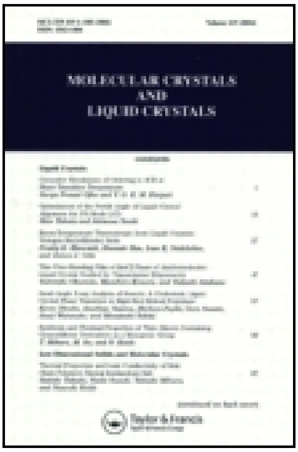

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Resonance Raman Scattering and Its Annealing Effect for Photo-Induced Defect States in Quasi-One-Dimensional Mixed-Valence Compound $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$

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RESONANCE RAMAN SCATTERING AND ITS ANNEALING EFFECT FOR PHOTO-INDUCED DEFECT STATES IN QUASI-ONE-DIMENSIONAL MIXED-VALENCE COMPOUND $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$

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Abstract Resonance Raman spectra for the photo-induced defect states in quasi-one-dimensional mixed-valence compound $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ (en = ethylenediamine) were measured. After making corrections due to the penetration depth of the incident light and the reabsorption of the scattered light, we clearly observed the resonance enhancement of several Raman lines for the photo-induced absorption band. We also found that the thermal bleaching of these Raman lines well coincides with that of the photo-induced absorption bands.

INTRODUCTION

Halogen-bridged mixed-valence metal complexes (HMMCs) are quasi-one-dimensional systems not only in the crystal structure but also in the electronic state. Since the photo-induced absorption bands (named as A and B bands) due to defect states were found below the intervalence charge transfer absorption band of HMMCs, many studies to elucidate the defect states have been carried out both experimentally and theoretically[1-4]. Recently, Los Alamos's group found that several Raman lines, which are observed below the symmetric stretching mode of $[Pt(en)_2][Pt(en)_2Cl_2](ClO_4)_4$ (hereafter PtCl), resonantly enhance the intensity for the A and B bands[5,6].

Here, we report a clear evidence of the resonance enhancement of several Raman lines of the photo-induced defect states, thereby taking into account the correction due to the penetration depth of the incident light and the reabsorption of the scattered light. We also indicate that the thermal bleaching of these Raman lines well coincides with that of the A and B bands.

EXPERIMENTAL

PtCl single crystals were synthesized by the procedure previously described[7]. The PtCl samples were mounted on a copper block and kept in a temperature-controlled cryostat.

The light source of the resonance Raman spectroscopy was provided by a Ti:sapphire laser and a DCM dye laser pumped by an Ar ion laser. The excitation photon energy was varied from 1.44 to 1.83 eV, corresponding to the energy region of the A band.

The incident light impinged near-normally upon the sample's surface and the Raman scattering was measured in the backward scattering configuration. The scattered light was analyzed by a triple-monochromator and a CCD detector cooled by liquid nitrogen[8]. The polarization of the incident and scattered light was parallel to the b-axis of the PtCl sample (**E**//**b**). All of the Raman spectra were measured at 16 K.

Photolysis of the samples was performed for 150 minutes at 16 K by using the 365 nm line (3.4 eV) from a mercury lamp. The average power of the UV light was 1 mW/cm^2. The quantum efficiency for the generation of the photo-induced defects is large for the light excitation of the UV light[2] and the absorption coefficient of the UV light is not so large[9]. Therefore the photo-induced defects were effectively produced even inside of the PtCl crystal in this study.

RESULTS AND DISCUSSION

Figure 1 shows the resonance Raman spectra of PtCl with different excitation photon energies in the A band region after the photolysis. We found four Raman lines (278, 284, 287 and 293 cm^{-1}) below the symmetric stretching mode ν_1 (310 cm^{-1}) of PtCl. The half width of the 284 and 287 cm^{-1} lines is about 2-3 cm^{-1}, being equivalent to the resolution of the experimental equipment. On the other hand, the half width of the 278 and 293 cm^{-1} lines is 5-6 cm^{-1} and lager than the resolution, implying complexities of these lines. However, we tentatively assume that the observed 270-300 cm^{-1} Raman bands consist of four Raman lines, because we could not clearly observe any extra Raman lines even if the excitation photon energy changes from 1.44 to 1.83 eV. The ratios of the intensity among the Raman lines depend on the excitation photon energy in the A band region as seen in Fig. 1.

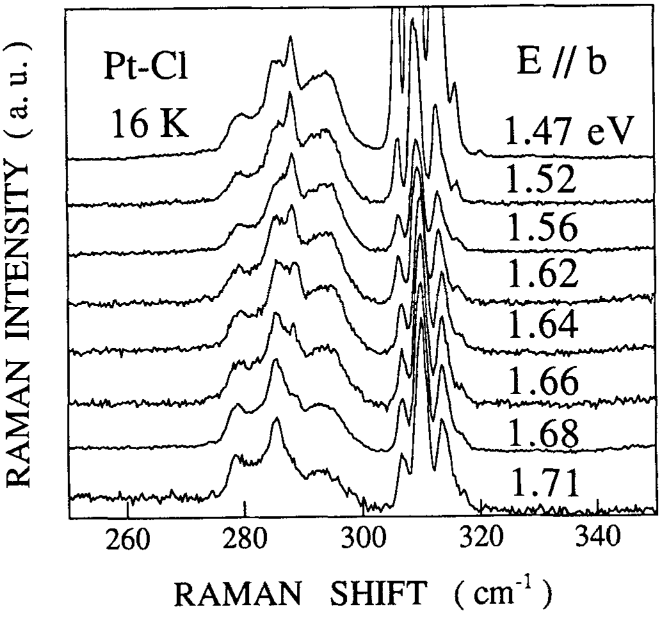

FIGURE 1 Resonance Raman spectra of PtCl with different excitation photon energies in the A band region after the photolysis.

