

# Group Theory Analyses of Fano Resonance Spectra in the System of $C_{3v}$ and $C_{4v}$ Metallic Multinanoparticles-Thin Film

Mengjun Li<sup>1,2,\*</sup>, Xiaoming Li<sup>3</sup>

<sup>1</sup>Institute of Modern Optics, College of Electronic Information and Optical Engineering, NanKai University, Tianjin, China

<sup>2</sup>Department of Physics, Tangshan Normal University, Tangshan, China

<sup>3</sup>Nanophotonics Research Centre, Shenzhen Key Laboratory of Micro-Scale Optical Information Technology, Shenzhen University, Shenzhen, China

## Email address:

aiwomengjun123@126.com (Mengjun Li), lxmqlq1818@163.com (Xiaoming Li)

\*Corresponding author

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**Abstract:** The original mechanism of Fano resonance spectrum dip resulting from the system of metallic multinanoparticles-thin film belonging to  $C_{3v}$  and  $C_{4v}$  is deduced in detail using group theory. Based on our previous study, this paper verifies that there is only four LSPP electric dipole moment resonant modes in the system of  $C_{nv}$  multinanoparticles-thin film according with the same irreducible representation  $E$  when illuminated by linearly polarized light: only three of them lie in the plane where the multiparticles locate, and among them, the ring-particles own two, the central particle is one. These results are completely the same with that of  $D_{nh}$ . The direction of the electric dipolar moments is perpendicular to the multiparticles plane although the last one has the same symmetry with the other three, and it is not applied usually to the experimental study or application of surface plasmon resonance relative to the other three. In addition, the systems of metallic nanoparticles-thin film belonging to  $C_{nv}$  and the metallic nanoparticles belonging to  $D_{nh}$  point groups hold the similar spectrum lineshape, however, there is some redshift or blueshift of spectrum dip(peak) in the system of nanoparticles-thin film if the thin film exists. This work can provide some references for designing the optical properties and its extended applications about the system of metallic multinanoparticles-thin film.

**Keywords:** Surface Plasmon Resonance Spectrum, Metallic Multinanoparticles-Thin Film, Group Theory, Fano Resonance Spectral Dip, Spectral Red (Blue) Shift

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## 1. Introduction

Surface plasmon polariton (SPP) has been the focus since its prediction before half a century [1], SPP has become one of the hot spots during the recent decades based on the unique optical responses and the extensive practical applications, springing out a great quantity of theoretical, simulated and experimental study [2-18]. Localized surface plasmon polariton (LSPP) confined to the metallic nanoparticles has turned gradually into the hot research because of the tunable optical responses and the super sensitivities, thus resulting in the wide applications of LSPP on surface enhanced Raman spectroscopy [19-20], light harvesting [21], bio-chemical sensing [22-23] and medical applications [24]. The optical

properties of metallic nanoparticle-thin film have attracted a great deal of interest [25-26], and some important research improvements have emerged from the early study of P. K. Aravind [27], W. R. Holland [28] and Howard R. Stuart [29] to the recent researches [4-5, 30-34]. There has been some developed theoretical and experimental study within the system of metallic single nanoparticle-thin film, while the researches about the system of metallic nanoparticles-thin film mainly focus on the simulation and experiment. The existing theoretical study mostly based on surface plasmon hybridization and discrete electric dipole coupling, but the mathematical calculation possesses a little of complexity.

Since the first being proposed by Ugo Fano in 1961, there is a continuous study of Fano resonance about its production

mechanism and extensive application [35], and the concept of Fano resonance has been expanded gradually from the early quantum system of physics to surface plasmon nanoparticle system including the symmetric one, the symmetry-breaking one, the plasmon metamolecule system within/without the substrate [36], optical crystal and electromagnetic metamaterial. The Fano resonance dip of symmetric plasmon metamolecule attracted especially more and more interests [23, 37]. As regards the origin of Fano resonance dip, there is a generally accepted view that the Fano dip results from the coupling of wide super-radiation bright mode and narrow low-radiation dark mode. While there is also some different viewpoints suggested in recent years [38-39], and we consider the difference resulting from the different base vectors based on the different resonant modes.

