

Resonant Raman effect and Fano distortion in the stage-2 graphite donor intercalation compound C/Rb

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(Received 5 March 1990)

Raman scattering of the C-C vibration with E_{2g_2} symmetry in stage-2 C/Rb has been studied with different incident photon energies. Resonant enhancement occurs for laser energies in the blue region, close to the threshold for the valence- to conduction-band electronic transition Ω_T . The results were fitted with a two-band resonance enhancement model and the fitting procedure yields $\Omega_T = 2.6 \pm 0.15$ eV, with a broadening of 0.13 eV. In the red spectral region, the Raman line exhibits a Fano-type distortion, indicating an interaction between the discrete one-phonon excited state, and a continuum which is attributed to electronic excitations.

I. INTRODUCTION

Recently, two effects have been observed^{1,2} in the Raman scattering measurements of stage-1 C/AsF₅, an acceptor-type graphite intercalation compound (GIC). Firstly, the C-C vibration with E_{2g_2} symmetry^{2,3} is resonantly enhanced for incident (scattered) photons with energies close to the threshold for direct electronic transitions from the Fermi level to empty states in the conduction band. However, when the incident photons are not in strong resonance with the graphitic electronic system, then a pronounced distortion of the line shape has been observed, indicating an interaction between the single phonon excitation and some continuum, which was attributed to electronic excitations.¹ In this report we extend the research to stage-2 donor-type GIC's. These materials have been extensively studied by Raman spectroscopy⁴⁻⁶ but only with laser energies in the blue-green spectral region where the Raman line exhibits a relatively small distortion. Here we focus on stage-2 C/Rb and study the Fano-type distortion and the resonant Raman scattering and show a correlation between the two effects. The distortion decreases when the excitation energy is close to resonance with the electronic system. This observation is important for generalizing both effects to all GIC's for which the electronic system is governed by the properties of the graphitic layers.

II. EXPERIMENTAL DETAILS

The stage-2 C/Rb compounds were prepared from Union Carbide HOPG (highly oriented pyrolytic graphite) in the usual manner⁷ and mounted in a rectangular Pyrex tube. The quality of the samples was determined by optical means. The color of the samples was blue, sug-

gesting a pure stage 2. (Stage 1 has a goldlike color and stage 3 is observed to be black.) Comparing our Raman data with previous work⁴ on donor-type GIC's supports this conclusion for the following reasons. The line shape is completely different from the well-known broad line of stage 1. There is no evidence for a Raman peak near 600 cm^{-1} as is the case of stage-1 alkali-metal GIC's. Furthermore, there is only a single Raman line near 1600 cm^{-1} and not two well-resolved peaks as in stage-3 donor-type GIC's.

The Raman measurements were performed in the backscattering configuration with a beam power less than 35 mW to avoid local heating. As light sources we used Ar⁺ and Kr⁺ lasers. The scattered light was analyzed using a double monochromator equipped with a GaAs photocathode and a single-channel photon-counting system. All the spectra were taken with instrumental resolutions of 3–5 cm^{-1} . The spectra for each laser excitation were normalized to the 320- cm^{-1} Raman line of CaF₂. This line has no resonant enhancement in the visible region and thus can be used⁸⁻¹⁰ to correct for the energy (Ω) dependence of the instrumental response and for the dipole radiation prefactor of Ω^4 .

III. RESULTS

Three representative Raman spectra taken with the incident laser beam in the blue, yellow, and red spectral regions are shown in Fig. 1. Each trace in this figure is plotted with a different magnification scale (without normalization to the absorption), as indicated on the right side of each curve. Several authors had previously studied the Raman spectra of stage-2 donor-type GIC's (C/K, C/Rb, C/Cs) (Refs. 4–6) using only the 4880- and 5145-Å laser lines. They^{5,6} noticed a small line-shape distortion even in this spectral region. However, no attempt was previously made to investigate the dependence of the