The intensity of the ν_1 mode is strong and its Raman efficiency does not indicate resonance enhancement in the energy region of the A and B bands[10]. The absorption coefficient of the incident light, in the energy region except for the lower energy part of the band tail of the A band, becomes quite large after the photolysis, implying that the penetration depth of the incident light is within the thickness in which the photo-induced defects exist. On the other hand, the absorption coefficient of the scattered light in the energy region of the ν_1 and 270-300 cm^{-1} Raman lines is considered to be almost the same, since the difference of the frequency among them is quite small. Thus the corrected intensity due to the penetration depth of the incident light and the reabsorption of the scattered light for the 270-300 cm^{-1} Raman lines can be obtained, by normalizing the intensity of these Raman lines by that of the ν_1 mode.

Figure 2 shows the normalized Raman intensity of the 270-300 cm^{-1} Raman lines as a function of excitation photon energy in a logarithmic scale. Typical photo-induced absorption bands of PtCl is also shown in a linear scale in the figure. The solid curves drawn through the data points are the eye guided ones. All of the four Raman lines show strong resonance enhancement in the energy region of the A band. This result strongly indicates that the four Raman lines are associated with the photo-induced defect states. Furthermore, the 278 and 284 cm^{-1} lines show the resonance enhancement in the whole energy region of the A band, while the 287 and 293 cm^{-1} lines do not show the enhancement in the higher energy side of the A band. This result suggests that two kinds of the defect states may exist in PtCl.

The normalized Raman intensity of the 270-300 cm^{-1} Raman lines shown in Fig. 2 was reduced to 1/3 and 1/20 after the annealing at 250 and 300 K, respectively[11]. On the other hand, the intensity of the A and B bands at low temperature is reduced to 1/3 and 1/16 after the annealing at 243 and 293 K, respectively[2]. Thus the thermal bleaching of the Raman lines well fits to that of the A and B bands. This result also indicates that the 270-300 cm^{-1} Raman lines are related to the photo-induced defect states.

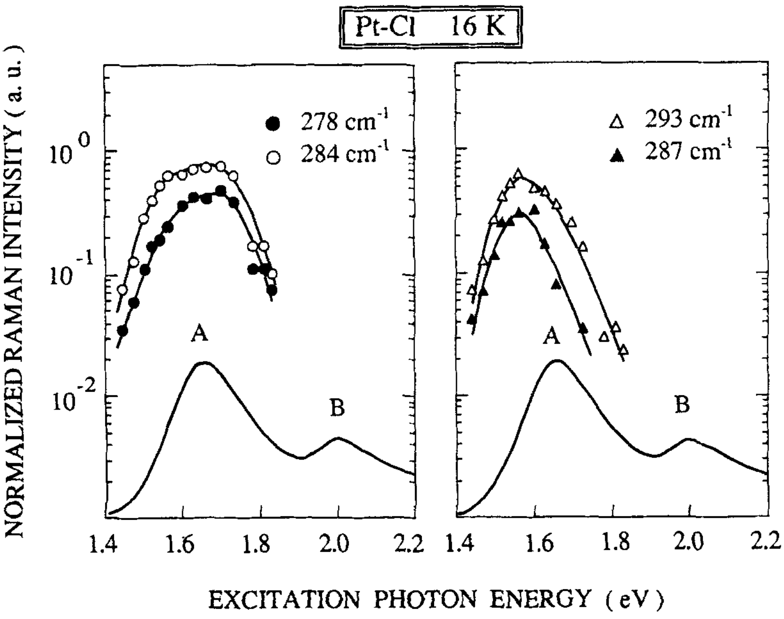

FIGURE 2 Normalized Raman intensity of the 278(●), 284(○), 287(▲), and 293(△)cm^{-1} Raman lines as a function of excitation energy in a logarithmic scale. Typical photo-induced absorption bands (A and B bands) are also shown in a linear scale in the figure.

Los Alamos's group also found several Raman modes (263,270-300 cm^{-1}) associated with the photo-induced defect states. They pointed out that the intensity of the 263 cm^{-1} mode shows the resonance enhancement in the energy region of 1.29-1.44 eV and 1.92-2.10 eV, and that of the 270-300 cm^{-1} modes shows the resonance enhancement in the energy region of 1.41-1.75 eV and 2.18-2.47 eV. According to some theoretical consideration, the Raman frequency of the electron polaron is softer than that of the hole polaron[5,6]. The three-quarter-filled two-band model[3] also predicts the electronic asymmetry between the hole and electron polarons. Thus they attributed the origin of the 263 cm^{-1} mode to the electron polarons and that of the 270-300 cm^{-1} modes to the hole polarons, although no photo-induced absorption bands were observed in the energy region below 1.44 and above 2.3 eV[2]. However the 263 cm^{-1} Raman mode did not observed for the A band in this study.

Thus we speculate that the 263 cm^{-1} mode is not related to the photo-induced defect states.

We observed not only the clear resonance enhancement of the 270-300 cm^{-1} Raman lines for the A band but also the slight difference of the resonant behavior among these Raman lines. We also found that thermal bleaching of these Raman lines well coincides with that of the A and B bands. These results suggest that two kinds of photo-induced defect states (for example, hole and electron polarons) exist in PtCl. However further experiment will be requested in order to identify the type of the defect states concerned with these Raman lines.

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