Group theory has been applied to the study of plasmon metamolecule in recent ten years, it has a wide range application on SPP because of its simplicity. The researchers of [11] set forth that how to structure the symmetric multiparticles plasmon mode resulting from the single particle one based on the principle from atomic orbital theory to molecule orbital theory, but this work did not involve the center particle and the substrate. The paper of [40] expounded in detail how to construct different symmetric multidiscs plasmon mode resulting from the single disc one making use of molecule point group character table, and this method is then used to the hierarchical multidiscs. The article of [36] accounted for the splitting subgroup and Fano resonant dip of symmetric multiparticles with center one utilizing group theory. Our paper thinks about the effect of substrate on the spectrum of plasmon metamolecule based on the study of [36], and provides the particular computation using the group theory, at last we demonstrate a more uniform view of Fano resonant dip in metal nanomultiparticles-thin film.

## 2. The Basic Principle of Group Theory

Figure 1 shows the symmetric metal four/five nanoparticles on the surface of thin film belonging to  $C_{3v}/C_{4v}$  point group (Appendix 1 shows their character tables respectively). The irreducible decompositions of four/five nanoparticles systems based on the equation (2) of [36] are as follows (Appendix 2):

$$\Gamma_4 = 3A_1 + A_2 + 4E \quad (1)$$

$$\Gamma_5 = 3A_1 + A_2 + B_1 + 2B_2 + 4E \quad (2)$$

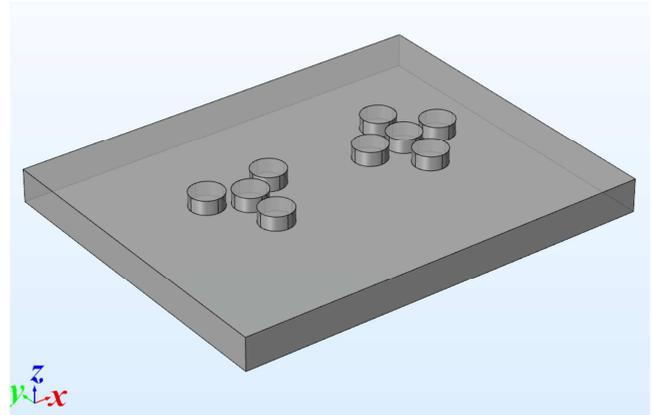
This paper talks about the resonant spectra of four/five nanoparticles systems under the linearly polarized stimulation light, that is to say the electric dipole moment of LSPP and the extra electric field must satisfy  $\vec{P} \cdot \vec{E} \neq 0$ , and they have the same irreducible decomposition:

$$\Gamma_{\vec{P}} = \Gamma_{\vec{E}} \quad (3)$$

Because the direction of the extra electric field is along x/y, we have  $\Gamma_{\vec{E}} = \Gamma_{xy}$ . According to Appendix 1, the two nanoparticles systems both have the same two-dimension irreducible decomposition  $E$  whose base vector is x/y. That is:

