

Emissions from Surface Chemical Reactions by QED induced EM radiation

T. V. Prevenslik
Discovery Bay, Hong Kong

Abstract

Over a century ago, chemical reactions of gaseous reactants with solid surfaces were identified as the source of exoelectron emissions (EEE). Photon emission (PE) was later found to accompany EEE, the PE taking the form of chemiluminescence (CL). But how gaseous reactants acquire the electromagnetic (EM) energy necessary to excite the electronic system to emit EEE and PE has remained a mystery. The proposed EM energy source is the thermal kT energy of the gas reactant molecules that by collisions is transferred to a thin layer of nanoparticles (NPs) covering the surface. Here k is Boltzmann's constant and T is absolute temperature. The NPs have high EM confinement frequencies, and therefore the low frequency kT energy accumulated from collisions is frequency up-converted by quantum electrodynamics (QED) to produce a continuous source of high frequency EM radiation, the theory called QED induced EM radiation. In this arrangement, QED induced EM radiation in NPs posited in the solid surface provides the excitation that by photoluminescence produces the EEE and PE emissions.

Keywords: exoelectron emission, photon emission, nanoparticle, QED

1. Introduction

Historically, chemical reaction induced EEE and PE were first observed even prior to Einstein's celebrated explanation [1] of the photoelectric effect in 1905. In 1887, Hertz found [2] light arcs in gases to be formed from other light arcs and Hallwachs [3] showed solids could be ionized by light. Just prior to Einstein's paper, Lennard showed [4] in 1902 that the photo-electric induced voltage depends on the wavelength of light and not its intensity.

Perhaps the most important work in chemical reactions in solids was performed in 1905. Thomson showed [5] light was not necessary to produce negative ions, but rather by simply exposing liquid alkali metals to small quantities of gases. Recently, Greber [6] stated that Thomson was the first to ask the question, although he never answered it - what is the source of EM energy for the continuous EEE and PE?

Later, Haber and Just [7] studied the ionizing action of gases on alkali metals and alloys and concluded the reaction of bromine and phosgene with NaK alloys leads to electron emission. It was not until 1935 that Denisoff and Richardson [8] with accurate experiments initiated the notion of non-adiabatic EEE and PE.

In the 1950's, the Kramer effect described [9] EEE induced by exothermic processes even though Thomson earlier showed EEE to occur isothermally by non-adiabatic processes.

Recently, the understanding of chemical reactions at surfaces was significantly advanced by many researchers, although it was Ertl and Hasselbrink [10] who showed that collisions of molecules with surfaces could lead to non-adiabatic processes and produce EEE and PE. E.g., the finding that translational energies in NO desorption from Pd surfaces were about 140 meV showed desorption was non-thermal. Otherwise, thermal desorption in an adiabatic process would have required an unphysical surface temperature of 800 K. Of interest to QED induced EM radiation, the EEE was concluded to be likely initiated by ultraviolet (UV) photons in photochemical processes in the metallic substrate, although the mechanism by which the UV photons are generated was not identified.

Nevertheless, Ertl [11] meticulously showed that EEE and PE are evidence of non-adiabatic processes and cannot be adiabatic processes. In 2007, Ertl was awarded the Nobel Prize in Chemistry for his methodical work in extending our understanding of the interaction of gas molecules and chemical surfaces. In an adiabatic process, the excited system is treated as a perturbation on the ground state potential energy surface (PES) with the system relaxing without jumps. This means the electronic system satisfies the Born-Oppenheimer condition where the electronic system is in thermodynamic equilibrium with the motion of the atomic nucleus. But in non-adiabatic processes, the electronic system relaxes in jumps that produce EEE and PE.

In non-adiabatic processes, the electronic system is no longer in thermal equilibrium [11] with the atomic nucleus evidenced by the facts that not only does EEE occur with the surface at ambient temperature, but the PE spectrum differs from that of a black body (BB). This is proof positive the process is non-adiabatic and not in thermal equilibrium with the atomic nuclei at the substrate temperature.

