

# THERMO-INFRARED-SPECTROSCOPY ANALYSIS OF DIMETHYL-SULFOXIDE-KAOLINITE INTERCALATION COMPLEXES

S. Yariv\* and I. Lapidés

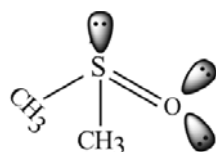
Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Dimethylsulfoxide (DMSO) kaolinite complexes of low- and high-defect kaolinites were studied by thermo-IR-spectroscopy analysis. Samples were gradually heated up to 170°C, three hours at each temperature. After cooling to room temperature, they were pressed into KBr disks and their spectra were recorded. From the spectra two types of complexes were identified. In the spectrum of type I complex two bands were attributed to asymmetric and symmetric H–O–H stretching vibrations of intercalated water, bridging between DMSO and the clay-O-planes. As a result of H-bonds between intercalated water molecules and the O-planes, Si–O vibrations of the clay framework were perturbed, in the low-defect kaolinite more than in the high-defect. Type II complex was obtained by the thermal escape of the intercalated water. Consequently, the H–O–H bands were absent from the spectrum of type II complex and the Si–O bands were not perturbed. Type I complex was present up to 120°C whereas type II between 130 and 150°C. The presence of intercalated DMSO was proved from the appearance of methyl bands. These bands decreased with temperature due to the thermal evolution of DMSO but disappeared only in spectra of samples heated at 160°C. Intercalated DMSO was H-bonded to the inner-surface hydroxyls and vibrations associated with this group were perturbed. Due to the thermal evolution of DMSO the intensities of the perturbed bands decreased with the temperature. They disappeared at 160°C together with the methyl bands.

**Keywords:** dimethylsulfoxide (DMSO), H-bonds, kaolinite, infrared spectra, inner-surface hydroxyls, intercalation complexes, O-planes, perturbation

## Introduction

The intercalation of dimethylsulfoxide (DMSO, Scheme 1) into kaolinite has been widely studied. Several investigators showed that small amounts of water are essential for this intercalation (e.g. [1]). In spite of the fact that the resulting complex forms an ordered structure [2, 3], the contribution of water is not clear. Franco Duro *et al.* [4] and Franco *et al.* [5] studied by IR spectroscopy the hydrazine-kaolinite and hydrazine–dickite complexes and showed differences due to the presence or absence of water. Kristóf *et al.* [6] and Horváth *et al.* [7] studied by controlled rate thermal analysis the hydrazine–kaolinite and hydrazine–halloysite complexes and showed that the intercalated organic compound was hydrated. Hydrazine-hydrate was evolved from kaolinite in a temperature range between 50 and 85°C whereas molecular hydrazine was evolved between 85 and 130°C.



Scheme 1 Dimethylsulfoxide (DMSO)

Costanzo and Giese [8] related the enhanced ability of halloysite to form intercalates to the presence of residual interlayer water molecules even if the mineral appeared to be almost dehydrated. They synthesized a 0.84 nm hydrated kaolinite in which water molecules keyed into the ditrigonal holes in the O-planes. In comparison with untreated kaolinite, this hydrated clay intercalated more easily and with a greater number and variety of organic compounds [9]. Kristóf *et al.* [10] studied the thermal behavior of DMSO-kaolinite complex by TG-DTA-EGA and TG-MS. Evolution of DMSO occurred in two steps, at 117 and 173°C. Most of the water was lost up to 80°C during the first step of decomposition but some water was released at 173°C. From the thermal evolution patterns of DMSO they suggested that the guest molecules were bonded at least in two different ways in the interlayer space.

Recently DMSO-kaolinite complexes of low- and high-defect Georgia kaolinite (KGa-1 and KGa-2, respectively) were studied by thermo-XRD-analysis in our laboratory [11]. X-ray powder diffraction (XRD) results showed intercalation complexes of DMSO in both kaolinites with a  $d(001)$ -value of 1.11 nm (type I complex). The samples were gradually heated up to 170°C and diffracted by X-ray at room-temperature. With the rise in temperature,

\* Author for correspondence: yariv@vms.huji.ac.il

due to the thermal evolution of the guest molecules, the relative intensity of the 1.11 nm peak decreased and that of the 0.72 nm peak (neat kaolinite) increased indicating that the fraction of the non-intercalated tactoids increased. The 1.11 nm peak disappeared at 130°C. During the thermal treatment of DMSO-KGa-1 and DMSO-KGa-2 complexes an additional peak appeared at 110 and 120°C, respectively, indicating the formation of a new phase (type II complex). The  $d(001)$ -value of this peak decreased with the rise in temperature from 0.94 to 0.79 nm and from 0.86 to 0.81 in the diffractograms of DMSO-KGa-1 and DMSO-KGa-2 complexes, respectively. The intensity of this peak increased with temperature up to 130°C. With further heating it decreased and disappeared at 160°C. At higher temperatures only the 0.72 nm peak was recorded, indicating the complete escape of DMSO.