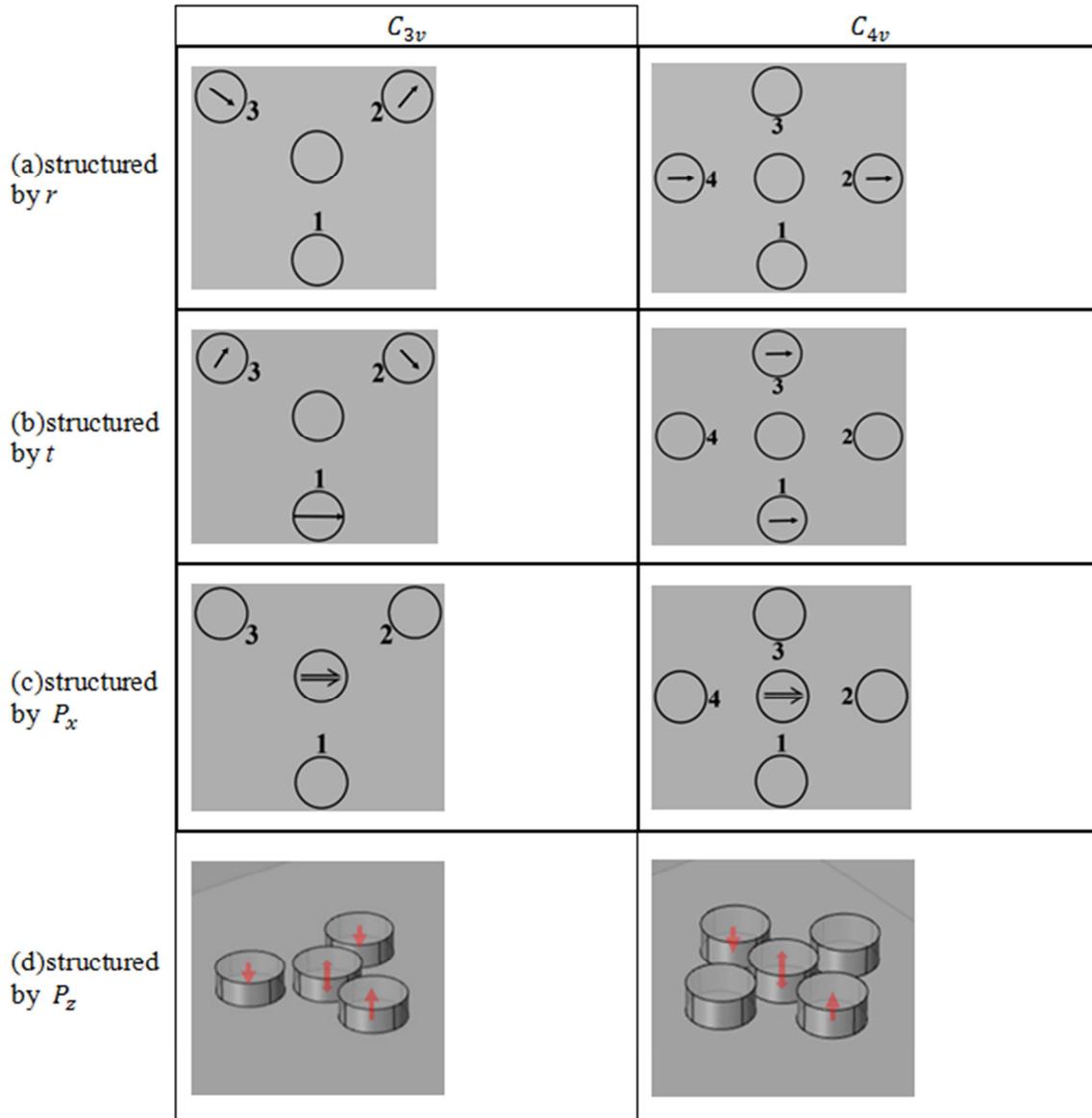
$$\Gamma_{\vec{P}} = \Gamma_{\vec{E}} = \Gamma_{xy} = E \quad (4)$$

So from equation (1) and (2), the four/five nanoparticles systems on the thin film both have 4 two-dimension degenerate LSPP electric dipolar moment resonant modes  $E$ .



**Figure 1.** System of metallic multinanoparticles on thin film, the radius of the cylinders is 70nm and the height is 60nm, the distance between the central particle and the ring-particles is 20nm.

As pointed out in [11], the symmetric LSPP electric dipolar moments in x/y plane based on  $D_{3h}/D_{4h}$  point group are the same with those of  $C_{3v}/C_{4v}$  point group.  $C$  point group is short of the symmetric operation of mirror reflection according to  $D$  point group, thus it produces that the LSPP electric dipolar moment out of x/y plane is the same with that in x/y plane which are both belonged to irreducible representation  $E$ , this means that the LSPP electric dipolar moment out of x/y plane is no longer dipole transition forbidden and could interact with the extra stimulation electric field. In addition, we can see from [36] that four/five nanoparticles of  $D$  point group only have three two-dimension degenerate LSPP electric dipolar moment resonant symmetric modes  $E'$  or  $E_u$  in x/y plane, and the ring particles have two modes, the center particle owns one independent resonant symmetric mode which is the same with that of the ring particles. So the four/five nanoparticles in this work also only have three two-dimension degenerate  $E'$  or  $E_u$  modes in x/y plane, although the other one mode has the same symmetry with that three modes, its electric dipolar moment direction is along z direction, which is perpendicular to that of extra electric field, and this is out of our discussion in our paper. Figure 2 shows the LSPP electric dipolar moment resonant symmetric modes of four/five nanoparticles, the electric dipolar moment direction of modes (a), (b) and (c) is located in x/y plane (shown in two dimension), and the direction of mode (d) is in z plane (shown in three dimension).



