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SIZE EFFECTS ON THE RAMAN EXCITATION PROFILES OF MIXED-VALENCE
COMPOUNDS WITH METAL-HALIDE CHAIN

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ABSTRACT - The Raman excitation profile of a metal - halide chain compound occurs near the gap frequency. The position of profiles of small particles depends strongly on the size of particles.

RÉSUMÉ - On montre que le profil d'excitation est situé au voisinage de la fréquence de gap. La position des profils de petites particules dépend de la taille de particules.

In our previous work /1/ - /3/ we showed that the position, the shape and the intensity of bands in the absorption spectra of mixed-valence compounds with a metal-halide chain depend on the size, the shape and the aggregation of the crystals. We also observed a small shift in the Raman excitation profiles (REP) when we changed the dispersed medium /3/. In this paper we describe the changes (position, shape, intensity) in the REP when one changes the size (the shape, and the aggregation) of crystals of mixed valence compounds with the chain $-M(II)-X-M(IV)-M(II)-X-$ ($M=Pt$ or Pd , $X=Cl$, Br or I). We consider as an example the compound $Pt(dapn)_2Pt(dapn)_2Br_2(ClO_4)_4$ (where $dapn=1,2$ -diaminopropane) of which the absorption bands occur in the visible region /1/, /2/.

$Pt(dapn)_2Pt(dapn)_2Br_2(ClO_4)_4$ has been prepared as in /4/ and recrystallized twice from water containing small amount of $HClO_4$. Large crystals (1x1x5mm) have been obtained by slow cooling aqueous solutions of the compound. It is soluble in water, methanol, acetonitrile, etc. but insoluble in carbon tetrachloride, carbon disulphide and ether. We made use of this property to prepare suspensions of the complexes in the last three liquids. The samples were prepared as follows. (A) 25mm³ of saturated solution of the compound in acetonitrile were injected slowly into 20cm³ carbon tetrachloride which was stirred vigorously. The suspension obtained was red in colour. (B) 25mm³ of the same saturated solution in acetonitrile were added at once to 2cm³ carbon tetrachloride without stirring; after 1min, 18cm³ carbon tetrachloride were added and the suspension was stirred. This suspension was violet in colour. Electron micrographs showed that the samples (A) and (B) consisted of small particles 150 and ~900Å in diameter respectively. We also prepared thin deposits of compound on quartz plates /1/-/3/. These deposits consist of small needles (1000-2000Å) and are blue in colour. After rubbing the deposits with a soft paper the particles become spheres (150Å) and the colour turns to red.

The single - crystal reflectance spectra were recorded from 350 to 1500 nm with an instrumentation

described in /2/. The absorption spectra were recorded with a Cary 17 spectrophotometer. The Raman spectra were recorded as described previously /3/ using Helium-Neon and Argon Lasers and rhodamine dyes. Excitation profiles were measured with respect to 317cm⁻¹ band of CCl_4 . All measurements were made at room temperature.

The results of measurements are presented in Figs. 1, 2. Fig. 1 shows the single crystal reflectance spectra of $Pt(dapn)_2Pt(dapn)_2Br_2(ClO_4)_4$ in the visible region with the wave vector of light parallel ($E||Z$) and perpendicular ($E\perp Z$) to the needle axis (Z). These spectra show semiconductor behaviour in one dimension (Z). We made a least-square fit to Reflectance (for $E||Z$) from 350nm to 1500nm using a single Lorentzian dielectric function. The best fit was obtained with the following parameters: $\epsilon_\infty=3.4$, $\omega_p=26000\text{cm}^{-1}$, $\omega_g=16000\text{cm}^{-1}$ (625nm), $\Gamma=3300\text{cm}^{-1}$. A polycrystalline pellet of compound shows qualitatively the same spectrum as that of Fig. 1a.

Single crystal Raman spectra of compound show a resonance enhancement of the band $\omega_1=179\text{cm}^{-1}$ due to symmetric vibration of the chain when $E||Z$ and a normal Raman spectrum when $E\perp Z$. Polycrystalline pellet shows only the resonance enhancement. The intensity of ω_1 depends strongly on the excit. frequency. Fig. 1 shows also the REP obtained from a polycrystalline pellet of compound and the calculated one via the Pinczuk-Burstein eqn /6/ (see also /3/). One can see that the maximum occurs near the gap frequency (ω_g) of semiconductor.

The absorption spectra and REP of suspension in CCl_4 or of deposits on quartz depend on the size of particles. Figure 2 shows the absorption spectra of samples A and B and the corresponding REP of $Pt(dapn)_2Pt(dapn)_2Br_2(ClO_4)_4$. One can see that the maxima are shifted to lower frequencies as the particle size increases. Also we observed that the maximum positions depend on the shape and the aggregation of the particles. The maxima of needle-like particles and aggregated samples occur at lower frequencies than those of spherical particles.

