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INFRARED AND RESONANCE RAMAN SPECTROSCOPIC STUDIES OF AgTCNQ

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Abstract AgTCNQ has been prepared, and studied by infrared and Raman spectroscopies. The various preparation techniques were found to lead to the same $Ag^{+}TCNQ^{-}$ composition. The Raman spectra show strong resonance enhancement of the totally symmetric modes. Differences in the degree of coupling of these modes with the electronic transitions were observed. The infrared spectra also show the presence of the totally symmetric modes, which become infrared active through the electron-phonon coupling mechanism.

INTRODUCTION

TCNQ(tetracyanoquinodimethane) forms a variety of charge-transfer compounds with inorganic and organic donors[1]. The common structural characteristic of these materials is the face-to-face stacking of the TCNQ species, to form pseudo-one-dimensional columns, which results in highly anisotropic physical properties.

It was recently demonstrated that AgTCNQ and CuTCNQ show interesting non-linear transformation and memory phenomena, when exposed to an electric field, a laser beam or an electron beam[2-4]. These

electrical switching and phototransformation properties are of interest from both fundamental and technological points of view[5]. In this paper we wish to report on the infrared and Raman spectroscopic study of AgTCNQ, which has been undertaken in an effort to understand better the properties of this material in relation to its vibrational characteristics.

EXPERIMENTAL

AgTCNQ can be prepared by various methods, each leading to a different physical form. Differences in composition may exist as well. AgTCNQ in powder form was prepared by the reaction of $AgNO_3$ and LiTCNQ in CH_3CN (Method I)[1]. This preparation is known to result in the Ag^+TCNQ^- anion radical salt. A polycrystalline film was prepared by dipping a clean Ag foil into a boiling CH_3CN solution of TCNQ (Method II)[2,3]. Homogeneous, smooth thin films can be prepared, on various substrates, by vapor depositing layers of Ag and TCNQ under vacuum, and then causing their reaction by heat treatment at 100°C (Method III)[3]. Single crystals were prepared by electrochemical reduction of a $TCNQ/CH_3CN$ solution, utilizing Ag electrodes (Method IV)[6], or by electrolysis of a mixture of $AgNO_3$ and $TCNQ/CH_3CN$, using Pt electrodes (Method V)[7]. The single crystals thus prepared were too small, however, for single crystal spectroscopic measurements to be performed. Infrared and Raman spectra of the products obtained by the different preparation routes

were measured to study the vibrational properties, and thus establish the degree of charge-transfer between Ag and TCNQ. This yields useful information about the composition of the materials under investigation.

Raman spectra were measured on a Ramanor HG 2S Jobin-Yvon spectrometer, employing the lines of an Argon-ion and a He-Ne laser. The power of the laser beam was less than 5mW, to avoid phototransformation of the material to neutral TCNQ and to metallic silver[3]. Infrared spectra were recorded on a Fourier-transform Bruker 113 v vacuum spectrometer. Samples were in the form of KBr pellets for the mid-infrared, and nujol mulls pressed between polyethylene plates for the far-infrared. All Raman and infrared spectra were measured in vacuum to avoid possible oxidation of the $TCNQ^-$ anion.

RESULTS AND DISCUSSION

Raman Spectra

The Raman spectra of a polycrystalline AgTCNQ film (II), prepared by Method II, were measured with several excitation lines and are presented in Fig.1. The spectrum of a thin AgTCNQ film on SiO_2 substrate (III), prepared by Method III, was measured with 514.5 nm excitation and is also shown in Fig.1 for comparison. Obviously this spectrum is similar to the corresponding spectrum of form II measured with the same line, indicating that both films are of the same composition. Raman spectra of AgTCNQ powder prepared by Method(I) are also identi-