**Figure 2.** Schematic of LSP dipolar resonance symmetric modes for  $C_{3v}$  and  $C_{4v}$  multinanoparticles. The modes (a) and (b) are built respectively from the radial and angular vector basis; the modes (c) are the only one belonging to the center particle. The modes (d) are built by the LSP electric dipole moments aligned in z. The lengths of arrows in modes (a) and (b) represent the magnitude of the dipole moments; a different kind of arrows is used for modes (c); according to modes (d), the lengths of red unidirectional arrows in out-ring particles represent the magnitude of the dipole moments, and the red bidirectional arrows in the center particles stand for the uncertainty of the magnitude and the direction of the electric dipole moments

### 3. Analysis and Discussion

Figures 3 and 4 show the electric field distributions of the four/five nanoparticles with and without the substrate. We can see from figure 3-(2), (4) that the two kinds of four nanoparticles have nearly the same electric field distributions at the long exciting wavelengths. They both could be combined by mode (a) and mode (c) in Figure 2, and the coefficient of without the substrate is larger than that of with the substrate resulting from the intensity of the electric field. At the same time, the two kinds of four nanoparticles also have relatively the same electric field distributions at the short exciting wavelengths, they both could be combined by mode (a), mode (b) and mode (c) in Figure 2. The coefficient of mode (a) must be negative while the others are positive when

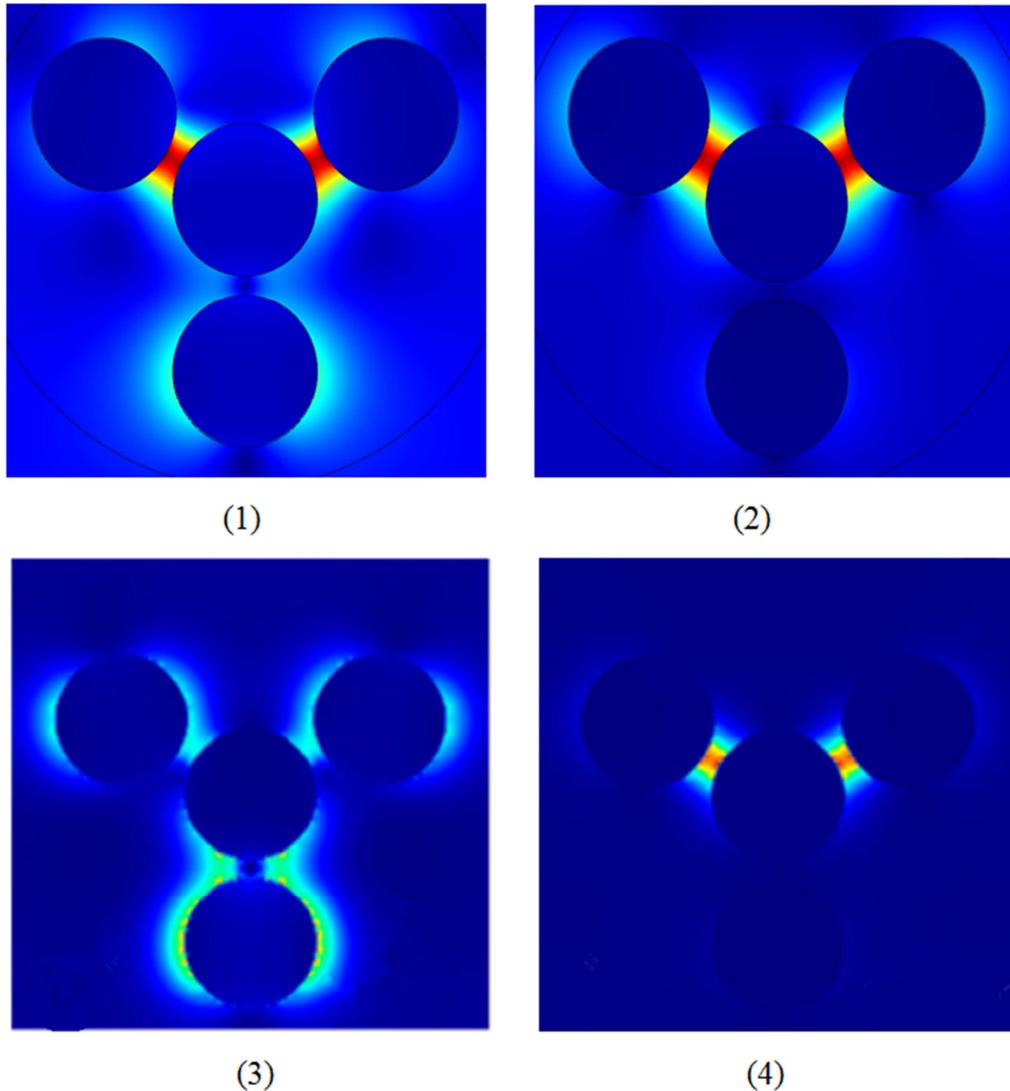
the extra electric field is along x direction based on the study of [36]. Provided that the coefficient of mode (b) is fixed beforehand, the absolute value of mode (a) coefficient without the substrate is larger than that of with the substrate resulting from the intensity of the electric field, and the coefficient of mode (c) with the substrate is far smaller than that without the substrate. According to Figure 4, the demonstration is the same with that of Figure 3, we will do not discuss in our paper.