However, whether EEE and PE are non-adiabatic processes is not yet resolved. In 2006, Hasselbrink [12] questioned the likelihood of non-adiabatic process in EEE and PE. Instead of resolution, complex non-adiabatic mechanisms including (i) charge transfer, (ii) delayed charge transfer, and (iii) oscillating charge were proposed.

In contrast, the EEE and PE mechanism proposed here is of relative simplicity. The question asked is that of Thomson rephrased: What mechanism makes it possible for EEE and PE to occur from low frequency kT energy present in gas molecules colliding with a surface?

It is immediately obvious that any answer to this question must rely on some mechanism to convert low frequency kT energy into high frequency EM radiation, at least to vacuum ultraviolet (VUV) levels. One such VUV mechanism is called QED induced EM radiation, but requires NPs. See e.g., Prevenslik [13]. In fact, the QED enhancement in chemical reactivity by nanocatalysts [14] was recently proposed.

Nanocatalysts are by definition NPs, but solid surfaces are generally thought to be smooth and continuous. However, it is reasonable to posit NPs in chemical reaction surfaces because NPs are inherent in all fabrication processes. E.g., surface enhanced Raman Scattering (SERS) was found [15] enhanced by a factor of 10^7 with NPs in roughened surfaces.

The Raman enhancement by roughened surfaces is thought [16] caused by exciting the surface plasmon modes in separated NPs or in structured hemispherical NP bumps on surfaces. But the enhancement is very sensitive to the distance between adjacent NPs with the optimum occurring when adjacent NPs are almost touching instead of being widely dispersed as usually observed. What this means is the field enhancement of the electric field by surface plasmon is most likely not the source of SERS enhancement.

In contrast, QED induced EM radiation is applicable for any dispersion of NPs on the surface and any location on the NPs. In fact, SERS was included as an extension to the application [17] of QED induced EM radiation to quantum dots (QDs) under near infrared (NIR) radiation.

In surface chemical reactions, there are no NIR lasers, but this is inconsequential because the NPs posited in the surface in collisions by reactant gas molecules accumulate EM thermal kT energy only to be frequency up-converted by QED to VUV levels. Planck energy at VUV levels is created everywhere within the NP, and therefore reactant molecules adsorbed anywhere on the NP surface undergo instantaneous chemical reaction. Otherwise the QED induced VUV in NPs irradiates the substrate to produce EEE and PE by photoluminescence.

2. Purpose

The purpose of this paper is to explain surface chemical reactions by treating the roughened surface at the nanoscale as a collection of NPs that accumulate EM thermal kT energy in collisions with reactant gas molecules that by QED is up-converted to VUV levels.

3. Theory

NPs under molecular collisions find similarity with QDs under NIR laser radiation [17] in that both NPs and QDs partially absorb EM radiation. In QDs, NIR laser radiation is absorbed; whereas, in NPs the EM thermal kT energy at far infrared (FIR) frequencies is absorbed by molecular collisions. Like QDs, the NPs are absent specific heat, and therefore cannot conserve the accumulated kT energy by an increase in temperature. Conservation may then only proceed by the NPs inducing the accumulated kT energy to undergo frequency up-conversion to the EM confinement frequency of the NP, typically beyond the VUV.

Consider the collision of reactant gas molecules A and B with NPs posited in the surface of a chemically reactive solid producing EEE and PE from the substrate shown in Fig. 1.

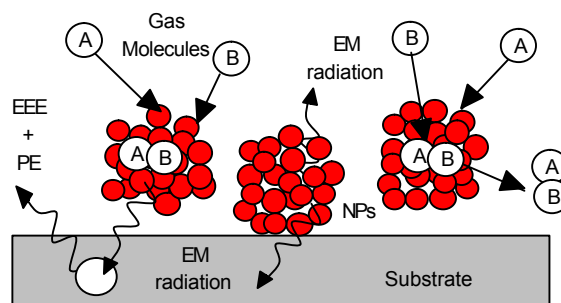


Figure 1. Collisions of gas molecules with NPs in surface of a chemically reactive solid to produce EM radiation that also causes EEE and PE from the substrate.

