Monitoring the Course of Intercalation by Spectroscopic Means. Insertion of Gaseous $SbCl_5$ into Graphite

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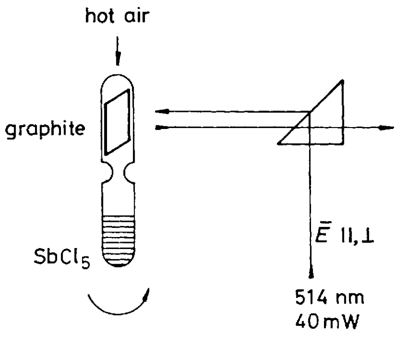
In situ studies, using Raman spectroscopy, enable the extent of intercalation of $SbCl_5$ into graphite to be evaluated from changes in the frequency of the in-plane E_{2g} lattice mode of the graphite host, and the nature of the intercalated guest to be deduced from accompanying changes in the low frequency 'molecular' vibrational modes.

In this communication we show that: (1) following intercalation, significant changes occur in the vibrational modes of $SbCl_5$; (2) the progress of intercalation can be followed by monitoring the changes in the lattice modes of graphite;[1] (3)



Scheme 1

the survival of bending vibrational modes and the gradual elimination of Sb–Cl stretching modes as intercalation proceeds are consonant with recent studies[2] of this system with other techniques; and (4) the spectral features of adsorbed $SbCl_5$ on carbon or graphite are distinct from those of the intercalated species.

On the basis of previous work (see comprehensive review ref. 1a) we expect the frequency of the in-plane E_{2g} ('C–C' stretch) mode of the graphite host to increase during the formation of acceptor graphite intercalates. Indeed the intensity changes as between the original peak at 1582 cm^{-1}, characteristic of pristine graphite, and the new one at 1624 cm^{-1},[1a,2c] characteristic of a single graphitic sheet bonded between $SbCl_x$ layers can be used to monitor the extent of antimony halide intercalation. Until recently, the molecular vibrations of the assimilated guest, expected in the range of 50—500 cm^{-1}, could not be detected, unlike the corresponding modes of adsorbed and partially hydrolysed $SbCl_5$, which, in the work of Eklund *et al.*,[3] were just detectable.

In a previous communication[4] we reported the observation of molecular modes diagnostic of several octahedral and tetrahedral derivatives of $SbCl_5$. In order to confirm that these derivatives are indeed intercalated we used the set-up shown in Scheme 1 thereby allowing the conversion of $SbCl_5$ *during* reaction to be directly observed. A single flake (*ca.* $1.5 \times 1.5 \times 0.05$ mm^3) of natural graphite (S40, Kropfmuhl[5]) is mounted in one compartment of a Pyrex capillary tube (3 mm diameter, 10 cm length), the lower part of which contained pure $SbCl_5$ which, by heating, could be vaporized and so effect intercalation (preceded by adsorption) in the upper compartment. For blank experiments a hard carbon black of low porosity (CK3, Degussa) which only adsorbs $SbCl_5$, but will not intercalate it, was placed in the upper compartment.

Spectra were recorded on a Cary-82 Raman spectrometer using a focussing back-scattering geometry. An Ar^+ laser (514 nm wavelength) with 40 mW output at the sample position was used as source: this could be plane polarized and focussed to an area of 0.05×2.0 mm^2 at the specimen. The spectral width was, as reported in the previous communication,[4] set to 6 cm^{-1}; for the wide scans of Figure 2 and in order to record satisfactorily the broad peaks, the spectral width had to be increased to 10 cm^{-1}.

First we focus on the Raman features associated with adsorbed and partly hydrolysed $SbCl_5$, using carbon black as the non-intercalatable adsorbent. Figure 1(a) shows the Raman spectrum after exposure of the carbon to $SbCl_5$ vapour at room temperature for 48 h. This spectrum is closely akin to that of pure $SbCl_5$[6] and clearly reveals the intense Sb–Cl stretching vibration at *ca.* 360 cm^{-1}. In addition two new peaks at 125 cm^{-1} and at *ca.* 200 cm^{-1}, associated with macroanionic species arise after several days of exposure of the carbon black to $SbCl_5$ (see later). The spectrum in Figure 1(b) results after the adsorbed $SbCl_5$ had been exposed to air for 48 h. Indistinguishable spectra were obtained when either glass or graphite were used as adsorbents, but with no intercalation in the latter case. This new spectrum is attributable[7] to species such as $SbCl_{5-x}(OH)_x$. Note that the Sb–Cl stretching frequency still stands out clearly in the spectrum of this air-exposed sample.

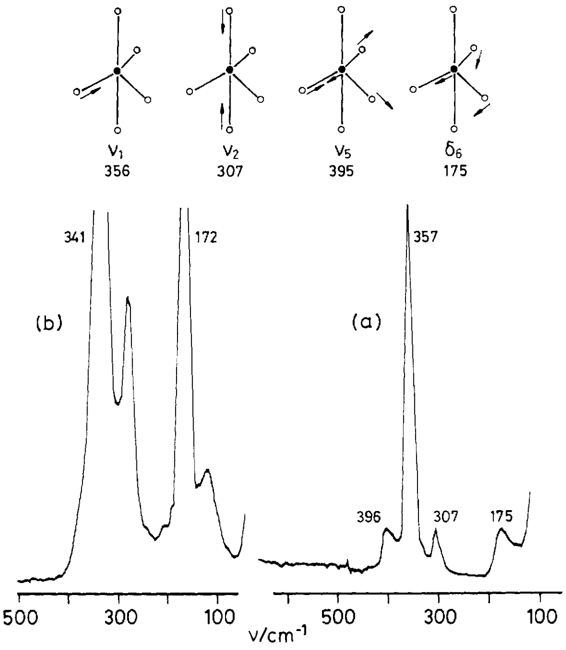


Figure 1. Raman spectra in the region of molecular vibrations for $SbCl_5$ (a) adsorbed on carbon black and (b) after exposure to air for 48 h. The frequencies in the schematic representations of some Raman-active fundamental vibrations relate to pure liquid $SbCl_5$.

