ENHANCEMENT OF IR ABSORPTION OF BIOMOLECULE ADSORBED ON SINGLE WALL CARBON NANOTUBES AND GRAPHENE NANOSHEETS

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Bukovel, 2012

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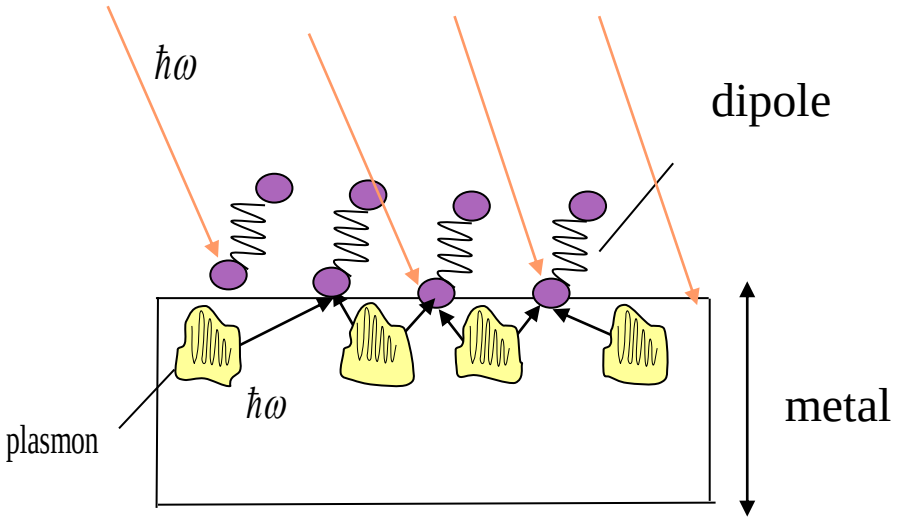
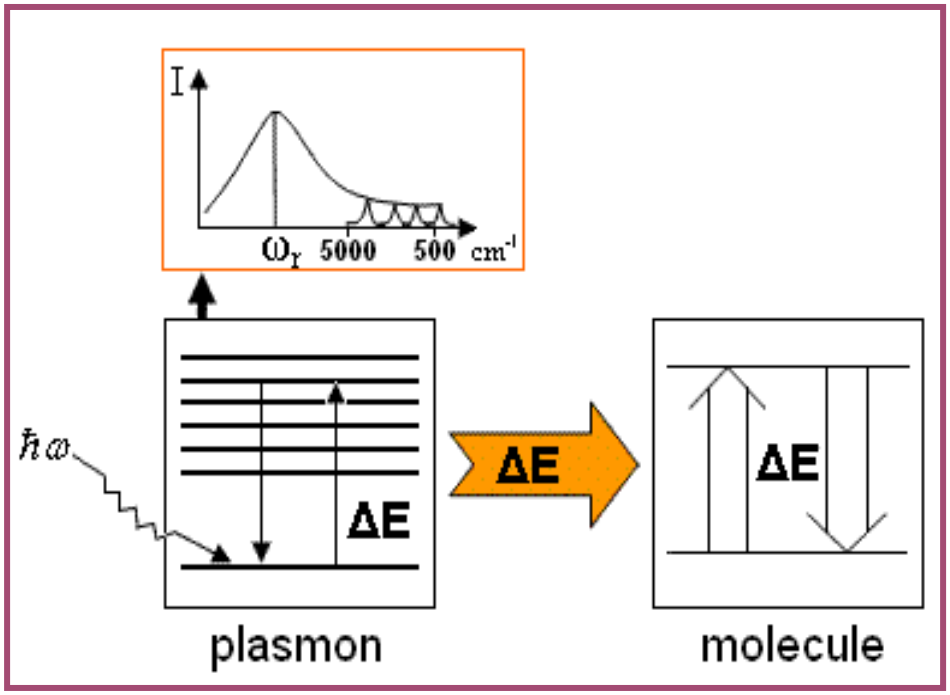
Outline

- Surface enhanced spectroscopy – SEIRA;
- Characterization of single wall carbon nanotubes (SWCNT) and graphene nanosheets;
- Enhancement of IR absorption by molecule (thymine) adsorbed on SWCNT and graphene nanosheets;
- Possible mechanism of enhancement of IR absorption for molecule adsorbed on the stated carbon nanomaterials;
- Conclusions.

