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## RAMAN SCATTERING STUDY OF ALKALI-MOLECULAR TERNARY GRAPHITE INTERCALATION COMPOUNDS

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## Summary

We have studied the room temperature Raman spectra of several stages of ternary GICs prepared by sequential intercalation of potassium-binary GICs with either furan, THF or  $\text{NH}_3$ . A Raman study, which detects the shift of the graphite intralayer vibrational frequency due to intercalation, provides a useful tool for the probe of charge transfer of these novel materials. For all three stage 1 compounds, we have observed an intralayer graphite vibrational frequency at  $\sim 1606 \text{ cm}^{-1}$  (upshifted from the pure graphite peak at  $1582 \text{ cm}^{-1}$ ), which is Fano broadened and has a Raman profile similar to that exhibited by  $\text{LiC}_6$  and  $\text{EuC}_6$ . These results are compared and contrasted with those for the alkali binary GICs.

## 1. Introduction

The study of graphite intercalation compounds (GICs) continues to be an exciting field of interest [1, 2]. These interests stem primarily from the possibility of studying 2D systems and their corresponding phase transitions. Another aspect, which has been the subject of considerable debate, has been the nature and quantitative value of the charge transfer to the host lattice [3].

Most work to date on GICs has been on binary systems where there is an intercalation of only one species in the graphite host. For a ternary GIC, however, there exists the possibility of an even richer variety of phases and also of intercalation of competing (donor *versus* acceptor) species. This, in turn, may give a better understanding of 2D phase transitions and the nature of the interaction between the intercalant and the host [3].

In this paper, we present the Raman spectra for three different graphite ternary systems; K-furan, K-THF and K- $\text{NH}_3$  GICs. X-Ray studies [4 - 8] on these materials have shown that these ternaries exhibit different stages and also undergo interesting staging phase transitions. Our Raman results

supplement the X-ray data and also give further insight into the above mentioned aspects of intercalant-host bonding. We compare and contrast our results with corresponding binary potassium GICs.

## 2. Sample preparation and experimental procedure

The molecular ternaries were prepared by exposing the potassium binary GICs (previously made by using the standard two-bulb technique) [9] to the molecular species involved (*i.e.*, furan, THF and  $\text{NH}_3$ ). A long glass tube with a break seal initially isolated the molecular liquid from the graphite-potassium system. After preparation of the alkali binary, the seal was broken and the sample exposed to the molecular liquid. Intercalation took place through the molecular vapor or through direct contact with the liquid. The tube was then further sealed to isolate the ternary GIC with just the molecular liquid to avoid interactions of the bare potassium with the liquids (furan and THF react with potassium over a period of time). Several samples were made in this manner with starting binaries of stages 1, 2 and 3. With  $\text{NH}_3$ , a ternary was also made with an initial potassium stage 4 binary. Table 1 indicates the stages of the resulting ternaries which resulted from intercalation of the various initial binaries.

An argon ion laser provided the incident beam ( $\lambda = 4880 \text{ \AA}$ ) for the scattering studies. The power of the beam was measured at  $\sim 30 \text{ mW}$  near the sample. A Jarell-Ash double grating monochromator was used for the analysis of the scattered light. Alignment of the sample consisted of focussing a line image of the beam onto the GIC surface. The scattered light was collected and focussed on the spectrometer slit in the back scattering  $90^\circ$  geometry arrangement. The incident beam was polarized in the scattering plane to obtain a maximum coupling of the incident radiation to the sample.

TABLE 1

Stages of the ternary GICs produced with different initial potassium binary GICs

Initial K binary	Stage of resulting ternary after intercalation*		
	Furan	THF	$\text{NH}_3$
$\text{KC}_8$	—	—	1
$\text{KC}_{24}$	2	1	1**
$\text{KC}_{36}$	2	2	1 + 2
$\text{KC}_{48}$	—	—	2 + 3

\*Verified by X-rays.

\*\*A different stage 1 from the one made by  $\text{KC}_8$ .

