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Local field distribution and configuration of CO molecules adsorbed on the nanostructure platinum surface*

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This paper shows that the local electric field distribution near the nanostructure metallic surface is obtained by solving the Laplace equation, and furthermore, the configuration of CO molecules adsorbed on a Pt nanoparticle surface is obtained by using Monte Carlo simulation. It is found that the uneven local electric field distribution induced by the nanostructure surface can influence the configuration of carbon monoxide (CO) molecules by a force, which drags the adsorbates to the poles of the nanoparticles. This result, together with our results obtained before, may explain the experimental results that the nanostructure metallic surface can lead to abnormal phenomena such as anti-absorption infrared effects.

Keywords: local electric field, adsorbed molecules, nanostructure metal surface
PACC: 7155, 7340, 3640

1. Introduction

Much progress has been made in science, engineering and technology based on the ability to organize, characterize, and manipulate matter systematically at the nanoscale. A fundamental understanding of nanoscale phenomena underpins innovations in critical areas ranging from manufacturing to medicine. Recently, much attention has been paid to the nanoscale effect of adsorption on a nanostructure metal surface.[1−3] It has been reported that CO molecules adsorbed on a nanostructure metal film exhibit abnormal infrared absorption behaviour in association with the geometrical features of the surface.[4−6]

Instead of a Gaussian-type spectral line shape, an enhanced asymmetric line shape of anti-absorption (abnormal infrared effects (AIREs)) has been found,[4−6] some of which can be classified as Fano-like line shapes.[7−10] Similar enhanced anti-absorption (positive-going peak) with an increased band width were also detected for agglomerated nanoparticles. These phenomena have been observed in various metals: platinum and rhodium, among others.[3,5]

Scientific reports on the adsorption of different adsorbates such as helium,[11] nitric oxide,[12] hydrogen,[13] or even copolymer sequences[14] on a solid surface using numerical simulations are abundant in the literature.[15] Many studies have shown that there is a strong connection between surface roughness and adsorption.[16,17] Albano and Martin computed the equilibrium concentration profiles of adsorbed particles at step and terrace sites at various degrees of coverage and temperatures by means of a Monte Carlo simulation.[18] Thostrup *et al* proposed that a strong binding to low-coordinated atoms may induce a step formation.[19] Much effort has been made to unveil the mechanisms responsible for the deviation of spectral line shape from Gaussian-type,[9,20] such as electronic damping,[21−23] dielectric behaviours of substrates,[24,25] and interactions between the adsorbed molecules.[26,27]

We would like to believe that the geometry and roughness of a metallic nanostructure surface, such as step and terrace, may influence the distribution of local field, and as a result, determine the configuration and the coverage of adsorbates, which plays an important role in the abnormal adsorption like AIREs. The abnormal line shape is closely related to the configuration of CO molecules determined by the geometrical features of the nanostructure surface.[26,27] The

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distribution of CO molecules adsorbed on the metal surface thus appears to be important to interpret the infrared absorption spectra.[26] However, due to the complicated geometrical description of a nanostructure surface, the calculation of the local field distribution at the surface remains a challenge. In this paper, an approximate solution is proposed to study the local field distribution of a half space bounded by a metallic nanostructure surface, and the configuration of CO molecules on a nanoparticle surface is obtained by Monte Carlo simulation. It is found that the roughness of the nanostructure surface plays an important role to agglomerate adsorbates on the surface. The agglomeration collectively increases the interaction between adsorbates, and result in the abnormal effect on the nanostructure surfaces.

2. Analysis

2.1. Electric potential

In order to illustrate the system in an intuitive way, we consider an array of half-spherical nanoparticles in a two dimensional hexagonal configuration grown out of a metal plane. An external electric field is applied in the normal direction with respect to the surface. Since there are no free charges in the upper space, the electric potential distribution Φ satisfies the Laplace's equation

$$\nabla^2 \Phi = 0, \tag{1}$$

which is restricted by the condition that the nanostructure surface is grounded. If the number of nanoparticles is large enough, it is reasonable to treat them in an identical manner (since all nanoparticles are equivalent). For convenience's sake, we consider a close-packing structure, i.e. a hexagonal packing of nanoparticles on a two-dimensional plane, and use a non-orthogonal $2\pi/3$ coordinate system with its origin fixed on the centre of one of the nanoparticles, as shown in Fig.1, to index the position of each nanoparticle. The position of interest is expressed in spherical coordinates. In view of the sixfold symmetry of the nanoparticle distribution and the spatial inversion symmetry in z-direction, we consider an approximate solution of Eq.(1) and obtain