It can be seen from above that the Fano resonant spectrum of four/five nanoparticles system with thin film could be analyzed by the four/five nanoparticles model without thin film in [36], that is to say that the actual LSP electric dipolar moment modes must be the linear combination of three basic resonant symmetric modes (a), (b) and (c) in Figure 2 when the exciting electric field is in x/y plane, however, the group

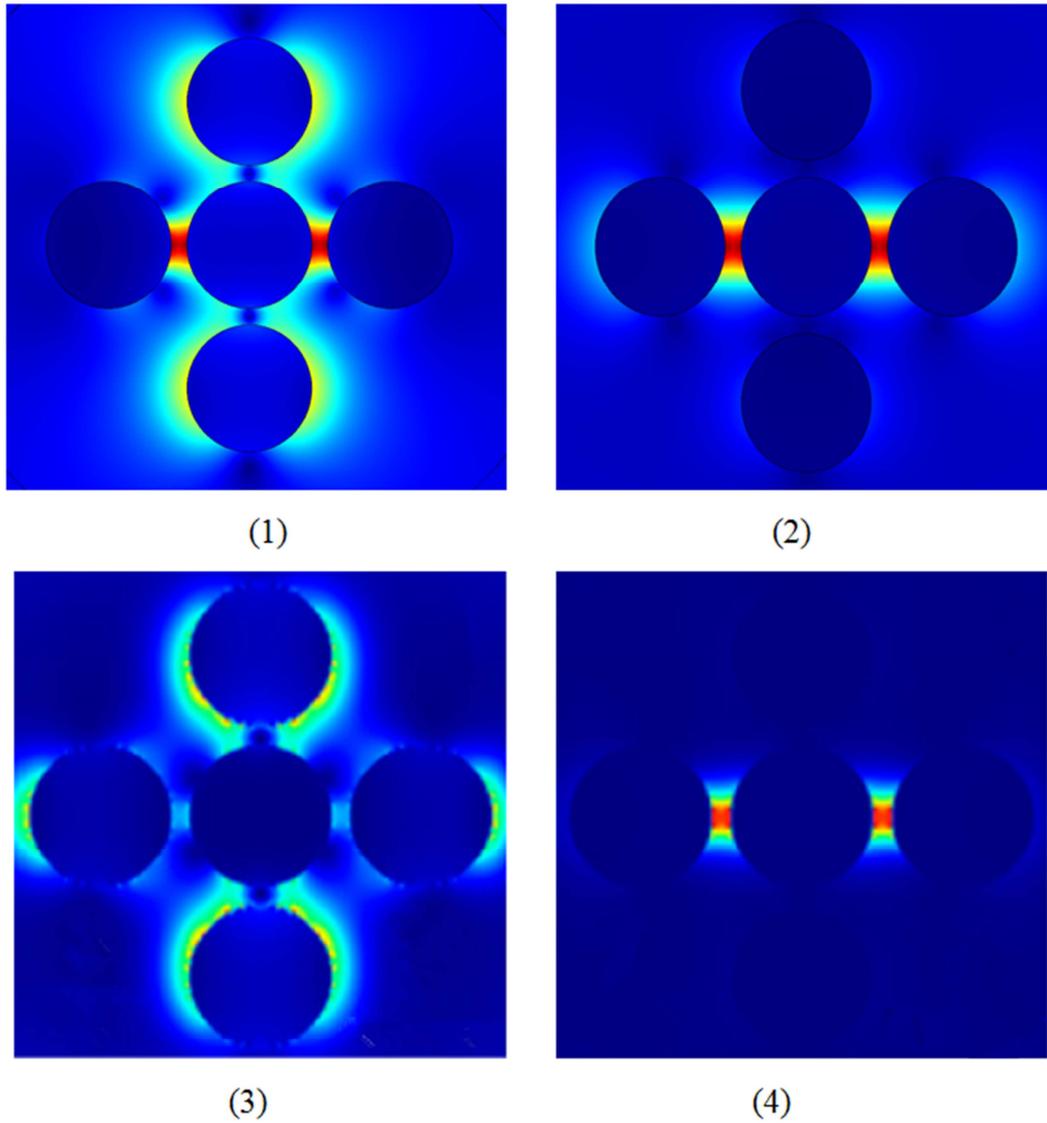
theory cannot provide the coefficients precisely, and we must seek help from theoretical numerations or experimental results. The Fano resonant dip also comes from the destructive interference of two neighboring modes which contain the same orthogonal base vectors in  $x/y$  plane.

