Resonance Raman Scattering from the High Frequency Intralayer Phonons in Graphite-H₂ SO₄ via Interband Absorption

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Introduction

The Raman-active (E_{2g}), graphitic intralayer modes (~ 1600 cm⁻¹) in graphite intercalation compounds (GIC's) have been studied extensively over the past several years [1]. These zone center phonons have been shown in a variety of acceptor- and donor-type GIC's to provide valuable stage index information in a probe depth of about 1000 A. The mode in pristine graphite (1582 cm^{-1}) is perturbed by the insertion of the intercalate layers to produce a Raman-active doublet (stage n>2) or a Raman-active singlet (n=1,2) in the spectra of GIC's. The high- and low-frequency components of the doublet have been identified [1] with intralayer carbon atom displacements taking place primarily in the bounding and interior layers, respectively. Studies of the stage dependence of the relative line intensities (or relative Raman cross sections) of the doublet were made to establish this identification. However, no attention has been given to the laser frequency dependence of the Raman cross section of these graphitic intralayer modes. In this paper we present the first results of such a study. For the stage 1,2 compounds of graphite- H_2SO_4 , we find that the Raman cross section does indeed exhibit a marked dependence on laser frequency. We present results of model calculations that show this frequency dependence is associated with the threshold for interband absorption between valence and conduction band states located within a few eV of the Fermi surface.

Experimental Details

The experiments were carried out in situ through the quartz walls of the electrochemical cell used to prepare the compounds. Details of the cell have been given elsewhere [2]. The samples were intercalated electrochemically by submerging ~ one half of a highly oriented pyrolytic graphite (HOPG) plate into concentrated (96-98%) Baker Analyzed H_2SO_4 . The Raman cross section data were collected in the Brewster-angle backscattering geometry with the laser beam (~20 mW) incident on the c-face region of the GIC plate above the acid

level. Various laser lines from Argon and Krypton lasers were used to study the incident photon frequency dependence of the Raman cross section. Using results from previous coulometric and x-ray studies on graphite-H2SO4 [3], the stage and stoichiometry of the samples were determined from the electrochemical charge passed during the reaction. Using this information, in addition to recent results of Raman scattering studies of staging kinetics in graphite-H₂SO4 [4], stage 1 and 2 compounds were prepared for the present study. The stoichiometry of these compounds have been shown [3] to be of the form $C_p^+(HSO_4^-)(H_2SO_4)$. We present results on the stage 1 C_{28}^+ , C_{21}^+ and stage 2 C_{60}^+ , C_{48}^+ compounds.

Results and Discussion

In Fig. 1 we show the normalized Raman cross section data vs incident photon energy for the respective stage 1,2 compounds. The solid lines in the figure are guides for the eye. We define the normalized cross section in this study to be the integrated Raman line intensity (counts) per incident laser power (mW) divided by the cube of the scattered photon frequency. As can be seen in the figure, the cross section data appear to be well-described by a series of peaks several tenths of an eV wide which shift to higher photon energy with increasing charge transfer f=1/p (i.e. f=1/60, 1/48, 1/28, 1/21). These peaks are positioned near the anticipated thresholds for interband transitions in these componds.

The band structure [5] for a stage 1 acceptor-type compound near the K-point in the Brillouin zone is shown schematically in the inset to Fig. 2, where the electronic energy is plotted vs basal plane wavevector. The threshold for interband absorption is indicated by the vertical arrow marked ω_T (=2E_F). The band structure for the stage 2 compound is similar to that shown, except two parallel valence and two parallel conduction bands (split by ~ .4 eV) are present, which generate the same form of interband absorption with threshold energy 2E_F [5]. In Fig. 2 we show the results of model calculations for the Raman scattering



Fig. 1

Experimental values for the normalized Raman cross section vs photon energy for the C_{60}^+ , C_{48}^+ , C_{28}^+ and C_{21}^+ graphite-H₂SO₄ compounds.

cross section utilizing the p.A interaction and the standard three step process involving (1) the absorption of the incident photon causing an interband transition, (2) the scattering of the excited electron or hole while creating the phonon and (3) the emission of the scattered photon while recombining the electron and hole. The calculations were carried out using the framework for backscattering in metals developed by Camely and Mills [6]. The standard assumption that electron-phonon and hole-phonon matrix elements are independent of interband energy was used. Also, since the data was not available, a constant refractive index for the GIC was used. As can be seen in the figure, the model calculations predict a peak in the cross section at ω_T . The width of the calculated peak stems from the incorporation of a damping factor \sim .3 eV to simulate the lifetime of the excited electron-hole pairs. The calculations are in good agreement with the data. Our analysis suggests that the peak in the cross section data can therefore be used as a measure of the Fermi level position. Accordingly, we find that the charge transfer within a given stage index in the stage 1,2 graphite- H_2SO_4 compounds shifts the Fermi level about ~.15 eV.

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Fig. 2

Calculated values for the normalized Raman cross section vs photon energy for the interband absorption thresholds of 2.1 and 2.4 eV.

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