Based on the thermal analysis of Kristóf *et al.* [10] we hypothesized that a complex of type II was obtained by the escape of water from type I complex. Thermo-IR-spectroscopy seems to be a reliable tool for proving this hypothesis. IR spectroscopy was previously used by several investigators to study the fine-structure of type I complex (e.g. [2, 3, 12–14]). However, most attention was given to changes in O–H stretching vibrations of the clay hydroxyls. These studies showed that the inner-surface-OH group was involved in the complex formation by donating protons and forming H-bonds with the S=O group of the DMSO. In the present study we used thermo-IR-spectroscopy analysis to obtain the IR spectrum of type II complex and to get some information about its fine-structure. We also studied the effect of intercalation on the Si–O vibrations to get information about the involvement of the clay-O-plane in the structures of both complex types.

## Experimental

### Materials

Low- and high-defect Georgia kaolinite (KGa-1 and KGa-2, previously referred to as well- and poorly-crystallized, respectively), supplied by the Source Clay Minerals repository (The Clay Minerals Society), were gently ground to 80 mesh. Chemical pure DMSO supplied by Merck, Germany, was used without further purification.

### Preparation of DMSO-Kaolinite intercalation complexes [12]

The complexes were prepared as follows: 5 g of kaolinite (KGa-1 or KGa-2) was stirred for one week

in a closed bottle containing 150 mL of DMSO and 50 mL of H<sub>2</sub>O. The suspension was centrifuged. The separated slurry was aged at 70°C for another week and dried in air. X-ray diffraction results of both kaolinites showed an intercalation complex of DMSO with a  $d(001)$ -value of 1.11 nm, similar to that obtained by Olejnik *et al.* [13]. The intensities of the 1.11 and 0.72 nm peaks (intercalated and neat kaolinite, respectively) showed that the intercalation of KGa-1 was nearly complete whereas that of KGa-2 was smaller.

### Thermo-IR-spectroscopy-analysis [15]

The DMSO intercalated kaolinites were gradually heated as powders at 110–170°C, three hours at each temperature, and were then kept in a desiccator at room temperature. KBr disks (2 mg sample in 200 mg KBr) of the untreated and of the thermal treated samples were prepared and their IR spectra were recorded. FTIR spectra were recorded by Bruker FTIR spectrometer (model Tensor 27) at room temperature. Some absorption bands were analyzed by curve-fitting calculations.

## Results and discussion

The expansion of the basal spacing as determined by XRD [2, 3, 11, 13], proves that DMSO molecules intercalated into newly formed interlayer spaces. The adsorption of DMSO by KGa-1 was higher than by KGa-2 and consequently perturbations of the kaolinite vibrations are more significant in the spectra of the former. Locations in  $\text{cm}^{-1}$  of the different bands in the IR spectra of KBr disks of neat KGa-1 and KGa-2, heated at 170°C, assignments according to Farmer and Russell [16], symbols labeled by Miller and Oulton [17, 18] and Yariv *et al.* [19] and relative intensities are depicted in Tables 1 and 2. Locations of these bands and their relative intensities in the DMSO-kaolinite spectra, before and after thermal treatments (three hours at each temperature) are also given in the Tables. Some representative spectra are shown in Figs 1 and 2.

### Spectra in the region 3800–3000 $\text{cm}^{-1}$

After the adsorption of DMSO by KGa-1 or KGa-2 the absorbance of band A (OH stretching vibration of inner-surface hydroxyls), located at 3695  $\text{cm}^{-1}$  in the spectrum of neat kaolinite, is considerably reduced, very much in KGa-1 and to a smaller extent in KGa-2, accompanied by the appearance of a new band at 3663  $\text{cm}^{-1}$ , ascribed as a perturbed band A [3, 13, 19, 20] and labeled here by A'. The perturba-

**Table 1** Locations (in  $\text{cm}^{-1}$ ), assignments, symbols and relative intensities of absorption bands in the IR spectra of KBr disks of neat KGa-1, heated at 170°C, and of DMSO-KGa-1 complex gradually heated to 170°C

