

A NEXAFS STUDY OF THE ORIENTATION OF BENZOATE INTERCALATED INTO A LAYER DOUBLE HYDROXIDE

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Abstract—NEXAFS is shown to be an excellent technique, of potentially widespread application, for the determination of the orientation of organic molecules intercalated in preferentially oriented thin films of polycrystalline, layered minerals. A NEXAFS study of $[\text{Mg}_2\text{Al}(\text{OH})_6]^+\text{C}_7\text{H}_5\text{O}_2^- \cdot n\text{H}_2\text{O}$, a layered anionic clay, is described. This material shows a transition from a layer spacing of 15.4 Å to only 9 Å at a remarkably low temperature (below 100°C). This is shown to be accompanied by a change in the angle of the plane of the benzoate molecule to the 00 l planes from $35^\circ \pm 10^\circ$ to $0^\circ \pm 10^\circ$. The tilt of the benzoate anion in the room temperature structure demonstrates the presence of an interaction between the phenyl ring and the positively charged, brucite-like layers. Furthermore it is suggestive of the importance of hydrogen bonding in determining the interlayer spacing and stability.

Key Words—Double hydroxide, Hydrotalcite, NEXAFS, Organic intercalates, Preferred orientation.

INTRODUCTION

There is significant commercial and academic interest in layered materials (anionic and cationic clays) both due to their potential as industrial catalysts and adsorbates (Reichle, 1985; Miyata, 1975; Drezdon, 1988; Ocelli *et al.*, 1984) and because of their possible role in the origin of life (Cairns-Smith, 1965, 1975; Paecht-Horowitz *et al.*, 1970; Kuma *et al.*, 1989; Borja and Dutta, 1992), either simply in concentrating metabolic precursors or taking a more active, catalytic role (“the clay hypothesis”). In both these general areas, the way in which organic intercalates behave within the inorganic layers is of great significance. Powder diffraction provides a powerful method of investigating the layer expansion due to organic intercalation, but the impossibility of growing single crystals and the low X-ray scattering cross section of organics makes detailed structural determination very difficult.

Near Edge X-ray Absorption Fine Structure (NEXAFS) at the carbon edge provides a means of determining the orientation of organic molecules relative to a planar surface (and can give some information on bonding interactions). It has traditionally been used to investigate organic adsorbates on single crystal surfaces (Solomon *et al.*, 1991; Hoffmann *et al.*, 1990; Tourillon *et al.*, 1987), but to the knowledge of the authors has never been applied to the determination of the orientation of molecules within a polycrystalline solid. Due to their platy habit, it is possible to orient thin films of many layered materials onto flat surfaces; thus the possibility exists of determining the orientation of organics within their layers using NEXAFS.

A particular class of layered minerals is the Layered Double Hydroxides (LDHs) (Frondel, 1941; Allmann, 1968, 1970; Taylor, 1969, 1973; Serna *et al.*, 1982),

having the general formula $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}\text{A}_{x/m}^{m-} \cdot n\text{H}_2\text{O}$, one type of which is the hydrotalcite-like group of minerals (Miyata, 1975; Drezdon, 1988; Brindley and Kikkawa, 1979; Gatucho *et al.*, 1967; De Waal and Viljoen, 1971), in which the cations are Mg^{2+} and Al^{3+} . These grow as very small, platy, hexagonal crystals. Their structure can be seen as derived from brucite, each cation being octahedrally surrounded by hydroxides; the octahedra form sheets by sharing edges. These sheets carry excess positive charge due to the Al^{3+} cations, which is balanced by anions incorporated within the interlayer. As a consequence of the excess positive charge on the brucite-like layers it is energetically favorable to expand the layers, provided that the negative charge can also be separated. Thus sizeable anions can be intercalated into the interlayer, giving large layer expansions (Drezdon, 1988; Kuma *et al.*, 1989; Borja and Dutta, 1992) and it is this which produces the interesting properties of the materials both for catalysis and the storage and orientation of biological precursors.

The system we have chosen to study here is $[\text{Mg}^{2+}\text{Al}^{3+}(\text{OH})_6]^+\text{C}_7\text{H}_5\text{O}_2^- \cdot n\text{H}_2\text{O}$ (hereafter referred to as LDH Benzoate). This has been previously investigated by powder X-ray diffraction, solid state NMR and thermal analysis (Vucelic, personal communication) and found to display some interesting and perplexing properties. The incorporation of benzoate into the interlayer causes the 003 layer spacing to expand to 15.4 Å (compared to 7.8 Å for the carbonate form). This in itself is somewhat surprising since it leaves a gallery height of 10.5 Å (assuming a brucite-like layer of 4.9 Å) compared with only 6 Å for the length of the benzoate anion. So although it may seem logical to assume a vertical orientation for the benzoate, it is clearly not

this which is determining the gallery height. Furthermore, on heating the layers collapse to a spacing of only 9 Å at remarkably low temperature (less than 100°C) and this effect is completely reversible over a few days in air. It is presumably dependent on dehydration and rehydration of the crystals and indicates the existence of two easily interconverted forms with quite different interlayer packing but very similar energies. So the question arises as to the geometry of the benzoate within the layers in these two forms. Perhaps the simplest explanation would be that the benzoate is vertical in the low temperature form and flat in the high temperature one, but up to now no evidence has existed as to the benzoate's orientation. This problem is directly addressed in this paper by using NEXAFS on thin, preferentially oriented films of LDH Benzoate.

EXPERIMENTAL METHODS

The LDH Benzoate was prepared by direct synthesis; a stoichiometric mixture of $Mg(NO_3)_2$ and $Al(NO_3)_3$ was dribbled into excess benzoic acid dissolved in sodium hydroxide solution over a period of several hours with vigorous stirring at room temperature. The final pH was around 11. The resulting amorphous slurry was then heated at 75°C for 18 hours with vigorous stirring to allow crystallization. All the preceding operations were carried out in an atmosphere of nitrogen and using pre-boiled water to minimize carbonate contamination. Powder diffraction indicated that the crystals had dimensions of about 15 nm in the [001] direction and 30 nm in the [110] directions (by application of the Scherrer formula). The crystals were filtered, washed to neutrality, but never allowed to dry, and diluted in water to produce a roughly 1% suspension. These last two operations were carried out in air and are the most likely sources of the carbonate contamination which was observed. As will be seen later this contamination proved highly fortuitous.

