental Science Division, Lancaster, LA1 4YQ, U.K.

Abstract. The adsorption of 4, 4′-bipyridyl by natural sepiolite and smectite group clay minerals (bentonite, hectorite and saponite) from Anatolia (Turkey) has been studied using vibrational spectroscopy. Investigation of Fourier-transform infrared and Fourier-transform Raman spectra of adsorbed 4, 4′-bipyridyl indicate the presence of chemisorbed species. However, any evidence for the generation of anionic species on the surface of the phyllosilicates has not been detected. It is proposed that the adsorbed bipyridyl molecules on sepiolite are centrosymmetric and H-bonded to the surface hydroxyls through both the nitrogen lone pairs as bidentate ligands. The adsorbed bipyridyl molecules on the smectite group clays are coordinated to exchangeable cations both directly and also indirectly through water as monodentate ligands. XRD patterns of the clays studied are also recorded.

Key words: FT-IR spectroscopy, FT-Raman spectroscopy, clays, sepiolite, bentonite, hectorite, saponite, 4, 4′-bipyridyl, adsorption, XRD.

1. Introduction

Phyllosilicates such as smectites and sepiolites have been widely used as catalysts for oxidation and/or polymerization reactions of aromatic molecules [1–5]. They have the ability to sorb selectively both polar and nonpolar organic molecules [3, 6–11].

Sepiolite has a fibrous structure consisting of talc-like ribbons parallel to the fibre axis [12]. Structurally, it consists of blocks and channels extending in the *c*-axis direction (Figure 1). Serratoza [1] has classified the active sorption centres of sepiolite as follows: (1) oxygen ions (which behave as weak electron donors), on
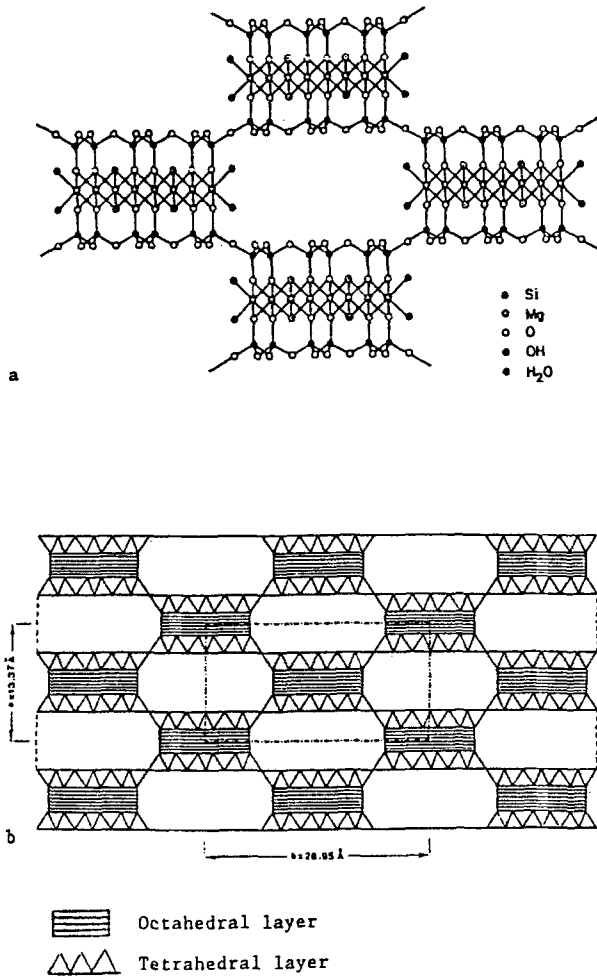
---

* Author for correspondence.

Fig. 1. (a) [100] projection of the sepiolite structure according to Brauner and Preisinger [12]. (b)
Outlines of the blocks and channels of the sepiolite structure. Dotted lines indicate the unit cell ($a =$
13.37 Å; $b = 26.95$ Å).

the tetrahedral sheet of the ribbons; (2) water molecules coordinated to magnesium
ions, at the edges of structural ribbons; (3) SiOH groups; the broken Si–O–Si
bonds of the terminal silica tetrahedra on the ribbons at the external surfaces
compensate their residual charge by accepting a proton or hydroxyl and form Si–
OH groups. These Si–OH groups react directly with organic reagents [3, 4] and
form true covalent bonds. In our previous study, the oxidative property of sepiolite
in reaction with N, N-dimethylaniline was reported [13].

Bentonite is a dioctahedral smectite group clay mineral, whilst saponite and

hectorite are trioctahedral minerals. They are well known as a major class of molecular sieves and to react with aromatic molecules forming radical ions [5, 6, 14–16].

Adsorption of 4, 4'-bipyridyl on MgO has been previously studied using IR spectroscopy and the formation of the bipyridyl radical anion together with neutral surface species were reported [17]. In this study we have investigated FT-IR and FT-Raman spectra of 4, 4'-bipyridyl adsorbed on natural sepiolite, bentonite, hectorite and saponite samples from Anatolia (Turkey). It is interesting to compare both IR and Raman results since the molecule is highly symmetric. It has however been difficult to obtain Raman spectra from clay samples using visible excitation sources due to problems with background fluorescence. The advent of FT-Raman spectrometers using near-IR excitation has now largely overcome this problem. Vibrational spectroscopic analysis therefore sheds much light on the orientation of the two phenyl rings of the adsorbed molecule and also on its coordination state (i.e. mono- or bidentate), if it acts as a ligand.