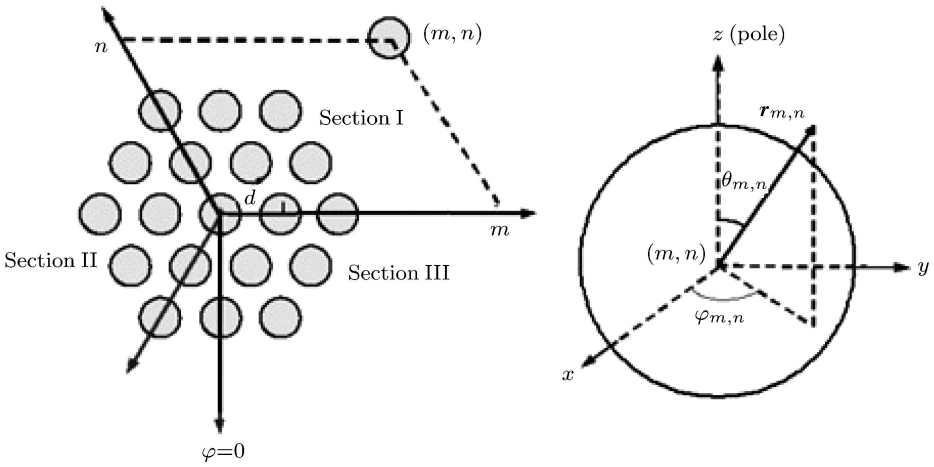


Fig.1. Hexagonal array of nanoparticles and the spherical coordinates for nanoparticle (m, n).

$$\begin{aligned}\Phi(r,\theta,\varphi) = &- Er\cos\theta + c_1 \sum_{m,n}\left(ER^3\frac{\cos\theta_{m,n}}{r_{m,n}^2}\right) + c_2\sum_{m,n}\left[ER^5\frac{P_3(\cos\theta_{m,n})}{r_{m,n}^4}\right]\\ &+ c_3\sum_{m,n}\left[ER^7\frac{P_5(\cos\theta_{m,n})}{r_{m,n}^6}\right] + c_4\sum_{m,n}\left[ER^9\frac{P_7(\cos\theta_{m,n})}{r_{m,n}^8}\right]\\ &+ c_5\sum_{m,n}\left[ER^9\frac{P_7^6(\cos\theta_{m,n})\cos 6\varphi_{m,n}}{r_{m,n}^8}\right].\end{aligned} \tag{2}$$

Here E is the external field, R is the radius of the nanoparticles, r is the distance of the position of interest from the origin, and subscripts (m,n) represent the position of the nanoparticles. $r_{m,n}$, $\theta_{m,n}$, and $\varphi_{m,n}$ denote the distance of the position of interest, the polar angles, and the azimuthal angles respectively. They can be given by r,θ,φ and (m,n) by geometrical relations (see Appendix). The numerical coefficients c_1, c_2, c_3, c_4 and c_5 are determined by boundary conditions for the contributions of terms 2–6 in Eq.(2) respectively. $P_3(\cos\theta_{m,n})$, $P_5(\cos\theta_{m,n})$, and $P_7(\cos\theta_{m,n})$ are Legendre polynomials, and $P_7^6(\cos\theta_{m,n})$ is an associated Legendre polynomial. Legendre polynomials with even degree are not taken into account due to the symmetry of the system.

Equation (2) is in fact a solution expressed in multipole expansion. The first term of Eq.(2) is the potential generated by the external field, the second term is the electric dipole moment contribution, the third, the fourth and the fifth terms are the higher-order electric moment due to the sixfold surface charge distribution on each nanoparticle, and the last term is the sixfold potential distribution, which reflects the symmetry of the nanoparticle configuration. It is apparent that Eq.(2) reflects the sixfold symmetry of the system.