### 3. Results and discussion

The Raman spectra of graphite (or HOPG) has been known for some time [10, 11]. There are two Raman active bands corresponding to a low frequency shear mode at  $42\text{ cm}^{-1}$  and a prominent intralayer mode at  $1582\text{ cm}^{-1}$ . The changes of the  $1582\text{ cm}^{-1}$  mode due to the intercalation of potassium in different stages have also been well studied [12]. Recently, the vibrational modes of the intercalant have also been observed directly [13, 14].

Figure 1(a) shows a spectrum for the  $\text{KC}_8$  stage 1 GIC. The  $1582\text{ cm}^{-1}$  band has been considerably Fano broadened [12] due to an electronic continuum arising from the strong coupling between the potassium donor and the host [15]. There also exists a low frequency  $563\text{ cm}^{-1}$  band arising from both disorder induced scattering and the  $(2 \times 2)\text{R}0^\circ$  ordering of the potassium in the plane [16]. However, the spectrum of a stage 1 ternary GIC,  $\text{K-THF}$  in this case, is noticeably different and is shown in Fig. 1(b). The sample was prepared by the intercalation of  $\text{KC}_{24}$  with THF vapor, as indicated in Table 1, and also characterized by X-rays to be a pure stage. Note from Fig. 1(b) that the intralayer mode has been shifted to  $1606\text{ cm}^{-1}$  and is considerably narrower. The spectrum in fact is more like that of stage 2  $\text{KC}_{24}$  or stage 1  $\text{EuC}_6$  [17]. Indeed, the color of the sample here is a deep blue, as in  $\text{KC}_{24}$ , rather than the gold expected of  $\text{KC}_8$ . The narrowness of the peak ( $\Delta\tilde{\nu} \sim 22\text{ cm}^{-1}$ ) implies a weaker coupling between the  $1582\text{ cm}^{-1}$  mode and the continuum than in the  $\text{KC}_8$  case. Interestingly, this peak is even narrower than in  $\text{KC}_{24}$  ( $\Delta\tilde{\nu} \sim 29\text{ cm}^{-1}$ ). The disappearance of the low frequency  $563\text{ cm}^{-1}$  band is consistent with the X-ray observation [7] of disorder in the plane.

A similar comparison has been made of the spectrum for the ternary (K-furan)  $\text{C}_{24}$ . Here, the resulting ternary prepared from  $\text{KC}_{24}$  (see Table 1) is also stage 2. Again, the carbon intralayer mode of the ternary is sharper ( $\Delta\tilde{\nu} \sim 23\text{ cm}^{-1}$ ) than that in  $\text{KC}_{24}$ , as shown in Fig. 2. Since one would not expect any appreciable change in the graphite phonon modes in the two cases, the width seems to be related to the charge transfer between the host and intercalant. We suggest that the furan molecule, being an acceptor, reduces the charge transfer to the host from the potassium donor. There is no appreciable shift in frequency between the two compounds.

Studies performed on the  $(\text{K-NH}_3)\text{C}_{24}$  system are shown in Fig. 3. Here, again, the ternary was prepared *via* the  $\text{NH}_3$  intercalation of  $\text{KC}_{24}$ . At room temperature, where the vapor pressure of  $\text{NH}_3$  surrounding the sample is  $\approx 10\text{ atm}$  (there is an excess amount of  $\text{NH}_3$  liquid in the sample tube), the ternary is a pure stage 1 [8]. It has been shown from the X-ray results [8] that as the vapor pressure of the  $\text{NH}_3$  is reduced by maintaining the excess  $\text{NH}_3$  at liquid  $\text{N}_2$  temperatures, for which the vapor pressure surrounding the sample is  $< 0.1\text{ Torr}$ , the sample evolves into a three phase system containing  $\text{KC}_8$ ,  $\text{KC}_{24}$  and pure stage-2  $\text{K}(\text{NH}_3)_{1.66}\text{C}_{23.86}$ . These changes are clearly reflected in the Raman spectra as well. The appearance of