2. Experimental

Natural sepiolite and saponite were obtained from Mihalliccik–Eskisehir, bentonite and hectorite were obtained from the Küçükhacibey–Çankiri and Çankiri regions of Anatolia (Turkey), respectively. The samples were first identified by X-ray diffraction, differential thermal and IR spectroscopic analyses. Some calcite impurity was detected in the hectorite sample. Chemical analyses of the samples were carried out on a GE SPG-7 X-ray fluorescence spectrometer, a Jarrell Ash optical emission spectrograph or using conventional wet analytical methods for some elements. The results are summarized in Table I.

4, 4'-Bipyridyl treated samples were prepared by immersing air-dried clays in a benzene solution of 4, 4'-bipyridyl (B.D.H.) in sealed bottles, at room temperature, for two days. They were then filtered and washed several times with benzene and dried. During the course of this study it was found that 4, 4'-bipyridyl molecules can also be intercalated in the clays by solid–solid exchange reactions analogous to the solid–solid reaction between 2, 2'-bipyridyl and Co-montmorillonite [6].

The FT-IR spectra of KBr discs were recorded on a Nicolet 510 spectrometer. The FT-Raman spectra of the samples 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.

X-ray powder diffraction patterns of the samples were recorded on a Jeol JDX 19C diffractometer.

TABLE I

Chemical analyses of the clays (wt. %).

Sample	Sepiolite	Bentonite	Hectorite	Saponite
SiO_2	58.0	58.0	37.7	57.9
MgO	25.5	2.5	15.3	8.0
Al_2O_3	0.5	17.0	0.7	15.4
K_2O	0.5	0.6	0.15	1.5
CaO	0.5	1.0	23.4	2.2
$\sum (FeO + Fe_2O_3)$	0.05	5.0	0.5	6.3
TiO_2	0.05	0.6	0.05	0.5
Na_2O	0.05	1.1	1.3	0.1
MnO	n.d.[a]	0.01	0.01	0.1
P_2O_5	n.d.	0.1	0.01	0.1
Ni	0.1	0.01	n.d.	n.d.
Cu	n.d.	0.002	n.d.	n.d.
LOI[b]	14.5	14.2	21.0	8.0
	99.75	100.12	100.12	100.1

[a] Not detected.

[b] Loss on ignition.

3. Results and Discussion

In contrast to the colouration of MgO on adsorption of $4, 4'$-bipyridyl [17], the colours of the natural sepiolite and smectite samples did not alter on adsorption of $4, 4'$-bipyridyl. In order to characterize the species formed upon adsorption an attempt was made to compare the vibrational wavenumbers of adsorbed $4, 4'$-bipyridyl to those of the free molecule, the coordinated molecule and the bipyridyl radical anion. However, very few IR data have been reported on $4, 4'$-bipyridyl [18–20] and its complexes [20–22], no complete Raman spectral assignment has so far been reported on $4, 4'$-bipyridyl, although its Raman spectrum has been published [19], and the only available vibrational data for the $4, 4'$-bipyridyl radical anion reported up to now are its resonance Raman spectrum [19] and the IR spectrum of the radical anion formed on a MgO surface [17]. Therefore IR wavenumbers and assignments of crystalline $4, 4'$-bipyridyl [20], the $4, 4'$-bipyridyl radical anion generated on MgO [17] and the Cd $(4, 4'$-bipy)Ni(CN)$_4$ complex [20] are tabulated in Table II, together with the IR data obtained from $4, 4'$-bipyridyl treated sepiolite and smectite group clays. The Raman wavenumbers of bipyridyl adsorbed on the clays are given in Table III *without* a complete assignment. Our measurements on crystalline $4, 4'$-bipyridyl and on the Cd$(4, 4'$-bipy)Ni(CN)$_4$ complex [23], together with the resonance Raman spectrum of the $4, 4'$-bipy anion [19] are included for comparison.

TABLE II

Infrared spectral data (cm^{-1}) for 4,4'-bipyridyl in complexes and adsorbed on clays.

Symmetry and assignment [20]	4,4'-Bipy [20]	4,4'-Bipy⁻ on MgO [17]	Cd(4,4'-Bipy) Ni(CN)$_4$ [20]	4,4'-Bipy on sepiolite	4,4'-Bipy on bentonite	4,4'-Bipy on hectorite	4,4'-Bipy on saponite
ν_3; ν_{ring}, B_{3u}	1598vs	1580s	1605vs	1602vs	1603s	1602s	1603s
ν_{12}; ν_{ring}, B_{2u}	1532s	1500m	1534s	1539m	1536w	1535m	1536m
A_g	1514*	–	–	–	1517vw	1517sh	1517w
ν_4; ν_{ring}, B_{3u}	1481s	1470s	1488m	1490w	1491w	1490w	1592m
ν_{13}; ν_{ring}, B_{2u}	1413s	1400–1440	1414s	1412s	1414m	1414m	1414s
ν_{14}; ν_{ring}, B_{2u}	1324s	1267m	1315m	1318vw	1320vw	1322vw	1320vw
ν_{15}; δ(CH), B_{2u}	1223s	1200ms	1219sh	1222m	**	1223vw	1221vw
ν_7; ν_{ring} + δ_{ring}, B_{3u}	967vw	956vs	976w	–	–	–	–
ν_{20}; γ(CH), B_{1u}	810vs		803vs	804s	804s	803s	806s
ν_{21}; γ_{ring}, B_{1u}	737s		729s	735m	733w	733w	732vw
ν_9; δ_{ring}, B_{3u}	615m		632vs	620s	620m	617m	620m
ν_{23}; γ_{ring}, B_{1u}	367s		386m	379sh	**	379sh	**

* Observed in the Raman spectrum.

