

Theoretical studies on one-photon and two-photon absorption properties of platinum acetylide complexes

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Abstract. The one-photon and two-photon absorption properties of platinum acetylide complexes that feature highly π -conjugated ligands substituted with π -donor or π -acceptor moieties are investigated by use of the analytic response theory at DFT level. The numerical results show that these molecules have relatively strong two-photon absorption activities. While the platinum insert into the ligands, TPA cross sections of the metal compounds are significantly enhanced. Metal clusters can also extend the π -conjugated length, which plays an important role in increasing the TPA cross section. Moreover, the NLO properties of metal clusters can be enhanced by the introduction of metal \rightarrow ligand and ligand \rightarrow metal charge-transfer states. The charge-transfer process is analyzed when the molecule is excited from the ground state to charge-transfer state.

1. Introduction

For several decades there has been extensive research in the area of two-photon absorption (TPA) both theoretically and experimentally. TPA process is one which occurs through the simultaneous absorption of two photons via virtual state in a medium. Materials possessing large TPA response have opened up a number of unique applications in photonics and biophotonics[1-6], such as two-photon excited fluorescence microscopy[2], optical limiting[3], upconverted lasing[4], three-dimensional optical datastorage [5], and microfabrication [6]. Lots of experimental synthesis and theoretical calculations have been carried out to find non-linear optical materials with strong TPA. Extensive research efforts have been centered on organic complexes owing to low density, mechanical flexibility, and high nonlinear response [7-9]. However, Metal clusters are reported to be excellent candidates for NLO materials [10,11], since their high damage threshold and fast response time in comparison to organic compounds, and they involve $d\pi$ - π delocalized systems and $d\pi$ - $d\pi$ conjugated systems[12]. These compounds have a large variety of structures and diverse electronic properties that can be tuned by virtue of the coordinated metal[13-15]; thus the opportunity exists to tune the NLO properties of metal complexes. Metal clusters can also extend the π -conjugated length, which plays an important role in increasing the TPA cross section. Moreover, the NLO properties of metal clusters can be enhanced by the introduction of metal \rightarrow ligand and ligand \rightarrow metal charge-transfer states [16]. Although many methods can be used to promote the NLO properties of metal clusters, the origination of the NLO properties is the delocalization of the π -electron cloud [17-19]. This delocalization in metal clusters is mainly brought about by metal ions constructing the skeleton and organic ligands fixing the skeleton, thus both the metal ions and the organic ligands should be important for the nonlinear optical properties of the clusters. Many early studies confirm that heavy-metal ions play very important roles on the third-order NLO properties of metal

clusters because their incorporation introduces more sublevels into the energy hierarchy, which permits more allowed electronic transitions to take place and hence a larger NLO effect to be produced [20,21].

Recently, Rogers et al synthesized a series of platinum acetylide complexes that feature highly π -conjugated ligands (noted as L1-L3) substituted with π -donor or π -acceptor moieties, and measured their one-photon and two-photon excitation spectra [22]. The design of new two-photon absorbing chromophores (noted as Pt1- Pt4) coupled with Pt complexes to produce materials that exhibit large intrinsic 2PA cross-sections, coupled with efficient intersystem crossing to afford long-lifetime triplet states.

Metal ions can assemble organic ligands in a variety of multipolar arrangements which show interesting electronic and optical properties [23-26]. The systems which are the focus of this investigation incorporate one or more platinum centers. Platinum is used because of its large spin-orbit coupling which gives rise to rapid intersystem crossing and high effective triplet yields. In order to understand optical properties of these compounds, and the effect of the metal ions on the NLO properties, a theoretical analysis for their one-photon absorption (OPA) and TPA properties by means of the response theory at density functional theory (DFT) level is provided.