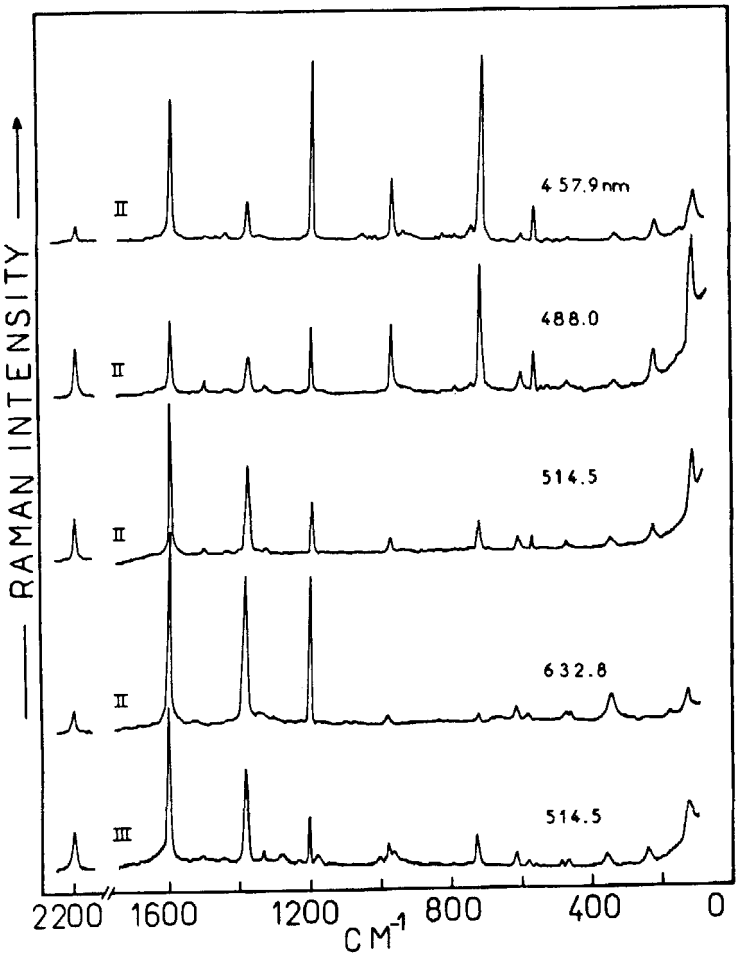

FIGURE 1. Raman spectra of AgTCNQ, prepared by Methods II and III. For details see text. Numbers next to spectra indicate excitation wavelength.

cal to those shown in Fig.1, implying that the films are also of the $Ag^{+}TCNQ^{-}$ composition.

If we assume the D_{2h} point group symmetry for $TCNQ^{-}$, then the distribution of the intramolecular modes is as follows:

$$\Gamma_{red}=10A_g(R)+9B_{1g}(R)+5B_{2g}(R)+3B_{3g}(R) \\ +4A_u+5B_{1u}(IR)+9B_{2u}(IR)+9B_{3u}(IR) \quad (1)$$

where R and IR denote Raman and infrared activity respectively. The Raman spectra of AgTCNQ are dominated by the totally symmetric (A_g) modes of the $TCNQ^-$ anion. On the basis of the vibrational analysis of $TCNQ^-$ and the reported spectra of alkali metal-TCNQ salts[8-10], we assign the bands of AgTCNQ observed at 2212,1606,1386,1206,982,732,583, 350 and 130 cm^{-1} to the $\nu_2,\nu_3,\nu_4,\nu_5,\nu_6,\nu_7,\nu_8,\nu_9$, and ν_{10} A_g modes of $TCNQ^-$ respectively. The notation of ref.8 is used in this paper. While all these modes involve contributions from various stretching and bending vibrations, we may note that ν_2 involves mainly C≡N stretching, ν_3 C=C (ring) stretching, ν_4 C=C (wing) stretching, ν_5 C=C-H bending, ν_6 and ν_7 C-C (ring)+C-C(wing)stretching, ν_8 C-C=N bending, and ν_9 and ν_{10} are combinations of ring deformations. Weak bands at 1650,1625,1507, 1450,1375,1122,1066,950,761,620,488 and 242 cm^{-1} originate from vibrations of B_g symmetry[8-10].