Preferentially oriented samples were produced by drying, at room temperature, LDH Benzoate suspensions onto glass cover slips (Drezdon, 1988). The thickness of the film thus produced was varied by diluting the suspension up to 1000 times before drying onto the glass. Initially this was done in air, but preliminary NEXAFS experiments showed carbonate contamination increasing in extent as the film thickness decreased, until for films of a few tens of nanometers the product was almost entirely LDH Carbonate. Hence it is clear that even after crystallization, the LDH Benzoate is labile with respect to carbonate ions in solution. To reduce this problem, thin films (less than a few hundred nanometers) were produced by preparing and drying the suspension in an inert atmosphere. Relatively small carbonate contamination resulted.

It is somewhat unfortunate that the 006 and 0012 reflections of the expanded LDH Benzoate structure

correspond almost exactly to the 003 and 006 basal reflections of LDH Carbonate at 7.8 Å and 3.9 Å. This makes the assessment of small amounts of carbonate impurities very difficult on the grounds of diffraction alone. However there are several pieces of evidence that, with the exception of extremely thin films dried in air, the material is indeed overwhelmingly LDH Benzoate. The 01 $\bar{1}$ reflection positions are highly indicative of the real layer spacing and the complete absence of appropriate peaks for LDH Carbonate demonstrates that this material can only be present in low concentrations. On heating the LDH Benzoate, the layer spacing collapses to 9 Å removing the basal reflections from interference with the LDH Carbonate peaks. Large amounts of LDH Carbonate are not revealed. Finally NEXAFS confirms that only a small fraction of the carbon present is in the form of carbonate. The question remains as to whether the carbonate impurity is present as a separate phase or co-intercalated with the benzoate. Sedimentation experiments suggest that it is predominantly a bi-phasic material, though small amounts of carbonate within the LDH Benzoate layers cannot be entirely ruled out. LDH Carbonate is about 10% denser than expanded LDH Benzoate and it is thus possible to separate the materials by sedimentation.

The thickness of a film was estimated from the ratio of the 110 reflection intensities of the oriented film and a randomly oriented, powdered sample (0.1 from Figures 1a and 1b). The density, ρ , and average absorption cross section, σ (Berger and Hubbell, 1993), can be calculated from the unit cell contents. Five water molecules per unit cell are assumed. Assuming random orientation for the majority of the sample of Figure 1b, the film thickness, λ , can be found:

$$\begin{aligned} \int_0^\lambda \exp(-2x\rho\sigma/\sin\theta) dx \\ = 0.1 \int_0^\infty \exp(-2x\rho\sigma/\sin\theta) dx \\ \Rightarrow \lambda = \sim 10^4 \text{ nm.} \end{aligned}$$

The thickness of all other films has then been estimated by dividing this value by the additional dilution of the suspension before drying.

A very rough estimate can also be made of the thickness of the oriented layer. The enhancement of the 006 reflection in a perfectly oriented sample relative to a randomly oriented one is:

$$2\pi R \sin 2\theta/\gamma\Delta\theta \cos\theta = \sim 1800$$

($\Delta\theta$ = FWHM of the diffraction peak, γ = length of collector slit, R = sample to slit distance; $\Delta\theta = 0.6^\circ$ for the 006, $\gamma = 1$ cm, $R = 15$ cm in our case).

The 006 intensity of Figure 1b (oriented sample) is

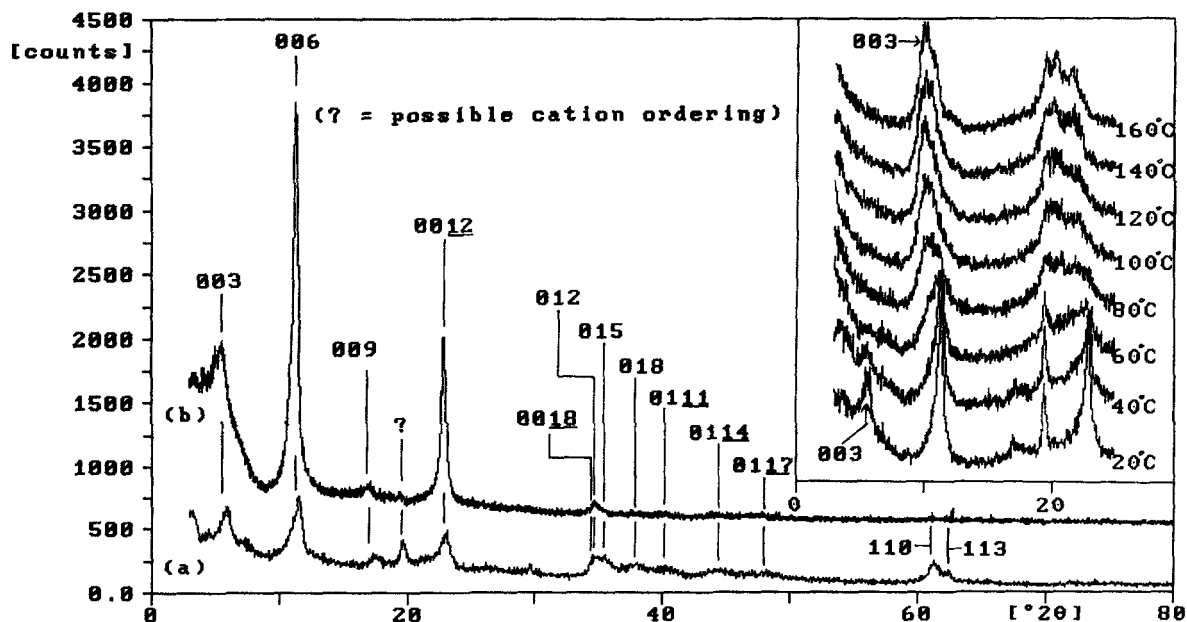


Figure 1. Powder X-ray diffraction patterns of LDH Benzoate; (a) randomly oriented, powdered sample (b) approximately 10,000 nm thick preferentially oriented film, dried in air. Inset—Temperature dependent powder patterns of LDH Benzoate, showing the collapse of the layer spacing (003 reflection) from 15.4 Å to 9 Å.

about 8 times that of Figure 1a (randomly oriented sample). So we have:

$$\begin{aligned}
 1800 \int_0^{\mu} \exp(-2x\rho\sigma/\sin\theta) dx \\
 &= 8 \int_0^{\infty} \exp(-2x\rho\sigma/\sin\theta) dx \\
 &\Rightarrow \mu = \sim 100 \text{ nm}
 \end{aligned}$$

where μ = thickness of a perfectly oriented layer required to give an equivalent 006 reflection to that of Figure 1b.