According to the electrostatic boundary condition, i.e. Φ=0 on the metal plane as well as on the nanoparticle surfaces, and a given homogeneous field far from the plane, we have

$$\Phi = \begin{cases} -Er\cos\theta & (r\to\infty), \\ 0 & (r_{m,n}=R). \end{cases} \tag{3}$$

Since Eq.(2) is an approximate solution due to including finite terms of Legendre polynomials, it is impossible to determine coefficients c_1, c_2, c_3, c_4 and c_5 to satisfy the zero-potential condition on the nanoparticle surfaces ($r_{m,n}=R$). Instead we determine the coefficients by finding the minimum mean value of Φ^2 at the spherical surfaces of nanoparticles to ensure that the absolute value of Φ approaches to zero, that is

$$\frac{\partial\langle\Phi^2\rangle}{\partial c_i}=0, \quad i=1,2,3,4,5, \tag{4}$$

where

$$\langle\Phi^2\rangle=\frac{1}{2\pi}\int_0^{2\pi}\int_0^{\pi/2}\Phi^2\sin\theta\mathrm{d}\theta\mathrm{d}\varphi, \tag{5}$$

which is also a measure for the precision of our calculation. When Φ is obtained, the local field on a metallic nanoparticle surface is given by

$$\boldsymbol{E}_{\mathrm{loc}}=-\frac{\partial\Phi}{\partial r}\boldsymbol{e}_r, \tag{6}$$

where $\boldsymbol{e}_r$ is the unit vector in the r-direction.

2.2. Total energy

When CO molecules are adsorbed on the nanostructure platinum surface, they produce equivalent dipole moments which interact with each other as well as the local electric field. It is apparent that each CO molecule with dipole moment μ is oriented perpendicular to the nanoparticle surface, and results in an interaction energy

$$\begin{aligned} W_1 &= -\mu\sum_{i=1}^{N}\boldsymbol{e}_{R_i}\cdot\boldsymbol{E}_{\mathrm{loc}}(\boldsymbol{R}_i) \\ &= -\mu\sum_{i=1}^{N}E_{\mathrm{loc}}(\boldsymbol{R}_i). \end{aligned} \tag{7}$$

Here μ is the dipole moment of the CO molecules, $\boldsymbol{R}_i$ denotes the adsorption site of CO molecules on nanoparticles, and N is the number of CO molecules. Besides the dipole–field interaction, on nanostructure platinum surface, CO molecules interact with each other through an equivalent dipole–dipole interaction, for which we use a function for the CO–Pt system in Ref.[28]. Incorporating with the CO–Pt interaction, we have

$$W_2=\frac{1}{2}\sum_{i,j,i\neq j}\left\{-E_0^{\mathrm{AM}}\left[1+a(r_{i,j})\right]\mathrm{e}^{-a(r_{i,j})}\right\}. \tag{8}$$

Here

$$a(r_{i,j})=\alpha\left(\frac{r_{i,j}}{r_0}-1\right), \tag{9}$$

the parameters had been provided by the literature [28] to meet the available density functional theory (DFT) and experimental data of the CO–Pt system. E_0^{AM}=1.77eV/atom is related to the energy of adsorption (which is E_0^{AM}/e estimated from the equation above), r_0 = 0.24nm relates to the CO–Pt distance, α = 10.75 relates to the rigidity of adsorbed CO or the vibrational properties of the CO–Pt bond. The interaction between dipoles attached to different nanoparticles are neglected due to their distance. Eqs.(7) and (8), which can be expressed in terms of r, θ, and φ, correspond to two kinds of forces acting on CO molecules, one (Eq.(7)) to agglomerate the CO molecules to the poles of nanoparticles and the other (Eq.(8)) to repel CO molecules from each other

if they are too closely packed. It is assumed that the global minimum of the total energy $W = W_1 + W_2$ determines the configuration of CO molecules (dipoles) adsorbed on Pt nanoparticles.

3. Simulation and discussion

3.1. Local field distribution

In the computational simulations, a total of 1141 identical Pt nanoparticles in a two-dimensional hexagonal array are considered. It corresponds to $(m,n)_{\max} = (20,20)$ in Fig.1. An external field $E = 6 \times 10^{13}$V/m, which is estimated according to the typical spectra of CO adsorption, is applied in the z-direction to the nanostructure Pt surface. The centre-to-centre distance between neighbouring Pt nanoparticles d and the radius of Pt nanoparticles R, both are in nanoscale, which are chosen properly for the calculation of the electrostatic potentials and the local fields. Figure 2 is the numerical coefficients $c_i (i = 1, 2, \ldots, 5)$ determined by Eq.(4) for various geometries. These coefficients decrease substantially with order. It suggests that the sixfold structural symmetry is not a major contribution to the electric field. It is also found that the coefficients c_i does not depend on radius R and nanoparticle separation d independently but on R/d. Figure 3(a) depicts how the magnitude of the local field produced on one nanoparticle depends on the polar angle θ as φ is fixed. It is shown that the nanostructure surface produces the largest local field at the poles of nanoparticles, which can be easily understood, as a pole protrudes out of a conductor surface, tends to accumulate charges and generates larger local field than other places. The dependence of the local field distribution on the polar angle θ on one nanoparticle implies that an electrostatic force