Symbol [17, 18, 19]	Assignment [16]	KGa-1		DMSO-KGa-1 intercalation complex				
		Thermal treatments/°C						
		170°C/3 h	Before thermal treatment	110°C/3 h	120°C/3 h	130°C/3 h	140°C/3 h	170°C/ 3h
A	OH str.	3694 vs	3694 vw	3700 w	3699 m	3698 s	3697 vs	3695 vs
B	OH str.	3670 vw	–	–	–	3670 sh	–	3672 vw
A'	Per. OH str.	–	3663 vs	3662 s	3659 m	3657 m	3656 m	–
C	OH str.	3653 w	–	–	–	3650 sh	3652 sh	3653 w
D	OH str.	3620 s	3621 s	3621 s	3622 s	3621 s	3621 s	3621 s
	intercalated water	–	3538 s	3536 m	3533 w	–	–	–
	intercalated water	–	3503 m	3500 w	3497 vw	–	–	–
E'	Per. Si–O str.	–	1122 w	1122 wsh	1122 vw	–	–	–
E	Si–O str.	1114 w	–	1114 wsh	1113 wsh	1113 w	1113 w	1114 w
P	Si–O str.	1098 m	1097 m	1097 m	1098 m	1097 m	1098 m	1097 m
F'	Per. Si–O str.	–	1038 vs	1038s	1038 wsh	–	–	–
F	Si–O str.	1033 vs	–	1031 s	1031 vs	1033 vs	1033 vs	1034 vs
G'	Per. Si–O str.	–	1018 s	1018 s	1018 sh	–	–	–
G	Si–O str.	1010 s	–	–	1010 s	1010 s	1010 s	1010 s
H'	Per. AlO–H def.	–	958 vw	958 vw	958 vvw	958 vvw	958 vv	–
H	AlO–H def.	937 w	937 vvw	937 sh	937 sh	937 w	937 w	937 w
I	AlO–H def.	914 m	–	912 w	913 m	913 m	913 m	914 m
I'	Per. AlO–H def.	–	905 w	–	–	–	–	–
J		791 vw	790 vw	790 vw	790 vw	790 vw	790 vw	791 vw
K		754 vw	742 vw	749 vw	752 vw	752 vw	753 vw	754 vw
L		695 w	685 w	688 w	691 w	691 w	693 w	694 w
M'	Per. Al–O def.	–	551 m	552 m	552 sh	552 wsh	552 vwsh	–
M	Al–O def.	540 m	–	538 m	538 m	539	539 m	540 m
N	Si–O def.	471 m	–	–	–	471 m	471 m	471 m
N'	Per. Si–O def.	–	465 m	468 m	470 m	–	–	–
O'	Per. Si–O def.	–	435 w	434 w	433 w	–	–	–
O	Si–O def.	431 w	–	–	–	432 w	432 w	431 w

Per.: perturbed band; str.: stretching vibration; def.: deformation vibration; v: very; s: strong, m: medium; w: weak; sh: shoulder

tion of band A implies that the inner-surface hydroxyls interact with the guest molecules. In this interaction the inner-surface OH groups donate protons to oxygens of the S=O groups of the intercalated DMSO. A three-dimensional structure determination showed that the DMSO molecules are triply H-bonded and are situated above vacancies in the octahedral sheets of the kaolinite [2, 3]. The very weak band B is not detected in the spectra of both kaolinite complexes. Weak band C is detected as a shoulder in the spectrum of DMSO-KGa-2 but not in that of DMSO-KGa-1. These two bands are also

attributed to inner-surface hydroxyls and their diminution is probably associated with this interaction. Inner hydroxyls are not expected to react with the intercalated molecules and consequently band D is not expected to be perturbed. Ratio of absorbance of band A relative to that of band D in the spectra of natural KGa-1 and KGa-2, before any thermal treatment are 1.4 in both clays. This ratio drops to 0.4 and 0.8 in the spectra of DMSO treated KGa-1 and KGa-2, in agreement with their high and low adsorptions of DMSO, respectively.

**Table 2** Locations (in  $\text{cm}^{-1}$ ), assignments, symbols and relative intensities of absorption bands in the IR spectra of KBr disks of neat KGa-2, heated at  $170^\circ\text{C}$ , and of DMSO-KGa-2 complex gradually heated to  $170^\circ\text{C}$ 

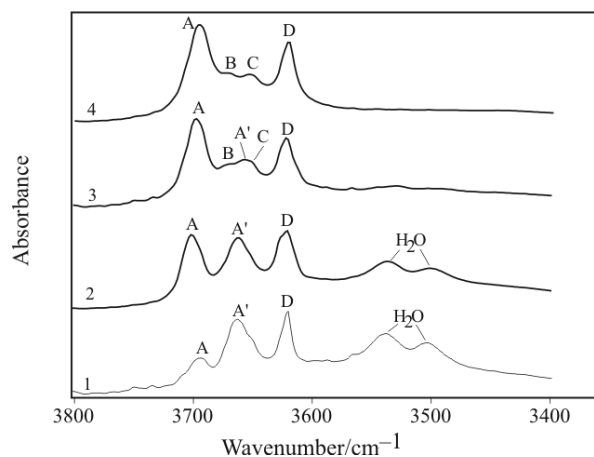
Symbol [17–19]	Assignment [16]	DMSO–KGa-2 intercalation complex						
		KGa-2		Thermal treatments/ $^\circ\text{C}$				
		170 $^\circ\text{C}/3$ h	Before thermal treatment	110 $^\circ\text{C}/3$ h	120 $^\circ\text{C}/3$ h	130 $^\circ\text{C}/3$ h	140 $^\circ\text{C}/3$ h	170 $^\circ\text{C}/3$ h
A	OH str.	3696 vs	3697 m	3698 s	3698 s	3698 vs	3697 vs	3697 vs
B	OH str.	3670 vw	–	–	3669 sh	3669 sh	3668 sh	3670 vw
A'	Per. OH str.	–	3663 s	3662 s	3658 m	3657 w	3656 vw	–
C	OH str.	3651 w	3651 sh	3651 sh	3651 sh	3650 w	3650 w	3651 w
D	OH str.	3621 s	3621 s	3621 s	3621 s	3621 s	3621 s	3621 s
	intercalated water	–	3539 m	3539 w	3538 vw	–	–	–
	intercalated water	–	3503 w	3504 vw	3503 vw	–	–	–
E'	Per. Si–O str.	–	–	–	–	–	–	–
E	Si–O str.	1113 sh	1112 sh	1112 wsh	1112 vwsh	1114 vwsh	1114 vwsh	1114 vwsh
P	Si–O str.	1104 m	1101 m	1101 m	1102 m	1103 m	1103 m	1103 m
F'	Per. Si–O str.	–	–	–	–	–	–	–
F	Si–O str.	1033 vs	1034 vs	1033 s	1032 vs	1033 vs	1032 vs	1033 vs
G'	Per. Si–O str.	–	1014 s	1012 s	1010 s	–	–	–
G	Si–O str.	1009 s	–	–	–	1009 s	1009 s	1009 s
H'	Per. AlO–H def.	–	958 vw	958 vvw	959 vvw	958 vvvw	958 vvvw	–
H	AlO–H def.	937 w	938 vvw	938 vw	937 vw	937 w	938 w	938 w
I	AlO–H def.	914 m	–	–	–	–	–	914 m
I'	Per. AlO–H def.	–	911 w	912 w	912 m	913 m	913 m	–
J		791 vw	791 vw	791 vw	791 vw	791 vw	791 vw	791 vw
K		754 vw	747 vw	750 vw	752 vw	752 vw	753 vw	753 vw
L		697 w	688 w	690 w	692 w	693 w	694 w	696 w
M'	Per. Al–O def.	–	544 m	543 m	543 sh	543 wsh	543 vwsh	–
M	Al–O def.	540 m	–	–	540 m	539 m	540 m	539 m
N	Si–O def.	470 m	–	469 m	469 m	469 m	470 m	470 m
N'	Per. Si–O def.	–	466 m	–	–	–	–	–
O'	Per. Si–O def.	–	433	433 w	433 w	–	–	–
O	Si–O def.	431 w	–	–	–	432 w	432 w	431 w