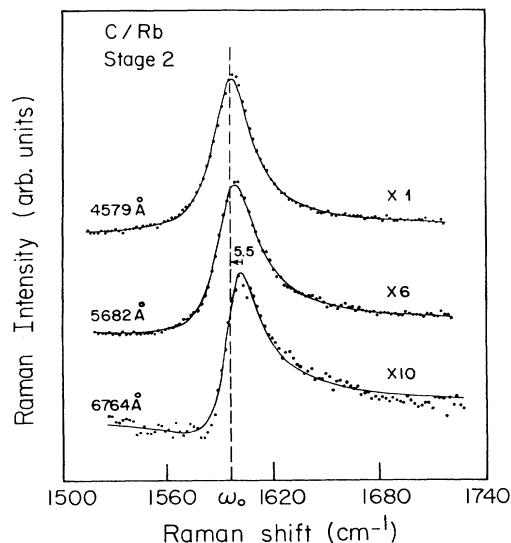


FIG. 1. Room-temperature Raman spectra of stage-2 C/Rb taken with different laser lines. The curves are plotted with different magnification scales marked on the right side. The solid lines represent the fit to the Fano line shape [Eq. (3)]. In the red region (6764 Å), a shift of 5.5 cm^{-1} for the peak from ω_0 is noted.

line shape and of the line intensity upon the incident laser energy.

The change in the Raman intensity for different laser excitation energies (Fig. 1) is a clear indication of a resonant enhancement effect. This resonant enhancement effect is a direct consequence of the charge transfer between the graphite and the intercalate layers and thus provides information on the electronic properties in accordance with the following argument. In donor (acceptor) -type GIC's, the Fermi level increases (decreases) upon intercalation. The onset of interband transitions for donor compounds is from a valence level to an empty state at the Fermi level, thereby giving rise to a sharp increase in $\epsilon_2(\Omega)$ for interband transitions as Ω passes through the threshold frequency Ω_T . Correspondingly, the Raman line is intensified when the energy of the incident photons is close to the threshold energy. Therefore one can obtain complementary information on Ω_T from the peak in the resonance Raman curve and from the rapid increase in the imaginary component of the complex dielectric function as Ω increases to Ω_T .

The Raman efficiency S^* can be obtained by normalizing the measured integrated intensity S (which has already been corrected for the instrumental response and for the Ω^4 dipole radiation prefactor) to the absorption and the reflection:¹¹

$$S^* = S \frac{\alpha_L + \alpha_S}{(1 - R_L)(1 - R_S)}, \quad (1)$$

where R_i and α_i are the reflection and the absorption coefficients for the incident ($i=L$) and scattered ($i=S$)

photons, respectively. Close to the Brewster angle, the reflection in the interesting energy region is only a few percent and does not vary significantly with the photon energy. We therefore used $R_i \sim 0$ in Eq. (1). The absorption coefficient was calculated from the complex dielectric function for stage-2 C/K which was derived by a Kramers-Kronig analysis of the reflectivity measurements¹² in the range 0–6 eV, since no corresponding data were available for C/Rb. Note that the normalization with respect to stage-2 C/K rather than to stage-2 C/Rb might introduce some error due to the possibility of a different charge transfer. However, we assume this difference to be small, since both compounds have very similar structures and electronic properties.^{4,13}

The Raman intensity versus photon energy is presented in Fig. 2(a). The crosses represent the measured values S and exhibit an increase of almost an order of magnitude in intensity between the red and the blue spectral regions. The circles in Fig. 2(a) represent the Raman efficiency S^* , which were obtained from the measured S by the normalization procedure given by Eq. (1). It should be noted that the order-of-magnitude increase in $S(\Omega)$ from the red to the blue region of the spectrum is further enhanced by a factor of 5 through the normalization procedure.

In a previous paper² the Raman cross sections for two- and three-band resonant scattering processes were calculated using the electronic structure for GIC's.¹³ It was shown that the first process is much more efficient and describes the experimental results for stage-1 C/AsF₅ well. The intensity of the Raman line is resonantly enhanced when the energy of the incident photons is close to Ω_T , the threshold for electronic transitions from the valence band to the Fermi level in the conduction band. This threshold in the electronic joint density of states is a direct consequence of the shift in the Fermi level due to the intercalation process. The present results for stage-2 C/Rb are consistent with the suggested model² with a threshold energy Ω_T of $2.58 \pm 0.15 \text{ eV}$, and a broadening parameter equal to 0.13 eV. The accuracy of these parameters is limited because we could not take data with a laser energy higher than 2.71 eV. However, the threshold energy of 2.58 eV very nearly corresponds to the value of 2.8 eV obtained from reflectivity measurements on stage-2 C/K.¹² It is also worth noting at this point that the model for resonant Raman scattering includes two poles^{2,3} at $\Omega = \Omega_L$ and at $\Omega = \Omega_S$ [see Eq. (1)]. However, as shown by Ohana, Yacoby, and Schmeltzer,² two peaks can be observed in the Raman spectrum when the broadening parameter is smaller than 0.02 eV, as, for example, in stage-1 C/AsF₅. In both stage-1 and -2 C/H₂SO₄ and stage-2 C/Rb the broadening parameters are greater than 0.12 eV and, in this regime, the two peaks cannot be individually resolved.