2. Computational methods

The one-photon absorption (OPA) strength between the ground $|0\rangle$ and excited $|f\rangle$ state is described by the oscillator strength

$$\delta_{op} = \frac{2\omega_f}{3} \sum_{\alpha} |\langle 0 | \mu_{\alpha} | f \rangle|^2,$$

Where ω_f is the excited energy and μ_{α} is the dipole moment operator. The summation runs over the molecular axes: $\alpha \in (x, y, z)$.

The TPA cross sections of randomly oriented systems can be directly related to the imaginary part of the third susceptibility. Alternatively, the TPA cross section can be obtained by computing the individual TP transition matrix elements $S_{\alpha\beta}$ between the initial state $|0\rangle$ and final state $|f\rangle$,

$$S_{\alpha\beta} = \sum_i \left[\frac{\langle 0 | \mu_{\alpha} | i \rangle \langle i | \mu_{\beta} | f \rangle}{\omega_i - \omega_f / 2} + \frac{\langle 0 | \mu_{\beta} | i \rangle \langle i | \mu_{\alpha} | f \rangle}{\omega_i - \omega_f / 2} \right], \quad (1)$$

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where $\alpha, \beta \in (x, y, z)$, ω_i and ω_f are the excitation energy to the intermediate state $|i\rangle$ and the final state ω_f , respectively. The summation here includes all intermediate, initial, and final states.

The TPA cross section is given by orientational averaging over the two-photon absorption probability [27]

$$\delta_{ip} = \sum_{\alpha\beta} [F \times S_{\alpha\alpha}^* S_{\beta\beta}^* + G \times S_{\alpha\beta}^* S_{\alpha\beta}^* + H \times S_{\alpha\beta}^* S_{\beta\alpha}^*], \quad (2)$$

The coefficients F, G and H are related to the incident radiation. For the linearly polarized light, F, G and H are 2, 2 and 2, but for the circular case, they are -2, 3, and 3, respectively. The summation goes over the molecular axes $\alpha, \beta = (x, y, z)$.

The TPA cross section that can be directly compared with the experiment is defined as

$$\sigma_{ip} = \frac{4\pi^2 a_0^5 \alpha}{15c_0} \times \frac{\omega^2 g(\omega)}{\Gamma_f} \delta_{ip}, \quad (3)$$

where a_0 is the Bohr radius, c_0 is the speed of light in vacuo, α is the fine structure constant, ω is the photon energy of the incident light, $g(\omega)$ denotes the spectral line profile that is assumed to be a δ function here, and the level broadening Γ_f of final state is assumed to have the commonly used value $\Gamma_f = 0.1$ eV [28], corresponding to a lifetime of a few femtoseconds.

The straightforward application of Eq. (1) to calculate the TP transition matrix elements is limited since it requires the knowledge of all excited states. Another rigorous method to calculate the TP transition matrix elements is by using of response theory [29]. In this framework the summation over excited states is substituted by the solution of a set of coupled response equations, where the TP transition matrix elements can be identified from the residue of the quadratic response function.