Sodium Benzoate was produced by reaction of a stoichiometric mixture of NaOH(aq) and benzoic acid—a thick crystalline layer was produced by drying the resulting solution at 60°C onto platinum coated glass.

Powder diffraction patterns were collected using a Phillips PW1710 diffractometer with a Cu anode and a $1/2^\circ$ divergence slit. Scans were taken from 3° to 80° 2θ with a step size of 0.02° .

The NEXAFS experiments were carried out on the SACEMOR beamline (SA72) at the Super-ACO storage ring, LURE. A high energy TGM monochromator (resolution of 90 meV at the Carbon edge, 200 meV in routine mode) was used. With the exception of the sodium benzoate standard, all spectra were recorded over about one hour in fluorescence mode. I_0 was recorded by using a channeltron to collect the electrons emitted from a gold reference grid at the entrance to the analysis chamber. The fluorescent photons were

collected using a channel plate; the geometry of this channel plate and analysis chamber limited the angle of the beam to between 20° and 50° to the surface normal. To avoid reabsorption problems, the sodium benzoate standard spectrum was recorded in electron yield mode using a second channeltron, collecting the electrons emitted from the sample. Electron yield measurements were also attempted on the LDH Benzoate samples, but the signal was found to be dominated by surface contamination. For this reason the NEXAFS were recorded by collecting fluorescent photons. In this mode of operation, reabsorption phenomena may distort the spectra if the sample is too concentrated. The striking similarity between the benzoate NEXAFS observed in the LDH samples and the sodium benzoate standard (cf particularly Figures 2 (inset) and 6) is taken as evidence that the benzoate is sufficiently dilute in the LDH that reabsorption is not a significant problem when operating in fluorescence mode.

To remove the oxygen atomic absorption background, raw spectra were treated by subtracting the spectrum of a carbon-free, oxygen containing material. Data obtained in fluorescence from a highly sputtered Al_2O_3 single crystal was used (Figure 3 inset), this being the cleanest source of an oxygen background readily available. The oxygen-only spectra were scaled such that their pre-edge intensity is equal to that of the carbon + oxygen data, and then subtracted. The removal of this background is the equivalent of the removal of an impurity from a NEXAFS spectrum (Stöhr, 1992). In addition to the smoothly varying O-K edge

atomic absorption, relatively sharp features are apparent between 287 and 294 eV. These are due to absorption by carbon adsorbed on the optics and are not perfectly normalized out by I_0 due to the presence of the 2λ , 3λ , etc., harmonics in the beam. The background subtraction cannot be expected to remove these anomalous features [for this division by a carbon and oxygen free background would be required (Stöhr, 1992)]. The features before 285 eV are most likely O 1s σ^* resonances.

So our background subtraction can be expected to account well for smooth variations in the background and allow normalization. However correction for the attenuation of the beam due to adsorption on the optics is not adequate. This is a particularly severe problem between 287 and 289 eV, exactly the position of the C-O Π^* resonance. Indeed comparison with the sodium benzoate spectrum (inset Figure 1) shows this peak to be attenuated relative to the C-C Π^* resonance, as would be expected due to absorption on the optics. A similar but much less serious problem is apparent in the region of the first benzoate σ^* resonance. Finally, in connection with the background, the K $2p_{3/2, 1/2}$ signals which can be seen in Figures 3 and 5 need to be mentioned. These are due to potassium in the glass substrate and are more pronounced in the 150°C treated material because of the thinning of the sample as the layer spacing collapses from 15.4 Å to 9 Å. Their presence is evidence in support of the calculated film thicknesses, the fluorescent photon escape depth being about 150 nm.

In summary, the background subtraction and normalization procedures used allow quantitative analysis only of sharp, intense features appearing in regions of gently varying background. Such features are the benzoate C-C and carbonate Π^* resonances. It could be argued that the carbonate Π^* resonances are too small, particularly in the 20° to normal case, for accurate quantification. Fortunately, more highly carbonate contaminated films (see above) were available for analysis and gave very similar results to those discussed below, confirming the validity of the analysis given.

RESULTS

If any statement is to be made about the orientation of the intercalated organics within the LDH layers, it is obviously of vital importance to be certain of having a well oriented film of crystals. This can be monitored by powder diffraction where reflections from planes oriented parallel to the sample holder are massively enhanced at the expense of all others. This is shown in Figure 1. However, a problem presents itself at this juncture; whereas the sampling depth in powder diffraction is a few tenths of millimeters, the mean free path of the fluorescent photons is only expected to be about 150 nm (assuming an absorption cross section of about 10^6 barns/atom (Stöhr, 1992, 134–135)). Thus

a relatively thick film with a thin oriented layer at its base can be expected to give a good preferentially oriented diffraction pattern, but will appear completely disoriented in any NEXAFS experiment. So it is necessary not only to know that orientation is present but also to have a good estimate of the thickness to which this orientation can be expected to extend above the substrate and the total thickness of the film produced.

The sample of Figure 1b is about 10,000 nm thick, containing the equivalent of a perfectly oriented layer about 100 nm thick (see Experimental Methods section). Of course, in reality there will be a graduation from very good orientation at the bottom to completely random orientation in the upper layers. However, bearing in mind that the conditions for X-ray orientation ($\pm 1/2^\circ$) are much more stringent than those required to give a well oriented NEXAFS spectrum ($\pm 5^\circ$ would easily suffice), one can confidently expect a layer of at least 100–200 nm above the substrate to be very well oriented with respect to a NEXAFS experiment. It is now abundantly clear why it is so important to have a good estimate of both film thickness and degree of orientation.

A film of about 100 nm was chosen for the majority of the NEXAFS experiments. Such a film is thin enough that very good preferential orientation can be confidently assumed throughout its thickness, yet thick enough to give a good signal in fluorescence mode (the fluorescent photon escape depth being about 150 nm).

