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2328-24

Preparatory School to the Winter College on Optics and the Winter College on Optics: Advances in Nano-Optics and Plasmonics

30 January - 17 February, 2012

Theoretical background for enhancement of luminescence and Raman scattering in metal-based nanostructures

S.V. Gaponenko
Stepanov Institute of Physics
Minsk, Belarus

Strada Costiera 11, 34151 Trieste, Italy - Tel.+39 040 2240 111; Fax +39 040 224 163 - sci_info@ictp.it

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S. V. Gaponenko

B. I. Stepanov Institute of Physics,

National Academy of Sciences of Belarus

Minsk, Belarus

Trieste, febbraio 16, MMXII

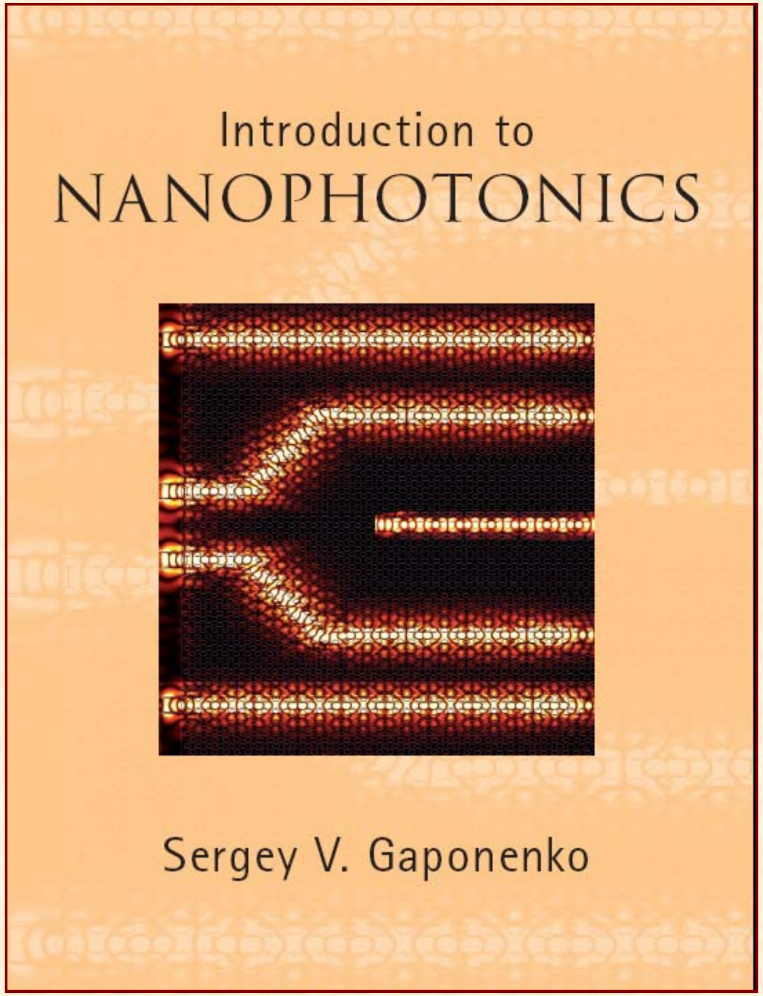
Outline:

1. Enhancement of secondary radiation in metal-dielectric structures

2. Role of photon density of states in plasmonics

3. Scattering enhancement versus luminescence enhancement

4. What is a “hot spot” in surface enhanced spectroscopies?



Cambridge University Press 2010

Elastic scattering (Rayleigh)

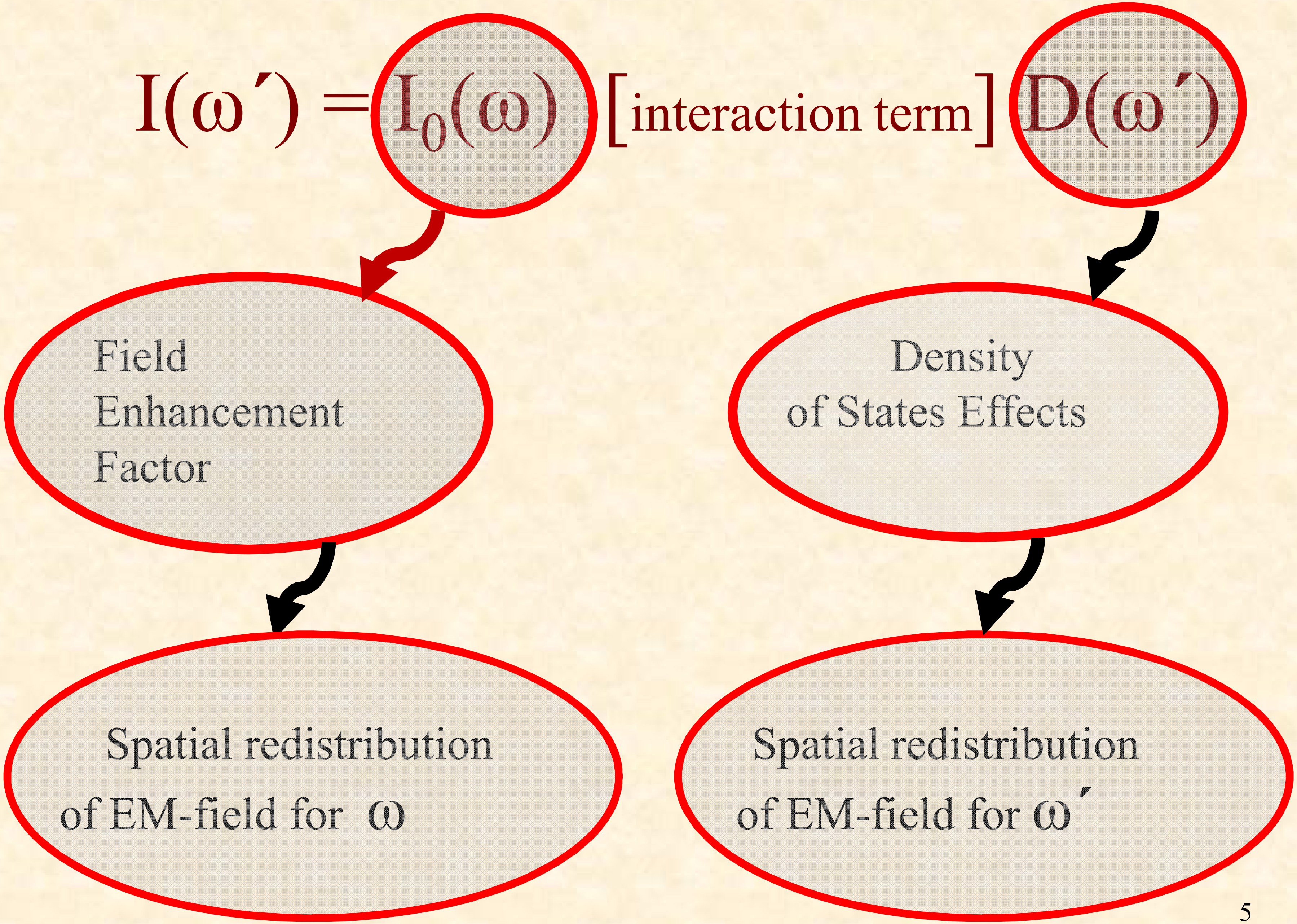
Excitation (virtual) $\hbar\omega$ $\longrightarrow$ emission $\hbar\omega$

Inelastic scattering (Raman)

Excitation (virtual) $\hbar\omega$ $\longrightarrow$ emission $\hbar\omega'$

Spontaneous emission

Excitation (real) $\hbar\omega$ $\longrightarrow$ emission $\hbar\omega'$


I(ω´) = I0(ω) [interaction term] D(ω´)
Field Enhancement Factor
Density of States Effects
Spatial redistribution of EM-field for ω
Spatial redistribution of EM-field for ω´

What is the challenge?

Single molecule detection in surface enhanced Raman scattering:

10^{14}-fold enhancement is not understood since 1997

K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. R. Dasari and M. S. Feld. *Phys. Rev.Lett.*, **78** (1997), 1667—1670.

S. Nie and S. R. Emory. *Science*, **275** (1997), 1102—1105.

Why the same luminescence enhancement has never been reported?

What is the ultimate luminescence enhancement?

C. V. Raman
1888—1970

A New Type of Secondary Radiation

C. V. Raman and K. S. Krishnan, Nature, *121(3048)*, 501, March 31, 1928

… a beam of sunlight was converged by a telescope objective of 18 cm. aperture and 230 cm. focal length, and by a second lens was placed the scattering material… To detect the presence of a modified scattered radiation, the method of complementary light-filters was used.
A blue-violet filter, when coupled with a yellow-green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapour. The reappearance of the track when the yellow filter is transferred to a place between it and the observer's eye is proof of the existence of a modified scattered radiation.
…Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree.

Katrin Kneipp Martin Moskovits
Harald Kneipp (Eds.)