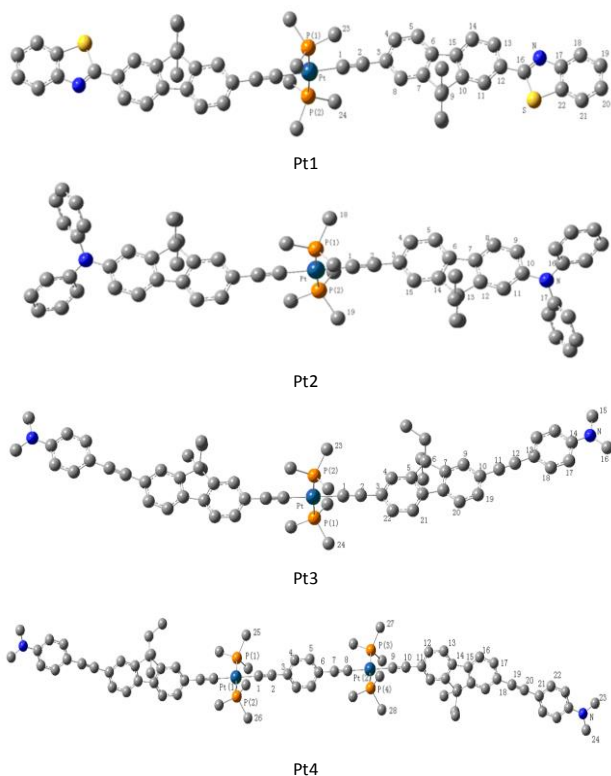


Figure 1: Optimized geometries of molecule Pt1-Pt4

3. Results and discussion

A. Computational details

The geometries of molecules are optimized using GAUSSIAN03 program [29] combined with basis sets 6-31G* for C, N, S, P and H atoms, and LANL2DZ for Pt atom, along with corresponding pseudopotential. The OPA and TPA calculations have been obtained using response theory at DFT/B3LYP level under the basis set of 6-31G* for C, N, S, P and H atoms, and ecp-sdd-pseudo for Pt atom, implemented with DALTON program. For purpose of assuring the convergence of numerical results, larger basis sets of 6-31G**, and hybrid functions B3PW91 and B3P86 are employed.

B. Molecular structures

The molecule structures optimized by DFT method are shown in **Figure 1**. In **Table 1** we list some selective bond lengths and angles of the platinum acetylide complexes. From **Table 1**, one can see that the bond lengths of Pt-C(1) (noted as B) in Pt1, Pt2, Pt3, and Pt4 are 2.0403 Å, 2.0523 Å, 2.0405 Å and 2.0519 Å respectively. And we can obtain the trace that B(Pt1) < B(Pt3) < B(Pt4) < B(Pt2). The same trend is happened in the bond length of the axetylene bonded to the platinum. This demonstrates that molecule Pt1 has a better conjugation from ligands to platinum. The backbones of both four molecules possesses perfect planarity, for instance, the angle of Pt-C(1)-C(2) in Pt1, Pt2, Pt3, and Pt4 are all 179.9°. And the atoms Pt, P(1) and P(2) also nearly on the same plane, the angles of Pt-P(1)-P(2) are ~176°. In compound Pt2, we noted that the angle between the fluorenyl carbon-nitrogenphenyl carbon atoms is ~120°, for example the angles are respective 119.9°, 119.9° and 120.2°, it is consistent with the experimental results [22], showing that the lone pair of electrons on the nitrogen has sp² hybridization, resulting in conjugation with the fluorenyl group and the attached phenyls.

C. One-photon absorption

The excitation energies and oscillator strengths of the states are calculated at the DFT/B3LYP level in gas phase as listed in **Table 2**. As shown in **Table 2**, our calculated results are in agreement with the experimental values. For the studied molecules, the transition to the first excited state dominates the OPA spectrum. As the platinum insert into the ligands, the maximum OPA wavelength of the molecules are successively red-shifted, For instance, the maximum OPA wavelength is from L1 (346.3 nm) to Pt1 (399.6 nm), L2 (363.5 nm) to Pt2 (376.7 nm), and from L3 (378.7 nm) to Pt3 (399.2 nm) Pt4 (394.9 nm). The singlet of state energy of the ligands follow the trend E(L3) < E(L2) < E(L1), while that of the platinum compounds follow the trend E(Pt1) < E(Pt3) ≈ E(Pt4) < E(Pt2). The magnitude of the

Table 1. The selective bond lengths and dihedral angle of the metal compounds.