Per.: perturbed band; str.: stretching vibration; def.: deformation vibration; v: very; s: strong, m: medium; w: weak; sh: shoulder

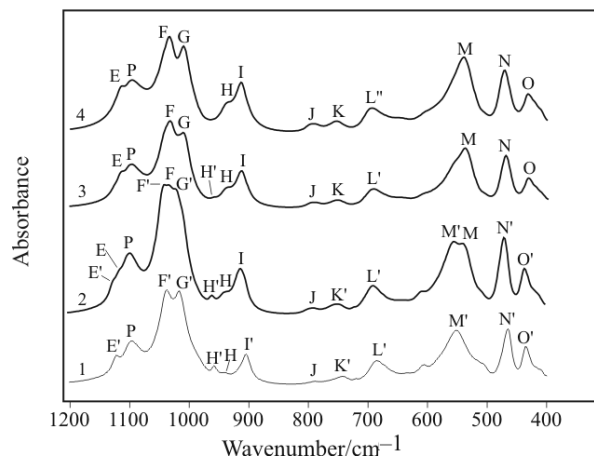
The thermal treatment of DMSO-Kaolinite complexes is associated with the evolution of the guest molecules. Consequently, the thermal analysis shows that the absorbance of band A gradually increases whereas that of band A' decreases. The latter is not observed after heating the complexes at  $160^\circ\text{C}$ . The frequencies of band A' decrease with the rise in temperature from  $3663\text{ cm}^{-1}$  before the thermal treatment to  $3656\text{ cm}^{-1}$  after heating at  $140^\circ\text{C}$  (Tables 1 and 2) indicating the thermal strengthening of the  $\text{O–H}\cdots\text{O}=\text{S}(\text{CH}_3)_2$  H-bond, probably due to water escape. As mentioned in the Introduction,

thermo-XRD-analysis showed that type II complex was obtained by the thermal treatment of type I complex. It appears that the absorption at  $3663\text{ cm}^{-1}$  represents type I complex where absorption at  $3656\text{ cm}^{-1}$  represents type II complex.

Absorbance ratios of bands A relative to D in the spectra of non-intercalated KGa-1 and KGa-2 heated at  $170^\circ\text{C}$ , were 1.4 and 1.7, respectively. These ratios in the spectra of DMSO-KGa-1 gradually heated were 0.4, 1.0, 1.2, 1.3 and 1.4 and in the spectra of DMSO-KGa-2 they were 0.8, 1.0, 1.1, 1.3 and 1.7 before and after heating at 110, 120, 130 and  $170^\circ\text{C}$ ,



**Fig. 1a** Thermo-IR-spectroscopy analysis of DMSO-KGa-1 complex in the spectroscopic region 3800–3400  $\text{cm}^{-1}$ . 1 – unheated, 2 – after heating the complex at 110°C, 3 – 130°C and 4 – 170°C. KBr disks were prepared after the thermal treatments



**Fig. 1b** Thermo-IR-spectroscopy analysis of DMSO-KGa-1 complex in the spectroscopic region 1200–400  $\text{cm}^{-1}$ . 1 – unheated, 2 – after heating the complex at 110°C, 3 – 130°C and 4 – 170°C. KBr disks were prepared after the thermal treatments

respectively, as a consequence of the thermal evolution of the guest molecules. The fact that after heating the samples at 170°C, this ratio in the spectrum of DMSO-KGa-1 is similar to that of KGa-1 and the ratio of DMSO-KGa-2 is similar to that of KGa-2 proves that at the end of the thermal treatment the inner-surface hydroxyls are not perturbed.