Surface-Enhanced Raman Scattering

Physics and Applications

With 221 Figures, 3 in color

Springer 2006

Chem. Rev. **1999,** *99,* 2957–2975

Ultrasensitive Chemical Analysis by Raman Spectroscopy

Katrin Kneipp,* Harald Kneipp, Irving Itzkan, Ramachandra R. Dasari, and Michael S. Feld

VOLUME 78, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1997

Single Molecule Detection Using Surface-Enhanced Raman Scattering (SERS)

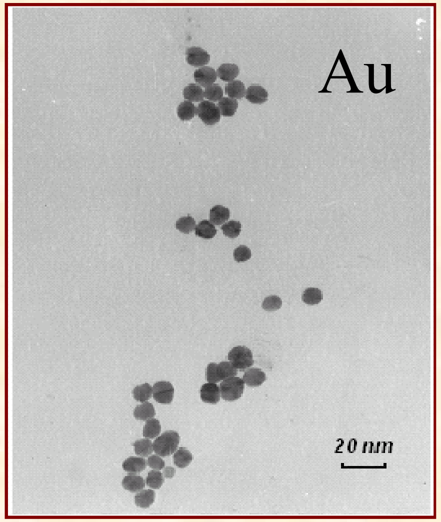
Katrin Kneipp, Yang Wang,* Harald Kneipp, Lev T. Perelman, Irving Itzkan,
Ramachandra R. Dasari, and Michael S. Feld

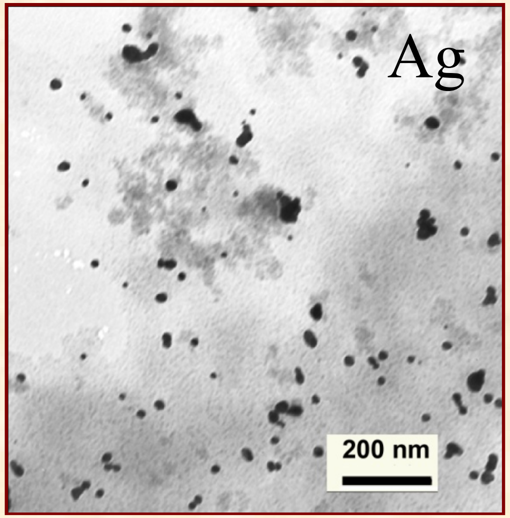
Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering

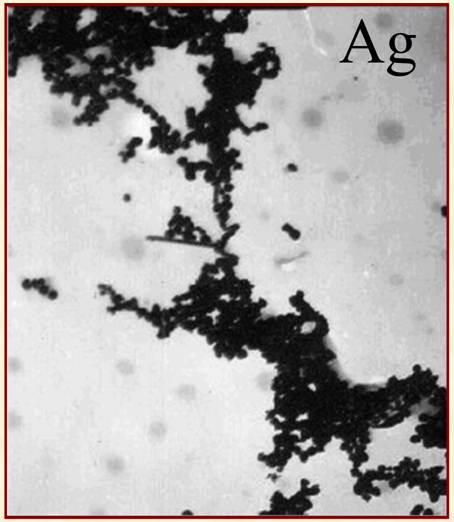
Shuming Nie* and Steven R. Emory

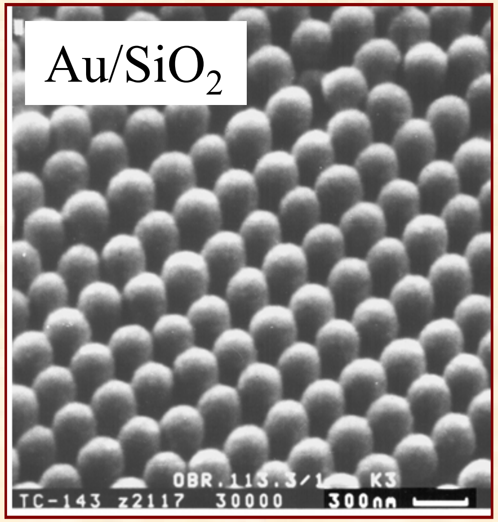
SCIENCE • VOL. 275 • 21 FEBRUARY 1997 1102

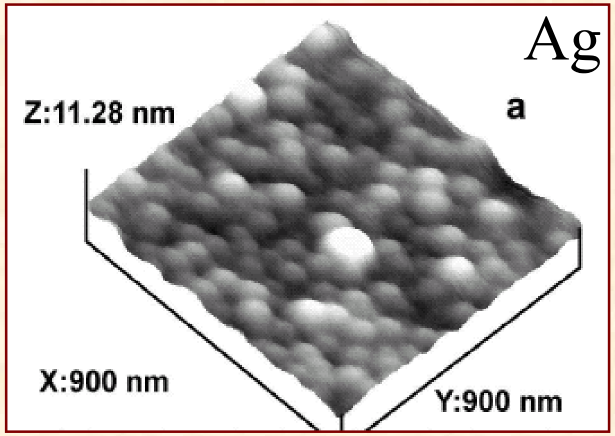
Typical nanostructures that exhibit strong enhancement of secondary emission

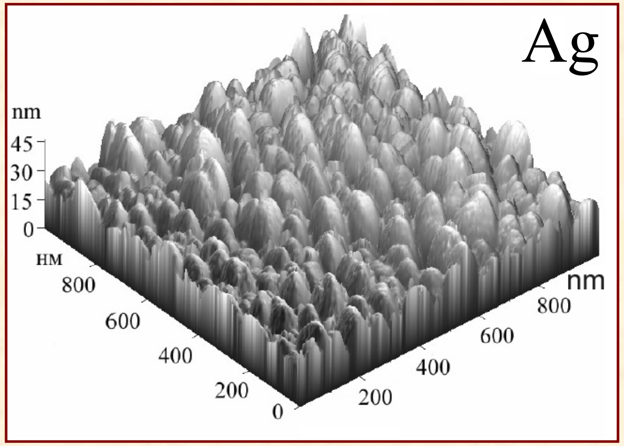


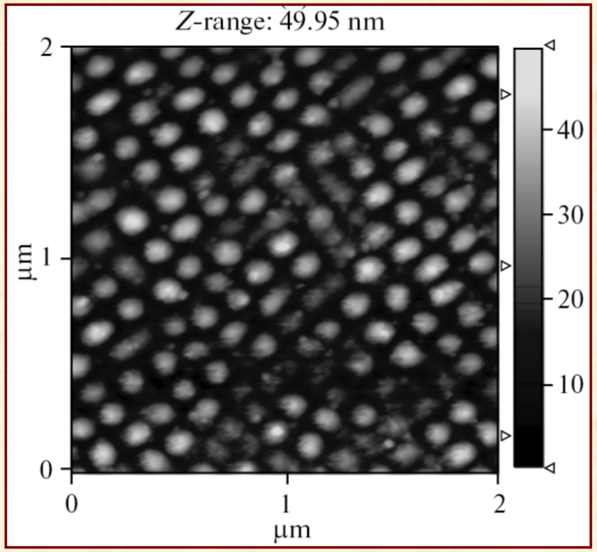






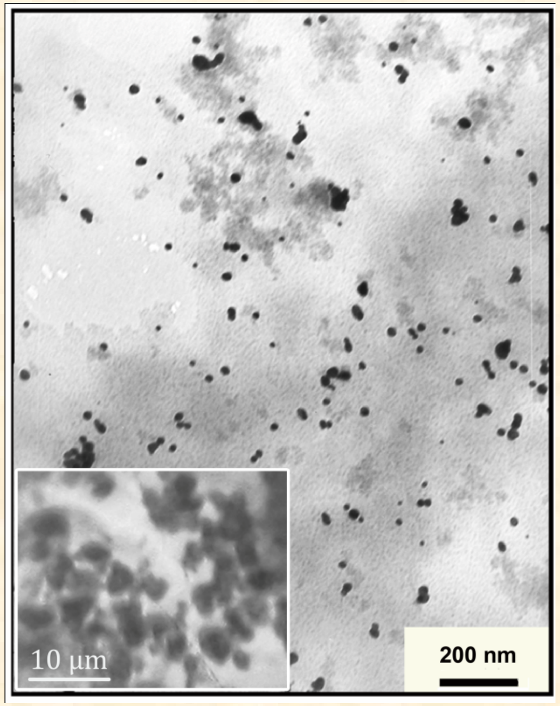


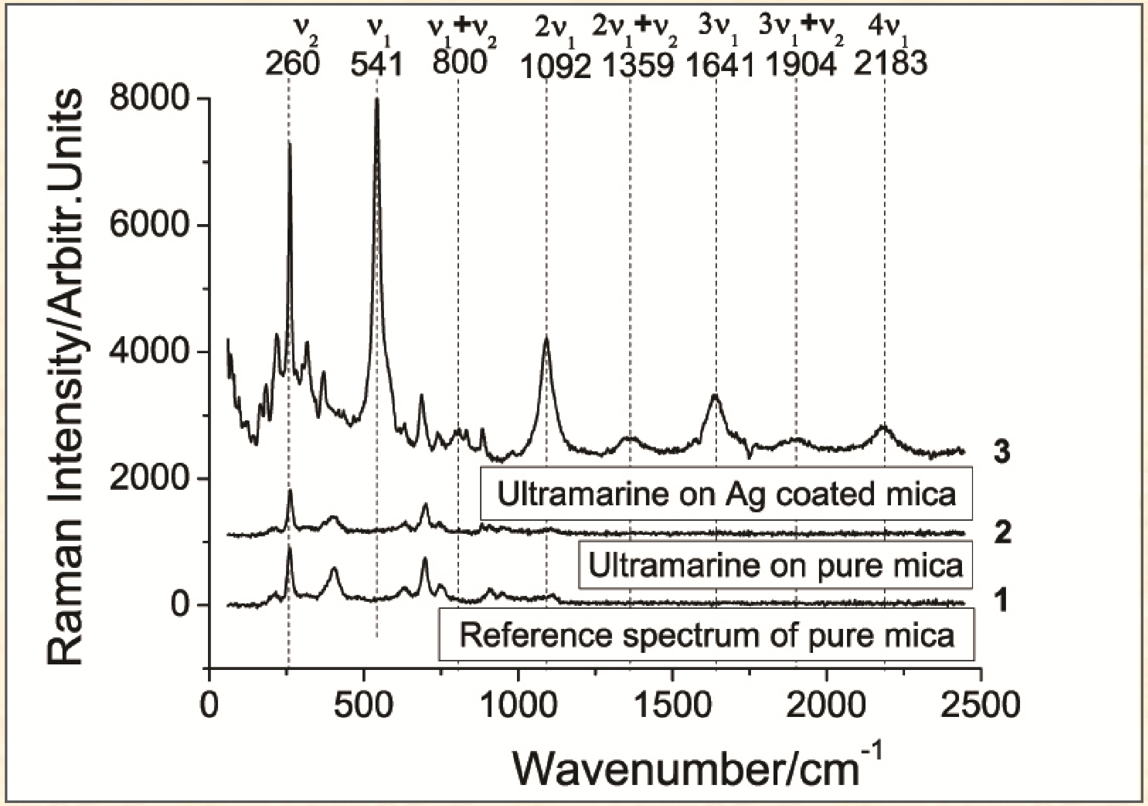




Au/Ge/Si

Kulakovich, Strekal, Vaschenko, Gaponenko,…. (2001—2011)