The frequency of the ν_4 mode is particularly sensitive to the degree of charge-transfer (ρ)from donor to TCNQ molecule[11]. Indeed, a linear dependence of ν_4 on ρ was recently shown[12]. The value of ν_4=1386 cm^{-1} obtained for AgTCNQ corresponds to complete charge-transfer from silver to TCNQ(ρ=1), and thus to the Ag^+TCNQ^- composition.

When the laser excitation line is changed interesting changes in relative Raman intensities are

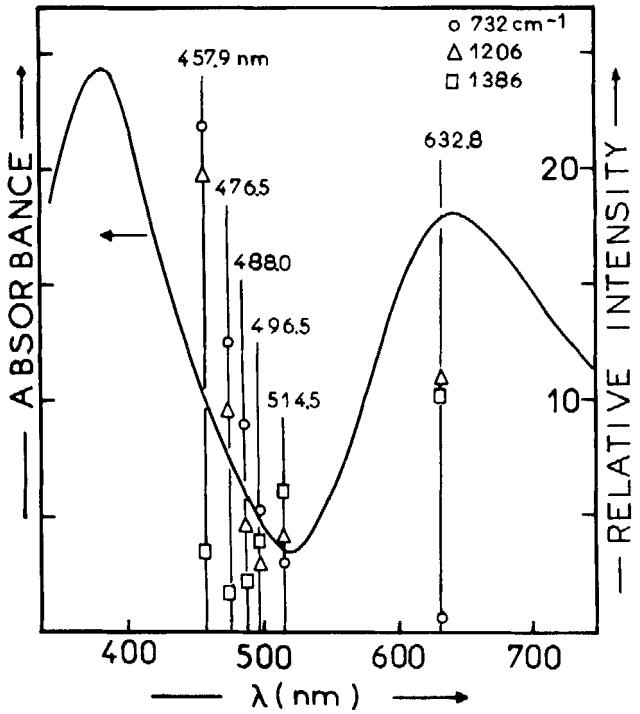

FIGURE 2. Visible spectrum of AgTCNQ, and relative Raman intensities of a few characteristic vibrational modes.

observed (Fig.1). Thus, while the spectra excited with lines in the 457.9-514.5 nm region are quite similar, the spectrum obtained with red line excitation shows big differences. Specifically, the bands at 982,732 and 583 cm^{-1} are greatly reduced in intensity. To understand this phenomenon we refer to Fig.2, which shows the visible spectrum of AgTCNQ, and the position of the excitation lines for Raman measurements. The absorption band at 640 nm is due to the $^2B_{2g}^{(1)} \longrightarrow {}^2B_{1u}^{(1)}$ electronic transi-

tion of $TCNQ^-$, while the one at 385 nm originates from the overlapping $^2B_{2g} \rightarrow {}^2B_{1u}^{(2)}$ and $^2B_{2g} \rightarrow {}^2A_u$ transitions[13]. All the blue laser lines are within the same absorption band, and thus they excite similar Raman spectra. The 632.8 nm line is within another electronic excitation, resulting in a substantially different resonance Raman spectrum.

Resonance Raman enhancement of a vibrational mode occurs when this mode can couple with an electronic excitation[14]. Thus, the selectivity in resonance Raman enhancement among the A_g modes is a consequence of the fact that they can couple differently with the electronic excitations. To further illustrate this point we examine the relative intensities of a few characteristic A_g modes. The 620 cm^{-1} band of B_g symmetry, whose intensity appears to be almost independent of excitation wavelength, is used as an internal standard. The wavelength dependence of the relative intensities is given also in Fig.2. Clearly, the ν_7 mode (732 cm^{-1}) shows strong coupling with the blue electronic absorption, and almost no coupling with the red absorption. The ν_4 mode (1386 cm^{-1}) shows the opposite behavior, while the ν_5 mode (1206 cm^{-1}) is capable of coupling with both electronic excitations. This is a clear demonstration of the selectivity of the resonance Raman enhancement process. For the case that a single electronic excitation is involved (Franck-Condon coupling), the degree of coupling of the various vibrational modes with the electronic excitation can be calculated, as previously shown[12].