$$\boldsymbol{F} = -\frac{\partial W_1}{R\partial\theta}\boldsymbol{e}_\theta = \mu\frac{\partial E_{\rm loc}(\theta,\varphi)}{R\partial\theta}\boldsymbol{e}_\theta, \qquad (10)$$

is exerted by the local field on the CO molecules which adsorbed on the surface. A direct gradient calculation of the local field with respect to θ in Fig.3(a) shows that the force will push CO molecules to the poles, leading to a correction to the steady distribution of adsorbates surrounding the poles in the absence of the external field. In order to figure out the characteristics of the local field, the magnitude of the local electric field is plotted against the azimuthal angle φ in Fig.3(b), which illustrates a sixfold symmetry again. It is clear that close to the poles, the spatial fluctuations of the local field with respect to the azimuthal angle φ are weak.

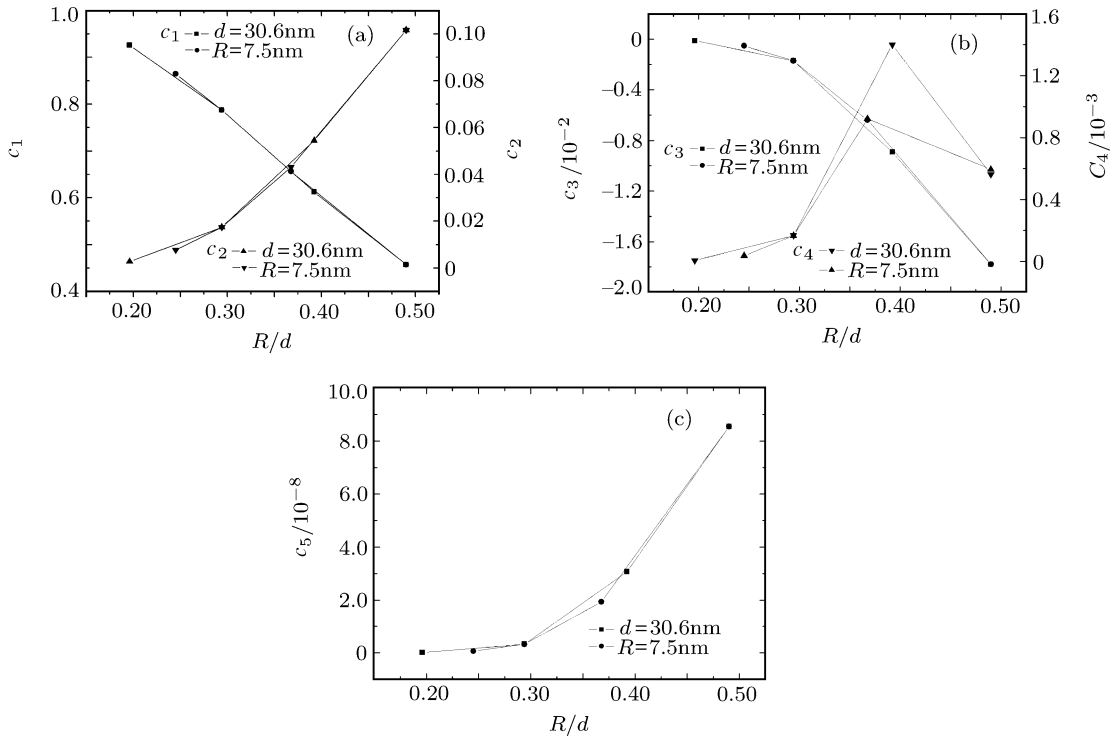


Fig.2. Dependence of (a) c_1 and c_2, (b) c_3 and c_4, and (c) c_5 on R/d.