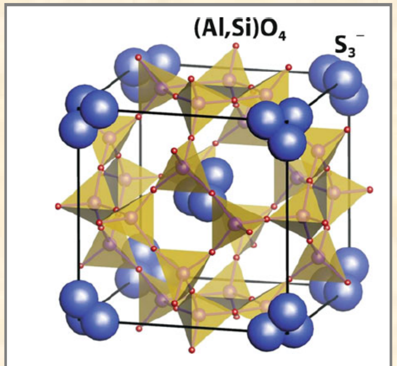


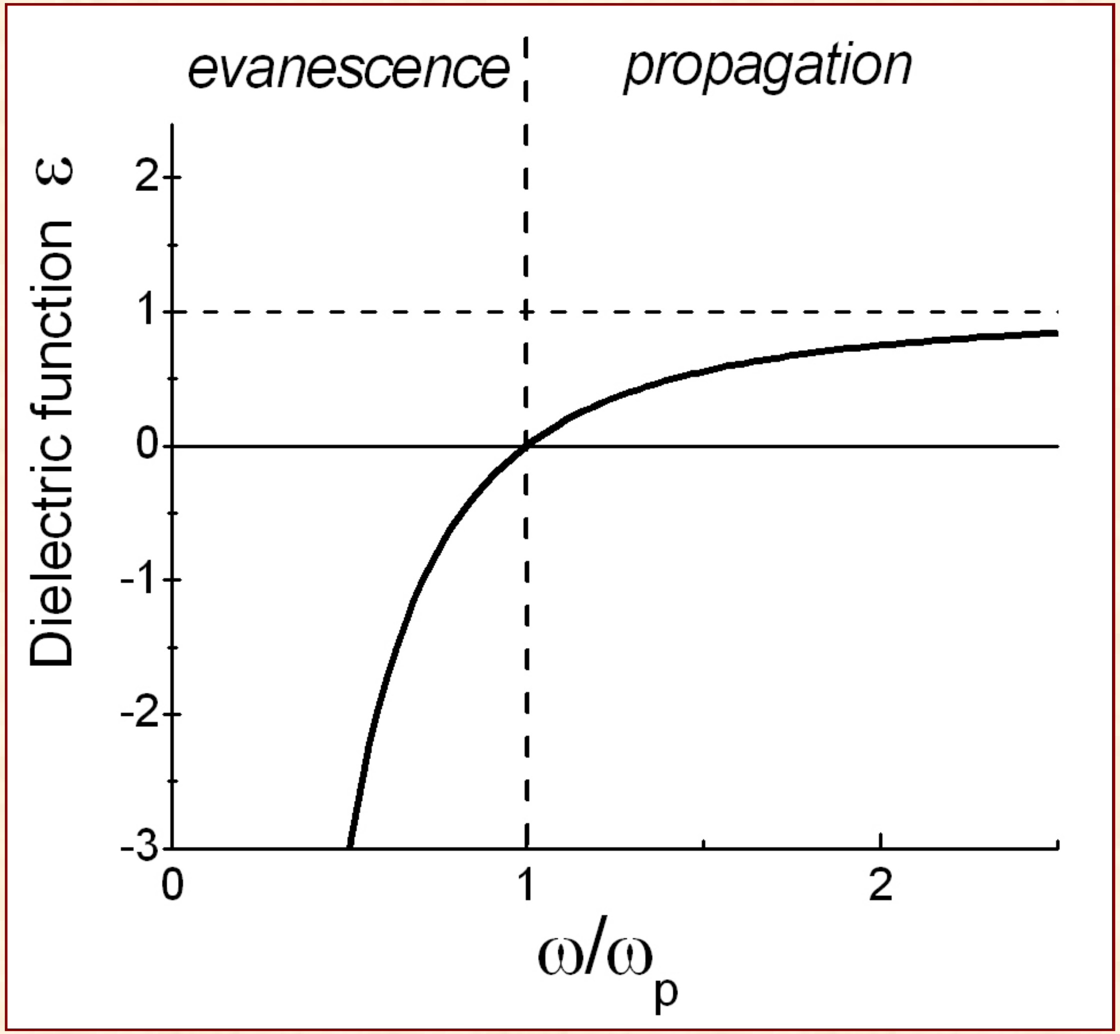
Fig. 4 Crystal cell of ultramarine

Klyachkovskaya et al. Plasmonics, 2011, **6**, 413; J. Raman. Spectr. 2012

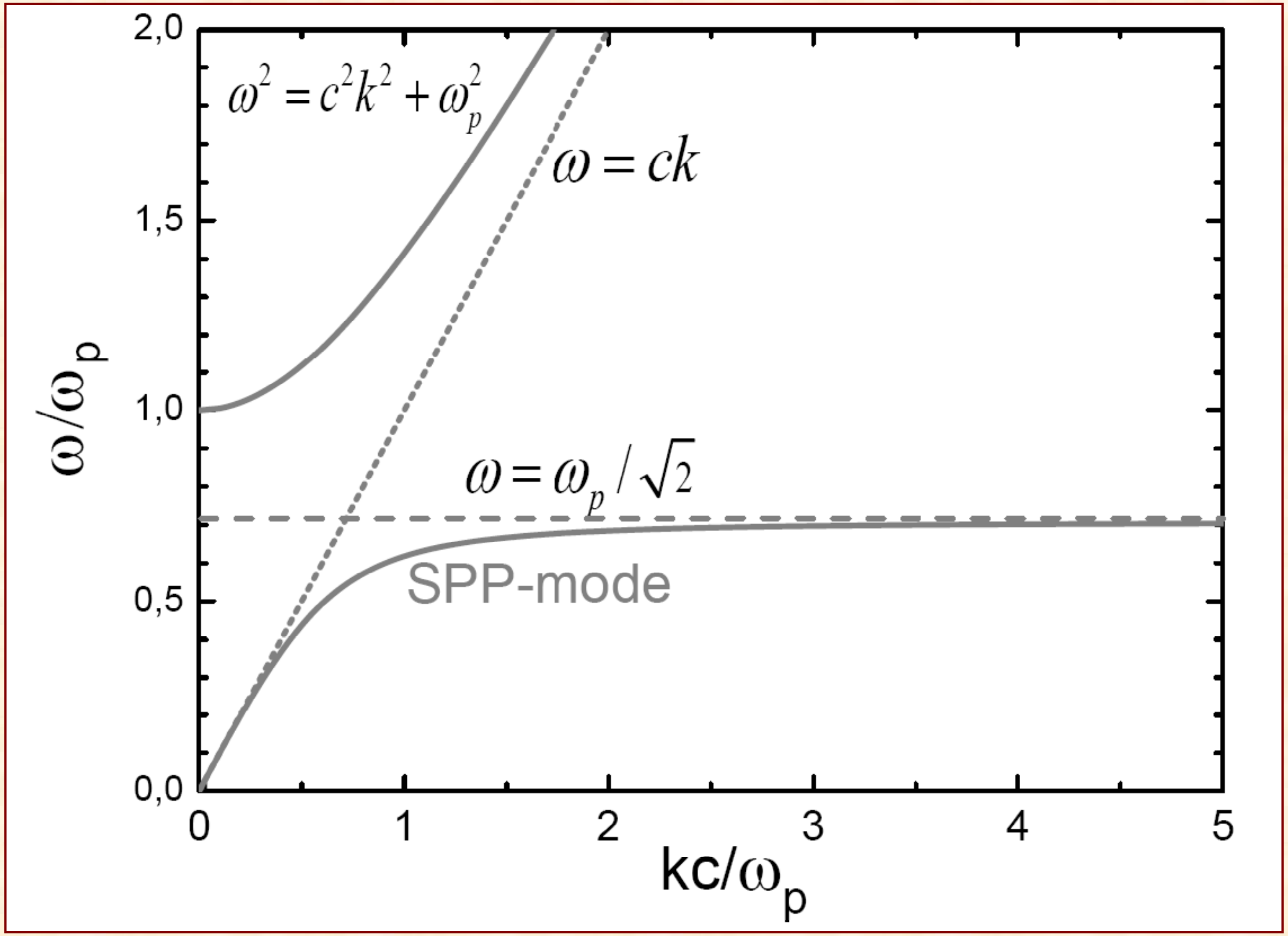
Dielectric function of ideal electron gas

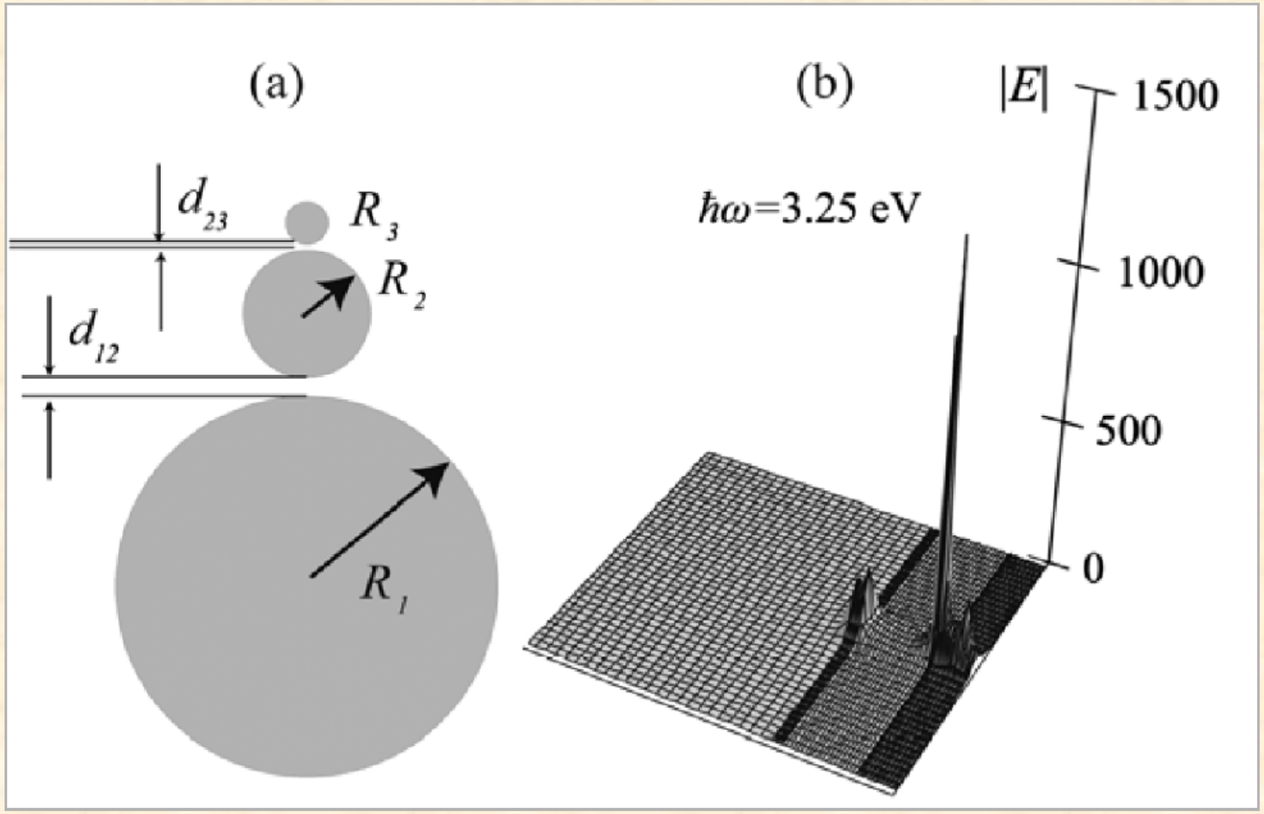
$$\varepsilon(\omega) = 1 - \frac{\omega^2{}_p}{\omega^2}$$