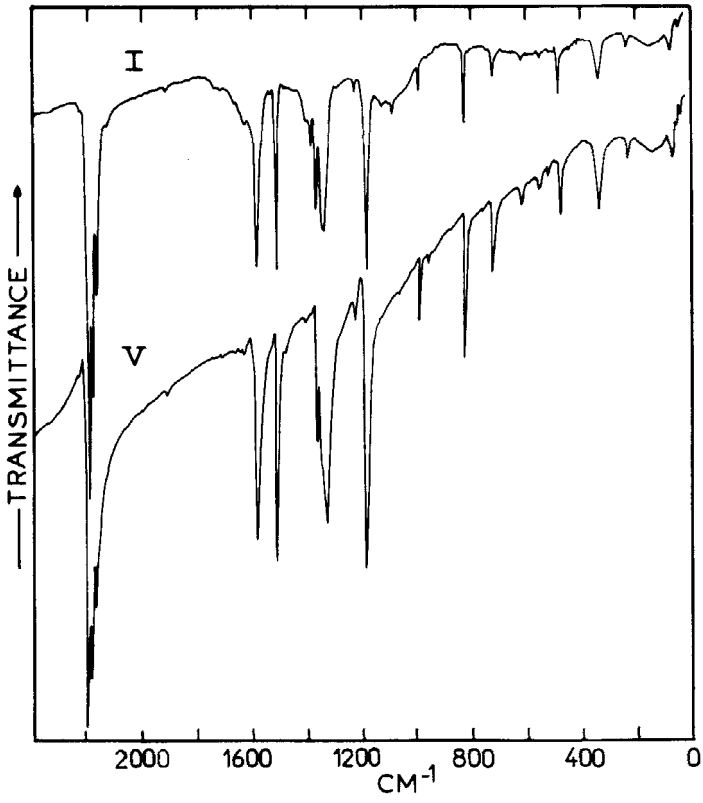

FIGURE 3. Infrared spectra of AgTCNQ, prepared by Methods I and V. For details see text.

Infrared Spectra

The infrared spectra of AgTCNQ powder (I), and of small crystals (V), are shown in Fig.3. The two sample forms give similar spectra, suggesting that the crystals are also of the $Ag^{+}TCNQ^{-}$ form, contrary to the composition $Ag_4(TCNQ)_3$ given in ref.7 for crystals prepared in a similar way. The IR spectrum of crystals prepared by Method IV is also si-

milar to those shown in Fig.3, and thus the materials are of the same composition, that is of $Ag^{+}TCNQ^{-}$.

It was shown previously that a total of 23 infrared active modes would be expected. However, a greater number of infrared bands has been observed. For example, if we consider only the C≡N stretchings, then the corresponding reducible representation can be written as follows:

$$\Gamma_{red}=1A_g(R)+1B_{1g}(R)+1B_{1u}(IR)+1B_{3u}(IR) \qquad (2)$$

The Raman active A_g mode has been observed at 2212 cm^{-1}, while the B_{1g} mode was probably too weak to be observed in the Raman spectrum. Two infrared active modes are predicted to appear in the C≡N stretching region. However, Fig.3 shows the presence of three strong bands at 2197, 2182, and 2169 cm^{-1}. Thus, one additional infrared C≡N stretching band has been observed.