The NPs accumulate kT energy from the adsorption of reactant A and B molecules that by QED is frequency up-converted to high frequency EM radiation at VUV levels. Subsequently, the EM radiation is absorbed in the substrate to produce EEE and PE by photoluminescence, or is emitted into the gas above the chemically reactive solid.

The gas molecules A and B adsorb on the NPs and react under the Planck energy induced at VUV levels in the NP to promptly initiate the chemical reaction,



where, h is Planck's constant and ν is the frequency of the EM confinement of the NP.

It is important to note the EM confinement frequency of the NP excited by FIR radiation from collisions of gas molecules is not that of lattice vibrations at microwave frequencies. Instead, the EM thermal kT energy excites the electrons in the NPs that by Mie theory [18] is subsequently scattered or absorbed. Typically, FIR radiation is mostly scattered by NPs, but FIR radiation in molecular collisions is expected to be fully absorbed because the molecules are small in relation to the NPs.

Regardless, the absorbed EM thermal kT energy must satisfy the boundary conditions imposed by the NP geometry. QED induces the accumulated kT energy from prior collisions to be up-converted to the VUV levels necessary for EEE and PE.

With regard to NPs under molecular collisions, QED restricts the kT energy of the NP atoms to vanishing small levels; whereas, the colliding reactant A and B molecules absent EM confinement have full kT energy. This may be understood by the Einstein-Hopf relation [19] for the harmonic oscillator at 300 K shown in Fig. 2.

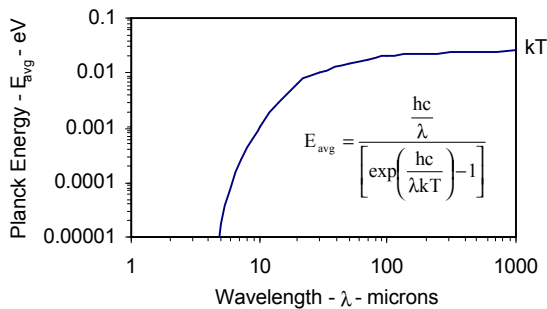


Figure 2. Harmonic oscillator at 300K.

In the inset, c is the speed of light, λ is wavelength.

In nanocatalysts, NPs having diameters $D < 5$ nm are of interest. The EM confinement has wavelengths $\lambda < 2D = 10$ nm. Fig. 2 shows at $\lambda \sim 6$ microns, $kT = 10^{-4}$ eV, and therefore at $\lambda < 10$ nm, $kT \ll 10^{-4}$ eV.

Hence, kT vanishes for NP atoms; whereas, colliding reactant molecules A and B not under EM confinement have full kT energy, say for $\lambda > 100$ microns in Fig. 2.

Collisions therefore transfer full kT energy to the NPs. But the absence of specific heat does not allow the accumulated kT energy to be conserved by an increase in temperature, and therefore conservation proceeds by the accumulation of Planck energy at the EM confinement frequency of the NP. For NPs having diameters $D < 100$ nm, the Planck energy exceeds 6 eV which is more than sufficient to complete the bond dissociation begun by adsorption to initiate the chemical reaction.

The generality of QED induced EM radiation finds application to EM radiation at VUV levels emitted from larger NPs than those used in catalysis, e.g., the oxidation [20] of hydrocarbon liquids in flow electrification and aging by NP impurities having $D < 100$ nm.

A. EM Confinement

Before considering NPs absorbing EM radiation from molecular collisions, it is instructive to consider the QD theory [17] under NIR laser radiation for the case of $D > \lambda$ shown in Fig. 3. For clarity, a single NIR photon is depicted to excite the polar, radial, and equatorial modes [21] of the NP.