Figures 2 and 3 show the raw NEXAFS data for a 100 nm LDH Benzoate film untreated and heated to 150°C, respectively. In each case the 20° and 50° to normal spectra have been scaled to give roughly the same pre-edge background intensity. This is a purely arbitrary procedure but makes visual comparison easier. The heating was performed outside the vacuum chamber (on the same sample as was used for the untreated spectra of Figure 2) and the sample transferred into the NEXAFS chamber entry lock whilst still hot, to avoid any possibility of rehydration on cooling. The spectra were then recorded at ambient temperature. Heating and cooling cycles whilst performing *in situ* XRD have shown this treatment to be an effective means of reducing the layer spacing in LDH Benzoate from 15.4 Å to around 9 Å (Vucelic, personal communication). The benzoate NEXAFS features have been identified by reference to the spectra obtained in electron yield from sodium benzoate (inset Figure 1); the assignment is confirmed by the close similarity to the NEXAFS spectrum of benzene (Johnson *et al.*, 1983; Horsley *et al.*, 1985), with the exception of the C-O Π^* resonance. Two features remain unidentified—a Π^* resonance at around 291 eV (see particularly 50° to normal of Figure 2, feature labelled $\text{CO}_3^{2-}\Pi^*$) and a σ^* resonance at about 300 eV. This latter feature was much more visible in the more highly contaminated thin films which were dried in air (see Experimental

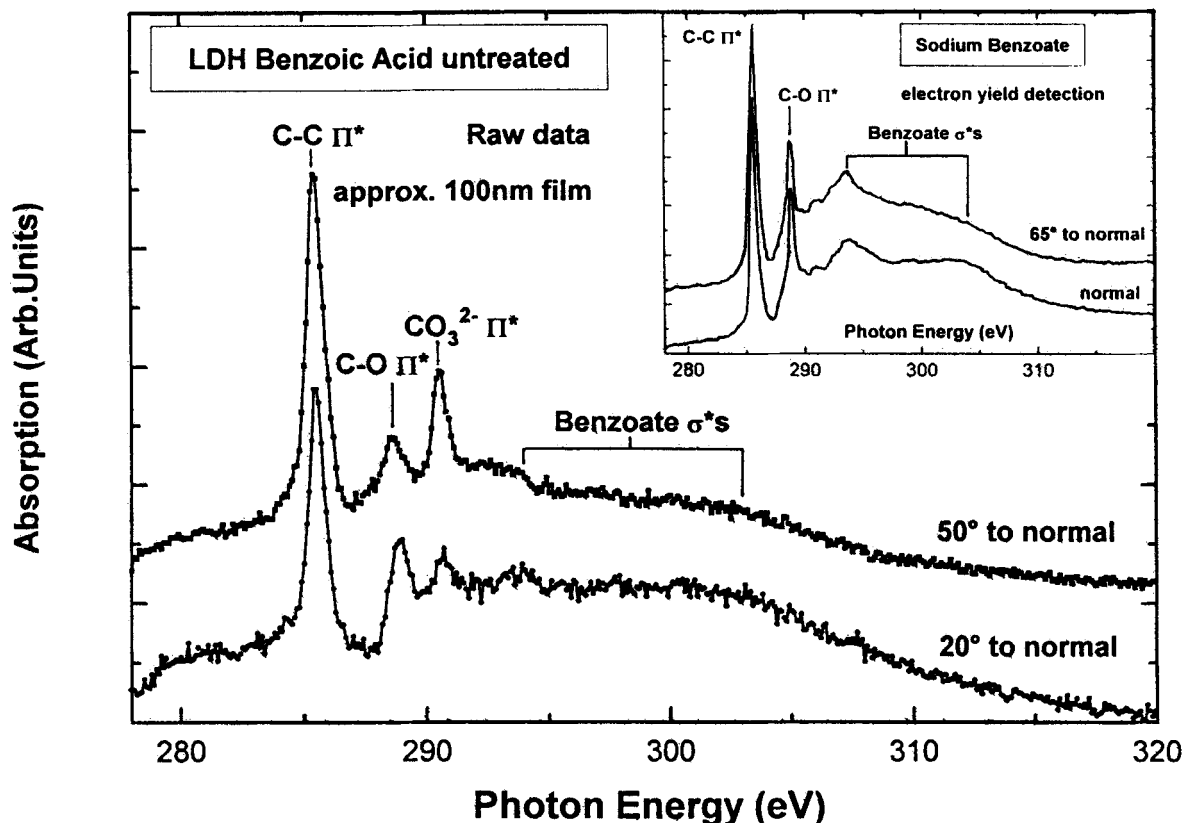


Figure 2. Raw NEXAFS data, recorded in fluorescence mode, of an approximately 100 nm LDH Benzoate film (dried under Ar). Inset—NEXAFS spectrum of Sodium Benzoate, recorded in electron yield mode.

Methods section), confirming the existence of the 300 eV σ^* resonance. Also the intensity of these two unidentified peaks was always seen to increase at the expense of the benzoate peaks in these more highly contaminated films, suggesting that they result from an anion which can substitute for benzoate in the LDH layers. The obvious candidate is carbonate, which indeed shows a Π^* resonance at 291 eV and a σ^* resonance at 300 eV, both as an adsorbate on Ag(110) and in bulk CdCO_3 (Madix *et al.*, 1988; Bader *et al.*, 1988). By good fortune, the presence of this carbonate impurity makes the interpretation of the NEXAFS data very much easier and more convincing, since it is extremely well established that carbonate lies flat within LDH layers (Miyata, 1975; Allmann, 1968; Taylor, 1973; Gastuche *et al.*, 1967). The angular dependence of a Π^* resonance originating from a double bond is given by the following expression (Stöhr, 1992, 279–283):

$$I = K (\cos^2\theta \cos^2\alpha + \sin^2\theta \sin^2\alpha \cos^2\phi + 2 \sin\alpha \cos\alpha \sin\theta \cos\theta \cos\phi)$$

where $\theta = 90^\circ$ —angle of incident beam to surface normal, $\alpha =$ angle of Π bond to surface (i.e., to LDH

planes), and $\phi =$ azimuthal angle of normal to P bond projected onto the surface (it has been assumed that the X-ray beam is completely plane polarized—in fact the polarization factor is around 0.85, but the difference made by including this refinement is small, and it would be stretching the data beyond credibility to consider it significant). If the z axis is taken as the surface normal, then the preferential orientation of the LDH crystals is only in the z direction, there being complete disorder in the xy plane. Thus in our case, we must integrate the above expression over all ϕ , to give:

$$I = K(2 \cos^2\theta \cos^2\alpha + \sin^2\theta \sin^2\alpha).$$

In the case of carbonate it is known that $\alpha = 0^\circ$ and so we expect

$$I(50^\circ)/I(20^\circ) = 2 \cos^2 40^\circ / 2 \cos^2 70^\circ = 5.0$$

i.e., the intensity of a flat lying Π^* resonance (e.g., carbonate) should increase 5 times on moving from 20° to 50° (in contrast a vertical Π^* resonance should decrease by 2 times).