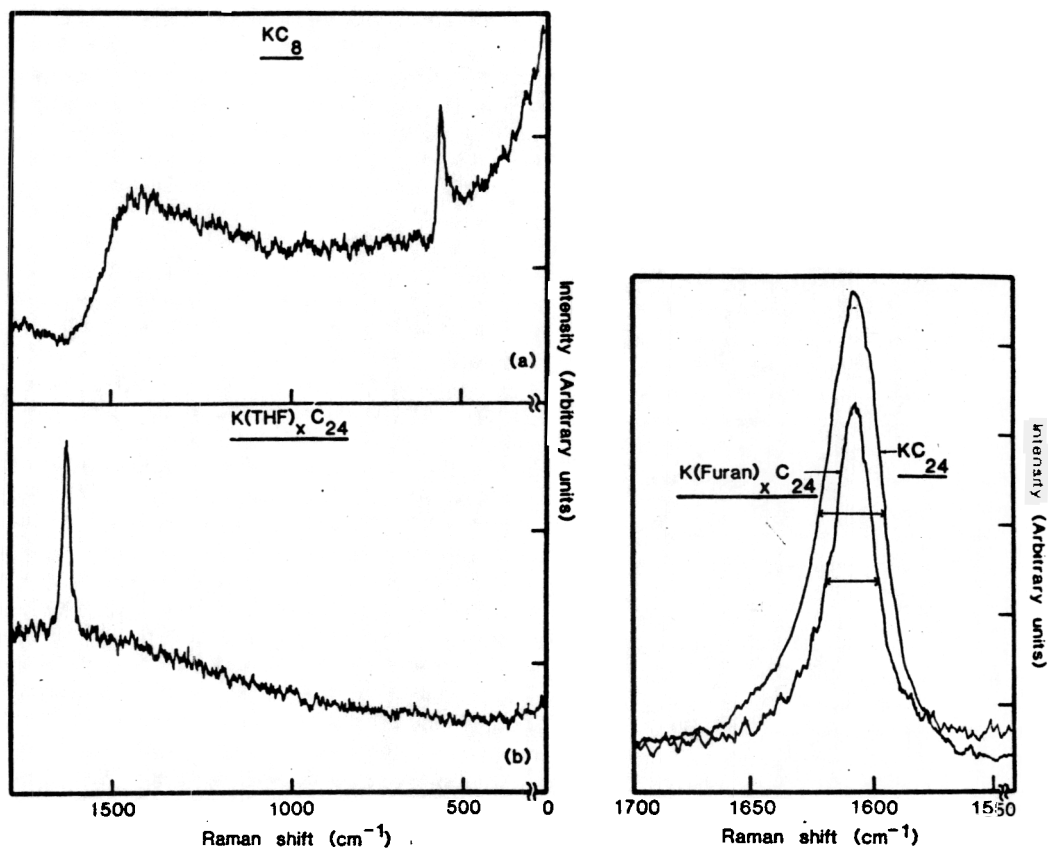


Fig. 1. The Raman spectra of an (a) stage 1  $KC_8$  and (b) stage 1 ternary  $K(THF)_xKC_{24}$ . The abscissa in this Figure and the Figures which follow is linear in wavelength rather than wavenumber.

Fig. 2. Comparisons of the widths of the graphite intralayer mode for samples  $KC_{24}$  ( $\Delta\tilde{\nu} = 29 \text{ cm}^{-1}$ ) and  $K(\text{furan})_xC_{24}$  ( $\Delta\tilde{\nu} = 23 \text{ cm}^{-1}$ ).