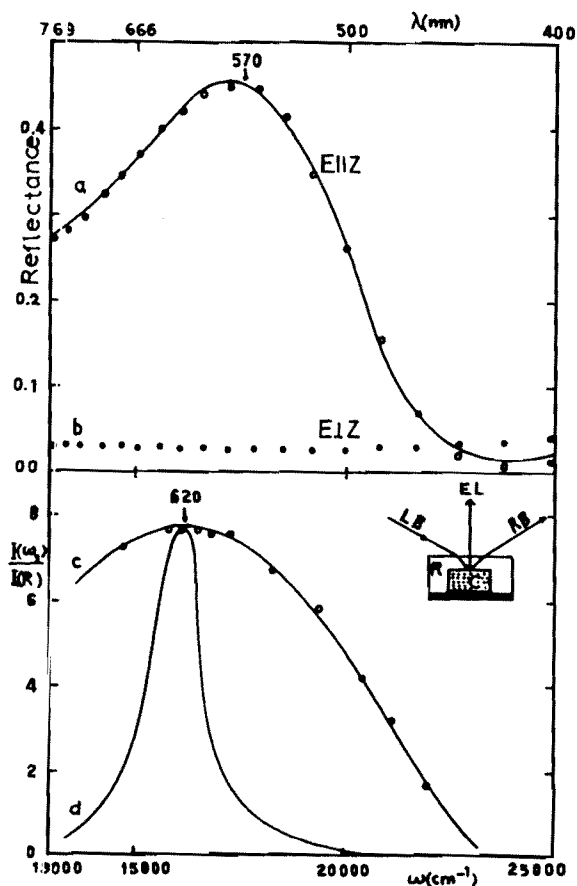


Figure 1. Single crystal reflectance spectra with $E_{||}Z$ (a) and $E_{\perp}Z$ (b).ooo experimental data, — Lorentzian fit. REP of a pellet (c) and the calculated one (d). LB=Laser beam, RB=Refl.beam, EL=Entrance lens, R=ref.liquid (CCl_4), C=compound.

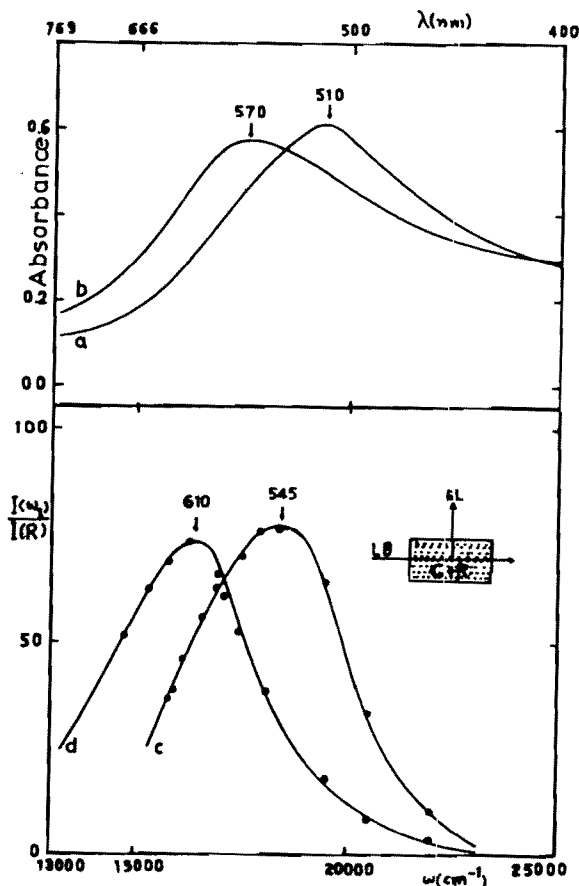


Figure 2. Absorption spectra (a),(b) of samples A and B and the corresponding REPs(c),(d).

and non-aggregated samples, respectively. Aggregated samples show REP-maxima near the ω_p (Fig.1c). In our previous experiments /3/ we did not observe strong shifts in REPs because we used aggregated samples. Also the REPs obtained from the overtone and the anti-Stokes bands showed similar effects.

Similar results have been obtained for other compounds with a metal-halide chain. The size effects in the absorption spectra are attributed to surface plasmons /1/, /7/. The size effects in REP can be considered as a consequence of size quantization of the gap-or exciton-frequency of semiconductor (see /8/-/11/ and refs. therein). The excitonic peaks appear in the spectra of $Pt(dapn)_2Pt(dapn)_2Br_2(ClO_4)_4$ observed at low temperature /11/.

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