$$\omega_p{}^2 = \frac{Ne^2}{m\varepsilon_0}$$

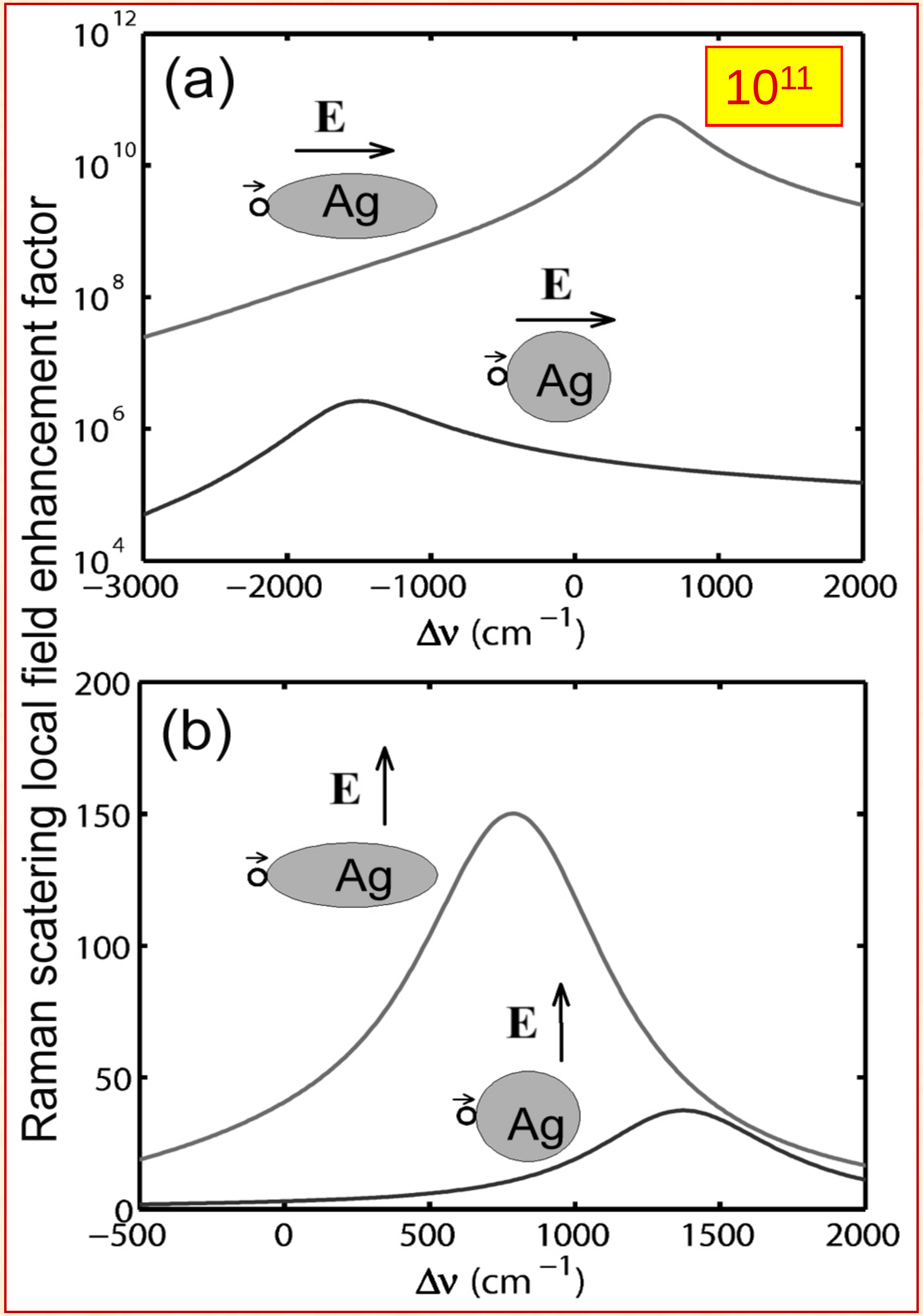


Incident field enhancement is promoted by generation of surface plasmon polaritons at metal—dielectric interface

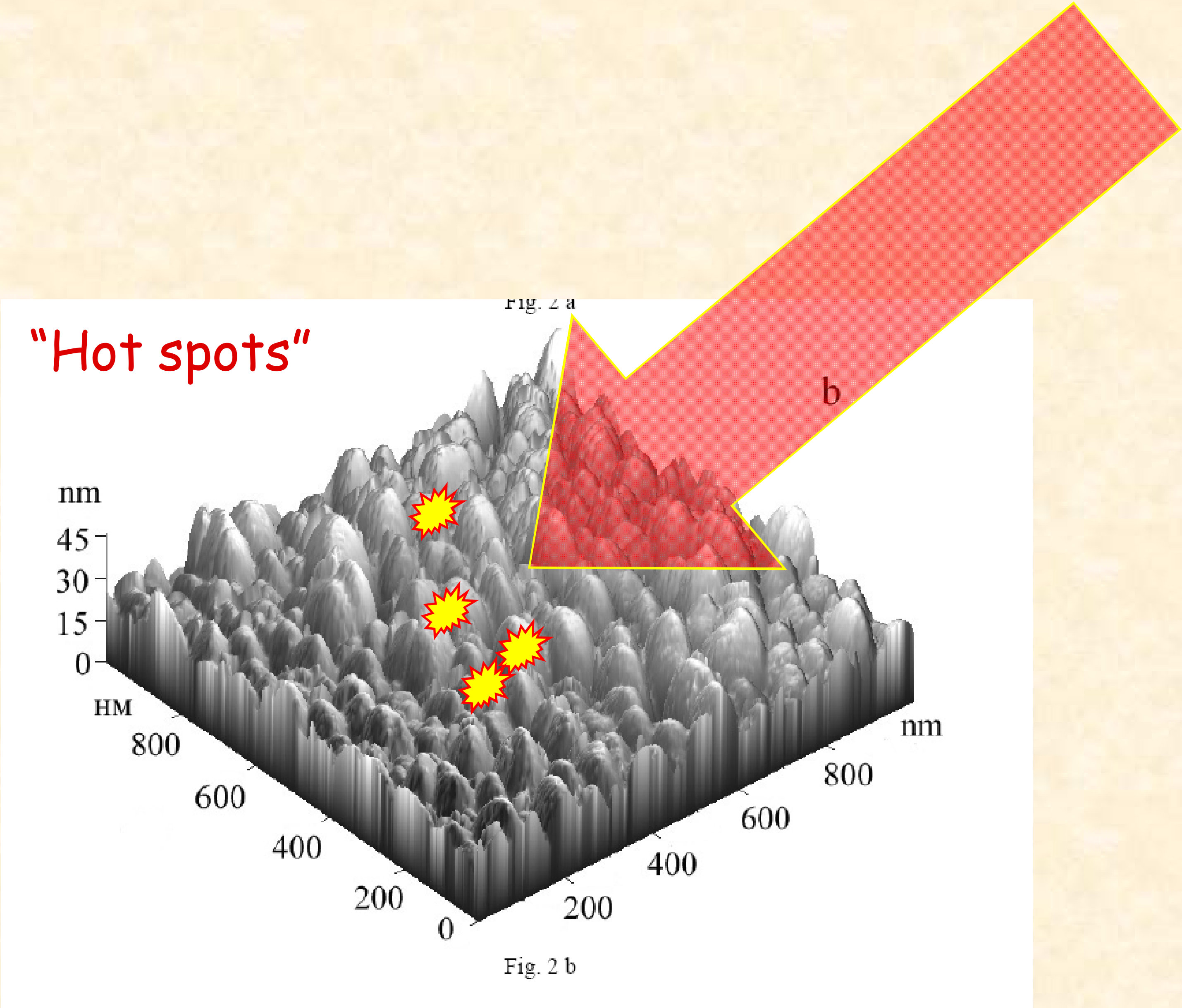




K. Li, M. I. Stockman, D. J. Bergman.
Phys. Rev. Lett., **91** (2003), 227402.



S. V. Gaponenko and D. V. Guzatov, Chem. Phys. Lett. **477** 411 (2009)


"Hot spots"
Fig. 2 a
b
nm
45
30
15
0
HM
800
600
400
200
0
200
400
600
800
nm
Fig. 2 b

How is a “hot spot” looking at the frequency of incoming light?

Concentration of light by means of microfocusing?

Not the case since purely linear optical response of a molecule is performed

It is rather light energy accumulation than focusing!