In addition, it could be seen from Figure 5 that the two finds of Fano resonant spectrum line shapes in four/five nanoparticles with and without the substrates are essentially the same. According to the four metallic nanoparticles without the substrate, the exciting wavelengths are 560nm and 760nm, and that with the substrate are 650nm and 850nm respectively.

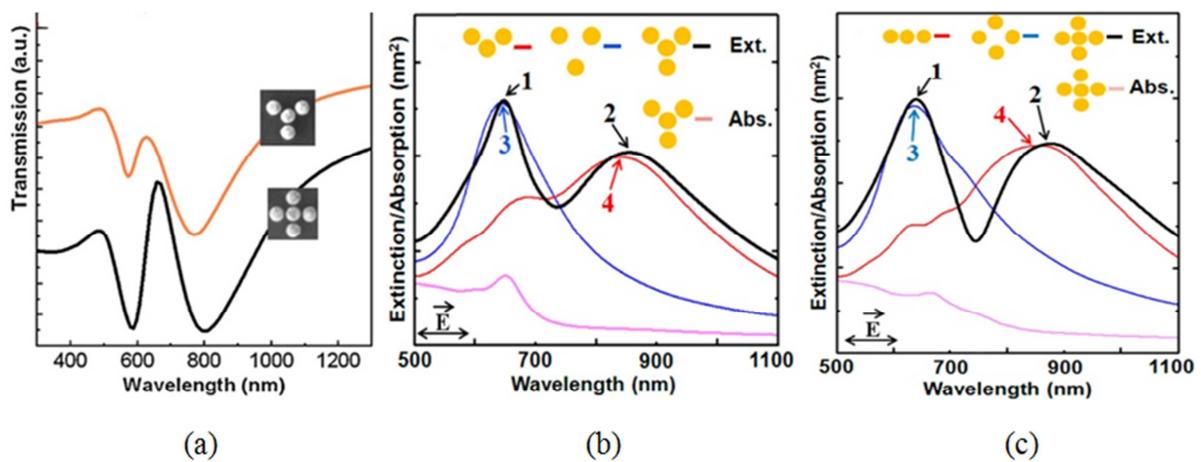
With respect to the five metallic nanoparticles without the substrate, the exciting wavelengths are 580nm and 800nm, and that with the substrate are 640nm and 880nm respectively. Thus we can conclude that both of the same multiparticles have the similar spectrum line shape, and the mainly difference is that there is some redshift or blue shift [4] of the exciting wavelength when adding the substrate to the four/five nanoparticles. The red shift of four nanoparticles is always 90nm, and that of five nanoparticles is always 80nm. The shift can be defined by the detailed parameters instead of the group theory.