** Overlapped with mineral framework vibrations.

vs = very strong; s = strong; m = medium; w = weak; vw = very weak; sh = shoulder.

TABLE III

Raman vibrational data (cm^{-1}) for 4,4'-bipyridyl in complexes and adsorbed on clays.

Symmetry species [19]	4,4'-Bipy [23]	4,4'-Bipy$^-$ (RRS) [19]	Cd(4,4'-Bipy) Ni(CN)$_4$ [23]	4,4'-Bipy on sepiolite	4,4'-Bipy on bentonite	4,4'-Bipy on hectorite	4,4'-Bipy on saponite
A_g	3056			3071	~3069	nm	nm
A_g	1617)s	1612s	1615vs	1610s	1620)	1620)	1615s
	1605)				1609)s	1609)s	
A_g	1514m	1509s	1518m	1512w	1516vw	1514vw	1516vw
A_g	1301vs	1350s	1295vs	1290vs	1292s	1295s	1292s
A_g	1230m	1230m	1230m	1221m	1237w	1233)	1236)
						1223)m	1221)m
B_{1g}	1076w		1085vw	1084w	~1085vw	*	1077w
A_g	-	1043vs	-	-	-	-	-
Ring breathing A_g	1000vs	990w	1022s	1014sh 1009s	1010m	1008s	1012s
B_{3g} or A_g	762m	742m	771m	764m	767w	765m	765m
B_{1g}	660m		663m	659m	660vw	659w	658m
	574w		567w	570vw	-	570vw	571vw
				382vw	-	380vw	382vw

nm = Not measured.

* Obscured by a mineral framework vibrational mode band.

3.1. BIPYRIDYL ADSORPTION ON SEPIOLITE

The IR and Raman spectra of $4, 4'$-bipyridyl treated sepiolite are illustrated in Figures 2 and 3, respectively. The examination of the vibrational data of bipyridyl treated sepiolite indicates that anionic surface species have not been generated. However the vibrational wavenumbers of the adsorbed molecule are found to exhibit all the characteristics of coordinated bipyridyl. For example, several modes of adsorbed $4, 4'$-bipyridyl have upward shifts, compared to those in the free molecule (see Tables II and III). Similar shifts are observed in pyridine [24] and $4, 4'$-bipyridyl complexes [20] and explained by the coupling with low frequency vibrations, particularly the metal–ligand (M–N) stretching frequency. In fact, the IR spectroscopic studies on the adsorption of pyridine [25], $2, 2'$-bipyridyl [26] and $4, 4'$-bipyridyl [17] on oxide surfaces showed that the ring breathing mode of the aromatic molecule around $990 \, cm^{-1}$, and the two ring stretching modes observed in the 1500–$1600 \, cm^{-1}$ region are very sensitive to the interaction with the adsorbing sites. They increase in frequency upon coordination of the lone pair on the nitrogen atom to Lewis acidic sides or upon formation of H-bonds through the nitrogen lone pair to surface OH groups. On the other hand, in addition to these vibrational modes, the IR active δ_{ring} (ν_9, B_{3u}) mode of $4, 4'$-bipyridyl, (corresponding to the ν_{10}, A_1 δ_{ring} mode of pyridine), is also found to be sensitive to the coordination of the molecule and shows an upward shift in frequency depending on the coordination strength [20].

The ring breathing mode out-of-phase component of $4, 4'$-bipyridyl is observed at $994 \, cm^{-1}$ in the IR spectrum of crystalline $4, 4'$-bipyridyl. It is unfortunately obscured by mineral framework vibrational modes [$\nu(Si - O)$] in the IR spectrum of the clay; however, its Raman active component (in-phase, A_g) has clearly been observed as a strong band at $1009 \, cm^{-1}$ with a shoulder at $1014 \, cm^{-1}$ in the Raman spectrum of $4, 4'$-bipyridyl treated sepiolite (Figure 3). This band is observed at $1000 \, cm^{-1}$ in the Raman spectrum of crystalline $4, 4'$-bipyridyl ($\Delta(\nu_{ads} - \nu_{cryst}) = 9$ and $14 \, cm^{-1}$) and at $1022 \, cm^{-1}$ ($\Delta = 22 \, cm^{-1}$) in the Raman spectrum of the Cd($4, 4'$-bipy)Ni(CN)$_4$ complex [20]. On the other hand, the coordination sensitive ring stretching and ring bending modes of $4, 4'$-bipyridyl are observed at 1602 (ν_3, ν_{ring}, B_{3u}), 1539 (ν_{12}, ν_{ring}, B_{2u}) and 620 (ν_9, δ_{ring}, B_{3u}) cm^{-1} in the IR spectrum of bipyridyl treated sepiolite, whereas the corresponding modes are observed at 1598, 1532 and $615 \, cm^{-1}$, respectively, in the IR spectrum of microcrystalline $4, 4'$-bipyridyl. Thus the vibrational wavenumbers of adsorbed bipyridyl are found to be closer to those of the coordinated molecule than those of the free molecule.