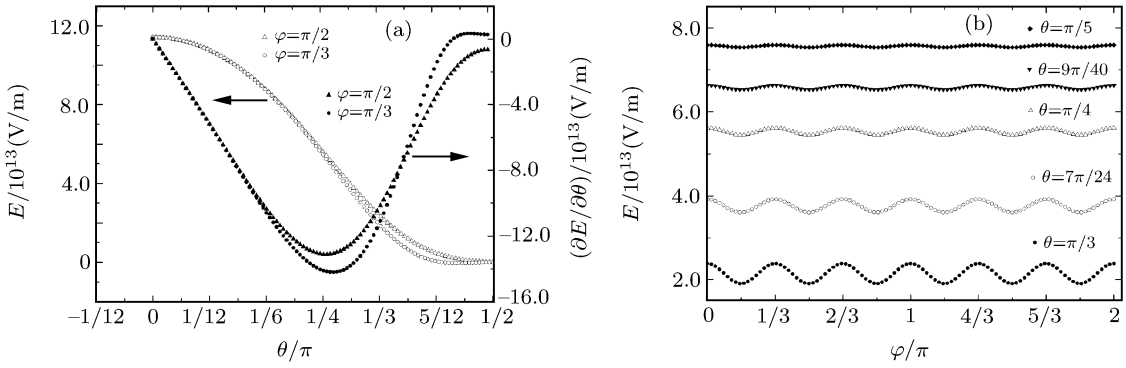


Fig.3. (a) The magnitude and gradient of the local electric field produced on one nanoparticle depending on θ as φ is fixed. (b) The magnitude of the local electric field produced on one nanoparticle depending on φ as θ is fixed.

3.2. Monte Carlo simulation of the configuration of CO molecules adsorbed on the nanostructure Pt surface

In order to investigate the configuration of CO molecules adsorbed on a nanostructure Pt surface, the off-lattice Monte Carlo simulations are carried out by using the total energy $W = W_1 + W_2$ given by Eqs.(7) and (8). However, the interaction energy among CO molecules on different nanoparticles is so weak that it can be neglected. Obviously, the distribution of CO molecules on one nanoparticle will show sixfold symmetry configuration due to the local field. For exhibiting the configuration and fitting the character of adsorption, each of the Pt nanoparticle is assumed to adsorb 2025 CO molecules in average, which comes from the initial distribution chosen in a way that CO molecules fully occupy sites of a 45×45 square lattice with respect to θ and φ on the Pt nanoparticle surface. It leads to a denser distribution around the pole than close to the equator of Pt nanoparticle. To attain a proper precision, each time a CO molecule is randomly chosen to move a step of arc length $\pi R/1000$ (R is the radius of the Pt nanoparticle) on the hemispherical surface in a tangential direction. The new position is selected according to Markovian chain of states, in which the influence of the environmental temperature is taken into account by a thermodynamic weight of probability. 2.025×10^7 iterations (equivalent to 10000 Monte Carlo Steps (MCS)) are carried out in our computation, which is proved to approach a stable result , and do not spend too long time for computation. For R=7.5 nm, d=15.3 nm, and room temperature T=300 K, the distribution of CO molecules adsorbed on a Pt nanoparticle is shown by a top view of the coverage (Fig.4(a)). A hexagonal coverage can be clearly seen due to the distribution of nanoparticles.

Whenever the specific properties of a nanostructure surface are examined, the study of different surfaces with varying geometrical parameter is inevitable. The dependence of the azimuthal CO coverage on the nanoparticle separation d (d=15.3, 20.4, 25.5, 30.6 nm) is shown in Fig.4(b). This is an analogue to the CO molecule adsorption on a number of agglomerated nanoparticles observed through experiments.[6] It can be seen from the polar angle distribution of the outermost molecules $\theta_{\max}$ with respect to the azimuthal angle φ in Fig.4(b) that the sixfold symmetry disappears quickly with the increase of the nanoparticle separation d. The coverage of the adsorbed CO molecules does not vary significantly with the separation d. This result reveals that the influence of the neighbouring Pt nanoparticles can be neglected except for the case when the neighbouring nanoparticles are close enough, which indicates that the adsorbates appear the sixfold domain pattern as nanoparticles agglomerate together.