**Figure 3.** Electric field intensity distributions on different exciting wavelengths, the exciting wavelength of (1) and (3) is 650nm, (2) and (4) is 850nm; the electric field intensity distributions of (1) and (2) is about the model of four particles, (3) and (4) is about the four particles on the thin film; (3) and (4) are adapted from Ref. [37].



**Figure 4.** Electric field intensity distributions on different exciting wavelengths, the exciting wavelength of (1) and (3) is 640nm, (2) and (4) is 880nm; the electric field intensity distributions of (1) and (2) is about the model of five particles, (3) and (4) is about the five particles on the thin film; (3) and (4) are adapted from Ref. [37].



**Figure 5.** (a) is the simulated transmission spectrum of the four/five particles without the existence of the base, (b) and (c) are the simulated extinction spectra of the four/five particles located on the base; (a) is adapted from Ref. [41], (b) and (c) are adapted from Ref. [37].

## 4. Conclusion

This paper demonstrates detailedly the Fano resonant dip spectrum line shape of symmetric metallic nanoparticles on the surface of thin film based on the group theory, and this method possesses some universality because of its simplicity. The system of metallic nanoparticles-thin film have more variables on the designing of Fano resonant line shape with respect to metallic nanoparticles model in [36]. Apart from the nanoparticles shape, size, material and symmetry, there are some others including the thin film size, structure, material and the gap between the nanoparticle and the thin film, and it can provide some references on the fields of optical designing, optical-electric sensor and biomedicine. Whether this method is fit pervasively for the Fano resonant spectrum of  $C_{nv}$  point group nanoparticles, the relationship between red/blue shift and the symmetry of nanoparticles, the variables of the thin film needs more study in the future.

## Appendix

### Appendix 1

Table 1.  $C_{3v}$  Character table.

$C_{3v}$	E	$2C_3$	$3\sigma_v$		
$A_1$	1	1	1	z	$x^2 + y^2, z^2$
$A_2$	1	1	-1	$R_z$	
E	2	-1	0	(x, y) ( $R_x, R_y$ )	$(x^2 - y^2, xy)$ (xz, yz)

Table 2.  $C_{4v}$  Character table.

$C_{4v}$	E	$2C_4$	$C_2$	$2\sigma_v$	$2\sigma_d$		
$A_1$	1	1	1	1	1	z	$x^2 + y^2, z^2$
$A_2$	1	1	1	-1	-1	$R_z$	
$B_1$	1	-1	1	1	-1		$x^2 - y^2$
$B_2$	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) ( $R_x, R_y$ )	(xz, yz)

### Appendix 2

$C_{3v}$ :

$$n_{A_1} = \frac{1}{6} (12 \times 1 \times 1 + 0 \times 1 \times 2 + 2 \times 1 \times 3) = 3$$

$$n_{A_2} = \frac{1}{6} [12 \times 1 \times 1 + 0 \times 1 \times 2 + 2 \times (-1) \times 3] = 1$$

$$n_E = \frac{1}{6} [12 \times 2 \times 1 + 0 \times (-1) \times 2 + 2 \times 0 \times 3] = 4$$

$C_{4v}$ :

$$n_{A_1} = \frac{1}{8} [15 \times 1 \times 1 + 1 \times 1 \times 2 + (-1) \times 1 \times 1 + 1 \times 1 \times 2 + 3 \times 1 \times 2] = 3$$

$$n_{A_2} = \frac{1}{8} [15 \times 1 \times 1 + 1 \times 1 \times 2 + (-1) \times 1 \times 1 + 1 \times (-1) \times 2 + 3 \times (-1) \times 2] = 1$$

$$n_{B_1} = \frac{1}{8} [15 \times 1 \times 1 + 1 \times (-1) \times 2 + (-1) \times 1 \times 1 + 1 \times 1 \times 2 + 3 \times (-1) \times 2] = 1$$

$$n_{B_2} = \frac{1}{8} [15 \times 1 \times 1 + 1 \times (-1) \times 2 + (-1) \times 1 \times 1 + 1 \times (-1) \times 2 + 3 \times 1 \times 2] = 2$$

$$n_E = \frac{1}{8} [15 \times 2 \times 1 + 1 \times 0 \times 2 + (-1) \times (-2) \times 1 + 1 \times 0 \times 2 + 3 \times 0 \times 2] = 4$$

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