# (FT-NIR) RAMAN SCATTERING IN PRESSED PELLETS OF
# BEDT-TTF BASED ORGANIC METALS

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## ABSTRACT

The low lying (1.25 eV) electronic state of a family of BEDT-TTF based organic metals has been investigated with FT-NIR resonant Raman scattering.

We assign the 1.25 eV electronic state to the BEDT-TTF cation radical. The enhanced Raman modes coupled with this electronic transition are discussed and assigned.

## INTRODUCTION

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is the donor moiety of a new family of 2-dimensional organic metals and superconductors [1,2]. In particular, all the organic superconductors with the highest transition temperature are radical salts of BEDT-TTF [3,4], and of special interest is the fact that bulk superconductivity in polycrystalline pressed samples has been recently discovered [5]. In this view, the utilization of organic superconductors for the preparation of electronic devices seems possible and spectroscopic studies on pressed samples have become important. The electronic structure of BEDT-TTF based superconductors is not yet well known [6,7]. Conductivity spectra of many compounds show approximately the same pattern of electronic bands, namely three peaks in the 1-3 eV range and are generally assigned to BEDT-TTF cation radical intramolecular excitations [8-10]. The Raman spectroscopy is a powerful tool to study the electronic manifold, because of the enhancement of selected Raman modes when resonance conditions with electronic states are fulfilled. Few Raman data have been reported in the literature [11-13], and only with visible excited laser lines. Aim of this paper is the study of the low lying (1.25 eV) electronic state of the BEDT-TTF cation radical moiety. For this reason we have performed resonant Raman scattering measurements exciting in the near infrared (NIR) at 1.16 eV, in $\alpha$ and $\beta$ phases of (BEDT-TTF)$_2$I$_3$ and in (BEDT-TTF)$_2$Cu(NCS)$_2$ organic metals.

## RESULTS and DISCUSSION

The materials studied in this work have been electrochemically grown as previously described [5,14,15]. The samples were prepared by grinding single crystals in an agate mortar toge-

ther with dry CsI. Pellets were obtained with an applied pressure of $10^4$ Kg/cm$^2$ and with a 0.5% weight concentration of the organic metal. FT-NIR Raman measurements were performed at the exciting wavelength of 1064 nm (1.16 eV) in a FT-IR 88 Bruker equipped with a FRA 106 Bruker attachment for Fourier Transform Raman Spectroscopy. Back scattering configuration, 4 cm$^{-1}$ spectral resolution and 50 mW of laser power were the working conditions. The NIR Raman spectrum of both protonated and deuterated $\alpha$(BEDT-TTF)$_2$I$_3$, see Fig.1, shows three strong bands at 501 cm$^{-1}$ ($\Omega_1$), 1464 cm$^{-1}$ ($\Omega_2$), 1489 cm$^{-1}$ ($\Omega_3$) and four medium and weak bands at 114 cm$^{-1}$ ($\Omega_4$), 888 cm$^{-1}$ ($\Omega_5$), 999 cm$^{-1}$ ($\Omega_6$) and 1965 cm$^{-1}$ ($\Omega_7$).
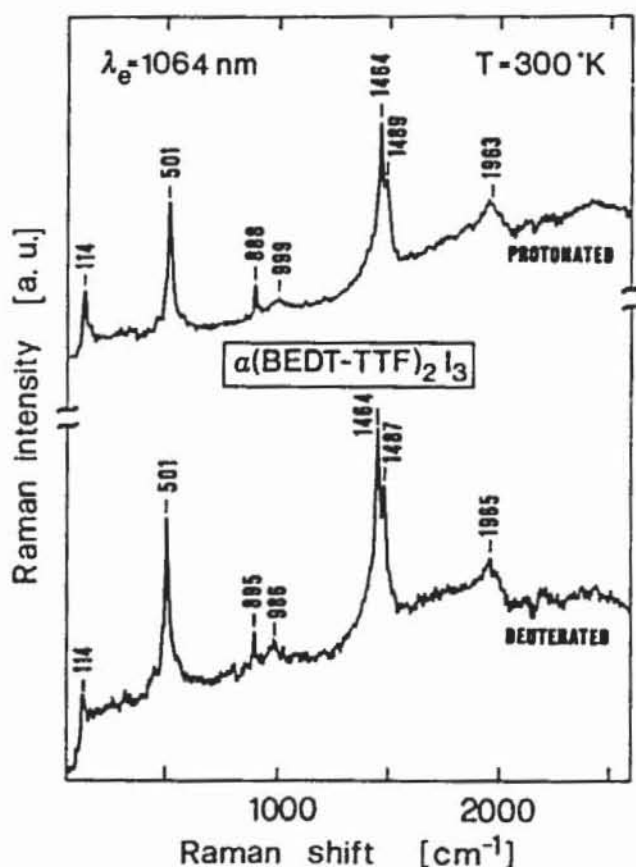


Fig. 1 FT-NIR Raman spectra of protonated (upper) and deuterated (lower) $\alpha$(BEDT-TTF)$_2$I$_3$