	Pt1	Pt2	Pt3	Pt4			
Pt-P(1)	2.4121	Pt-P(1)	2.4112	Pt-P(1)	2.4114	Pt(1)-P(1)	2.4107
Pt-P(2)	2.4121	Pt-P(2)	2.4112	Pt-P(2)	2.4115	Pt(1)-P(2)	2.4105
Pt-C(1)	2.0403	Pt-C(1)	2.0523	Pt-C(1)	2.0405	Pt(1)-C(1)	2.0519
C(1)-C(2)	1.2129	C(1)-C(2)	1.2140	C(1)-C(2)	1.2130	C(1)-C(2)	1.2139
C(2)-C(3)	1.4338	C(2)-C(3)	1.4358	C(2)-C(3)	1.4344	C(2)-C(3)	1.4360
P(1)-C(23)	1.8687	P(1)-C(18)	1.8716	P(1)-C(23)	1.8687	C(7)-C(8)	1.2142
P(2)-C(24)	1.8687	P(2)-C(19)	1.8716	P(2)-C(24)	1.8687	Pt(2)-P(3)	2.4107
N-C(16)	1.2756	N-C(10)	1.4235	C(10)-C(11)	1.1996	Pt(2)-P(4)	2.4110
N-C(17)	1.3952	N-C(16)	1.4208	C(11)-C(12)	1.4324	Pt(2)-C(9)	2.0530
S-C(16)	1.8422	N-C(17)	1.4210	N-C(14)	1.4520	C(9)-C(10)	1.2142
S-C(22)	1.8054	Pt-C(1)-C(2)	179.9	N-C(15)	1.4520	Pt(1)-C(1)-C(2)	179.9
Pt-C(1)-C(2)	179.9	C(1)-C(2)-C(3)	179.9	Pt-C(1)-C(2)	179.9	C(1)-C(2)-C(3)	179.9
C(1)-C(2)-C(3)	179.9	Pt-P(1)-P(2)	176.3	C(1)-C(2)-C(3)	179.9	Pt(1)-P(1)-P(2)	176.1
Pt-P(1)-P(2)	176.3	C(10)-N-C(16)	119.9	Pt-P(1)-P(2)	176.3	C(6)-C(7)-C(8)	179.9
C(16)-N-C(17)	114.3	C(10)-N-C(17)	119.9	C(10)-C(11)-C(12)	179.9	C(8)-Pt(2)-C(9)	179.9
C(16)-S-C(22)	87.3	C(16)-N-C(17)	120.2	C(11)-C(12)-C(10)	179.9	C(18)-C(19)-C(20)	179.9

red shift upon conversion of the ligand to the platinum complexes is noted as ΔE , we can obtain the trend $|\Delta E(Pt1)| > |\Delta E(Pt2,3,4)|$. The red shift in the metal complexes signals that there is conjugation through the Pt-acetylide units. Compound Pt1 has largest red shift in the platinum acetylide complexes. This indicates again that Pt1 has greater conjugation while the ligand L1 combine with the center metal platinum. In this series of platinum acetylide complexes, the ligand L1 is seen as an acceptor, and the ligands L2 and L3 are shown as donor. Namely, the compound Pt1 is classified as $A-\pi-A$ typed structure, while Pt (2, 3, 4) are $D-\pi-D$ typed structure. This demonstrates that there is a greater extent of conjugation in the $A-\pi-A$ compound Pt1 than in the $D-\pi-D$ complexes Pt2, Pt3 and Pt4. The calculated results are well consistent with the experimental measurement. Furthermore, the corresponding oscillator strengths of first excited state are significantly enhanced, while the ligands combined with platinum atom. That is, the oscillator strengths are increased from L1 (1.27) to Pt1 (2.30), from L2 (0.64) to Pt2 (2.59) and from L3 (1.31) to Pt3 (3.90), enhanced by two times more than those of ligands. The complex Pt4 contains a $Pt-c \equiv c-phenyl \equiv c-Pt$ unit, including two platinum atoms and a central phenyl ligand, the oscillator strength is increased to 4.43. There are metal \rightarrow ligand and ligand \rightarrow metal charge-transfer states, so the oscillator strengths are significantly increased in the platinum complexes.

