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Electronic band structure and Raman property of mixed MX chain: $\text{PtI}_x\text{Cl}_{1-x}$

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We investigated theoretically the electronic and optical properties of the mixed halogen-bridged-mixed-valence-transition-metal (MX) linear chain compounds $\text{PtI}_x\text{Cl}_{1-x}$. Similar to our earlier results for $\text{PtBr}_x\text{Cl}_{1-x}$ [1], $\text{PtI}_x\text{Cl}_{1-x}$ exhibits a segment length dependence of optical Raman spectra, but shows a different quantitative behavior. The competition between the PtI segment length and its characteristic coherence length, coupled with electron-lattice coupling results in the initial increase and then decrease of PtI Raman segment frequency as a function of its segment length. The PtI segment Raman modes and their accompanying PtCl modes have good agreement with the experimental data. A possible novel charge separation effect associated with photo-excitation (*e.g.* exciton) is discussed.

We have previously reported our study on the segment length dependence of optical Raman spectra in the mixed halogen-bridged-mixed-valence-transition-metal (MX) linear chain compound (hereafter referred as mixed halide) $[\text{Pt}^{II}(\text{en})_2][\text{Pt}^{IV}\text{X}_2(\text{en})_2]\text{ClO}_4$ ($\text{X} = \text{Cl}$ or Br), abbreviated as $\text{PtBr}_x\text{Cl}_{1-x}$ [1]. Pt^{II} (reduced) and Pt^{IV} (oxidized) denote two types of Pt valences. We were able to quantitatively associate the experimentally observed Raman frequencies with different PtBr segment lengths embedded in a PtCl environment. We found that the PtBr Raman frequency decreases monotonically as its segment length increases, and that there is a photo-excited charge separation effect as a result of hybridized energy levels [2].

In this paper, we study the mixed halide $\text{PtI}_x\text{Cl}_{1-x}$. Compared to $\text{PtBr}_x\text{Cl}_{1-x}$, where both PtCl and PtBr are relatively localized charge-density-waves (CDWs), $\text{PtI}_x\text{Cl}_{1-x}$ is a mixture of a strong (PtCl) and a weak (PtI) CDW materials. PtI is a delocalized CDW reflected by its small Peierls energy gap (1 eV) and long polaronic defect width (typically 30 sites) [3]. The big difference between CDW strengths of PtBr and PtI distinguishes $\text{PtI}_x\text{Cl}_{1-x}$ from $\text{PtBr}_x\text{Cl}_{1-x}$. Obviously the competition between two lengths, namely the PtI segment length and the PtI coherence length, will characterize the Raman behavior of $\text{PtI}_x\text{Cl}_{1-x}$.

To describe MX materials, we have developed the following extended two-band nearest-neighbor Peierls-Hubbard model Hamiltonian [3]:

$$H = \sum_{i,\sigma} \{ (-t_0 + \alpha \Delta_i) (c_{i,\sigma}^\dagger c_{i+1,\sigma} + c_{i+1,\sigma}^\dagger c_{i,\sigma}) + (e_i + \beta_i (\Delta_i + \Delta_{i-1})) n_{i,\sigma} \} \\ + \sum_i U_i n_{i,\uparrow} n_{i,\downarrow} + \sum_i \left\{ \frac{M_i}{2} \dot{x}_i^2 + \frac{K_{MX}}{2} \Delta_i^2 + \frac{\kappa_i}{2} (\Delta_i + \Delta_{i-1})^2 \right\}, \quad (1)$$

where $c_i^\dagger$ and c_i are the electron creation and annihilation operators at site i . t_0 , α and β are, respectively, the hopping integral between adjacent M and X atoms, inter-site and on-site electron-phonon couplings. e_i is the on-site energy, which equals $+e_0$ for Pt (d -orbital) and $-e_0$ for X (p -orbital). U_i is the on-site Coulomb interaction. The nearest neighbor V term is neglected here but discussed elsewhere. M_i is the mass of M or X, and K_{MX} is the spring constant between M and X, κ_i is the second-nearest-neighbor spring constant which we assume is none-zero only for κ_{MM} . Δ_i is the lattice distortion, defined as

$$\Delta_i = x_i - x_{i-1} - a, \quad (2)$$

where a is the average lattice constant.