No coincidences were observed between the IR and Raman wavenumbers of adsorbed $4, 4'$-bipyridyl, indicating that is possesses a centre of symmetry. On the other hand, in contrast to the spectra of $4, 4'$-bipyridyl adsorbed on MgO [17], no splittings of some vibrational modes of the molecule in which one component was at a frequency similar to that of microcrystalline $4, 4'$-bipyridyl were observed.
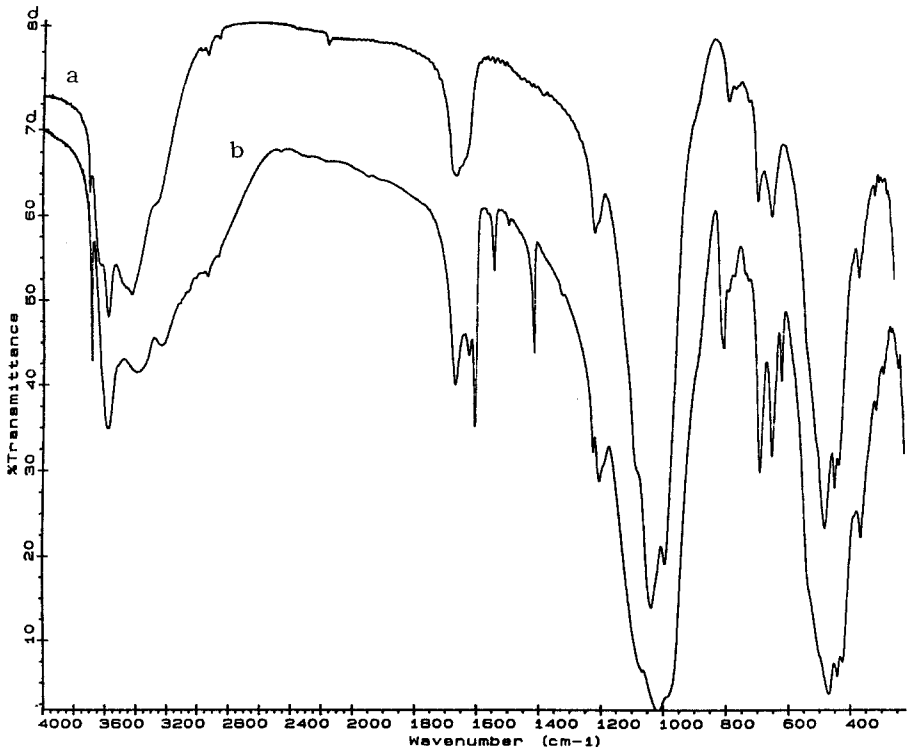
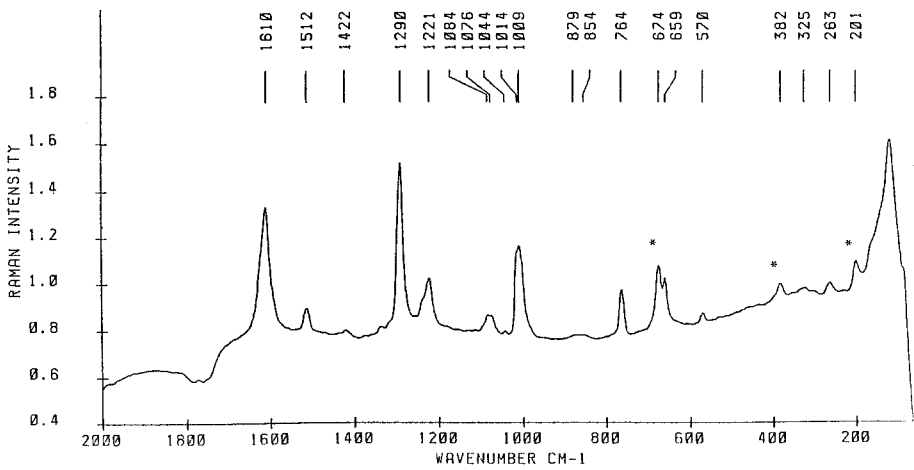Fig. 2.   FT-IR spectra of (a) natural (b) 4, 4′-bipyridyl treated sepiolite.

Fig. 3.   FT-Raman spectrum of 4, 4′-bipyridyl treated sepiolite. * Indicates bands arising from the sepiolite structure.

Therefore all the bipyridyl molecules adsorbed on sepiolite must be chemisorbed, no physical sorption species are detected. We propose that the adsorbed $4, 4'$-bipyridyl molecules are H-bonded to surface OH groups through the lone pairs of both nitrogens as bidentate ligands. Although nitrogen H-bonded pyridine exhibits weak interaction characteristics [25], both nitrogens of H-bonded bipyridyl may be expected to show a behaviour intermediate between the molecule strongly bonded to metal as a bidendate ligand (as in the case of the $Cd(bipy)Ni(CN)_4$ complex) and weakly bonded to surface hydroxyls through one nitrogen lone pair. The shoulder observed on the high wavenumber side of the ring breathing mode in-phase component in the Raman spectrum of bipyridyl treated sepiolite may be caused by coordination of surface hydroxyls with different strengths or by crystal field effects.

Bidentate coordination of $4, 4'$-bipyridyl to the Lewis acidic sides of sepiolite seems less possible to us when the interatomic distance of the $4, 4'$-bipyridyl molecule is compared with molecular dimensions of the idealized crystal structure of sepiolite (see Figure 1). On the other hand, it should be noted that adsorption of bipyridyl on sepiolite affects the hydroxyl group vibrations, which is further proof of a H-bonding interaction between bipyridyl and surface OH groups (Si–OH). The changes can be summarised as follows (Table IV and Figure 2): the shoulder observed at 3719 cm^{-1} in the IR spectrum of natural sepiolite, and ascribed to the OH stretching vibration of the Si–OH group in agreement with Ahlrichs *et al.* [27], disappears in the IR spectrum of $4, 4'$-bipyridyl treated sepiolite. In the latter case (in bipy treated sepiolite), the 3688 cm^{-1} band, ascribed to the OH stretching vibration of Mg_3OH in agreement with Ahlrichs *et al.* [23], increased in intensity and decreased in value. It is known that adsorption of polar and nonpolar molecules perturbs the stretching vibrations of Si–OH groups on the external surfaces and causes a shift to lower wavenumber [27]. If adsorbed bipyridyl molecules are H-bonded to surface Si–OH groups from both nitrogen ends, this will cause the OH stretching frequency of the Si–OH group to shift to lower value and may be overlapped by the OH stretching band of Mg_3OH groups, thus increasing its intensity. This is in agreement with the observed changes.