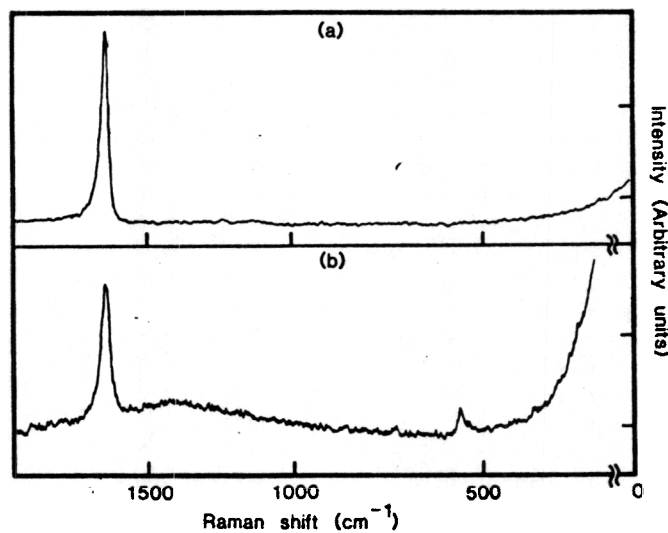


Fig. 3. The room-temperature Raman spectra of (a) stage 1  $K(NH_3)_{4.38}C_{23.86}$ , excess  $NH_3$ , at room temperature, and (b) stage-2  $K(NH_3)_{1.66}C_{23.86} + KC_8 + KC_{24}$ , excess  $NH_3$ , at 77 K.

the  $563\text{ cm}^{-1}$  peak is an indication of the presence of  $\text{KC}_8$  which, with  $\text{KC}_{24}$ , tends to reside on the sample surface. The superposition of the intralayer mode at slightly different wavenumber shifts for  $\text{KC}_{24}$  and  $\text{K}(\text{NH}_3)_{1.66}\text{C}_{23.86}$  has resulted in the broadening of the  $\sim 1580\text{ cm}^{-1}$  peak. Similar staging phase transitions may occur in the furan and THF systems as a function of intercalant vapor pressure as well.

Other higher stage phase transitions in the  $\text{K-NH}_3$  ternary GIC system, as seen by X-ray [18], have also been evident in the corresponding Raman spectra. Figure 4 shows the change to a stage 2 + 3 ( $\text{K-NH}_3$ ) ternary from a stage 4  $\text{KC}_{48}$  sample. Similar results were also seen for the THF and  $\text{NH}_3$  samples [19]. The relative intensities of the members of the doublets shown are consistent with the stage 4 and stage 2 + 3 designations.

It can be clearly seen that the results presented here indicate a richness in variety of possibilities for a better understanding of GIC systems. The Raman scattering results have also thrown light on understanding the width of the graphite intralayer mode. The Raman results are consistent with, and supplementary to, the X-ray results.

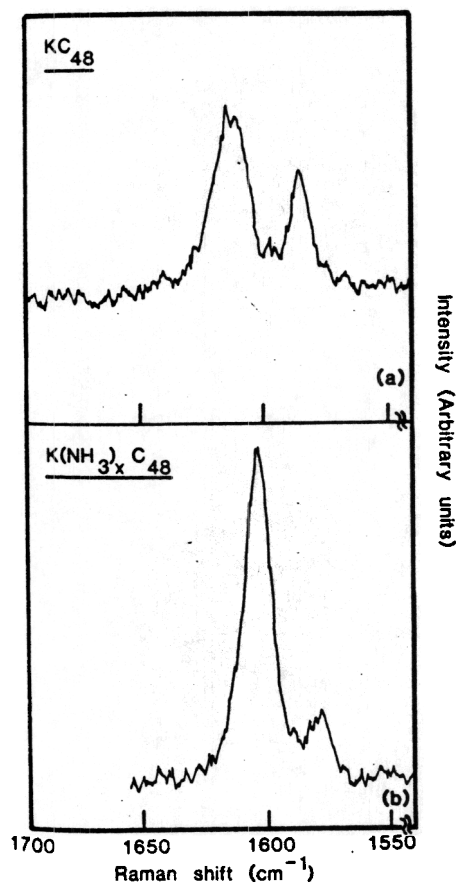


Fig. 4. Raman spectra showing the transformation of a stage 4  $\text{KC}_{48}$  binary GIC to a stage 2 + 3  $\text{K}(\text{NH}_3)_x\text{C}_{48}$  ternary GIC.

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