The presence of additional bands has been shown in the infrared spectra of alkali metal-TCNQ compounds as well[8-10]. Anderson and Devlin[15] have demonstrated that such bands are strongly polarized in the direction perpendicular to the TCNQ plane. Thus, they concluded that these bands originate from the totally symmetric (A_g) modes, which are normaly infrared inactive, but become activated through the electron-molecular vibration interaction mechanism[15]. On this basis we assign the IR bands at 2197, 1578, 1325, 1181, 988, 722, 555, 336, and 140 cm^{-1} to the ν_j (j=2-10) A_g modes respectively.

The frequencies of these infrared bands appear downshifted compared with their Raman counterparts, as it was similarly observed in the IR spectra of alkali metal-TCNQ salts[8-10], and theoretically predicted by Girlando et al [16,17].

The remaining infrared bands can be readily assigned to intramolecular B_u modes and to lattice modes. Thus, in the C≡N stretching region, the bands at 2182 (B_{3u}) and 2169 cm^{-1} (B_{2u}) are observed. The 1506 cm^{-1} band is due to C=C(wing) stretching. The out-of-plane C-H bending (B_{1u}) is observed at 825 cm^{-1}, while the band at 476 cm^{-1} is characteristic of the $C(CN)_2$ wagging mode (B_{1u}). The 230 cm^{-1} band is also intramolecular in nature (B_{1u})[10].

The band at 76 cm^{-1} is assigned to the translational lattice mode of the Ag^+ ion. The crystal structure determination of AgTCNQ has shown that silver is four-fold coordinated by nitrogen atoms, in a distorted tetrahedral configuration[6]. It is the ratling motion of Ag^+ ion in this anionic site that gives rise to 76 cm^{-1} band. Similar bands for Li^+, Na^+ and K^+ motions have been observed at 400, 202 and 155 cm^{-1} respectively. Fig.4 shows the frequency of the cation-motion band plotted versus $m^{-1/2}$, where m is the cation mass. The observed linear dependence provides additional evidence that these low-frequency bands originate from vibrations of cations in their sites. Such localized cation motions were recently modeled through a Born-Mayer type potential[18]. Thus, the cation motion frequency was associated with both cation and

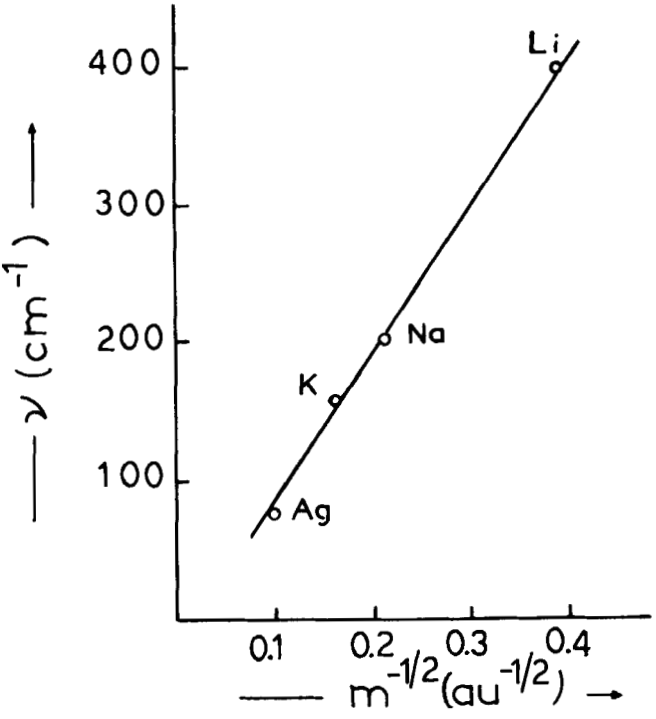

FIGURE 4. Cation-motion frequencies versus $m^{-1/2}$, where m is the cation mass.

anionic site parameters, and proved useful in probing the nature of the cation-anionic site interactions.

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