Then a hot spot looks like a high-Q microcavity

Then biuld-up of enhanced response needs finite time

Incident electromagnetic field enhancement

$$\text{Q-factor} = \frac{\text{energy stored in the system}}{\text{energy loss in a single period}}$$

Planar cavities $Q = 10^6 - 10^7$

Spherical microcavities $Q = 10^8 - 10^{10}$

Plasmonic enhancement $>10^{10}$?

Conclusion 1

Incident field enhancement in a “hot spot” occurs by means of light accumulation near a metal nanobody.

10^{11}-fold enhancement is feasible!

Remembering Lecture 1:

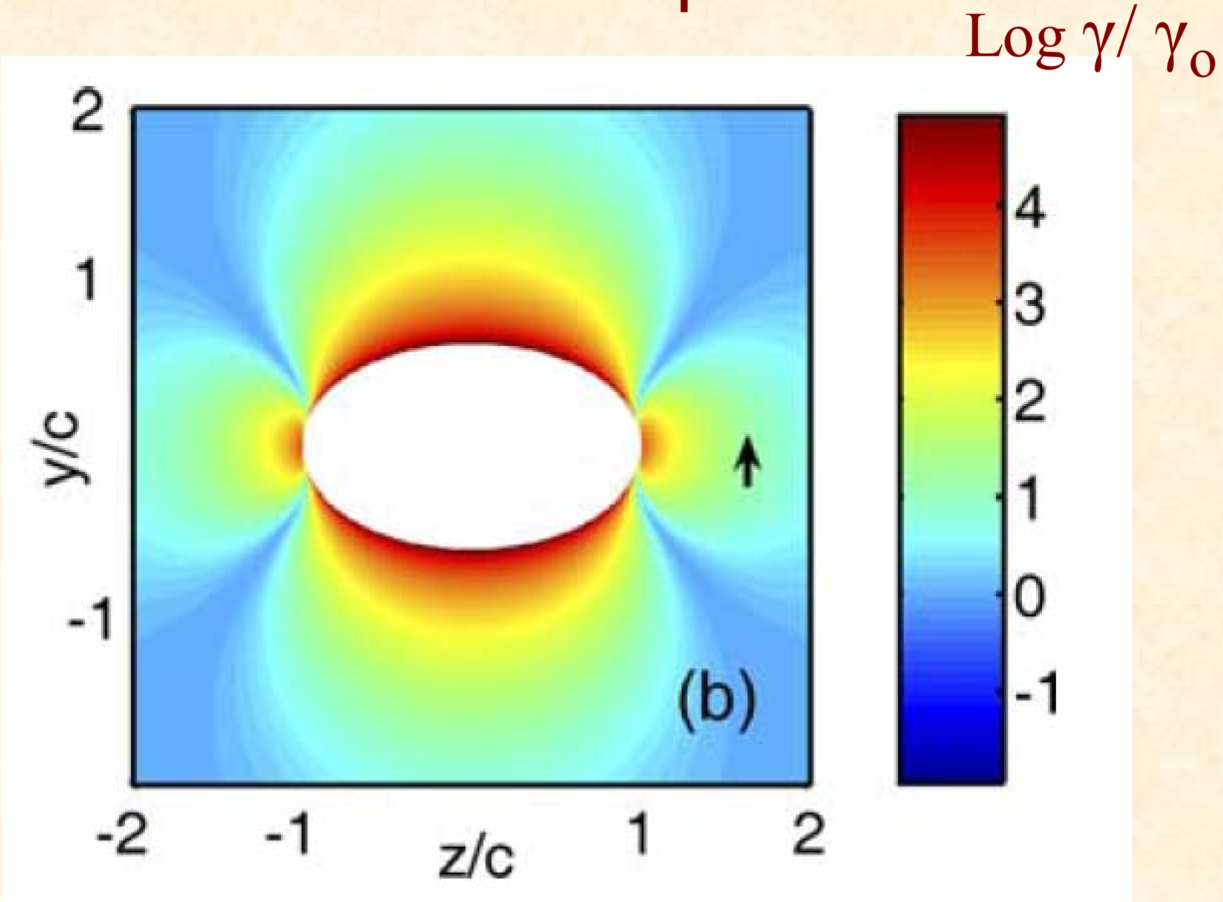
Include photon DOS effect to account for modification of photon spontaneous emission rate and photon spontaneous scattering rate in metal-based structures

How LDOS can be calculated near a metal nanobody?

V. V. Klimov, M. Ducloy. *Phys. Rev. A,* **69** (2004), 013812.

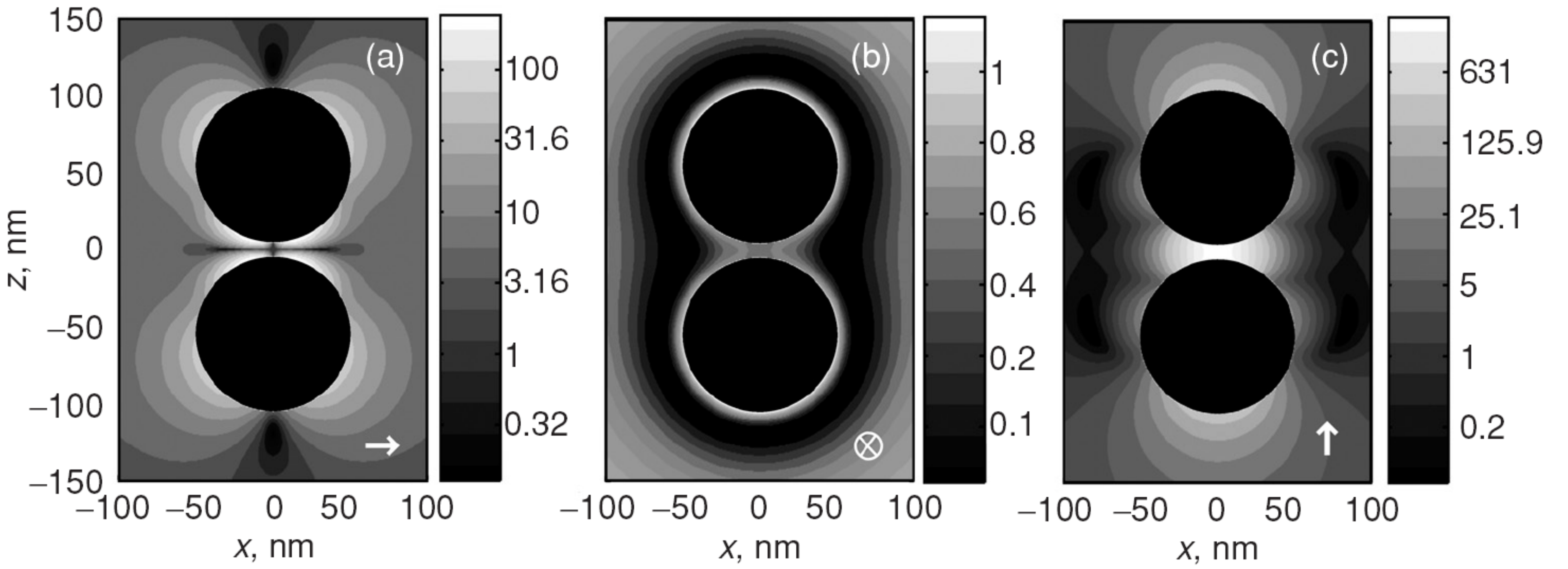
$$\left(\frac{W(\mathbf{r})}{W_0}\right)^{radiative} = \frac{\left|\mathbf{d_0} + \delta\mathbf{d}\right|^2}{\left|\mathbf{d_0}\right|^2}$$

Calculated spontaneous decay rate for a dipole near silver ellipsoid



Guzatov, Klimov. Chem. Phys. Lett. **412** (2005) 341

Radiative decay rates:



Klimov and Guzatov, Quantum Electronics 2005

DOS effects on resonant and Raman scattering

RAPID COMMUNICATIONS

PHYSICAL REVIEW B, VOLUME 65, 140303(R)

Effects of photon density of states on Raman scattering in mesoscopic structures

S. V. Gaponenko*
Institute of Molecular and Atomic Physics, National Academy of Sciences, Minsk 220072 Belarus
(Received 19 July 2001; revised manuscript received 19 February 2002; published 29 March 2002)

$$W_{RS}(\omega,\omega') = \frac{(2\pi)^2 \omega\omega' n}{\hbar^2} |S^2| \left[n' + \frac{\omega'^2}{(2\pi c)^3} \right]$$

G. Placzek, in: E. Marx (Ed.), Handbuch der Radiologie, vol. 6, part 2, Akademische Verlagsgellschaft, Leipzig, 1934, p. 205.

↓

$$\gamma_{RS}^{LDOS}(\omega,\omega') = \gamma_{RS}(\omega,\omega') \frac{D(\omega')}{D_0(\omega')}$$

Possible rationale for ultimate enhancement factor in single molecule Raman spectroscopy

S.V. Gaponenko [a,*], D.V. Guzatov [b]

[a] B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Minsk 220072, Belarus
[b] Y. Kupala State University, Grodno 230023, Belarus