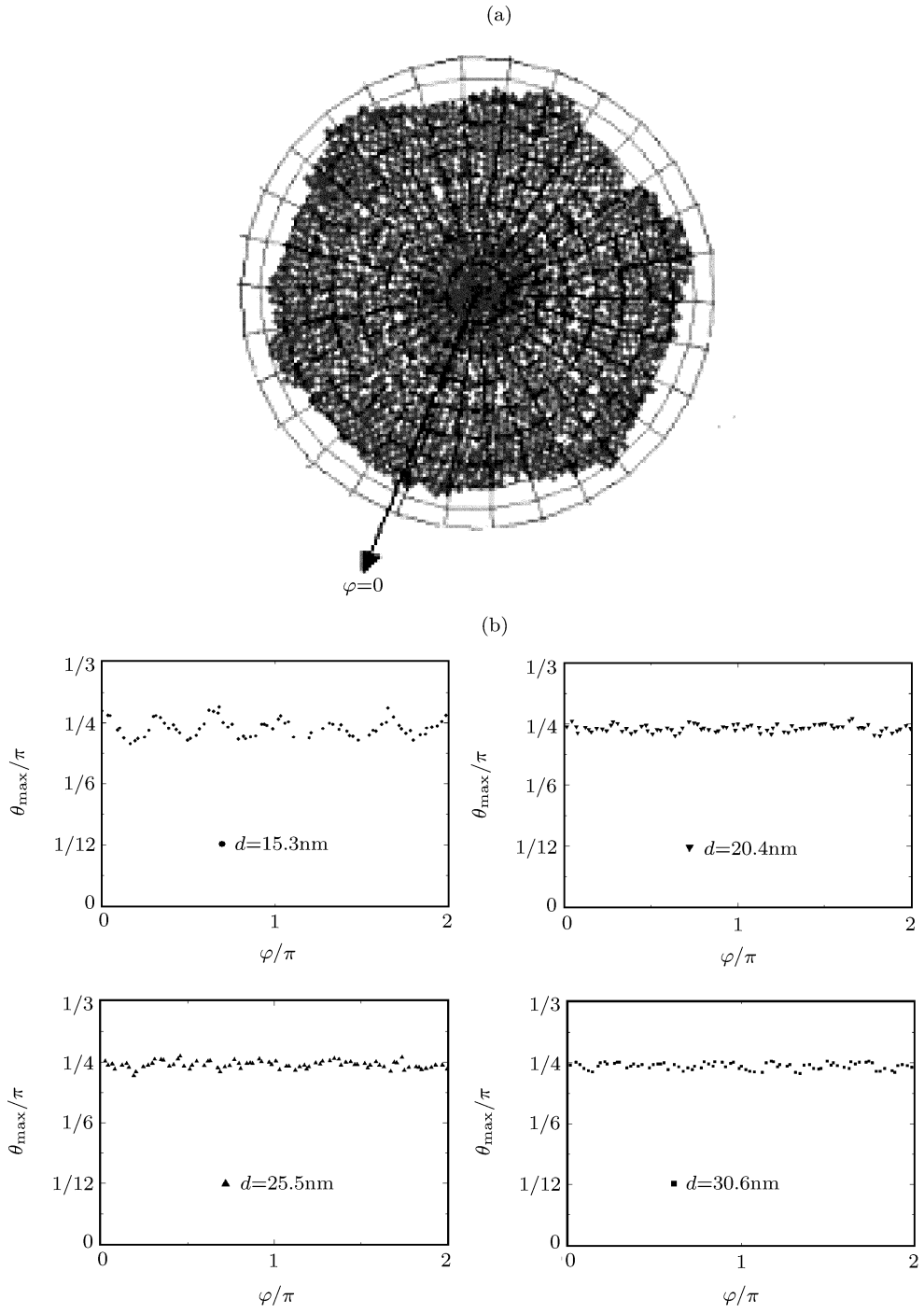


Fig.4. (a) Configurations of CO molecules on a nanoparticle (R=7.5 nm and d=15.3 nm). (b) Polar angle distribution of CO molecules at perimeter for different nanoparticle separations (d=15.3, 20.4, 25.5 and 30.6 nm).

The agglomeration of CO molecules and their configurations on a nanostructure Pt surface, found through present Monte Carlo simulations, provide a support for the fact that AIREs are found on a nanostructure Pt surface with a group of agglomerated Pt nanoparticles in two dimensions. The uneven local field distribution on the hemispheres produces a force, which attracts CO molecules to the poles of Pt nanoparticles, therefore, causes an agglomeration of CO molecules. Such a denser collective agglomeration of adsorbates, will increase the contribution of interaction factor $U(0)$ to the adsorption band,[27] and may finally lead to an abnormal infrared effect, as the model proposed by Ref.[26].