Two bands at 3538 and 3503  $\text{cm}^{-1}$  appear in the spectra of DMSO-KGa-1 and DMSO-KGa-2 complexes, attributed by some investigators to perturbed inner-surface hydroxyls [2, 3, 13, 14]. Similar absorptions were detected in the spectra of hydrated alkali-halide-kaolinite complexes and were assigned by Yariv *et al.* to asymmetric and symmetric H–O–H stretching vibrations of intercalated water [19]. Frost *et al.* [20] attributed these bands in the spectrum

of DMSO-kaolinite to water molecules adsorbed together with DMSO. They are of medium-size in the spectrum of the former and weak in that of the latter (Figs 1 and 2). A stretching OH vibration of monomeric non-hydrogen bonded water molecule in the vapor phase absorbs at 3755  $\text{cm}^{-1}$ . In clustered, as well as in liquid water, H-bonded molecules absorb at about 3455  $\text{cm}^{-1}$  and in ice at 3255  $\text{cm}^{-1}$  [21]. From the shapes and locations of the present bands it is obvious that the adsorbed water is not clustered [22] but occurs as discrete molecules involved in H-bonds [19], probably bridging between sulfur of DMSO and oxygens of the O-plane as follows,  $\text{Si-O}\cdots\text{H-O-H}\cdots\text{S(O)(CH}_3)_2$ . Sulfur atom may accept a proton at the non-bonding orbital with its lone pair electrons (Scheme 1).

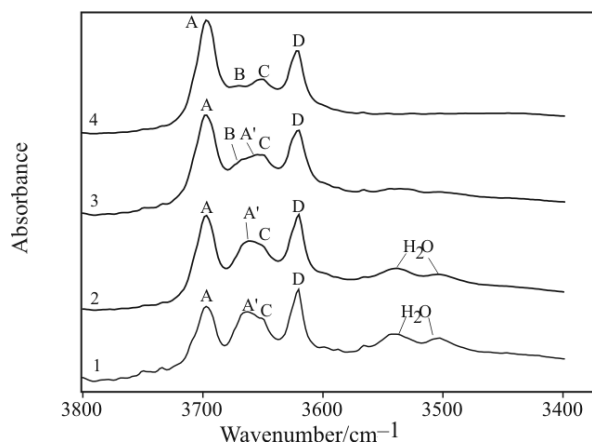
If this is the case, it is expected that the S=O stretching vibration will be perturbed. The spectroscopic absorption region of S=O group overlaps that of Si–O (see later) and the S=O bands are not identified in our spectra. Frost *et al.* [20] studied the Raman spectrum of DMSO-kaolinite complexes and found that these vibrations shifted from 1056, 1028 and 1004  $\text{cm}^{-1}$  in the spectrum of pure DMSO to 1066, 1023 and 1010  $\text{cm}^{-1}$  or 1058, 1040, 1026 and 1010  $\text{cm}^{-1}$  in spectra of DMSO intercalating low or high-defect kaolinite, respectively. Proton donation from the inner-surface hydroxyls to oxygens of the DMSO should also contribute to these shifts.

The absorbance of the two stretching water bands gradually decreases with temperature, due to the thermal escape of water molecules. The water bands disappear at 130°C. In the spectra of DMSO-KGa-2 the band frequencies do not change with the temperature of the thermal treatment (Table 2) but in those of DMSO-KGa-1 the frequencies of both asymmetric and symmetric absorptions decrease with the rise in temperature from 3538 and 3503  $\text{cm}^{-1}$  to 3529 and 3497  $\text{cm}^{-1}$ , respectively (Table 1), indicating the strengthening of the H-bonds in the system  $\text{Si-O}\cdots\text{H-O-H}\cdots\text{S(O)(CH}_3)_2$ .

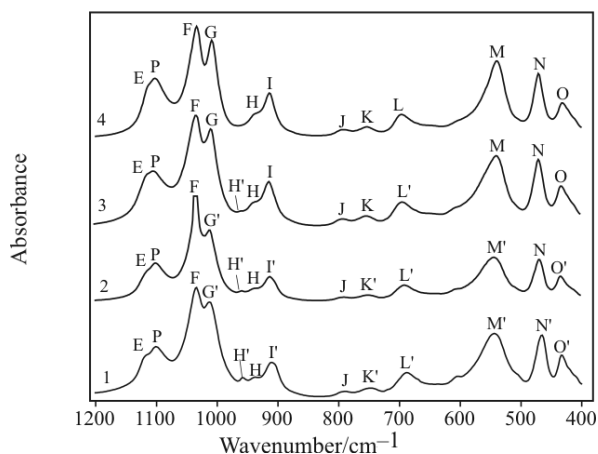
Heller-Kallai *et al.* [23] applied IR spectroscopy in the study of disorder induced in kaolinite by the de-intercalation of DMSO from the complex. They found that the removal of DMSO gave rise to changes in the OH-stretching region. In the present study the spectrum of KGa-1 shows broadening of bands A and D after the de-intercalation at 170°C. It appears that the de-intercalation of DMSO induces some disorder on KGa-1 but not on KGa-2.