Chemical Physics Letters 477 (2009) 411–414

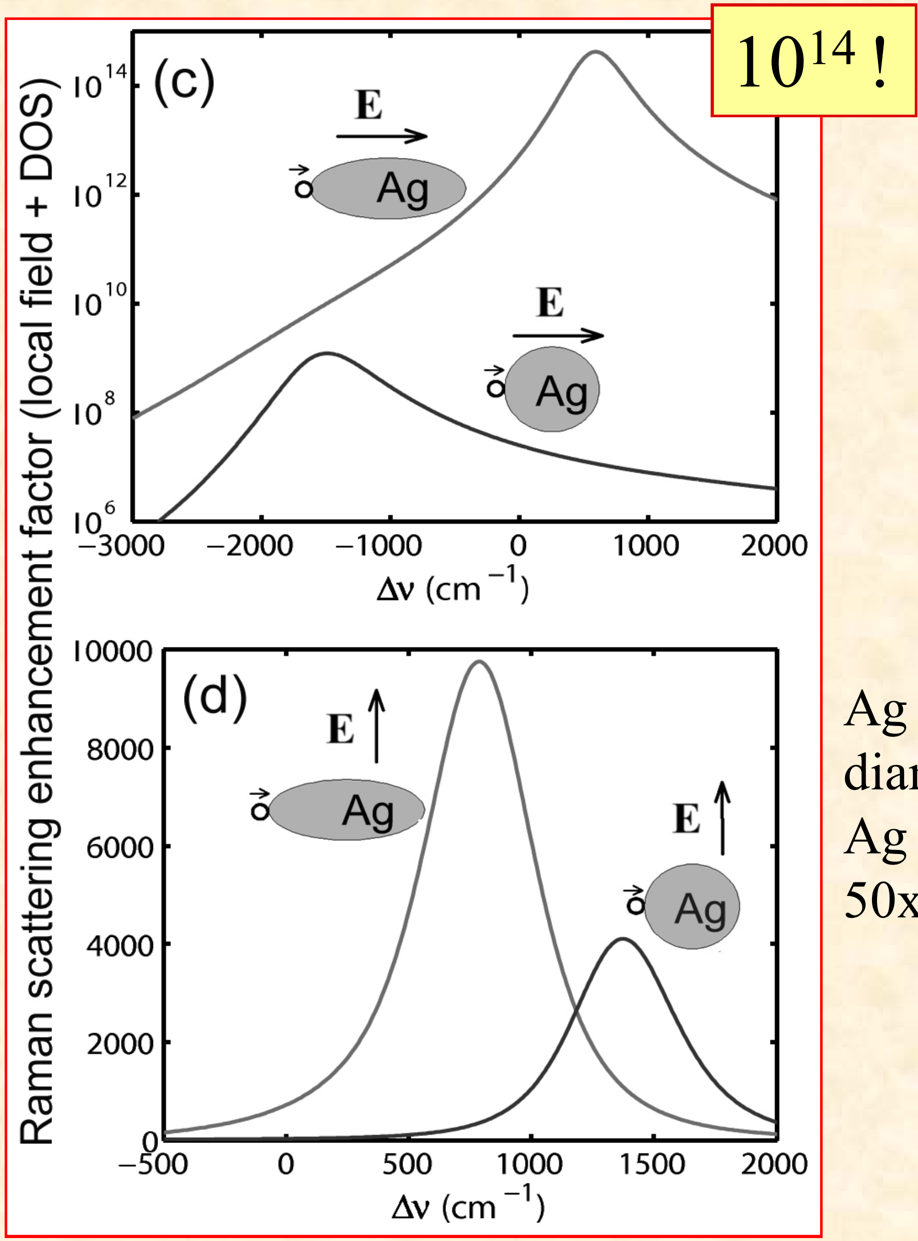
Correct enhancement factor

$$F = \frac{\left|\mathbf{E}(\mathbf{r},\omega)\right|^2}{\left|\mathbf{E}_0(\omega)\right|^2}\frac{D(\mathbf{r},\omega')}{D_0(\omega')}$$

Incorrect (inaccurate?) enhancement factor

$$F = \frac{\left|\mathbf{E}(\mathbf{r},\omega)\right|^2\left|\mathbf{E}(\mathbf{r},\omega')\right|^2}{\left|\mathbf{E}_0(\omega)\right|^2\left|\mathbf{E}_0(\omega')\right|^2} \approx \left|\frac{\mathbf{E}(\mathbf{r},\omega)}{\mathbf{E}_0(\omega)}\right|^4$$

DOS contribution to SERS



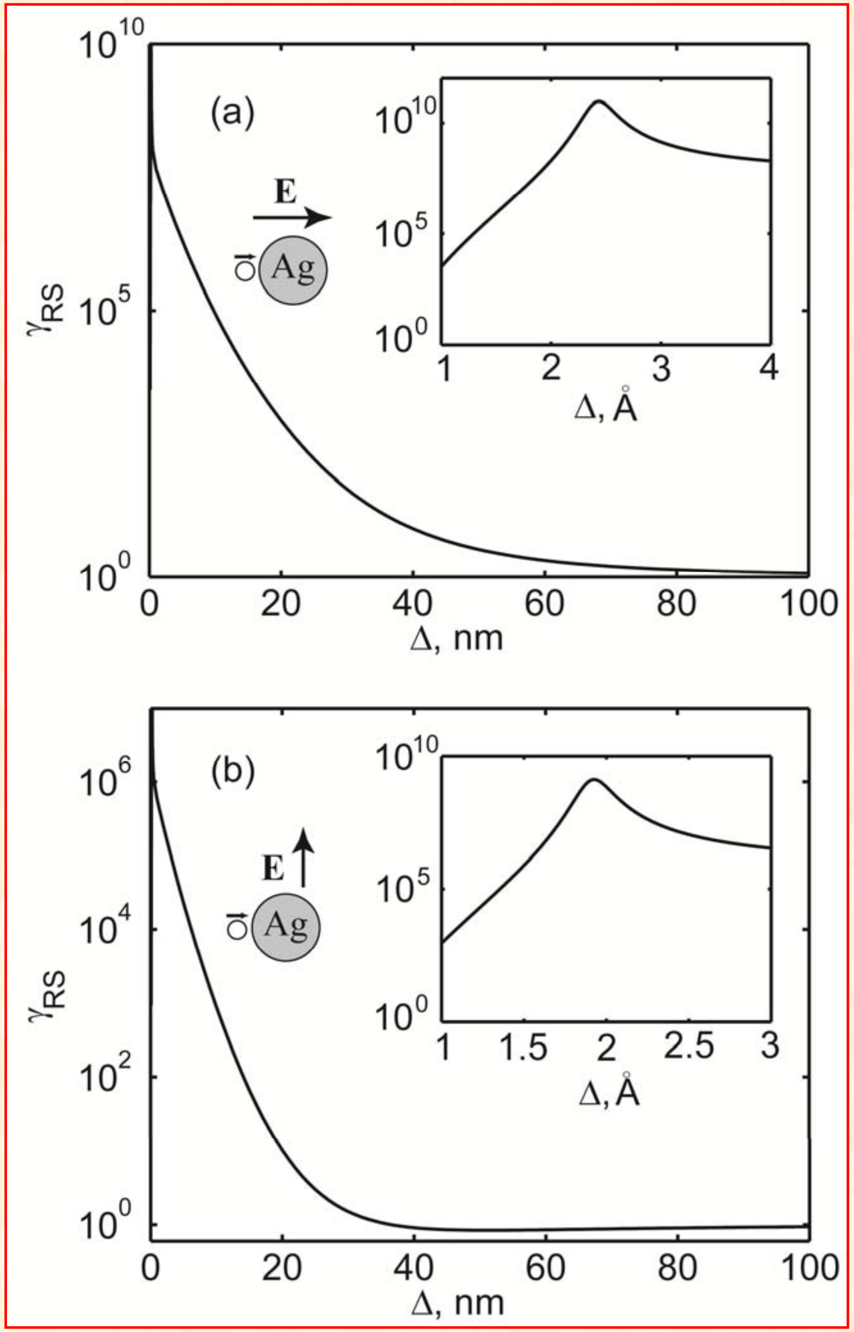
Ag nanoparicle diameter is 60 nm
Ag spheroid size 50x80 nm

Gaponenko and Guzatov, Chem. Phys. Lett., **477,** 411 (2009)

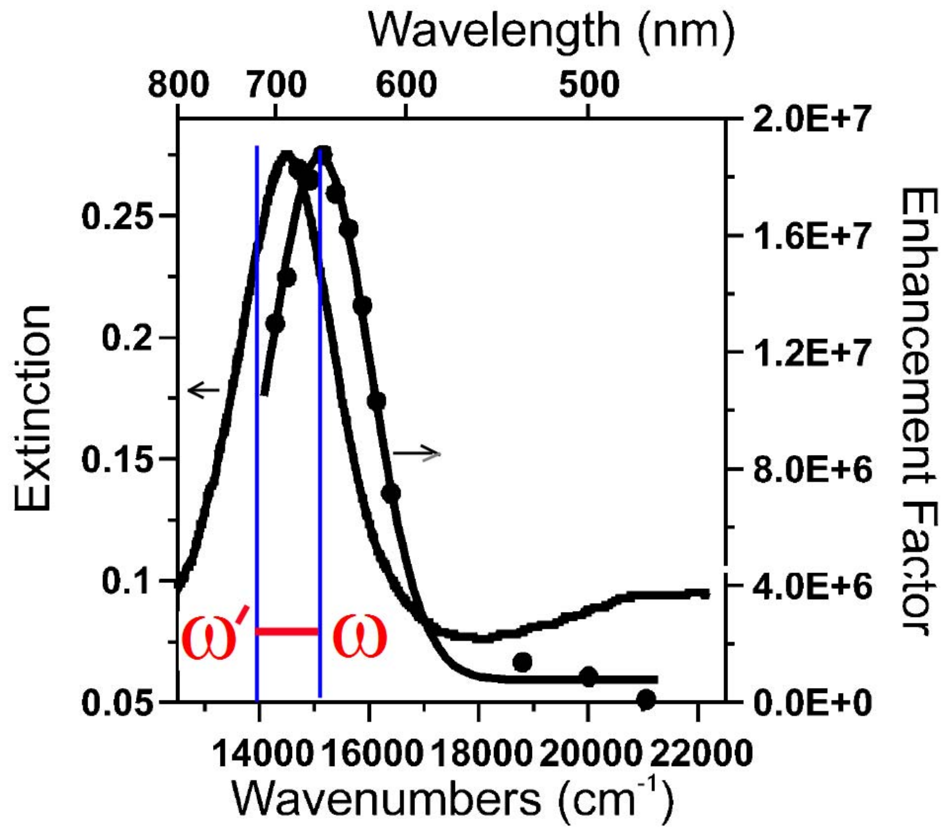
Strong distance dependence of SERS

Guzatov, Gaponenko et al
J. Raman Spectr. 2012

Ag nanoparicle
diameter is 20 nm



SERS excitation spectrum



benzenethiol on Ag array

George C. Schatz et al.