Even from the raw data of Figures 2 and 3, the qual-

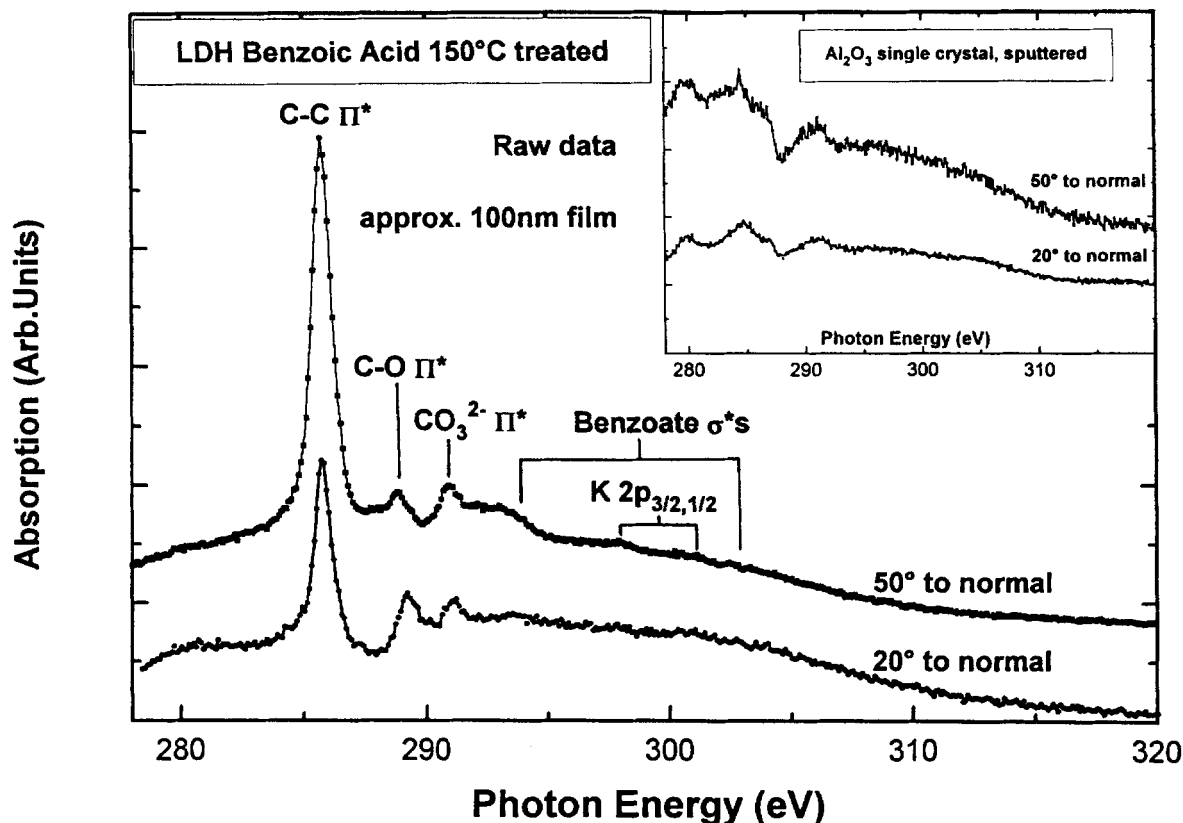


Figure 3. Raw NEXAFS data, recorded in fluorescence mode, of an approximately 100 nm LDH Benzoate film (dried under Ar) after heating to 150°C. Inset—Backgrounds used for subtractions from raw data, obtained in fluorescence mode from a highly sputtered Al_2O_3 single crystal.

itative features of the results now become apparent. The carbonate, as expected, appears flat in both cases, as does the benzoate after the 150°C treatment. However, in the untreated case, the benzoate seems to be intermediate between flat and vertical since the intensity of the C-C Π^* resonance increases on moving from 20° to 50°, but certainly not by as much as is the case for the carbonate Π^* .

To put these observations onto a sounder footing and to quantify the results, the spectra were normalized to the carbon edge step (see Experimental Methods section). Figure 4 shows the background subtracted data, normalized to the atomic absorption, for an untreated 100 nm LDH Benzoate film. The carbonate Π^* resonance shows an increase of about 5.4 times on changing from an X-ray incidence angle of 20° to normal, in excellent agreement with the value of 5 expected for a perfectly flat π orbital. This provides a highly convincing internal calibration of the background subtraction and normalization procedures, as well as confirming the highly oriented nature of such a thin film (as expected from the diffraction results).

The benzoate C-C Π^* resonance increases only 2.1

times on changing the photon incidence angle from 20° to 50° to the surface normal. Thus we have;

$$\begin{aligned} &2 \cos^2 40 \cos^2 \alpha + \sin^2 40 \sin^2 \alpha \\ &= 2.1(2 \cos^2 70 \cos^2 \alpha + \sin^2 70 \sin^2 \alpha) \\ &\Rightarrow \text{the angle of the benzoate to the} \\ &\quad \text{LDH layers, } \alpha = 35^\circ \end{aligned}$$

The angular dependence of the Π^* resonance depends on the normal to the plane of the phenyl ring; thus this angle is between the plane of the benzoate molecule and the 00 ℓ planes of the LDH.

It is important to make some estimate of the likely errors on this figure. Undoubtedly, the principal source of error is the normalization—the backgrounds, particularly pre-edge, at either end of the spectra are by no means perfectly flat and any error in estimation of the edge step will magnify directly onto the normalized peak intensities. Hence it would be unrealistic to suppose great accuracy in the determination of the ratio of Π^* resonances at the two angles. It seems reasonably safe, however, to assume that this ratio lies somewhere between 1.5 and 3 which limits the angle, α , to between