The XRD patterns of natural sepiolite and $4, 4'$-bipyridyl treated sepiolite are given in Figures 4a and 4b, respectively. Since sepiolite, in contrast to the smectites, is not an expandable clay the reflection peaks corresponding to the host structure are only slightly altered on adsorption of bipyridyl.

3.2. BIPYRIDYL ADSORPTION ON SMECTITES

The XRD patterns of the air dried natural clays, together with those of the $4, 4'$-bipyridyl treated clays are illustrated in Figure 4. The basal spacings of bipyridyl treated bentonite, hectorite and saponite are 15.0, 16.4 and 15.5 Å, respectively, compared with values of 12.4, 11.8 and 11.5 Å for the corresponding air-dried clays. These observations suggest that bipyridyl molecules intercalate into the interlayers

TABLE IV

OH group vibrations of natural and 4, 4'-bipyridyl treated sepi-
olite in the IR spectra.

Assignment [27]	Sepiolite	4, 4'-Bipyridyl treated sepiolite
ν(OH) SiOH	3719m,sh	–
ν(OH) Mg$_3$OH	3688s	3684vs
ν(OH) dioctahedral system	3636s	3626sh
ν(OH) coordinated water	3566vs	3584vs
ν(OH) zeolitic water	3407s,br	3395s,br
	3272sh	3243m,br

of smectites with a monolayer arrangement. The XRD diagrams of the bipyridyl
treated smectites also show a shoulder corresponding to the basal spacing of the
untreated clays at *ca.* 12 Å, indicating that the intercalated bipyridyl molecules do
not expand all the layers. A similar pattern is also observed in the XRD patterns
of 2, 2'-bipyridyl treated Co-montmorillonite when the amount of 2, 2'-bipyridyl
used in the preparation is not sufficient to fully occupy the interlayer space [6]. It
was not possible to increase the amount of 4, 4'-bipyridyl intercalated into these
natural smectites. Ion-exchanged clays, e.g. Sn- or Co-bentonite, have, however,
been found to adsorb much more bipyridyl than the natural ones.

The IR and Raman spectra of 4, 4'-bipyridyl treated bentonite, hectorite and
saponite are illustrated in Figures 5–8, respectively. Vibrational modes of the 4, 4'-
bipyridyl radical anion are not observed in any of the spectra. On the other hand, the
vibrational wavenumbers of bipyridyl adsorbed on these smectite group clays are
found to be closer to those of coordinated bipyridyl than those of the free molecule,
similar to the results obtained for sepiolite. However, it is worth mentioning three
major differences observed in the IR and Raman spectra of 4, 4'-bipyridyl adsorbed
on smectite group clay minerals as compared with the corresponding spectra of the
molecule adsorbed on sepiolite.

(a) The intensities of the 4, 4'-bipyridyl vibrational modes adsorbed on smec-
tites, particularly on bentonite, are found to be less than those when adsorbed on
sepiolite, indicating that the 4, 4'-bipyridyl adsorbing capacity of sepiolite is more
than that of natural smectites. As mentioned previously the ion-exchanged ben-
tonites adsorb more bipyridyl compared to the natural samples. This is in agreement
with the well known observation that the adorption capacity of clays depends on
the exchangeable cations [28].