K. Kneipp, M. Moskovits, H. Kneipp (Eds.): Surface-Enhanced Raman Scattering – Physics and Applications, Springer-Verlag Berlin Heidelberg 2006

High local density of photon states since Purcell's paper in 1946 can be treated as local space portions with high Q-factor

Conclusion 2:

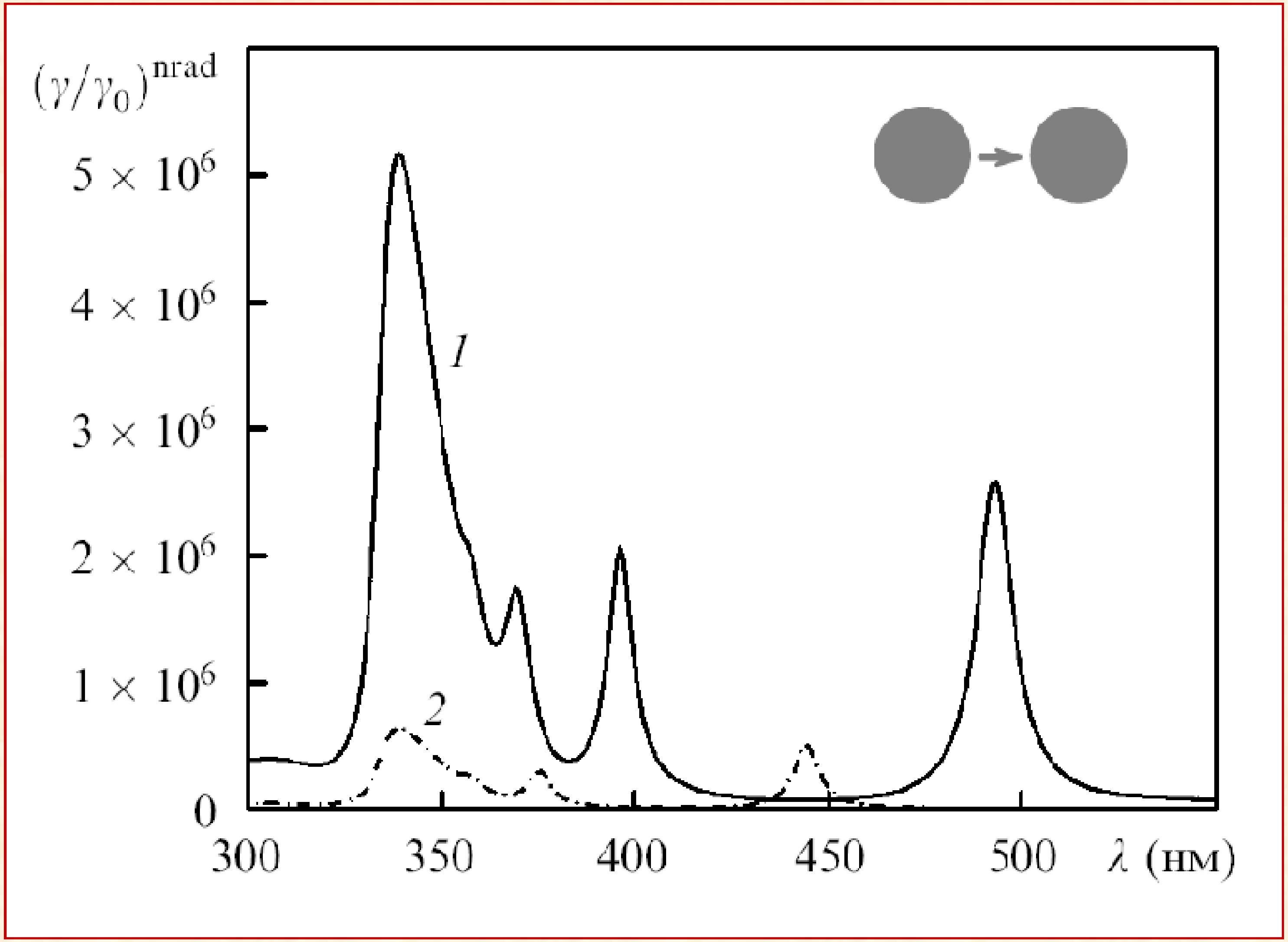
"Hot spot" is portion of space where simultaneously high Q-values develops for incident light frequency and for emitted (scattered light frequency)

Comment: DOS versus nano-antenna representation

Let us multiple intensity enhancement and DOS enhancement to arrive at ultimate 10^{14} PL enhancement

- not the case!!! ☹

Non-radiative decay enhancement



Klimov, Guzatov, Quant. Electron. 2007

One principal difference of Raman scattering and spontaneous emission at metal nanostructures

---

Proximity of metal surface results in enormous non-radiative relaxation channel – fast "by-pass"

Raman process has neither relaxation time nor lifetime

Therefore Raman scattering is non-sensitive to additional non-radiative "by-pass" promoted by metal

Contrary to Raman, quenching of PL at metal nanostructures dramatically overtakes FE and DOS effects in many experimental situations

It is for this reason SEPL will never be so strong as SERS

It is for this reason SEPL is more pronounced in case of <u>lower intrinsic quantum yield</u>

General recipe for SERS and SEPL

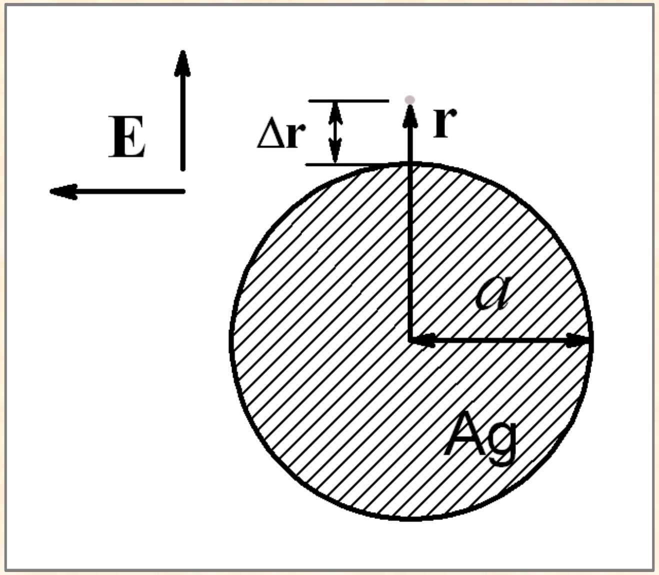
- Find a point where field enhancement at excitation frequency is high, LDOS at emission frequency is high

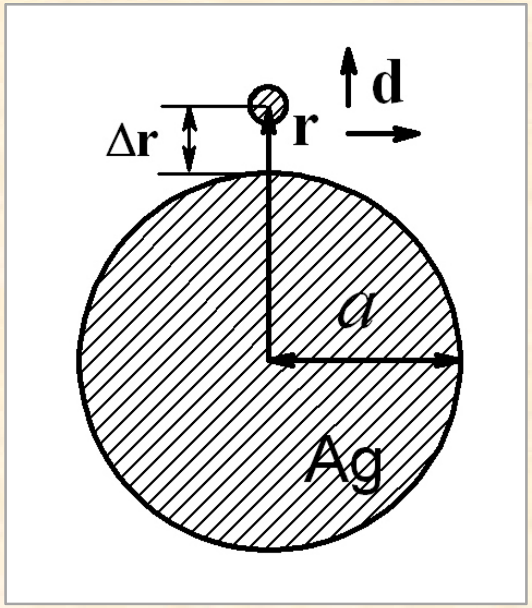
Additional recipe for PL enhancement

- Quenching of PL should be less than FE and LDOS enhancement factors – controllable spacing by means of dielectric interface or rare dispersion of metal colloids combined with luminophore particles (molecules, atoms).

For materials with strong Stokes shift field enhancement and DOS enhancement can be engineered <u>separately</u>