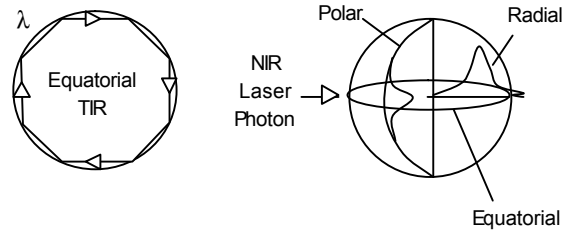


Figure 3 EM Energy Interaction with NP for $\lambda < D$

The equatorial mode shows the EM radiation trapped in the NP by total internal reflection (TIR) that may be understood by the number n of reflections of wavelength λ around the NP circumference, $n \sim \pi D / \lambda$. As $n \rightarrow 1$, the ratio $\lambda / D \rightarrow \pi$. For $n > 1$, the speed of light c is reduced in the NP, giving frequency f_{TIR} ,

$$f_{TIR} = \frac{c/n_r}{\pi D} = \frac{c}{\pi n_r D} \quad (2)$$

where, n_r is the index of refraction.

For NPs having $\lambda \gg D$, the TIR frequency f_{TIR} is modified [22] by a unity index of refraction,

$$f_{\text{TIR}} \sim \frac{c}{\pi D} \quad (3)$$

The radial Mie mode is analogous to the quantum mechanical analogy of creating photons of wavelength λ by supplying EM energy to a box having walls separated by $\lambda / 2$. For NPs the EM energy supplied is the absorbed kT energy accumulated from prior molecular collisions. With NP walls separated by diameter D , the QED photons created have wavelength $\lambda = 2D$. The frequency f_r radial mode,

$$f_r \sim \frac{c}{\lambda} = \frac{c}{2D} \quad (4)$$

B Vanishing Specific Heat

Upon absorption, the EM radiation is confined within the geometry of the NP. For the NP to conserve the absorbed EM radiation by an increase in temperature, the specific heat must be finite. Here, the specific heat of the NP generally follows the Einstein formulation, but differs in that instead of the specific heat given by atomic vibrations; it is given by the vibration of thermal photons, the atoms remaining stationary.

Prior to the absorption of kT energy, the thermal photons from the NP atoms are in equilibrium at temperature according to the Einstein-Hopf relation. But the absorbed kT energy disturbs the equilibrium during frequency up-conversion to the EM confinement frequency of the NP. Over this time, the NP momentarily has more kT energy than allowed by Bose-Einstein statistics at temperature. The specific heat is then given by the Einstein relation evaluated at the EM confinement frequency of the NP.

Although Einstein assumed the atoms are harmonic oscillators vibrating independent of each other, the thermal photons as oscillators vibrate coherently in the surface plasmon modes before being converted to the EM confinement frequency imposed by the NP. For each atom, one thermal photon is assumed for each degree of freedom (DOF). The total Planck energy U of a NP with N atoms, each atom having 3 DOF is,

$$U = 3N \frac{\frac{hc}{\lambda}}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1 \right]} \quad (5)$$

The NP specific heat C is,

$$C = \frac{\partial U}{\partial T} \quad (6)$$

In terms of the dimensionless specific heat C^* ,

$$C^* = \frac{C}{3Nk} = \frac{\left(\frac{hc}{\lambda kT}\right)^2 \exp\left[\frac{hc}{\lambda kT}\right]}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]^2} \quad (7)$$

All BB photons are coherent at the EM confinement frequency f ,

$$C^* = \frac{C}{3Nk} = \frac{\left(\frac{hf}{kT}\right)^2 \exp\left[\frac{hf}{kT}\right]}{\left[\exp\left(\frac{hf}{kT}\right) - 1\right]^2} \quad (8)$$

where, f is the frequency of the quasi-bound leaking radial mode, $f = f_r \sim c / 2D$. The dimensionless specific heat C^* in relation to wavelength λ at 300 K is observed to vanish at $D < 4$ microns in Fig. 4.