(b) The vibrational bands of 4, 4'-bipyridyl adsorbed on smectites are found
to be rather broad and mostly asymmetric on the high wavenumber side. This
is particularly evident for the highest wavenumber bands. This is probably due to
coordination to exchangeable cations of the clays with different strengths. Bipyridyl
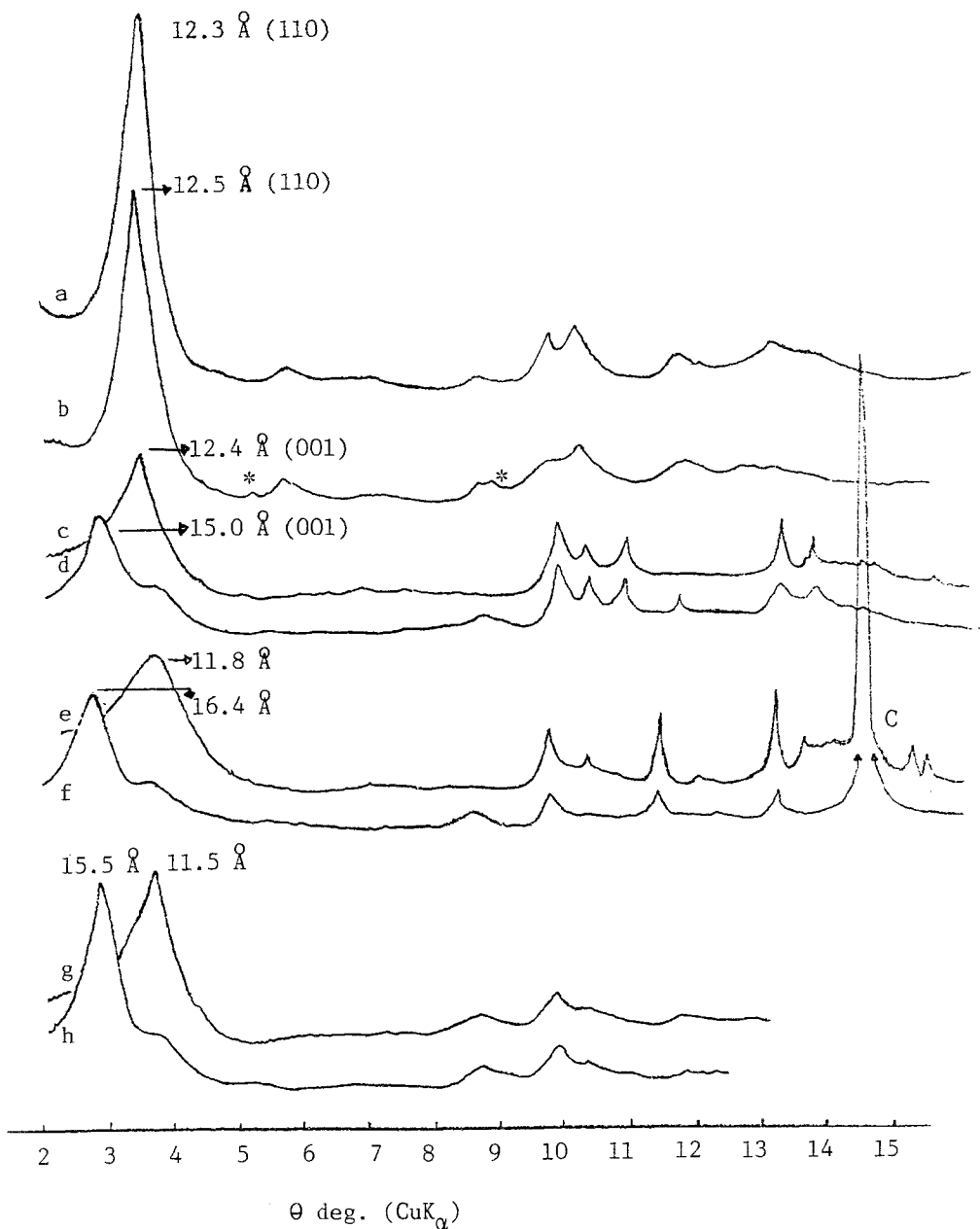
Fig. 4. XRD patterns of (a) natural sepiolite; (b) 4, 4'-bipy treated sepiolite. * Indicates 4, 4'-bipy reflection; (c) natural bentonite; (d) 4, 4'-bipy treated bentonite; (e) natural hectorite; (f) 4, 4'-bipy treated hectorite. C indicates a calcite reflection; (g) natural saponite; (h) 4, 4'-bipy treated saponite.
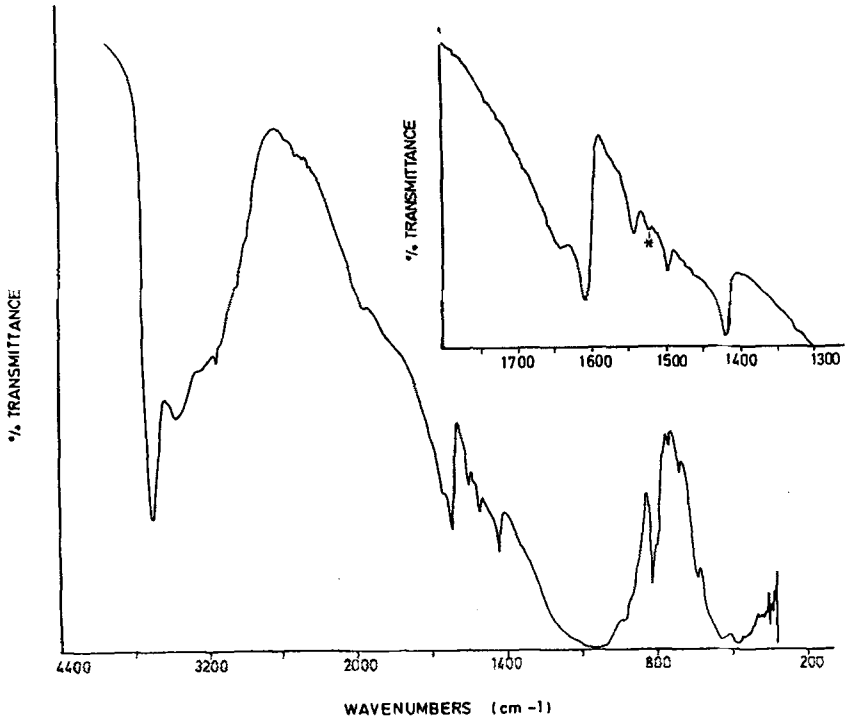
Fig. 5. FT-IR spectra of $4, 4'$-bipyridyl treated bentonite. The inset shows the 1800–1300 cm^{-1} region with the Raman active band (1517 cm^{-1}) marked*.
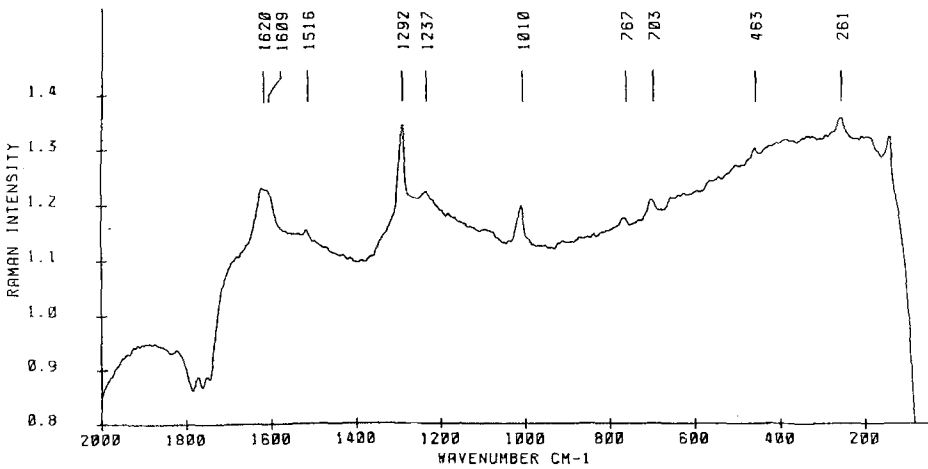