In order to compare with the experimental results properly [14], we carry out a Lorenz expansion of the one photon absorption, and the so-called OPA spectrum is given in **Figure 2**. It clearly to see that the red shift in compound Pt1 compared to that in ligand L1 is the largest of the metal complexes, while the red shifts in the others metal complexes Pt2, Pt3 and Pt4 are even small. Furthermore, it noted that the one photon absorption of Pt3 and Pt4 are very

Table 2. Oscillator strength δ_{op} (a.u.), the excited energy E(eV) and the corresponding wavelength λ_{op} (nm) of the six lowest excited states for all compounds.

MOL	E	λ_{op}	δ_{op}	MOL	E	λ_{op}	δ_{op}
L1	3.57	346.3	1.27	Pt1	3.10	399.6	2.30
		*351				*402	
	4.05	305.3	0.02		3.21	385.4	0.08
	4.34	285.4	0.01		3.38	366.0	0.48
	4.39	281.9	0.01		3.45	359.2	0.00
	4.47	276.8	0.01		3.50	353.8	0.15
	4.53	273.2	0.00		3.51	352.7	0.04
L2	3.40	363.5	0.64	Pt2	3.29	376.7	2.59
		*372				*383	
	3.87	319.8	0.01		3.43	362.3	0.00
	4.11	301.1	0.20		3.54	349.6	0.12
	4.26	290.9	0.00		3.70	334.2	0.01
	4.45	278.2	0.22		3.75	330.0	0.00
	4.49	275.8	0.11		3.75	329.9	0.00
L3	3.27	378.7	1.31	Pt3	3.10	399.2	3.90
		*371				*397	
	4.10	301.7	0.55		3.25	380.4	0.26
	4.16	297.8	0.00		3.29	376.1	0.41
	4.38	282.7	0.02		3.44	360.1	0.18
	4.43	279.3	0.07		3.62	341.8	0.00
	4.57	270.9	0.03		3.69	335.3	0.01
PE2	3.55	348.4	2.30	Pt4	3.13	394.9	4.43
						*397	
	3.73	331.7	0.44		3.18	388.8	0.30
	3.74	330.7	0.00		3.27	378.1	0.46
	3.85	321.4	0.00		3.40	364.6	0.18
	3.87	320.0	0.00		3.40	364.1	0.10
	3.88	319.5	0.42		3.55	349.0	0.00

similar, only with a smaller red shift and increased oscillator strength.

The calculated energies of the frontier orbitals at the B3LYP/6-31g level are reported in **Figure 3**. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the energy gap of HOMO and LUMO are given. One can see that, the energy gap between the HOMO and LUMO decreases from ligand L1 to L3, and follows the trend of first excited state excitation energy. In the platinum complex the energy gap is decreasing, and the molecular orbitals are becoming dense. This owing to that the heavy-metal atom play very important roles on their incorporation introduces more sublevels into the energy hierarchy, which permits more allowed electronic transitions to take place.

Furthermore, we also report the nature of the electronic transition in the CT state, as shown in **Table 3**. The same conclusions can be reached in a different way, by taking into account the electronic transition in the CT state. While introduce the platinum atoms into the ligands, there increased some transitions between the molecular orbitals, which also have contribution to the CT state. For instance, the transition between HOMO-1 and LUMO, HOMO and LUMO+1, besides HOMO-1 and LUMO+1. We also calculated the frontier molecular orbital of the studied compounds. It can be seen from **Figure 3** that the molecular orbital HOMO, LUMO, HOMO-1 and LUMO+1. We found that the charge-transfer of metal \rightarrow ligand, ligand \rightarrow metal and ligand \rightarrow ligand are all contributed to enhance the NLO properties. The results have clearly demonstrated that the heavy-metal atom play very important roles on enhancing the one photon absorption strength by increasing many channels of electronic transitions.