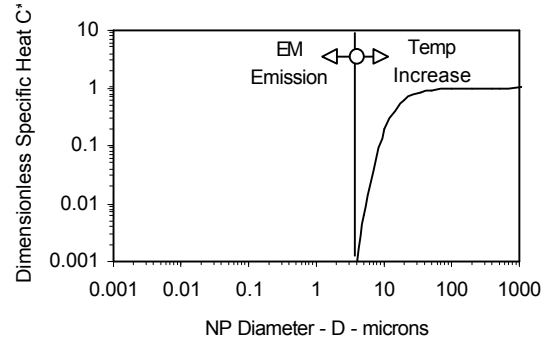


Figure 4. Dimensionless Specific Heat C^* at 300 K

C Collision Induced EM Radiation

The collisional EM power Q_C [23] in the NP,

$$Q_C = \frac{\pi}{2\sqrt{3}} pPD^2 \sqrt{\frac{kT}{m}} \quad (9)$$

where, p is the probability of EM energy transfer, and P is the ambient pressure. The mass m of colliding molecules is, $m = MW / N_{\text{avag}}$ where MW is molecular weight and N_{avag} is Avagadro's number.

D QED Induced EM Energy and Rate

Absent an increase in NP temperature, the collisional EM energy Q_C is conserved by the emission of EM radiation,

$$E_p \frac{dN_p}{dt} = Q_C \quad (10)$$

where, dN_p / dt is the rate of QED photons produced in the NP having Planck energy E_p ,

$$E_p = \frac{hc}{2D} \quad (11)$$

$$\frac{dN_p}{dt} = \frac{\pi}{2\sqrt{3}} \frac{pPD^2}{E_p} \sqrt{\frac{kT}{m}} \quad (12)$$

For NPs having $D < 100$ nm, $E_p > 6.21$ eV and the EM radiation is emitted in the VUV where most reactant molecules are activated. For probability $p = 1$ of full kT transfer, the Planck energy E_p and power Q_C at Planck energy E_p for oxygen and chlorine gases having MW = 18 and 70 are shown in Fig. 5.

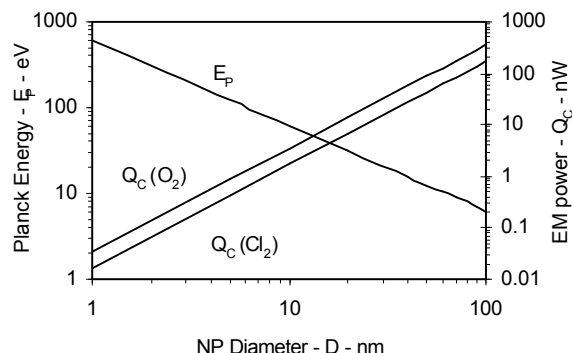


Figure 5. QED Induced Power Q_C - Planck Energy E_p

Under absorbed collisional kT energy, the NP is induced by QED to produce EM radiation at a power Q_C depending on its diameter D . For $D = 5$ nm NPs in O_2 and Cl_2 , Fig. 5 shows the power $Q_C \sim 1$ and 0.8 nW of EM radiation at ~ 120 eV.

4. Discussion

Currently, non-adiabatic EEE and PE processes are explained by spontaneous reactions using the phenomenological NNL model [6] with harpooning in combination with the chemical hole diving.

In contrast, the QED model explains EEE and PE including CL by the accumulation of kT energy from collisions of gas molecules with NPs posited in the metal surface that by QED is converted to VUV levels as illustrated in Fig. 6.