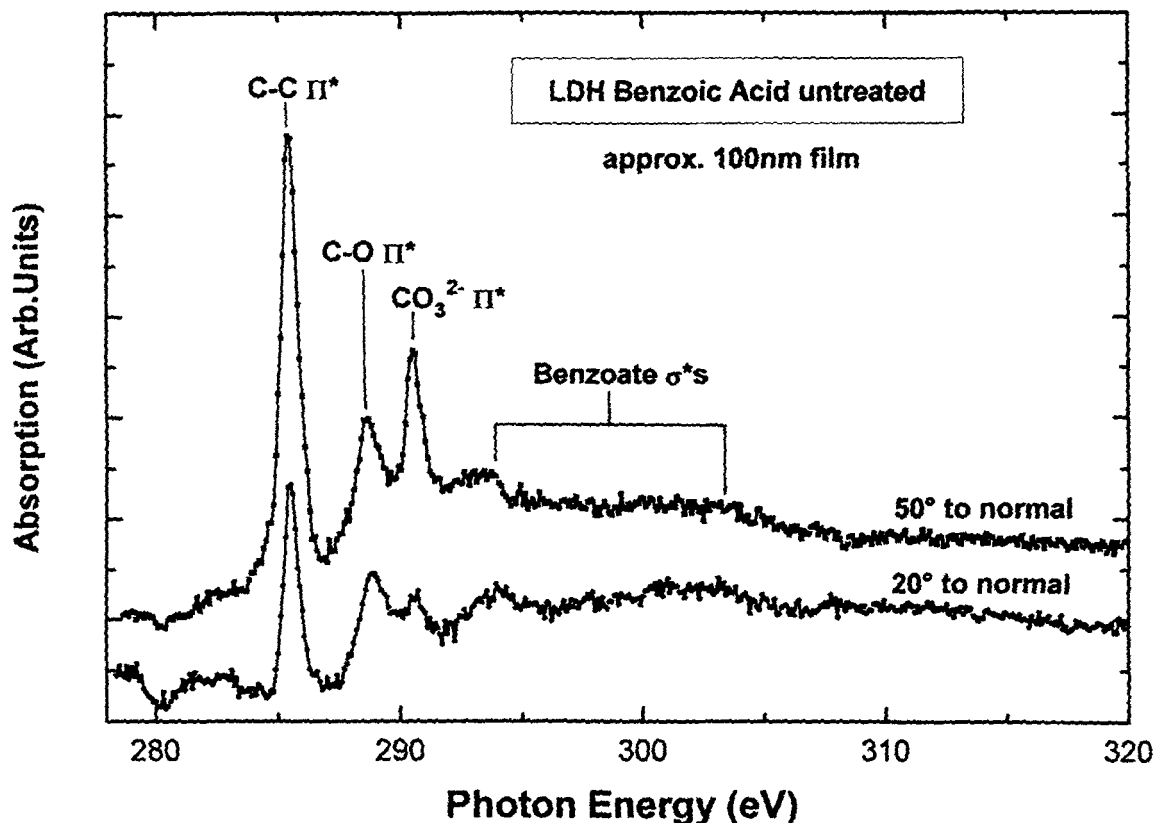


Figure 4. Background subtracted NEXAFS spectra of an approximately 100 nm LDH Benzoate film (dried under Ar), normalized to the carbon atomic absorption. Recorded in fluorescence mode.

25° and 44°. (Even if one lets the ratio vary from 1 to 4, α must still remain between 15° and 55°—this however seems needlessly pessimistic given the excellent agreement of the carbonate Π^* resonance with its expected behavior.) So $\pm 10^\circ$ seems a reasonable estimate of the accuracy of the measurement. This estimate of error was reinforced by checking the upper and lower limits for the edge step which seemed sensible given the level of background noise.

Figure 5 is similar to Figure 4, but displays data for the same sample after being heated to 150°C. The carbonate Π^* resonance now increases by approximately 3.8 times between photon incidence angles of 20° and 50° to normal, though in this case the exact ratio is rather difficult to estimate due to the small size of the carbonate features, relative to the very large benzoate Π^* resonances. Again the agreement with the expected value of 5 for flat lying carbonate is satisfactory. Meanwhile the benzoate C-C Π^* resonance increases by 4.3 times with the same increase in photon incidence angle to the surface normal. This is completely consistent with the benzoate now lying flat with respect to the LDH layers. Again an error of $\pm 10^\circ$ can be assumed to be reasonable.

Figure 6 shows background subtracted data, normalized to the atomic absorption, for an LDH Benzoate film of about 2000 nm thickness. Moving from a photon incidence angle of 20° to normal to 50°, the carbonate Π^* resonance now increases only approximately 2 times, whilst the benzoate C-C Π^* resonance increases 1.25 times. This is completely consistent with the data of Figure 4 if one assumes a lower degree of preferential orientation in the superficial layer of this much thicker film, compared to the 100 nm film. This is exactly what is expected from the earlier discussion of the diffraction data. It is interesting to note that significant preferential orientation still remains even at the surface of such a thick film. This orientation might, however, result in very little enhancement of the 00 l reflections, the criteria of “good” orientation in diffraction being much more stringent ($\pm 0.5^\circ$) than that for NEXAFS.

There are two reasons for including Figure 6. The first is to demonstrate convincingly that the background subtraction and normalization procedure is successful for more than one sample. It proved effective for a range of film thicknesses and carbonate impurity concentrations; these spectra are not shown as they are