- Examples – lanthanides, doped QD's

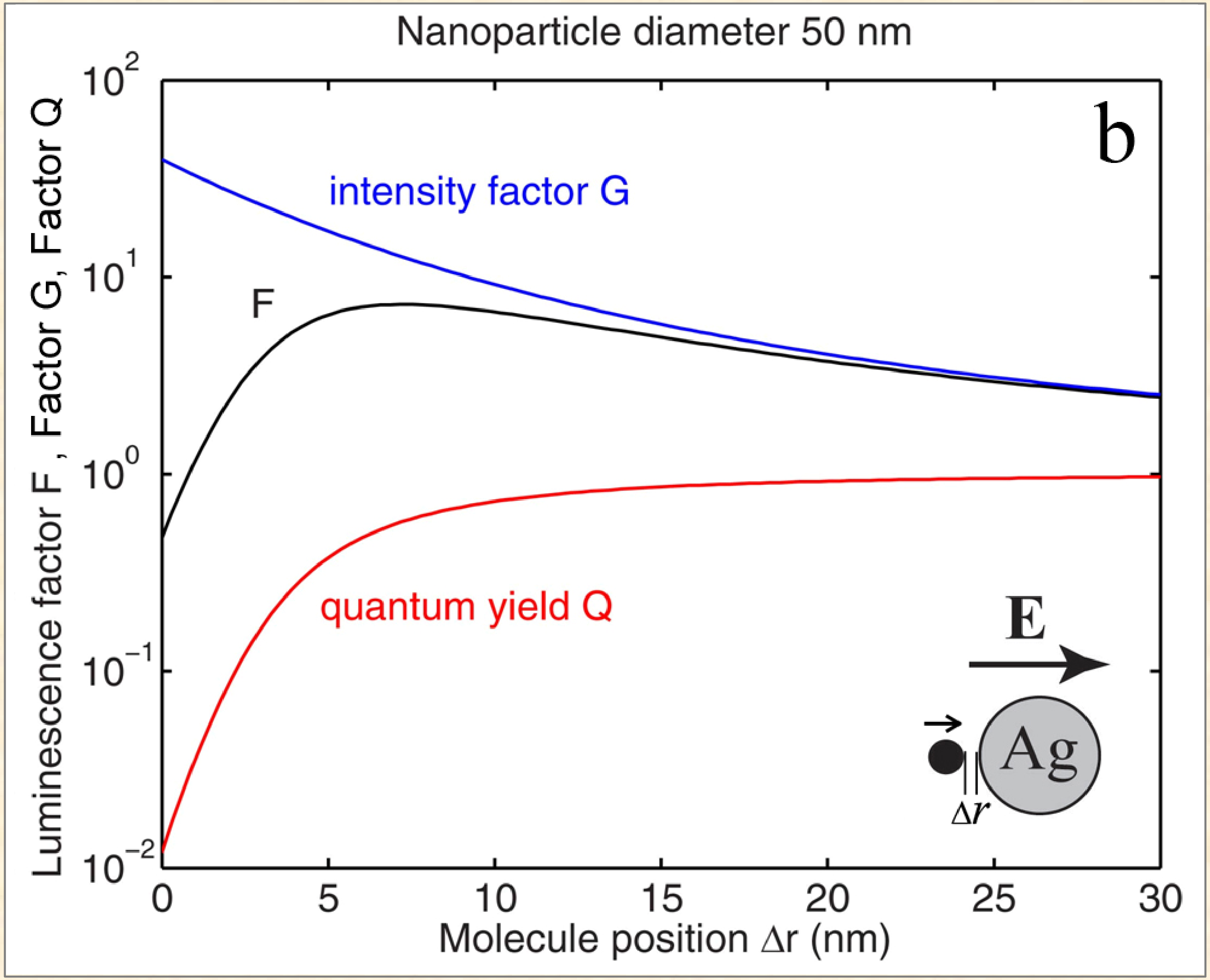




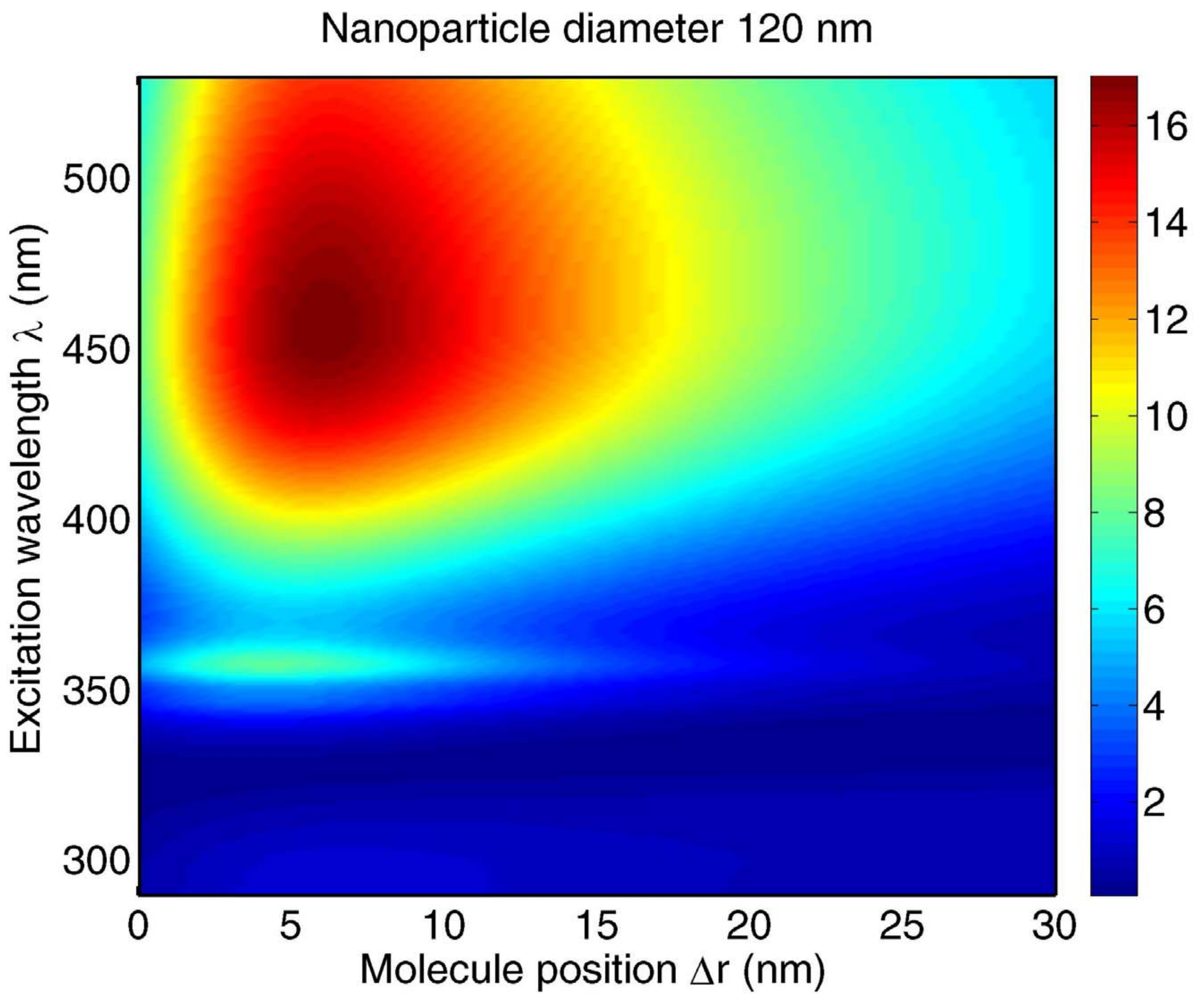
Field +metal body

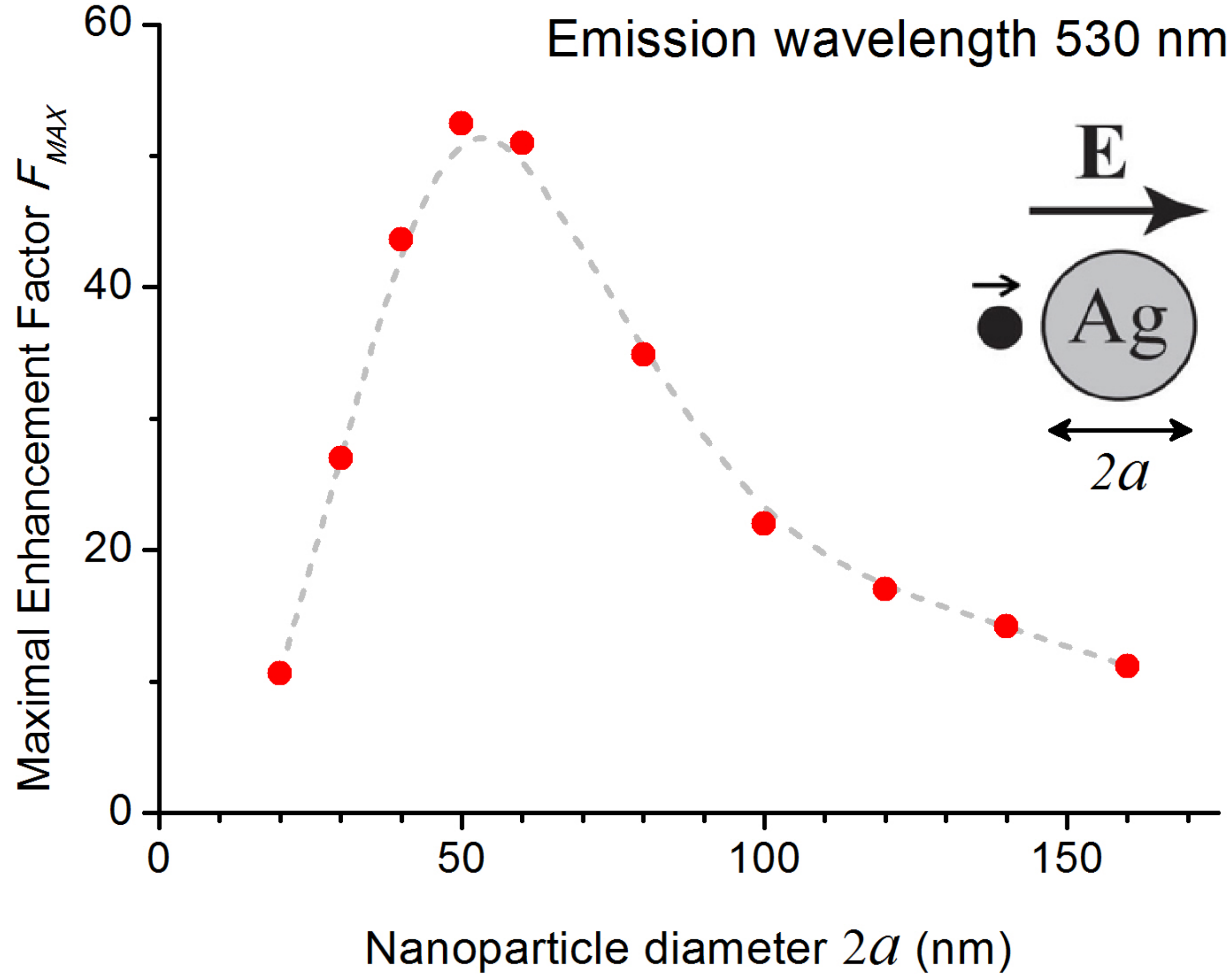
Metal body +molecule

$$F(\omega,\omega',\mathbf{r}) = G(\omega,\mathbf{r})\,Q(\omega',\mathbf{r}) = \frac{\left|\mathbf{E}(\omega,\mathbf{r})\right|^2}{\left|\mathbf{E}_0(\omega)\right|^2}\,\frac{\gamma_{rad}(\omega',\mathbf{r})}{\gamma_{rad}(\omega',\mathbf{r}) + \gamma_{nonrad}(\omega',\mathbf{r})}$$



Guzatov, …, and Gaponenko, J. Phys. Chem. 2012 - submitted


Nanoparticle diameter 120 nm
Excitation wavelength λ (nm)
500
450
400
350
300
0
5
10
15
20
25
30
Molecule position Δr (nm)
16
14
12
10
8
6
4
2



Emission wavelength 530 nm
Maximal Enhancement Factor F_{MAX}
Nanoparticle diameter $2a$ (nm)
E
Ag
$2a$
0
20
40
60
0
50
100
150

Conclusions

Modified spontaneous emission and scattering of light near metal nanobodies can be described in a similar manner in terms of incident field and local photon DOS enhancement

“Hot spot” is a portion of space where high Q-factor develops for incident and emitted (scattered) light frequency

Consistent SERS theory does needs QED-based approach including local photon DOS modification

Luminescence can be enhanced by about 50 times with a single spherical nanoparticle