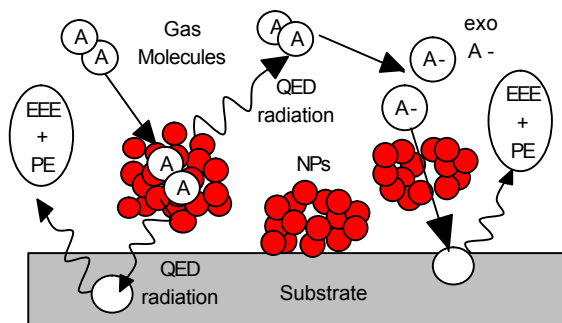


Figure 6. QED Induced EEE and PE

A. Harpooning

Generally, the Norskov-Newns-Lundqvist (NNL) charge transfer model [24] is applied to electropositive metals interacting with diatomic gases of electronegative atoms.

The charge-transfer [25] is thought to proceed by steps: (1) *harpooning* of the diatomic molecule AA as it approaches the metal surface by an electron transferred from the metal, (2) *dissociation* of AA into $2A^-$ ions which may be accelerated toward the metal surface, and (3) *exoemission* where the collision of A^- ions produces EEE and PE. The process transfers 2 electrons from the metal to the gas, the first in harpooning and the second in the collision of the A^- ions and the substrate.

In contrast, the QED model is depicted in Fig. 6. Collisions of the diatomic molecules AA with NPs accumulate kT energy by adsorption only to be frequency up-converted to VUV levels by QED. The QED radiation is emitted spherically to directly interact with other AA molecules, or directly with the substrate, either interaction producing EEE and PE.

The QED radiation may excite AA molecules approaching the surface that spontaneously dissociate into $2A^-$ ions, either of which may be accelerated toward the surface, or be expelled to the gas. Fig. 6 shows the A^- ion emission that passing through other NPs collides with the dense substrate to produce EEE and PE. Alternatively, the QED radiation from the NPs may directly be absorbed by the substrate to produce EEE and PE.

The interaction of QED radiation at VUV levels may dissociate the AA molecules into A^- ions at a distance from the surface, although upon adsorption the A^- ions are promptly dissociated. There is no requirement for the potential barrier between the work function of the substrate and the electron affinity of the AA molecule to be sufficiently small to allow dissociation of AA molecules by tunneling.

An important consideration in the production of QED radiation is the probability p of full kT energy transfer in surface collisions. In Fig. 5, the unit probability ($p = 1$) was assumed which is supported by vibrationally assisted sticking of molecules [26] to surfaces in chemical reactions.

B. Chemical Hole Diving

EEE is usually thought [6] to occur by the Auger de-excitation of a hole state that is injected into the Fermi sea of electrons. In a one electron analogy, the affinity level will try to dive to its ground state. The observation of EEE implies that in this hole injection process, the AA dissociation is so fast the holes may dive deeper than the work function and cause the emission of Auger electrons. For EEE, a second electron transfer is required for the dissociating molecule to undergo Auger emission. That the EEE is non-adiabatic is affirmed by injection velocities of about 2000 m/s for an effective temperature of 4800 K.

In contrast, QED induced EM radiation produces EEE at ambient lattice temperatures. The effective temperature translates into Planck energies of about 0.4 eV. The Planck energy induced in NPs is more than sufficient to produce Auger emission without a second electron emission. There is no need to invoke the chemical diving model to explain EEE.

C. CL

The CL response of alkali metals in collisions with halogen gas molecules is usually explained by the NNL model [24]. Enhanced CL induced current and photon response occurs by collisions of halogen gas molecules entrained in a molecular beam with alkali metal. The NNL model predicts both CL current and photon intensity to increase with beam velocity. Indeed, Cl_2 gas molecules impinging a potassium surface is found [27] to increase CL current with molecular beam velocity, but the CL photon intensity contrarily remains shows no increase at all.

Similarly, the QED model predicts both CL current and photon intensity to increase with beam velocity. Unlike the QED model, the NNL model does not expect high frequency EM radiation to be produced in the surface. Indeed, the photomultiplier in the CL experiment [27] has a short wavelength cut-off of 200 nm which excludes Planck energies beyond 6.2 eV. Fig. 5 shows most QED photons induced in NPs < 100 nm diameter would not be detected. What this means the CL photon intensity does increase with beam velocity, but was not detected in the experiment.