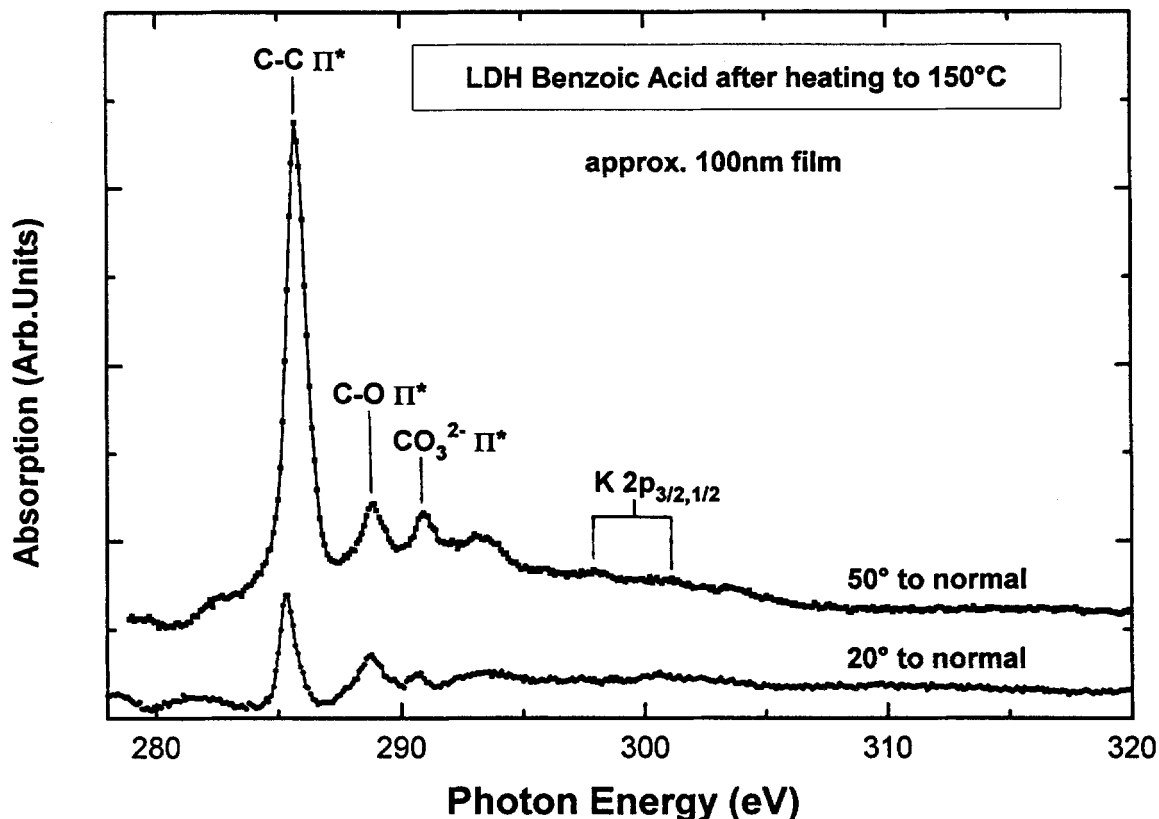


Figure 5. Background subtracted NEXAFS spectra of an approximately 100 nm LDH Benzoate film (dried under Ar) after heating to 150°C, normalized to the carbon atomic absorption. Recorded in fluorescence mode.

generally similar (the data quality decreasing with film thickness) and show high degrees of carbonate contamination. Secondly, if one compares Figure 6 with Figure 4 there is a definite improvement in the form of the spectra, relative to the standard benzoate spectra of Figure 1 (inset). In particular, the ratio of the C-O π^* resonance intensity to that of the C-C π^* resonance is improved and the background in the region of the first σ^* resonance appears much flatter. The conclusion must be that the use of thicker films is desirable, both because it removes interference effects from the substrate and minimizes the errors in the background subtraction, presumably by maximizing the fluorescence signal from carbon. Hence a film of perhaps 200 nm thickness might be optimal for future experiments. Such a film can still be expected to be very well oriented and the fluorescence photon escape depth will have been exceeded, so maximizing the signal.

Another obvious improvement on this experiment would be to use for the background subtraction a material closer in structure to LDH Benzoate, e.g., LDH Nitrate or Brucite. It would, however, be essential to ensure the complete absence of carbon from such materials, which is where the use of an Al_2O_3 single crystal

has its great advantage. The oxygen background subtraction could also be improved by deposition of the LDH onto an oxygen free substrate ensuring that the oxygen contribution to the background was both minimized and originated from a single material. Ultimately a method of removing the 2λ contamination from the incident beam would make data treatment for an experiment such as this one trivial. Not only would the oxygen background disappear but also the effect of the carbon on the optics would be completely removed after division by I_0 .

Whilst future experiments could certainly be improved with the above considerations, even using the methods described in this paper it has been unequivocally demonstrated that NEXAFS is an excellent method for determining the orientation of organic molecules within layered compounds, to a good degree of accuracy.

DISCUSSION

What is remarkable about LDH Benzoate is that it is able to form a stable and crystalline expanded structure, which collapses at very low temperature ($\sim 50^\circ\text{--}100^\circ\text{C}$) to a compressed phase. It is by no means un-

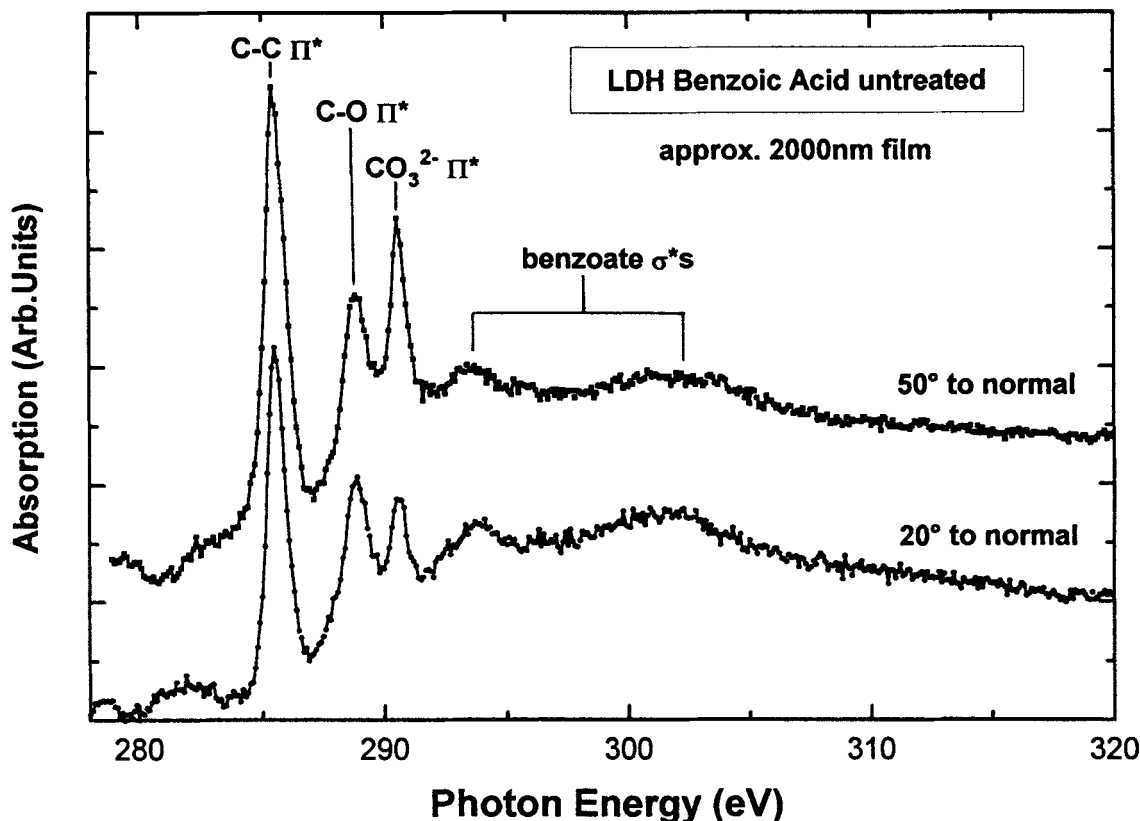


Figure 6. Background subtracted NEXAFS spectra of an approximately 2000 nm LDH Benzoate film (dried in air), normalized to the carbon atomic absorption. Recorded in fluorescence mode.

usual for clays and other layered minerals, notably vermiculites and smectites, to form such expanded structures as a result of sorption of water or organic molecules (Barrer, 1978). However, it is usual for the collapse of the structures to occur in a stepwise fashion over a range of temperatures, as sorbed molecules are gradually released or hydrocarbon chains slide over each other (Borja and Dutta, 1992). Also higher temperatures are usually required to cause complete collapse. It is presumably the rigidity of the benzoate molecule and the strong ionic anchoring of the acid groups to the brucite-like layers which causes this "binary" behavior with heating. Distortion of the benzoates is impossible and so the structure can adopt one of only two stable phases. The general analogy to other expanded layered minerals in terms of the importance of hydrogen bonding and hydrophobic-hydrophilic interactions in determining the most stable structure is obvious and illustrates the range of possibilities for the NEXAFS technique described.