Table 1: Parameter sets for PtCl and PtI. The units are, eV for t_0 , e_0 , and U , eV/Å for α and β , eV/Å² for K and κ_{MM} .

	t_0	e_0	α	β_M	β_X	U_M	U_X	K_{MX}	K_{MM}
PtCl	1.02	2.12	0.5	2.7	-1.35	1.9	1.3	6.8	2.0
PtI	2.45	2.0	2.53	0.51	-0.255	0.0	0.0	7.42	2.0

There are two steps in our calculation: first, the mean-field (MFA) electronic spectrum is calculated by self-consistently solving Hamiltonian (1) with the following equation, which minimizes the total energy with respect to lattice distortion:

$$K_{MX}\Delta_i + \kappa_i(\Delta_i + \Delta_{i+1}) + \kappa_{i-1}(\Delta_{i-1} + \Delta_i) = \sum_{\sigma} -\alpha_i \langle c_{i,\sigma}^{\dagger} c_{i+1,\sigma} + h.c. \rangle + \beta_i \rho_{i,\sigma} + \beta_{i+1} \rho_{i+1,\sigma} ; \quad (3)$$

second, the optical spectrum and Raman cross section are calculated using a real-space random phase approximation (RPA) method [4].

The parameter sets for PtCl and PtI are shown in Table 1. They are obtained by fitting to the experimental stoichiometric ground state properties of pure PtX materials. The experimental data and theoretical results using parameter in Table 1 (shown in parenthesis), of the ground state properties for PtCl and PtI are respectively: the Peierls dimerization 0.38 and 0.12 Å (0.384 and 0.128); the Peierls energy gap 2.5 and 1.0 eV (2.52 and 0.98); Raman frequency 305 and 113 cm⁻¹ (306 and 115); infrared frequency 358 and 240 cm⁻¹ (349 and 219).

We note that analytical expressions exist for the Fermi energy level (HOMO) and the lowest conduction band level (LUMO) of a pure MX material under our Hamiltonian (1), which in the case of $U_M = U_X = 0$ and for a given Peierls dimerization Δ , are given by

$$E^{LUMO} = \beta_M \Delta + \sqrt{2(t_0 + \alpha \Delta)^2 + (e_0 + \beta_M \Delta)^2}, \quad (4)$$

$$E^{HOMO} = -\beta'_M \Delta' + \sqrt{2(t'_0 - \alpha' \Delta')^2 + (e'_0 - \beta'_M \Delta')^2} + (e_0 - e'_0), \quad (5)$$

respectively. The last term ($e_0 - e'_0$) is added to keep the Pt on-site energy the same for two PtX materials. Comparing these two energy levels for two MX materials using Eqs. (4) and (5) can tell us whether or not we should expect *intrinsic* charge transfer effect when they are mixed. The parameters listed in Table 1 for the present PtCl/PtI material satisfy:

$$E_{PtCl}^{LUMO} > E_{PtI}^{HOMO}, \text{ and } E_{PtI}^{LUMO} > E_{PtCl}^{HOMO}, \quad (6)$$

implying that there will be no intrinsic charge transfer effect either from PtCl to PtI or vice versa. However, *photo-induced* charge transfer can still be observed in mixed PtBr_xCl_{1-x} [2] and probably in mixed PtI_xCl_{1-x} as well.

Table 2: PtI and accompanying PtCl Raman mode (cm⁻¹), and their resonance energy (eV) as function of PtI segment length.

	PtI	Pt ^{IV} I ₂	Pt ^{II} I ₂	PtI ₃	(Pt ^{IV} I ₂) ₂	(Pt ^{II} I ₂) ₂	PtI ₅	(Pt ^{IV} I ₂) ₃	(Pt ^{II} I ₂) ₇
PtI	156.5	172.1	166.2	176.3	153.7	143.0	160.8	143.6	
PtCl	none	302	none	302	300	none	301.5	295.9	125.6
E_{ν} †	1.82	1.36	2.0	1.36	1.9	1.48	1.39	1.5

Figure 1: Experimental Raman intensity data on mixed $\text{PtI}_x\text{Cl}_{1-x}$ with 5% PtI for several pumping energies.

We have systematically calculated the electronic band structure and optical Raman amplitude for $\text{PtI}_x\text{Cl}_{1-x}$ by varying the relative PtI and PtCl segment lengths. The calculated characteristic Raman modes for $\text{PtI}_x\text{Cl}_{1-x}$ are summarized in Table 2, while Fig. 1 shows a typical experimental measurement of Raman amplitude for a mixed $\text{PtI}_x\text{Cl}_{1-x}$ with 5% PtI. There are two regions in the Raman measurement, one for PtI in the range between 110 cm^{-1} to 176 cm^{-1} , the other for PtCl between 280 cm^{-1} and 310 cm^{-1} (the features beyond 400 cm^{-1} are due to overtones). The PtI segment and PtCl frequencies shown in Table 2 are quite consistent with the experimental observations. The coexistence of different PtI and PtCl Raman modes in experimental data suggests that the measured sample are composed of randomly distributed different (short) PtI segments.