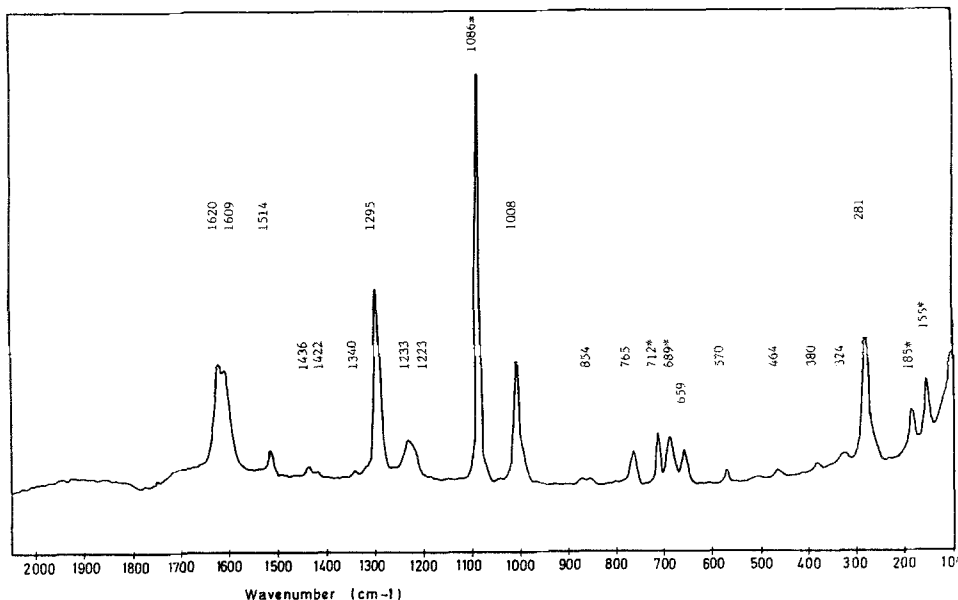Fig. 6. FT Raman spectrum of $4, 4'$-bipyridyl treated bentonite.

Fig. 7. FT-Raman spectrum of 4, 4'-bipyridyl treated hectorite. * Indicates bands arising from the hectorite structure.
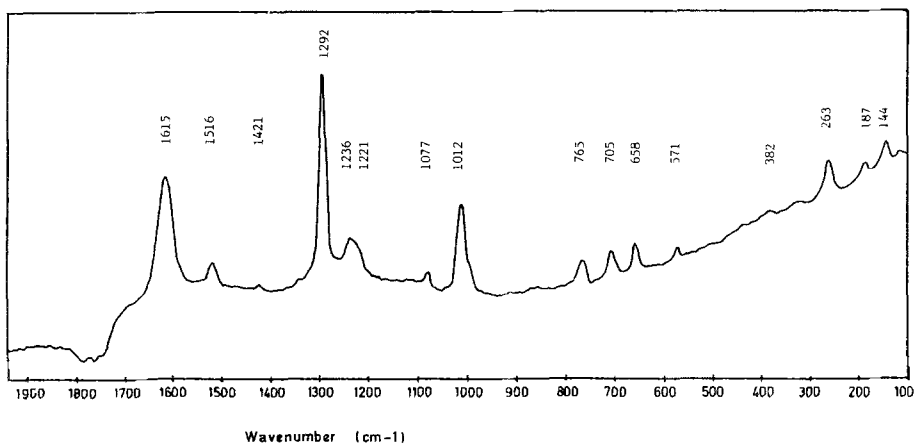

Fig. 8. FT-Raman spectrum of 4, 4'-bipyridyl treated saponite.

molecules may coordinate to exchangeable cations both directly and indirectly through water molecules.

(c) An additional band at $1517 \, \text{cm}^{-1}$ is observed in the IR spectrum of bipyridyl treated smectites (Figure 5), which is not present in the IR spectrum of bipyridyl treated sepiolite or in the IR spectrum of crystalline 4, 4'-bipyridyl. This band corresponds to the Raman active vibrational mode of 4, 4'-bipyridyl in D_{2h} symmetry, observed at $1514 \, \text{cm}^{-1}$ in the Raman spectrum of microcrystalline 4, 4'-bipyridyl

and at 1516–1512 cm^{-1} in the Raman spectra of bipyridyl treated smectites and sepiolite. The observation of at least one Raman active mode in the IR spectra of smectites indicates that the adsorbed molecule does not possess a centre of symmetry.