5. Conclusions

QED induced EM radiation produced by the accumulation of kT energy in collisions of diatomic molecules that stick to NPs posited on the metal surface provides the Planck energy necessary for the dissociation of gas molecules approaching the surface, or upon adsorption.

Harpooning or the resonant ionization of molecules colliding on surfaces is otherwise equivalent to VUV photolysis of the molecules by QED induced EM radiation.

EEE by the Auger process need not be triggered by a second electron transfer from the dissociating molecule. The NPs produce more than sufficient Planck energy for EEE.

Typical photomultipliers having a cut-off at 200 nm cannot detect the VUV photons expected in CL. But measurement of high energy QED photons is difficult.

References

- [1] A. Einstein, *Ann. Phys.* 17 (1905) 132.
- [2] H. Hertz, *Ann. Phys.* 31(1887) 983.
- [3] H. Hallwachs, *Ann. Phys.* 33(1887) 301.
- [4] P. Lennard, *Ann. Phys.* 8 (1902) 149.
- [5] J.J. Thomson, *Phil. Mag.* 10(1905) 584.
- [6] T. Grebar, *Surf. Sci. Repts.* 28(1997)1.
- [7] F. Haber and G. Just, *Ann. Phys.* 30(1909) 411.
- [8] A.K. Denisoff, *Proc. R. Soc.* 150 (1935) 495.
- [9] J. Kramer, *Z. Phys.* 125 (1949) 739.
- [10] G. Ertl and E. Hasselbrink, *Mol. Phys.* 76 (1992) 777.
- [11] G. Ertl, *Adv. Catal.* 45 (2000) 1.
- [12] E. Hasselbrink, *Current Opinion in Solid State and Material Science* 10 (2006) 192.
- [13] T.V. Prevenslik, available: http://www.geocities.com/thomas_prevenslik
- [14] T.V. Prevenslik, *Nanocatalysts by QED induced EM radiation*, 13th Nordic Symposium on Catalysis, Oct. 5-7, 2008, Goteborg.
- [15] M.J. Fleischmann, P.J. Hendra, and A.J. McQuillan, *Chem. Phys. Lett.*, 26 (1974)163.
- [16] R.J.C. Brown, J. Wang, R. Tantra, R.E. Yardley, and M.J.T. Milton, *Faraday Discuss.* 132 (2006) 201.
- [17] T.V. Prevenslik, *Quantum dots by QED*, Presented at Inter. Conf. Materials for Advanced Technologies (ICMAT), July 2-6, Singapore, 2007.
- [18] C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, J. Wiley & Sons, 1983.
- [19] R. W. Christy and A. Pytte, *Introduction to Modern Physics*, Benjamin, New York, 1965.
- [20] T. V. Prevenslik, *IEEE 16th Int. Conf. on Dielectric Liquids (ICDL)*, "Flow Electrification by Nanoparticle Impurities," Poitiers, June 2008.
- [21] B. Shortt, R. Carey, and S. Nic Chormiac, *Proc. SPIE*, Vol. 5827, pp. 47-57, Opto-Ireland, 2005.
- [22] A. O. Govorov, W. Zhang, T. Skeini, H. Richardson, J. Lee, and N. A. Kotov, *Nanoscale Res. Lett.*, 1 (2006) 84.
- [23] K. K. Das, Y. V. Rostovtsev, K. Lehmann, and M.O. Scully, *Optics Communications*, 246 (2005) 551.
- [24] J.K. Norskov, D.M. Newns, and B.I. Lundqvist, *Surf. Svc.* 80 (1979) 179.
- [25] H. Nienhaus, *Surf. Sci. Repts.* 45(2002)1.
- [26] J.W. Gadzuk and N.K. Norskov, *J. Chem. Phys.* 81 (1984) 2828.
- [27] L.A. Hellberg, J. Campbell, and B.Kasemo, *Surf. Sci.* 502-503 (2002) 399.