#### *Spectra in the regions 1000–900 and 600–500 $\text{cm}^{-1}$*

Absorptions of AlO–H deformation (bands H and I) and Al–O deformation vibrations (band M) occur in these



**Fig. 2a** Thermo-IR-spectroscopy analysis of DMSO-KGa-2 complex in the spectroscopic region 3800–3400  $\text{cm}^{-1}$ . 1 – unheated, 2 – after heating the complex at 110°C, 3 – 130°C and 4 – 170°C. KBr disks were prepared after the thermal treatments



**Fig. 2b** Thermo-IR-spectroscopy analysis of DMSO-KGa-2 complex in the spectroscopic region 1200–400  $\text{cm}^{-1}$ . 1 – unheated, 2 – after heating the complex at 110°C, 3 – 130°C and 4 – 170°C. KBr disks were prepared after the thermal treatments

regions [16]. These bands shift in the spectra of the complexes from their locations in the spectrum of the non-intercalated kaolinite (937, 914 and 539  $\text{cm}^{-1}$ ). Bands H and M shift to higher frequencies (958 and 552  $\text{cm}^{-1}$  in the spectrum of DMSO-KGa-1 and 958 and 544  $\text{cm}^{-1}$  in that of DMSO-KGa-2), and are labeled H' and M', respectively whereas band I shifts to lower frequencies (905 and 911  $\text{cm}^{-1}$  in the spectra of the two complexes, respectively) and is labeled I'. These perturbations occur due to the H-bonds between the inner-surface hydroxyls and the oxygens of the DMSO molecules, previously mentioned. Since these are deformation bands the extent of the shifts is not related to the strength of the H-bonds.

Non-perturbed bands I and M are not detected in the spectra of the DMSO-kaolinite complexes before

the thermal treatment. However, their existence as weak bands is confirmed by curve-fitting calculations. They appear during the thermal treatment.

The thermal behavior of the pairs H and H', M and M' and A and A' is very similar. The absorbance of bands H, M and A gradually increases with temperature whereas that of band H', M' and A' decreases (Figs 1 and 2). The perturbed bands disappear after heating at 160°C. This is not surprising since these pairs are associated with H-bonds between the inner-surface hydroxyls and the oxygens of the DMSO molecules.

#### *Spectra in the regions 1200–1000 and 500–400 $\text{cm}^{-1}$*

The IR absorptions of Si–O stretching bands (E, P, F and G) and deformation bands (N and O) are in these regions, respectively. In the spectrum of DMSO-KGa-1 bands E, F and G are not detected and instead, perturbed bands E', F' and G' appear at higher frequencies (Tables 1 and 2). These three bands are in-plane Si–O vibrations and the perturbation implies that the O-plane is involved in short range interactions such as H-bonds in which the oxygens accept protons. Since DMSO has no proton to donate, these H-bonds should be formed with water molecules adsorbed with the DMSO. In conclusion, adsorbed water molecules take part in the structure of type I complex, probably bridging between the clay-O-plane and the intercalated DMSO molecules by donating one proton to the DMSO-sulfur and the second to a clay-O-atom.

The perturbations of the Si–O bands are towards higher frequencies, indicating that the contribution of the double bond character to the overall Si–O bond in the tetrahedral sheet is higher in the DMSO complex than in the neat kaolinite [24]. In other words, the Si–O bond becomes stronger after the intercalation suggesting that the interaction between the O-plane and the guest molecules is weaker than that between the O-plane and the inner-surface OH plane in the neat kaolinite [25]. Shifts are also observed in the locations of bands N and O in the spectrum of KGa-1. The former shifts from 471 to 465  $\text{cm}^{-1}$  and the latter from 431 to 435  $\text{cm}^{-1}$  (bands N' and O', in Table 1).

In the spectrum of DMSO-KGa-2 only bands G, N and O are slightly perturbed from 1008, 470 and 430 to 1014, 466 and 433  $\text{cm}^{-1}$ , respectively. No perturbations of the other two Si–O in-plane stretching vibrations occur suggesting that with this clay weak H-bonds are obtained between the intercalated water molecules and the O-plane.

During the thermal treatment water is evolved, the perturbed Si–O bands gradually become weak and disappear at 120 or 130°C in the spectra of DMSO-KGa-2

or DMSO-KGa-1, respectively. Differences in the temperatures at which the perturbed Si–O bands disappear are due to the smaller amount of the DMSO adsorbed by KGa-2. Because of small differences in the frequencies of the perturbed and non-perturbed bands, results of curve-fitting calculations in this spectroscopic region are not reliable.

Band P cannot be taken into account in these considerations. This band represents an out-of-plane Si–O stretching vibration [16] and is very sensitive to grinding [17, 18, 26]. It appears at  $1098\text{ cm}^{-1}$  in the spectra of unground Georgia kaolinites (KGa-1 and KGa-2) and gradually shifts to higher frequencies (up to  $1104\text{ cm}^{-1}$ ) with grinding due to the delamination of the clay tactoids [27]. This band is obtained from the vibration of oxygens common to tetrahedral and octahedral layers, and consequently is not involved in the H-bonds with intercalated water molecules. However, the present spectra show that it shifts to lower frequencies compared with those of ground kaolinite, suggesting that the number of layers in tactoids of the intercalation complexes is higher than in the ground kaolinite. This requires further studies by other methods.