Referring to Fig. 1, an asymmetric line shape is observed for laser excitation energies in the red, far from the peak in the resonant enhancement curve (Fig. 2). An asymmetric Fano Raman line shape is generally observed when a discrete photon excited state interacts with a continuum. For a Fano Raman line shape, the frequency dependence of the Raman intensity is given by^{14,15}

$$I(\omega) = \frac{\pi\rho(E)T_e^2(\hbar\omega_0 - \hbar\omega - VT_p/T_e)^2}{[\hbar\omega_0 - \hbar\omega + V^2R(E)]^2 + \pi^2V^4\rho(E)^2}, \quad (2)$$

where V is the matrix element between the one-phonon excited state $|p\rangle$, with energy $\hbar\omega_0$, and a continuum of excited states $|e\rangle$. Here T_p and T_e are the transition probabilities from the ground state to the states $|p\rangle$ and $|e\rangle$, respectively, and $R(E)$ is the Hilbert transform of $\rho(E)$, the density of continuum states at an energy E where the excitation energy is equal to $\hbar\omega_0$. Equation (2) is related to the original Fano equation:¹⁴

$$I(\omega) = \pi\rho(\varepsilon)T_e^2 \frac{(q + \varepsilon)^2}{1 + \varepsilon^2} \quad (3)$$

through

$$q = [V(T_p/T_e) + V^2R(E)]/\Gamma \quad (4)$$

and

$$\varepsilon = [\hbar\omega - \hbar\omega_0 - V^2R(E)]/\Gamma, \quad (5)$$

where Γ is the Lorentzian half width at half maximum (HWHM) intensity:

$$\Gamma = \pi V^2\rho(E). \quad (6)$$

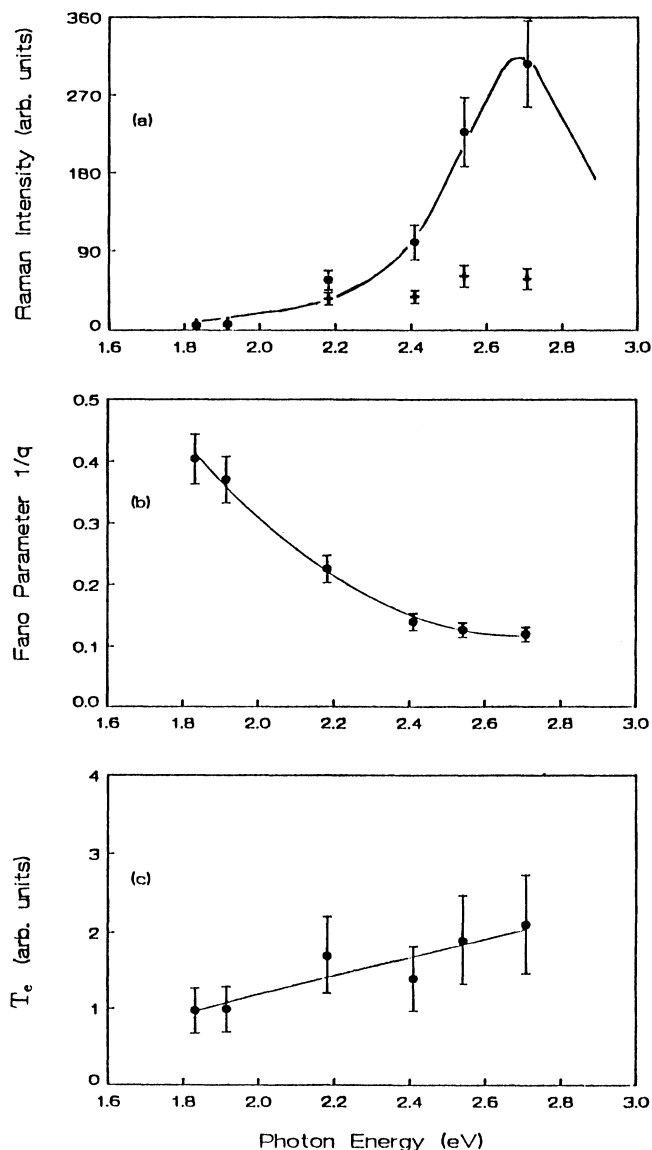


FIG. 2. The photon energy dependence of (a) the Raman intensity (+, before and ●, after the normalization), (b) the Fano parameter q^{-1} , and (c) the transition probability to the continuum, T_e . The solid line in (a) is a fit to a two-band resonant Raman enhancement model (Ref. 2). The solid lines in (b) and (c) are guides to the eye.

The experimental results of Fig. 1 fit well to Eq. (3) (the solid lines). The fitting procedure yields the undistorted peak position ω_0 , the linewidth Γ , and the Fano parameter q . The peak position and the linewidth are independent of the laser energy Ω_L and are equal to 1596 ± 1 and $12.5 \pm 0.15 \text{ cm}^{-1}$, respectively. The energy dependence of q^{-1} obtained from these fits is presented in Fig. 2(b). From a comparison of Figs. 2(a) and 2(b) it is seen that when the laser frequency is close to the resonance, the line shape is almost symmetrical [i.e., the Fano parameter ($1/q$) is small], and conversely when the laser frequency is off resonance, the Fano asymmetry factor is large.

Shown in Fig. 2(c) is the photon energy dependence of the product $q^{-1}[I(\omega_p)]^{1/2}$, which is proportional to T_e , the transition probability to the excited state. Here $I(\omega_p)$ is the peak Raman intensity. As was already pointed out in Ref. 1, the weak dependence of T_e on Ω_L cannot be explained if we assume that the continuum of states is associated with two-phonon excitations since the phonon process shows a strong dependence on laser frequency [see Fig. 2(a)]. We therefore suggest that the continuum is due to electronic excitations which are expected to possess a transition probability with a weaker dependence on the laser excitation energy.^{16,17}

The present results on the stage-2 C/Rb and the previous work^{1,2} on stage-1 C/AsF₅ suggest that the resonant Raman effect and the Fano distortion are general properties of GIC's. We expect these effects to be observed in all GIC's where the electronic system is governed by the electronic character of the graphite layers and is only slightly perturbed by the intercalation process. This should include all the GIC's except the stage-1 donor-type GIC's and the C/F compounds, where there is evidence for strong hybridization between the electronic wave functions in the graphite and those associated with the intercalate layers.

The Fano-type distortion cannot be explained only by the shift of the Fermi level (Blinowski-Rigaux model for acceptor GIC's¹⁸). However, it can be understood in terms of band models which take into account the in-plane perturbation of the electronic structure caused by intercalation.¹ As discussed in Ref. 1, zone folding effects can result in two conduction bands having an energy separation of about E_F which is comparable to, but greater than, the phonon frequency. The Fano-type distortion measurements can provide a tool for obtaining

qualitative and perhaps even quantitative information on the perturbation introduced by the intercalate layers on the electronic bands associated with the graphene layers.

In conclusion, we have shown that the Raman line associated with the C-C vibration in stage-2 C/Rb is resonantly enhanced when the laser energy is in the blue region, close to the threshold for interband transitions from the valence band to states at the Fermi level in the conduction band. However, when the laser energy is in the red region, the Raman line exhibits a Fano-type distortion which is attributed to an interaction between the one-phonon excited state and a continuum of electronic excitations. Based on the observation of the two effects in stage-1 C/AsF₅ and in stage-2 C/Rb compounds, we

suggest that these are general phenomena in all GIC's in which the electronic system is governed by the electronic properties of the graphene planes.

ACKNOWLEDGMENTS

The authors are grateful to Dr. D. Heiman for valuable discussions and encouragement. Part of the experimental work was done at the Francis Bitter National Magnet Laboratory (Cambridge, MA), which is supported by the National Science Foundation (NSF) Contract No. DMR-85-11789. The research work was supported by NSF Grant No. DMR-88-19896.

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