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## A RAMAN STUDY OF TRIHALIDE-CONTAINING ORGANIC CONDUCTORS

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We have recently prepared the organic conductors  $(\text{EDT-TTF})_2\text{X}$ , where  $\text{X}=\text{IBr}_2$ ,  $\text{AuI}_2$  and  $\text{EDT-TTF}=\text{ethylenedithiotetrathiafulvalene}$  [1]. For  $\text{X}=\text{IBr}_2$  the room temperature structure was found to be identical to that of the superconductor  $(\text{BEDT-TTF})_2\text{I}_3$ , where  $\text{BEDT-TTF}=\text{bis-EDT-TTF}$  [2]. We report here on the Raman spectra of both organic conductors (i.e.  $\text{X}=\text{IBr}_2, \text{AuI}_2$ ), since they are expected to be quite informative about the state of the polyhalide anion and the donor cation. Disorder or structural changes, such as those associated with the trihalide anions, have been recently found to affect the superconductivity exhibited by such materials [3].

The organic conductors studied here were prepared by electro-oxidation of the donor molecule in the presence of  $\text{Bu}_4\text{X}$ , in dichloromethane solvent and under a  $1\mu\text{A}$  constant current. Raman spectra were recorded at room temperature on pressed pellets, using for excitation the 476.5 nm line, operating at less than 10 mW. Spectra measured in two frequency regions are shown in Fig.1, where also those of pure donor ( $\text{D}=\text{EDT-TTF}$ ) and  $\text{Bu}_4\text{NX}$  are shown for comparison. The spectrum of  $\text{Bu}_4\text{NIBr}_2$  exhibits its strongest band at  $163\text{ cm}^{-1}$ , assigned to the symmetric stretch of the linear  $\text{IBr}_2^-$  anion, while its bending gives rise to the  $137\text{ cm}^{-1}$  band [4]. In the spectrum of  $\text{D}_2\text{IBr}_2$  the corresponding bands appear at 165 (broad) and  $135\text{ cm}^{-1}$  (shoulder), and thus they show the presence of the linear, symmetric  $\text{IBr}_2^-$  anion, in agreement with the crystal structure determination [2]. The intense feature at  $495\text{ cm}^{-1}$  is associated with the symmetric stretching of C-S bonds of the donor molecule [5]. Its enhanced intensity in the complex relative to that in pure donor could be attributed to its coupling with the conduction electrons [6]. A number of sharp peaks appearing below  $100\text{ cm}^{-1}$  arise from libration modes of the donor, since they also appear in the spectrum of pure donor. The spectrum of  $\text{Bu}_4\text{NAuI}_2$ , which is similar to that reported by Swietlik et al [3], exhibits a strong doublet at 106 and  $118\text{ cm}^{-1}$ , assigned to the symmetric stretch ( $\nu_1$ ) of the  $\text{AuI}_2^-$  anion. The splitting is due to crystal field effects. Overtones of  $\nu_1$  at  $210\text{ cm}^{-1}$  ( $2\nu_1$ ),  $314\text{ cm}^{-1}$  ( $3\nu_1$ ) and  $415\text{ cm}^{-1}$  ( $4\nu_1$ ) are clearly observed. The asymmetric stretch ( $\nu_2$ ) of  $\text{AuI}_2^-$  appears at  $157\text{ cm}^{-1}$ , while combinations of  $\nu_1$  with lattice modes give rise to the 178 and  $135\text{ cm}^{-1}$  bands. The spectrum of  $\text{D}_2\text{AuI}_2$  exhibits  $\nu_1$  at  $113\text{ cm}^{-1}$ , in addition to the strong band at  $165\text{ cm}^{-1}$ .

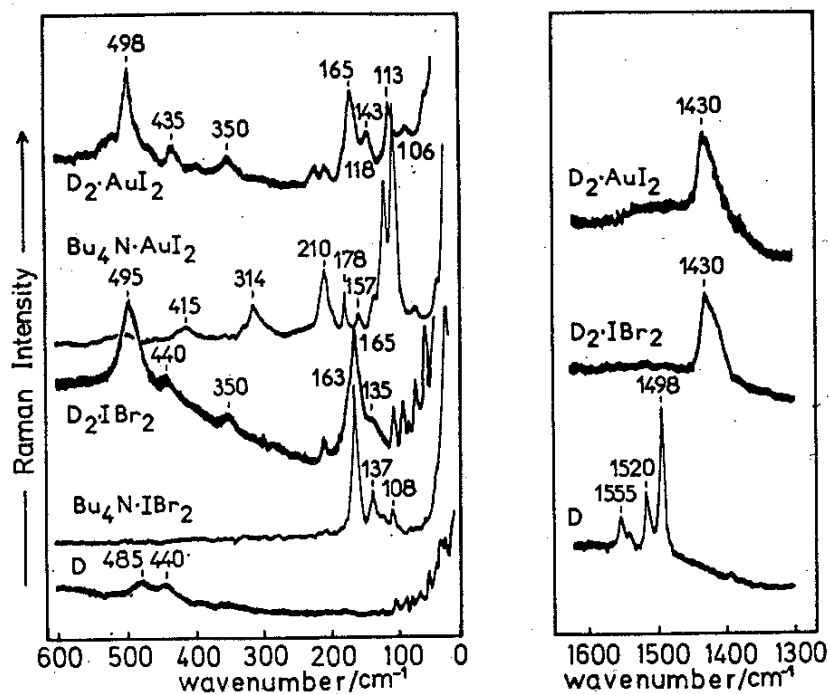


Fig. 1. Raman spectra of organic conductors

This band is probably associated with  $\nu_2$ , and thus its increased intensity relative to  $\nu_1$  denotes the distortion of  $AuI_2^-$  anion in the organic complex. The strong C-S stretching is also observed at  $498\text{ cm}^{-1}$ .

In the high frequency region the donor molecule exhibits the strongest bands at  $1498$ ,  $1520$  and  $1555\text{ cm}^{-1}$ , assigned to the stretching of the central and external C=C bonds [5]. Both complexes show an asymmetric, broad envelope centered at about  $1430\text{ cm}^{-1}$ . The downshift of this envelope relative to pure donor is indicative of the charge-transfer process from D to X, which appears to be the same for both organic conductors. Sugai and Saito [7] observed a number of bands superimposed on a broad envelope, extended from  $1400$  to  $1600\text{ cm}^{-1}$ , for  $\beta\text{-(BEDT-TTF)}_2X$ . However, we have noticed that a broad band centered at about  $1500\text{ cm}^{-1}$  appears, in addition to that at  $1430\text{ cm}^{-1}$ , when the excitation power exceeds  $20\text{ mW}$ . This can be the result of partial sample decomposition to pure donor. In all other cases the  $1430\text{ cm}^{-1}$  envelope appeared on a rather normal background.

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