#### *Spectra in the region $800\text{--}600\text{ cm}^{-1}$*

Band J is ascribed to an out of phase vibration of the hydroxyl groups of the octahedral sheet [16]. This band appears at  $790\text{ cm}^{-1}$  in the spectra of both kaolinites and is not shifted after the adsorption of DMSO. The thermal treatment has no effect on this band.

Band K is ascribed to perpendicular vibration of the octahedral  $\text{Al}^{3+}$  ions and the hydroxyl groups on the side of the tetrahedral sheet [16]. This band shifts from  $754\text{ cm}^{-1}$  in the spectra of both kaolinites to lower frequencies ( $742$  and  $747\text{ cm}^{-1}$  in the spectra of DMSO-KGa-1 and DMSO-KGa-2, respectively) proving the involvement of the gibbsite-like sheet in the intercalation complexes.

Band L is ascribed to a vibration in which hydroxyl groups of the octahedral sheet move in phase in the direction perpendicular or nearly so to the layers [16]. This band appears at  $697\text{ cm}^{-1}$  in the spectra of both kaolinites. It shifts to  $685$  or  $688\text{ cm}^{-1}$  in the spectra of DMSO-KGa-1 or DMSO-KGa-2, respectively. Curve-fitting calculations of this spectroscopic region resulted in a single component for K and a single for L.

The shifts of bands K and L to lower frequencies in the spectra of DMSO-kaolinite complexes occur due to a non-localized long-range electrostatic interaction between the horizontal layer of the intercalated DMSO molecules and the O–H plane of the gibbsite-like sheet. According to Thompson and Cuff [2] the intercalated DMSO molecules form

horizontal layers with their oxygens directed towards the octahedral sheets. As a result of the high dipole-moment of DMSO ( $13.03 \cdot 10^{-30}\text{ Cm}$ ) the O-plane of the intercalated DMSO layer is negatively charged. As well, as a result of the polarization of the O–H groups, the inner-surface-proton plane of the gibbsite-like sheet becomes positively charged [28]. During the thermal treatment of the DMSO-kaolinite complexes, bands K and L gradually shift to higher frequencies and at  $170^\circ\text{C}$  the frequencies are similar to those in the spectra of neat kaolinites recorded at this temperature (Tables 1 and 2).

#### *The methyl groups*

In the vapor of DMSO the asymmetric and symmetric stretching vibrations of the  $\text{CH}_3$  group are observed at  $2973$  and  $2908\text{ cm}^{-1}$ . The asymmetric deformation vibrations are observed at  $1440$ ,  $1419$  and  $1405\text{ cm}^{-1}$  and the symmetric deformations at  $1319$ ,  $1304$  and  $1287\text{ cm}^{-1}$ . In solutions of chloroform or carbon disulfide they shift to  $3000$ ,  $2918$ ,  $1436$ ,  $1416$ ,  $1404$ ,  $1325$ ,  $1306$  and  $1291\text{ cm}^{-1}$ , respectively [29]. In agreement with Olejnik *et al.* [13], the spectra of DMSO-kaolinites recorded in our laboratory show very weak  $\text{CH}_3$  bands at  $3022$ ,  $2937$ ,  $2919$ ,  $1431$ ,  $1412$ ,  $1397$  and  $1320\text{ cm}^{-1}$ , respectively. The intensities of these bands significantly decrease with the temperature but they disappear only at  $160^\circ\text{C}$ . At  $130^\circ\text{C}$  small shoulders appear attached to the  $3022$  band at  $3032$ ,  $3017$  (vw) and  $2995$  (vvw)  $\text{cm}^{-1}$ . The appearance of the  $\text{CH}_3$  bands in spectra recorded after heating the samples at temperatures between  $130$  and  $150^\circ\text{C}$  indicates that DMSO is present in the interlayers as a component of type II complex.

## Conclusions

- The thermo-IR-spectroscopy analysis established the role of water in the DMSO-kaolinite intercalation complexes. It confirmed the presence of water in type I complex and its absence from type II.
- In type I complex water molecules form bridges between the intercalated DMSO molecules and the O-planes of the clay. One proton of the water molecule is H-bonded probably to an S atom of DMSO and the second proton is H-bonded to oxygens of the clay-O-plane. Consequently perturbed Si–O bands of the kaolinite-tetrahedral sheet are detected in the spectrum and together with the two intercalated water bands are finger prints for the identification of this complex. Perturbed Si–O bands and two water stretching bands are detected in spectra of samples heated from room temperature up to  $120^\circ\text{C}$  but disappear at  $130^\circ\text{C}$ .