4. Conclusion

The local electric field distribution on a nanostructure Pt surface is obtained when an external electric field is applied. With a consideration of the interaction between equivalent dipoles of adsorbed CO molecules and local field as well as the interaction between CO molecules, the Monte Carlo simulations show that CO molecules tend to agglomerate to the poles of Pt nanoparticles. As a result, the distribution of CO molecules on a nanostructure Pt surface differs significantly from those configurations formed on a plane surface. This modified distribution patterns may serve as a starting point to explain the abnormal infrared spectra observed in such a system.

Appendix

As shown in Fig.1, the spherical coordinates $r_{m,n}$, $\theta_{m,n}$, and $\varphi_{m,n}$ with respect to the nanoparticle (m, n) can be written in terms of spherical coordinates r, θ and φ for the position of interest with respect to the origin and the non-orthogonal $2\pi/3$ coordinates (m, n) of the nanoparticle (m, n). Since the coordinate system for nanoparticles (Fig.1) divides the system into three sections, we have to treat them separately:

$$
\begin{aligned}
r_{m,n} =& \{[r\sin\theta\cos\varphi + d(m^2+n^2-mn)^{1/2}\sin\alpha]^2 \\
&+ [r\sin\theta\sin\varphi - d(m^2+n^2-mn)^{1/2}\cos\alpha]^2 + r^2\cos^2\theta\}^{1/2}, \quad \text{Section I} \\
r_{m,n} =& \{[r\sin\theta\cos\varphi + d(m^2+n^2-mn)^{1/2}\sin(\alpha+2\pi/3)]^2 \\
&+ [r\sin\theta\sin\varphi - d(m^2+n^2-mn)^{1/2}\cos(\alpha+2\pi/3)]^2 + r^2\cos^2\theta\}^{1/2}, \quad \text{Section II} \\
r_{m,n} =& \{[r\sin\theta\cos\varphi + d(m^2+n^2-mn)^{1/2}\sin(\alpha+4\pi/3)]^2 \\
&+ [r\sin\theta\sin\varphi - d(m^2+n^2-mn)^{1/2}\cos(\alpha+4\pi/3)]^2 + r^2\cos^2\theta\}^{1/2}, \quad \text{Section III}
\end{aligned}
$$

$$
\begin{aligned}
\theta_{m,n} &= \arccos\left[\frac{r\cos\theta}{r_{m,n}}\right], \\
\varphi_{m,n} &= 2\pi - \arcsin\left[\frac{d(m^2+n^2-mn)^{1/2}\cos\alpha - r\sin\theta\sin\varphi}{l_1^{1/2}}\right], \quad \text{Section I} \\
\varphi_{m,n} &= 2\pi - \arcsin\left[\frac{d(m^2+n^2-mn)^{1/2}\cos(\alpha+2\pi/3) - r\sin\theta\sin\varphi}{l_2^{1/2}}\right], \quad \text{Section II} \\
\varphi_{m,n} &= 2\pi - \arcsin\left[\frac{d(m^2+n^2-mn)^{1/2}\cos(\alpha+4\pi/3) - r\sin\theta\sin\varphi}{l_3^{1/2}}\right], \quad \text{Section III}
\end{aligned}
$$

where

$$
\begin{aligned}
\alpha &= \arccos\left[\frac{2m-n}{2(m^2-n^2-mn)^{1/2}}\right], \\
l_1 &= d^2(m^2+n^2-mn) + r^2\sin^2\theta - 2d(m^2+n^2-mn)^{1/2} r\sin\theta\cos(\alpha+\pi/2-\varphi), \\
l_2 &= d^2(m^2+n^2-mn) + r^2\sin^2\theta - 2d(m^2+n^2-mn)^{1/2} r\sin\theta\cos(\alpha+\pi/2+2\pi/3-\varphi), \\
l_3 &= d^2(m^2+n^2-mn) + r^2\sin^2\theta - 2d(m^2+n^2-mn)^{1/2} r\sin\theta\cos(\alpha+\pi/2+4\pi/3-\varphi).
\end{aligned}
$$

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