Figure 2: Calculated Raman characteristic phonon wave function for a $(\text{PtI})_4(\text{PtCl})_{20}$ chain: (a) PtI segment mode; and (b) accompanying PtCl mode. Unlabeled part is PtCl.

From Table 2 and Fig. 1, we observe the following features:

First, the PtI Raman *segment* mode depends on its segment length. The PtI segment Raman

frequency first *increases* with segment length until reaching Pt_2I_3 , a characteristic length beyond which it starts to decrease. It approaches its pure chain mode of 113 cm^{-1} as the PtI segment becomes very long.

Second, there are PtCl modes (sometimes none) accompanying the PtI segment modes. They correspond to various lengths of PtCl segment, surrounded by two neighboring short PtI segments with the vibrational amplitude mostly located on the PtCl segment but also penetrating across the PtI segments. Fig. 1 (a) and (b) show a typical PtI segment and its accompanying PtCl phonon mode.

The segment dependence of PtI Raman mode is quite different from $\text{PtBr}_x\text{Cl}_{1-x}$, where the PtBr Raman segment mode *monotonically* decreases with PtBr segment length [1]. This different behavior originates in the different CDW strengths of PtBr and PtI. PtBr is still a relatively localized CDW like PtCl, with a typical polaronic width of 4 sites, while PtI is a very delocalized CDW (and thus easily deformed, see [5]) with a typical polaronic width of ~ 30 sites. Since the coherence length is so short in PtCl, the PtCl segments on the two sides of a PtI segment act as hard boundaries for PtI. They also act as a strong perturbative force distorting the charge/lattice distribution in the weaker PtI segment. Therefore, a competition exists between the PtI segment length and its coherence length. Clearly, PtI can not fully relax if it is too short. The hard PtCl boundary dominates when the PtI segment length is below a characteristic length, while it has much less influence on PtI segment behavior above this length. In the case of $\text{PtBr}_x\text{Cl}_{1-x}$, however, the PtBr defect length is so short that even a short PtBr segment is almost fully relaxed. This is why we have different quantitative behavior for PtBr Raman mode in $\text{PtBr}_x\text{Cl}_{1-x}$ and PtI Raman mode in $\text{PtI}_x\text{Cl}_{1-x}$. The PtI segment, in turn, affects the PtCl Raman profile, reflected by the presence of PtCl mode, located near the interface of PtI/PtCl on the PtCl side.

Figure 3: Calculated quasi-particle wave-functions for the same chain as in Fig. 2. (a) HOMO level with dominant PtI character; and (b) LUMO level with mostly PtCl character.

In order to identify any charge transfer effect, we need characterize two quasi-particle energy levels: HOMO and LUMO. Fig. 3 and show the single particle wave functions of these two levels for a mixed $\text{PtI}_x\text{Cl}_{1-x}$. We see that the HOMO (Fermi) level is strongly localized in the PtI segment, and the LUMO level has dominant amplitude on the PtCl side near the interface. We would therefore expect that when a particle-hole is created, the hole will be localized in the PtI segment, while the particle will be mostly on the PtCl segment near the interface. Motivated by this idea, we have calculated the electronic band structure and charge distribution for a triplet exciton (by creating a particle-hole pair with spin flip). Fig. 4 shows the charge distribution pattern of such a

case. In this case, we found an extended hole bipolaron is formed in the $(\text{Pt}^{IV}\text{I}_2)_2$ segment (seen from the equal distribution of spin up and down densities) and two neighboring localized electron polarons formed on the PtCl segment near the interface. The corresponding Raman spectrum for a hole bi-polaron in PtI was also calculated. We found it has a characteristic frequency of 117 cm^{-1} , in the right experimental range for the strong peak near 116 cm^{-1} .

Figure 4: Calculated charge distribution of a triplet exciton for the same chain as Fig. 2. Solid line denotes spin up charge, and dotted line spin down. Both lines coincide in the PtI segment indicating a hole bipolaron, while two neighboring but separate (spin-up) electron polarons are formed in the PtCl segment.

In conclusion, in a combined experimental-theoretical efforts, we have studied systematically the segment length dependence of Raman frequencies in mixed halide $\text{PtI}_x\text{Cl}_{1-x}$. Unlike $\text{PtBr}_x\text{Cl}_{1-x}$, $\text{PtI}_x\text{Cl}_{1-x}$ shows a peak in the PtI segment Raman frequency at Pt_2I_3 . Accompanying the PtI segment Raman modes are PtCl segment modes, which are enhanced correlatively with the PtCl segment modes. The coherence length of MX, characterized, *e.g.* by its polaronic defect width, plays an important role in determining the electronic and optical properties of mixed halide MXX' materials. Numerical calculation on electronic band structure suggests a possible photo-induced charge transfer effect.

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