D. Two-photon absorption

The TPA cross sections in gas phase referring ten lowest excited states of the investigated compounds are listed in **Table 3**. One can see from **Table 3** that the metal compounds have relative strong TPA characteristics. It is noted that the fifth and sixth excited states of L2, and the eighth and ninth excited states of Pt3 are near-degenerate states, thus, the TPA cross section of the two states add up to one larger TPA cross section. As shown in **Table 3**, the

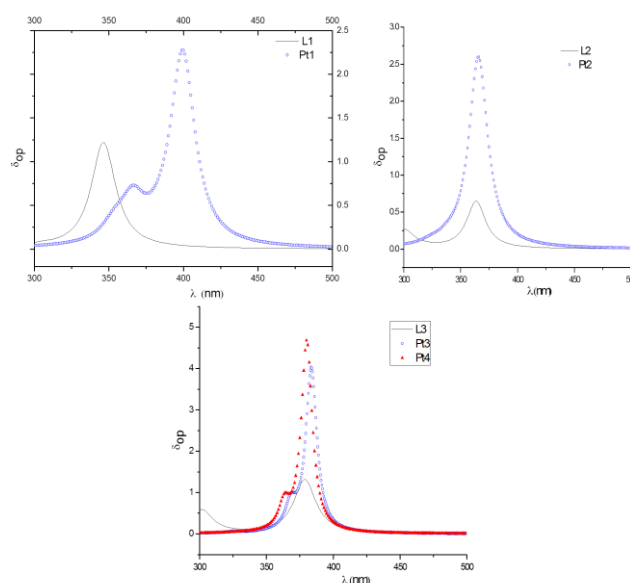


Figure 2: One photon absorption spectrum with a Lorenz expansion.

maximum TPA cross sections of the ligands L1, L2 and L3 are 1265.8, 580.0 and 1857.0 GM, when inserting the platinum into the ligands design the $A - \pi - A$ and $D - \pi - D$ typed structure Pt1, Pt2 and Pt3, the TPA activity is highly increased to 3437.9, 6146.4 and 8753.6 GM. It is clearly shown that the TPA cross sections of the metal compounds are significantly enhanced when the platinum insert into the ligands. That is mainly because the heavy-metal atom play very important roles on their incorporation introduces more sublevels into the energy hierarchy, which permits more allowed electronic transitions to take place.

4. Conclusions

We have numerically analyzed the one-photon and two-photon absorption properties of platinum acetylide complexes based on the response theory at the DFT/B3LYP level. The numerical results show that these molecules have relatively strong two-photon absorption activities. While the platinum insert into the ligands, TPA cross sections of the metal compounds are significantly enhanced. Metal clusters can also extend the π -conjugated length, which plays an

Table 3. Molecular electronic transition in the CT state.

Mol	CT state	Configuration	Coefficient	Mol	CT state	Configuration	Coefficient
L1	S_1	HOMO \rightarrow LUMO	0.65438	Pt1	S_1	HOMO \rightarrow LUMO	0.56859
L2	S_1	HOMO \rightarrow LUMO	0.67036			HOMO \rightarrow LUMO+1	0.32833
L3	S_1	HOMO \rightarrow LUMO	0.67053			HOMO-1 \rightarrow LUMO	0.14528
PE2	S_1	HOMO \rightarrow LUMO	0.63788	Pt2	S_1	HOMO-1 \rightarrow LUMO+1	-0.11320
		HOMO-1 \rightarrow LUMO	-0.10102			HOMO \rightarrow LUMO	0.49572
		HOMO \rightarrow LUMO+1	-0.18871			HOMO \rightarrow LUMO+1	0.27147
Pt4	S_1	HOMO \rightarrow LUMO	0.31515			HOMO-1 \rightarrow LUMO	-0.29475
		HOMO-1 \rightarrow LUMO	0.41694	Pt3	S_1	HOMO \rightarrow LUMO	0.48771
		HOMO \rightarrow LUMO+1	0.37508			HOMO \rightarrow LUMO+1	0.31184
		HOMO-1 \rightarrow LUMO+1	-0.12444			HOMO-1 \rightarrow LUMO	-0.29047
						HOMO-1 \rightarrow LUMO+1	0.17111