It is of interest to have as much information as is possible about the interlayer structure which mediates these interesting properties. As has been mentioned already, the gallery height available in the expanded structure (10.5 Å) is greater than the length of the ben-

zoate anion (6 Å). It is also interesting to note that the area per cation is about 24 Å² in the layers, which is very close to the area of a flat lying benzoate. Thus it is clear that the volume available in the interlayer is much larger than the volume required by a stoichiometric quantity of benzoate anions. So one can expect a large amount of water to fill the interlayer space in the expanded form. Thermogravimetric analysis confirms the loss of somewhere between four and six water molecules per unit cell as the structure collapses. Also, it seems likely that the hydrophobic phenyl rings will be repelled from the ionic layers and so it is hard to imagine the benzoates lying flat in the expanded structure. The details of the benzoate packing will be determined by hydrogen bonding and hydrophobic-hydrophilic interactions between benzoates and waters in the interlayer.

One can imagine that within a single interlayer the benzoates can either distribute themselves equally between the two hydroxide faces available or all bond to a single face. The latter case can be rationalized on the grounds of packing together all the hydrophobic phenyl groups. The expansion can then be explained by a layer of water between the hydrophobic phenyls and the ionic opposite hydroxide layer. However, this model is

hard to rationalize both on electrostatic grounds since the negative charge is not separated and because it is hard to understand the discrete layer expansion and collapse which is observed. If all that is maintaining the interlayer spacing is a "buffer zone" of water, it is hard to see why this should have only a single thickness. One might rather expect to see several different layer expansions with different numbers of water molecules per unit cell, as is the case in the vermiculites and smectites (Barrer, 1978). This structure would be unlikely to give rise to a concerted, single step interlayer collapse. Although this model cannot be ruled out by this study, it seems improbable for the reasons given above.

If one therefore assumes that the benzoates are equally distributed between opposing brucite-like layers, the interlayer spacing will be determined by the interaction between the phenyl rings facing each other, possibly mediated by water. It is well known from the crystal structures of poly(4-hydroxybenzoates) (Coulter *et al.*, 1989; Liu and Rybnikar, 1993) that phenyl rings prefer to pack edge to ring, presumably due to hydrogen bonding between the π -cloud and the hydrogens of the neighboring ring. So this can be expected to be the dominant hydrophobic interaction determining the interlayer spacing. Of course hydrogen bonding between the hydroxide layers and interlayer water will also be very important, but this is unlikely to be so critical in determining the exact layer spacing since the molecules lack the rigidity of benzoates.

Two models for the structure can be envisaged. The benzoates could stand vertically, the planes of the rings being rotated by 90° for benzoates standing on opposite faces. The phenyl rings from opposite faces would then overlap by about 2 Å, allowing good interaction between the hydrogens and π -clouds. It is interesting to note, though perhaps only accidental, that the unit cell parameters perpendicular to the chain direction in many poly(4-hydroxybenzoates) structures (Coulter *et al.*, 1989; Liu and Rybnikar, 1993) would overlay almost exactly onto the unit mesh of cations in the brucite-like layers. Thus this model is highly plausible from the point of view of stabilization of the structure. What is harder to comprehend is how this structure could easily collapse, since the flattening of benzoates would be hindered by neighboring phenyl groups. Alternatively the benzoates could form a herring bone type of structure, the terminal hydrogen of one benzoate hydrogen bonding to the π -cloud of a phenyl ring from the opposite layer. With the benzoate at angles between 30° and 50° , this would result in very plausible hydrogen bonding distances, around 2 Å. As well as seeming energetically reasonable, this model explains the great ease with which the structure collapses, the relatively small additional tilt required of the benzoates being unhindered by neighbors from the opposite face. The NEXAFS experiments described above unambiguously

support this herring bone type of structural model for the expanded LDH Benzoate.

CONCLUSIONS

At room temperature the plane of the benzoate molecule lies at $35^\circ \pm 10^\circ$ to the 00 l planes in LDH Benzoate. After heating to 150°C the benzoate was found to lie flat. This correlates well with diffraction results which shows the layer spacing collapsing from 15.4 Å to 9 Å over the same temperature interval. The surprisingly small change in orientation (and so presumably in energy) of the benzoate during the change in layer spacing helps to explain the remarkably low temperature (less than 100°C) and high degree of reversibility of this transition.

The tilting of the benzoate at room temperature within the LDH interlayers, despite the availability of ample room for it to stand vertically, provides strong evidence for some form of interaction between the brucite-like layer and the phenyl ring. The most likely explanation is delocalization of the benzoate's negative charge into the phenyl ring and coulombic attraction of this to the excess positive charge of the inorganic sheets. Thus the distribution of the negative charge between the oxygens and carbons will determine the tilt angle of the benzoate molecule. The flattening upon heating might then be explained by the entropy gain due to the loss of water of crystallization balanced against the coulombic energy lost due to the deviation from the optimum orientation of the benzoates relative to the brucite-like layers; what is certain is that this flattening is reversible and so must be of thermodynamic rather than kinetic origin. It is also interesting to note that a 35° tilt angle leaves a vertical distance of around 2–2.5 Å between the terminal hydrogen of a benzoate attached to one layer and the center of the phenyl ring of that bonded to the layer opposite—a suitable distance for hydrogen bonding. This is highly suggestive of the role of hydrogen bonding in stabilizing the crystal structure.

The general conclusion is that NEXAFS may have considerable potential as a method for determining the orientation of organic molecules intercalated within layered compounds. The potential applications of such a method are widespread, the behavior of organics within such materials being of great commercial and academic interest and the variety of such structures being vast.

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