- Type II complex is obtained from type I by the thermal escape of water. In the spectrum of type II complex water bands are not detected and the Si–O bands are not perturbed. Thermo-XRD-analysis identified type I complex from room temperatures up to 130°C and that of type II from 110 or 120°C up to 160°C [11]. Thermo-IR-spectroscopy failed to identify type II complex at 110 or 120°C, because the bands used in the identification of this complex are present also in the spectrum of type I complex.
- DMSO in the interlayer accepts protons from the inner-surface hydroxyls and O–H and AlO–H bands of the kaolinite-octahedral sheet are perturbed. These perturbed bands together with absorptions bands of the methyl groups are fingerprints for the identification of this complex. Perturbed O–H bands and methyl group bands are identified in spectra of samples heated from room temperature up to 150°C but disappear at 160°C. It should be noted that these bands are present in the spectra of both complexes.
- In the spectrum of the type I DMSO complex the Si–O stretching vibrations of the kaolinite-tetrahedral sheet are located at higher frequencies compared with those of the neat kaolinite. This implies that the short-range interaction of the O-plane with the guest molecules is weak compared with the interaction between this O-plane and the inner-surface OH plane in the neat mineral.

## References

- 1 A. Mata-Arjona, A. Ruiz-Amil and E. Inaraja-Martin, Proc. Reunion Hispano-Belga de Minerales de la Arcilla, Consejo Superior de Investigaciones Cientificas, Madrid 1970, p. 115.
- 2 J. G. Thompson and C. Cuff, *Clays Clay Miner.*, 33 (1985) 490.
- 3 M. Raupach, P. F. Barron and J. G. Thompson, *Clays Clay Miner.*, 35 (1987) 208.
- 4 F. I. Franco Duro, J. Gonzales Jesus and M. D. Ruiz Cruz, Proc. 2<sup>nd</sup> Mediterranean Clay Meeting, Aveiro 1998, (C. S. F. Gomes, Ed.), 2 (1998) 249.
- 5 F. I. Franco, M. D. Ruiz Cruz and M. Bentabol, Proc. 1<sup>st</sup> Latin American Clay Conf., Funchal 2000, (C. S. F. Gomes, Ed.) 2 (2000) 161.
- 6 J. Kristóf, R. L. Frost, W. N. Martens and E. Horváth, *Langmuir*, 18 (2002) 1244.
- 7 E. Horváth, J. Kristóf, R. L. Frost, Á. Rédey, V. Vágvolgyi and T. Cseh, *J. Therm. Anal. Cal.*, 71 (2003) 407.
- 8 P. M. Costanzo and R. F. Giese, *Clays Clay Miner.*, 33 (1985) 415.
- 9 P. M. Costanzo and R. F. Giese, *Clays Clay Miner.*, 38 (1990) 160.
- 10 J. Kristóf, R. L. Frost, J. T. Kloprogge, E. Horváth and M. Gábor, *J. Therm. Anal. Cal.*, 56 (1999) 885.
- 11 I. Lapidés and S. Yariv, Proc. ICTAC Congress 2008, paper in preparation.
- 12 S. Yariv, I. Lapidés, A. Nasser, N. Lahav, I. Brodsky and K. H. Michaelian, *Clays Clay Miner.*, 48 (2000) 10.
- 13 S. Olejnik, L. A. G. Aylmore, A. M. Posner and J. P. Quirk, *J. Phys. Chem.*, 72 (1968) 241.
- 14 C. T. Johnston, G. Sposito, D. F. Bocian and R. R. Birge, *J. Phys. Chem.*, 88 (1984) 5959.
- 15 S. Yariv, in *Organo-clay complexes and interactions*, (S. Yariv and H. Cross, Eds), Marcel Dekker, New York 2002, p. 345.
- 16 V. C. Farmer and J. D. Russell, *Spectrochim. Acta*, 22 (1966) 389.
- 17 J. G. Miller and T. D. Oulton, *Clays Clay Miner.*, 18 (1970) 313.
- 18 J. G. Miller and T. D. Oulton, *Clays Clay Miner.*, 20 (1972) 389.
- 19 S. Yariv, I. Lapidés, K. H. Michaelian and N. Lahav, *J. Therm. Anal. Cal.*, 56 (1999) 865.
- 20 R. L. Frost, J. Kristóf, G. N. Paroz and J. T. Kloprogge, *J. Phys. Chem. B*, 102 (1998) 8519.
- 21 H. W. van der Marel, H. Beutelspacher, *Atlas of infrared spectroscopy of clay minerals*, Elsevier, Amsterdam 1976.
- 22 L. H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, London 1966, p. 233.
- 23 L. Heller-Kallai, E. Huard and R. Prost, *Clay Miner.*, 26 (1991) 245.
- 24 S. Yariv, *Clay Miner.*, 21 (1986) 925.
- 25 S. Yariv, in 'Modern Approach to Wettability', (M. E. Schrader and G. Loeb, Eds), Plenum Press, New York 1992, p. 279.
- 26 S. Yariv, *Clays Clay Miner.*, 1975 (23) 80.
- 27 S. Yariv, *Powder Technol.*, 12 (1975) 131.
- 28 S. Yariv and H. Cross, 'Geochemistry of Colloid Systems', Springer-Verlag, Berlin 1979, p. 26.
- 29 F. A. Cotton and W. D. Horrocks, *Spectrochim. Acta*, 17 (1961) 134.

---

DOI: 10.1007/s10973-008-9459-3