Parallel to the above spectral changes, bipyridyl adsorption results in severe peturbations of the OH group stretching bands. In all the smectite type clay minerals studied, adsorption of this molecule causes the creation of a broad adsorption band centred arounds 3200 cm^{-1}, clearly due to the increase in the H-bonding interaction of intercalated water molecules, probably with the adsorbed bipyridyl molecules. In the case of hectorite, the OH stretching band observed at 3676 cm^{-1} in the IR spectrum of the natural clay is increased both in intensity and frequency (3686 cm^{-1}) and a shoulder appears at 3710 cm^{-1}. The frequency increase in the OH stretching mode of the layers indicates the decrease of the H-bonding interaction of these groups with intercalated water molecules due to the adsorption of bipyridyl.

Based on these spectroscopic investigations, we propose that bipyridyl molecules adsorbed on bentonite, hectorite or saponite coordinate to the exchangeable cations of the natural clays both directly and indirectly through water molecules as monodentate ligands.

4. Conclusions

Both IR and Raman vibrational investigations of 4, 4'-bipyridyl adsorbed on natural sepiolite, bentonite, hectorite and saponite are found to be very informative in shedding light on the nature of the surface species formed on clays. The use of an FT-Raman spectrometer enables the Raman spectra of these samples to be obtained and in particular the spectra of the 4, 4'-bipyridyl molecule in the 950–1100 cm^{-1} region, a region which is obscured by the broad adsorption bands of the silicate framework in the IR spectra of silicates.

The vibrational analyses indicate that 4, 4'-bipyridyl molecules adsorbed on sepiolite are centro-symmetric and act as a bidentate ligand whereas 4, 4'-bipyridyl molecules adsorbed on natural smectites coordinate to exchangeable cations as a monodentate ligand. The most probable coordination of 4, 4'-bipyridyl adsorbed on sepiolite is proposed as the coordination to surface hydroxyls from the lone pairs of both nitrogens.

References

1. P. Cloos, A. Moreale, C. Broers, and C. Badot: *Clay Miner.* **14**, 307 (1979).
2. A. M. Habib, M. Y. El-Sheikh, A. B. Zaki, and S. E. Morsi: *J. Incl. Phenom.* **4**, 169 (1986).

3. J. M. Serratoza: *Proc. Intern. Clay Conf. 1978* (Eds. M. M. Mortland and V. C. Farmer) pp. 99–109, Elsevier (1979).
4. M. N. F. Hernandez and E. R. Hitzky: *Clay Miner.* **14**, 295 (1979).
5. S. Akyüz and T. Akyüz: *Doga TU J. Chem.* **11**, 2 (1987).
6. M. Ogawa, T. Hashizume, K. Kuroda, and C. Kato: *Inorg. Chem.* **30**, 584 (1991).
7. R. M. Barrer, N. Mackenzie, and D. M. MacLead: *J. Phys. Chem.* **58**, 568 (1954).
8. R. M. Barrer and D. M. MacLead: *Trans. Faraday Soc.* **50**, 980 (1954).
9. V. C. Farmer and M. H. Mortland: *J. Chem. Soc. (A)*, 344 (1966).
10. R. M. Barrer: *J. Incl. Phenom.* **4**, 109 (1986).
11. B. L. Sawhney and M. P. N. Gent: *Clays Clay Miner.* **38**, 14 (1990).
12. K. Brauner and A. Preisinger: *Tschermaks Mineralog. Petrog. Mitt.* **6**, 120 (1956). *Chem. Abst.* **50**, 12767g.
13. S. Akyüz and T. Akyüz: *J. Incl. Phenom.* **5**, 259 (1987).
14. Y. Matsunaga: *Bull. Chem. Soc. Jpn.* **45**, 770 (1972).
15. H. E. Donor and M. M. Mortland: *Science* **166**, 1406 (1969).
16. S. M. F. Traynor, M. M. Mortland, and T. J. Pinnavaia: *Clays Clay Miner.* **26**, 318 (1978).
17. S. Coluccia, E. Garrone, and C. Morterra: *Z. Phys. Chem. Neue Folge* **124**, 201 (1981).
18. V. P. Gupta: *Indian J. Pure Appl. Phys.* **11**, 775 (1973).
19. H. Kihara and Y. Gondo: *J. Raman Spectrosc.* **17**, 263 (1986).
20. A. Sungur, S. Akyüz, and J. E. D. Davies: *J. Incl. Phenom.* **5**, 491 (1987).
21. S. Farquharson, P. A. Lay, and H. J. Weaver: *Spectrochim. Acta* **40A**, 907 (1984).
22. I. S. Ahuga, R. Singh, and C. P. Rai: *J. Inorg. Nucl. Chem.* **40**, 924 (1978).
23. S. Akyüz, J. E. D. Davies, and T. Akyüz: unpublished results.
24. S. Akyüz, A. B. Dempster, R. L. Morehouse, and S. Suzuki: *J. Mol. Struct.* **17**, 105 (1973).
25. C. Morterra, G. Ghiotti, F. Baccuzzi, and S. Coluccia: *J. Catal.* **51**, 299 (1978).
26. S. Coluccia, A. Chiorino, E. Guglielminotti, and C. Morterra: *J. Chem. Soc. Faraday Trans. 1* **75**, 2188 (1979).
27. J. L. Ahlrichs, C. Serna, and J. H. Serratoza: *Clays Clay Miner.* **23**, 119 (1975).
28. B. K. G. Theng: *The Chemistry of Clay-Organic Reactions*, Wiley, New York (1974).