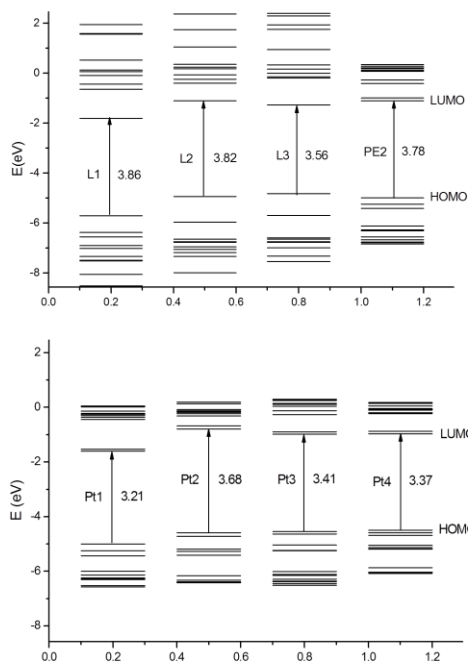


Figure 3: Calculated energies of the frontier orbitals at the B3LYP/6-31g level.

important role in increasing the TPA cross section.

Table 4. The excited energy E (eV), corresponding two photon wavelength λ_{tp} (nm), and TPA cross section σ_{tp} (GM) for studied molecules in the gas phase.

MOL	E	λ_{tp}	σ_{tp}	MOL	E	λ_{tp}	σ_{tp}
L1	3.57	690.8	20.6	Pt1	3.10	799.2	1.0
	4.05	609.1	5.5		3.21	770.8	3437.9
	4.34	569.8	1265.8		3.38	732.0	58.1
	4.39	562.0	50.7		3.45	718.4	0.0
	4.47	553.2	0.0		3.50	707.6	0.0
	4.53	545.9	301.8		3.51	705.4	169.7
	4.77	518.4	0.0		3.85	643.5	0.2
	4.94	500.6	3.2		3.88	637.6	17.2
	5.00	494.6	0.0		3.95	626.6	779.6
	5.05	489.7	2.1		4.08	606.6	2670
L2	3.40	725.2	155.9	Pt2	3.29	753.5	180.2
	3.87	637.4	1.9		3.43	724.0	6146.4
	4.11	601.7	25.2		3.54	699.0	115.8
	4.26	580.5	2.5		3.70	668.0	95.9
	4.43	555.7	358.4		3.75	660.0	30.2
	4.49	550.8	221.6		3.75	659.8	14.7
	4.55	543.5	14.4		3.77	657.6	128.4
	4.70	526.1	280.0		3.77	656.4	75.4
	4.90	504.7	1.8		3.89	635.5	168.7
	5.02	492.6	21.9		3.90	634.2	4640.4
L3	3.27	756.3	639.4	Pt3	3.10	798.0	20.6
	4.10	601.7	1857.0		3.27	760.5	21.3
	4.16	594.5	0.2		3.30	750.4	1604.2
	4.38	564.6	1.8		3.45	716.8	994.4
	4.43	557.0	107.9		3.68	683.6	64.5
	4.57	541.1	110.0		3.69	670.5	582.0
	4.77	518.4	7.6		3.75	659.5	9.9
	4.83	512.0	0.0		3.78	654.2	3832.6
	4.91	503.6	76.1		3.80	650.8	4921.0
	4.96	498.6	68.5		3.92	630.8	1497.8
PE2	3.55	696.8	55.1				
	3.73	663.4	1298.5				
	3.74	661.4	0.0				
	3.85	642.8	0.0				
	3.87	640.0	60.6				
	3.88	639.0	0.0				
	4.00	618.2	8.6				
	4.03	613.6	149.9				
	4.23	584.6	0.0				
	4.26	580.5	0.0				

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