The visible excited Raman scattering in the same compound shows only vibrations of the I$_3$ anions because of a very strong enhancement due to resonance with electronic transitions of the iodine moiety [11,12]. In the NIR excited Raman spectrum the I$_3$ stretching is still present ($\Omega_4$) but the band intensity is medium-weak. This is not the case of $\beta$ (BEDT-TTF)$_2$I$_3$ where the $\Omega_4$ is not clearly visible (see Fig.2). The I$_3$ electronic transition in the $\beta$ phase is $\approx$ 0.4 eV up-shifted compared to the $\alpha$ phase [9] and this may be the reason of the different behaviour of the $\Omega_4$. The $\Omega_5$ mode is generally assigned to a C-S stretching mode [10]. The band is weak in all the investigated compounds and up-shifted in the deuterated (see Figs. 1,2,3), suggesting an interaction with the terminal CH$_2$ groups. The frequency range of $\Omega_6$ has been assigned to C-C-H stretching in the BEDT-TTF neutral moiety [10,16]. In our measurements the $\Omega_6$ is present in all three organic metals and remains unshifted upon deuteration (see Figs. 1,2,3).
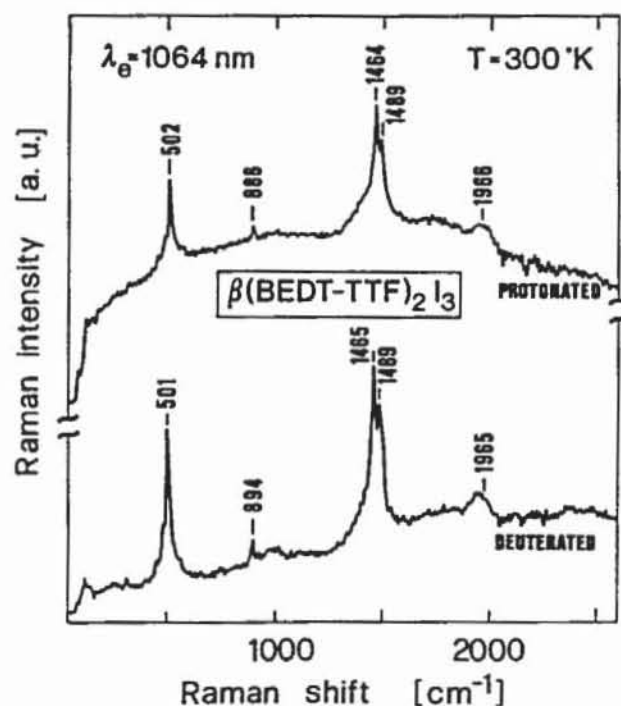
**Fig. 2 FT-NIR Raman spectra of protonated (upper) and deuterated (lower) β(BEDT-TTF)$_2$I$_3$.**



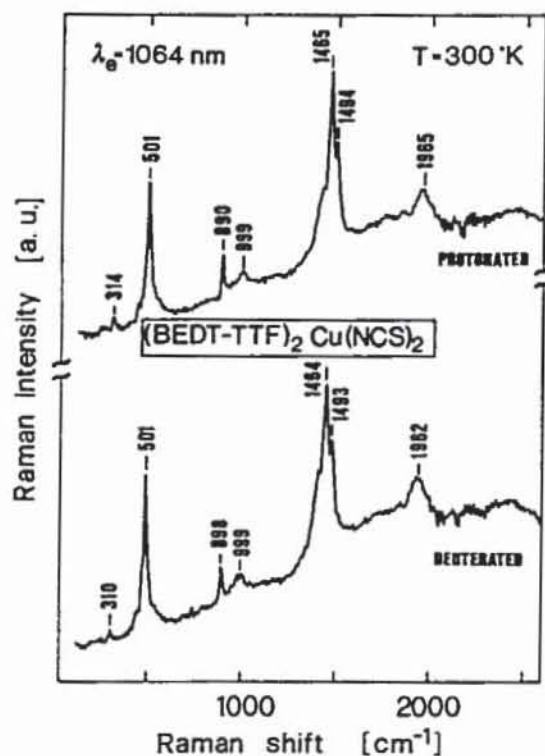**Fig. 3 FT-NIR Raman spectra of protonated (upper) and deuterated (lower) (BEDT-TTF)$_2$Cu(NCS)$_2$**

The behaviour of the $\Omega_6$ suggests to assign this mode to an overtone ($2\Omega_1$) of $\Omega_1$ and similarly for the $\Omega_7$ mode ($\Omega_1 + \Omega_2$).

In Fig. 3 we show the Raman spectrum excited in the NIR of the (BEDT-TTF)$_2$Cu(NCS)$_2$. As for the two other parent compounds the $\Omega_1$, $\Omega_2$ and $\Omega_3$ modes are the most coupled ones and the I$_3$ stretching ($\Omega_4$) is absent. We assign the $\Omega_1$ mode to the C-S internal stretching [10]

of the central TTF moiety of the BEDT-TTF cation radical. The unshifted frequency of the $\Omega_1$ in deuterated compounds supports this assignment. Furthermore, the $\Omega_1$, which is strongly enhanced when resonance conditions with the 1.25 eV electronic state are fulfilled, is not present in the visible excited resonant Raman scattering, as reported in a previous work [13] on (BEDT-TTF)$_2$Cu(NCS)$_2$ single crystal. Finally, the most intense modes $\Omega_2$ and $\Omega_3$ are assigned to the C=C stretching vibration. The former is related to the central bond, the latter to the ring bond [13]. All the resonant Raman spectra of the investigated compounds show a very similar behaviour and the most coupled vibrations involve the BEDT-TTF cation radical. This supports the attribution of the low lying electronic state to the donor moiety and seems common for BEDT-TTF based organic metals. In conclusion the low lying electronic state (1.25 eV) of a family of BEDT-TTF based organic metals has been investigated with resonant Raman scattering and assigned to the BEDT-TTF cation radical. The enhanced Raman modes coupled with this electronic transition have been discussed and assigned.

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