The spectroscopic features observed when a capillary filled with graphite was heated slowly up to 80 °C are shown in Figure 2. After the initial adsorbed state [see Figures 2(a) and 2(e)], but prior to the onset of intercalation, which can be detected by the symptomatic changes in the C–C stretch [see Figures 2(e)—(g)], new peaks appear in the molecular vibrational region [see Figures 2(a)—(d)] of the spectrum. Thus in addition to the $SbCl_5$ frequencies, there are new features at 125 cm^{-1} and 200 cm^{-1} which were also seen in the case of the carbon black (see above) suggesting the formation of Sb–Cl–Sb bridges,[8] which would, in turn, imply that an oligo- or macro-anionic species of the antimony halide forms at the exterior surface. These new features are just about visible, but much less well resolved, in the spectrum of Eklund *et al.*,[3] who did not comment upon their occurrence.

After monitoring the reactants for 12 h at 60 °C intercalation properly begins (see onset of a rather broad peak around 1620 cm^{-1} in the C–C stretch region) concomitantly a very broad new line, with a maximum at *ca.* 500 cm^{-1}, appears [Figure 2(c)]; but we still detect the molecular vibrations superimposed on this broad peak. After 24 h the intercalation is complete, at least within the probing depth (*ca.* 1 μm) of Raman spectroscopy. Note that the Sb–Cl stretching frequencies have now disappeared, but the bending vibrations remain, although, owing to the experimental conditions, they are rather less well defined than in the earlier study.[4]

Using polarized light, and by varying the orientation of the intercalated graphite with respect to the electric vector of the

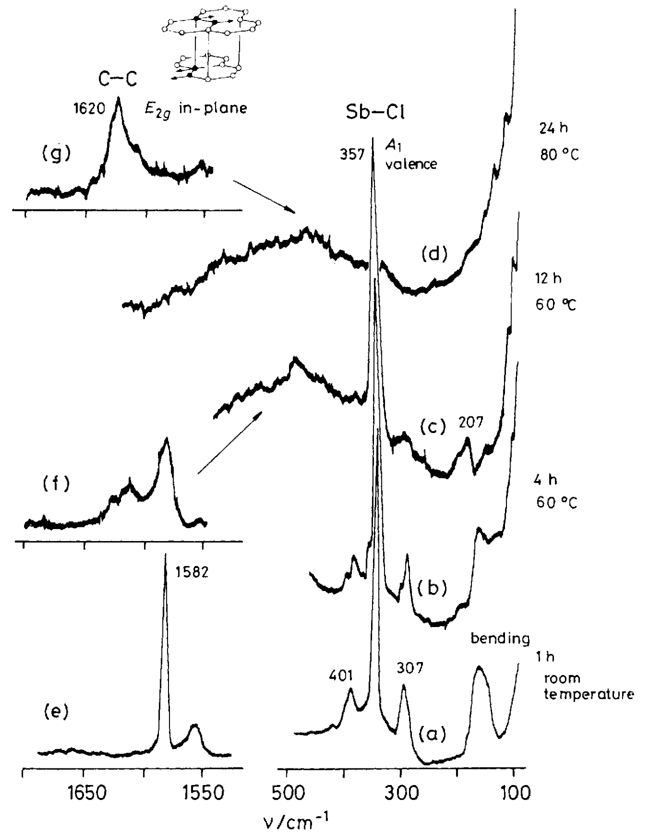


Figure 2. Raman spectra during intercalation of $SbCl_5$ into graphite. Spectra (a)—(d) display the region of molecular vibrations in low resolution (see text). Note the broad new feature replacing the Sb–Cl stretching vibrations. Spectra (e)—(g) illustrate the progress of intercalation as monitored by the gradual shift of the C–C stretching vibration.

stimulating source, we have established that the loss of the Sb–Cl stretching frequencies is not attributable to preferential orientation of the intercalated species. This disappearance alone shows that our spectra[4] do not refer to adsorbed entities, but are, instead, associated with a guest entity that is quite distinct from the initial $SbCl_5$ molecular species. Furthermore we exclude the possibility that the observed molecular modes may be ascribed to adsorbed (see Figure 1) $SbCl_5$ (or to its hydrolysis products) on the exterior surface of the graphite.

All these results support the hypothesis[2c,4,9] that the reaction of $SbCl_5$ with graphite results in the formation of an oligo- or poly-meric macroanion inserted between the graphite layers. The constitution and composition of the anion seem to be widely variable and dependent exclusively upon the preparation conditions.[2b]

One of us (R. S.) acknowledges a stimulating discussion with M. S. Dresselhaus and G. Dresselhaus. We thank the National Coal Board for support and Professor Breitinger (Erlangen) for generously permitting us access to his Raman spectrometer.

Received, 1st September 1983; Com. 1182

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