Surface enhanced infrared absorption





1) The increasing of electromagnetic field near rough metal surface and island metal films (***electromagnetic mechanism***);

2) The increasing of the dipole transition moment of the adsorbed molecules (***chemical mechanism***).

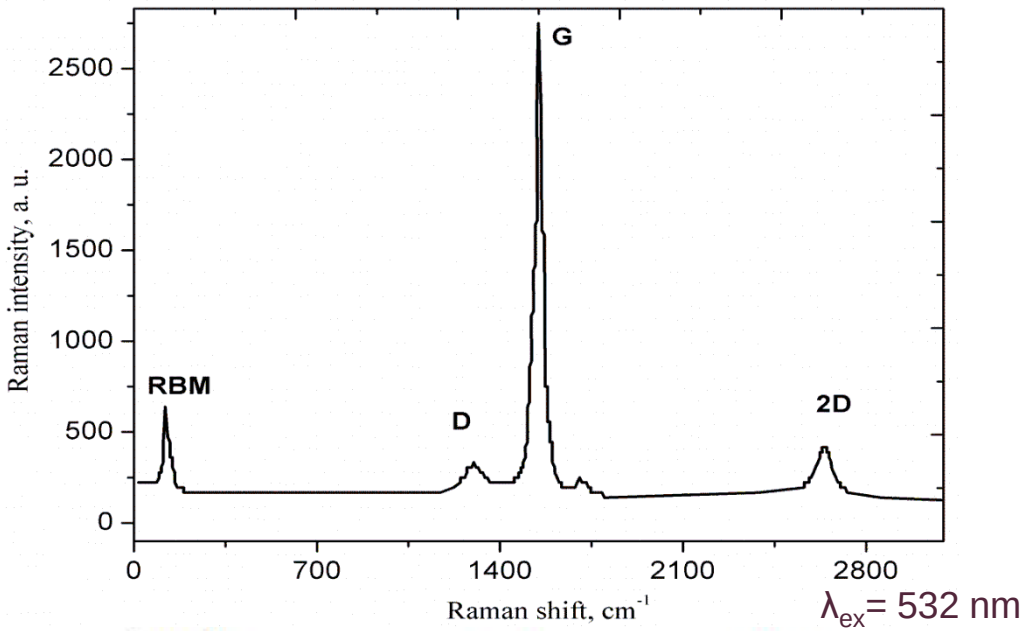
Dovbeshko G.I., Fesenko O.M., Chegel V.I., Shirshov Y.M. "Enhancement of optical transition near rough metal surface", Semiconductor physics, quantum electronics and optoelectronics, v.7, №4, 2004, p.215-225

Could carbon nanomaterials be used as enhancing substrate for IR absoption?

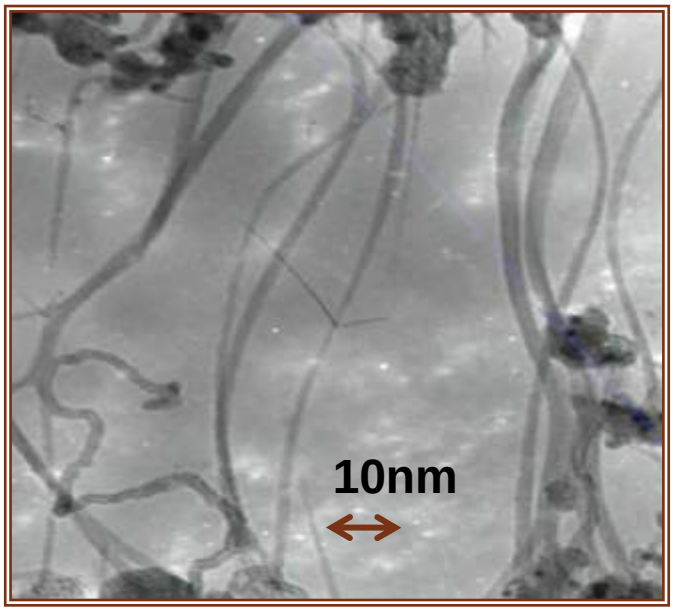
What is more efficient: SWCNT or graphene?

What is the mechanism of enhancement?

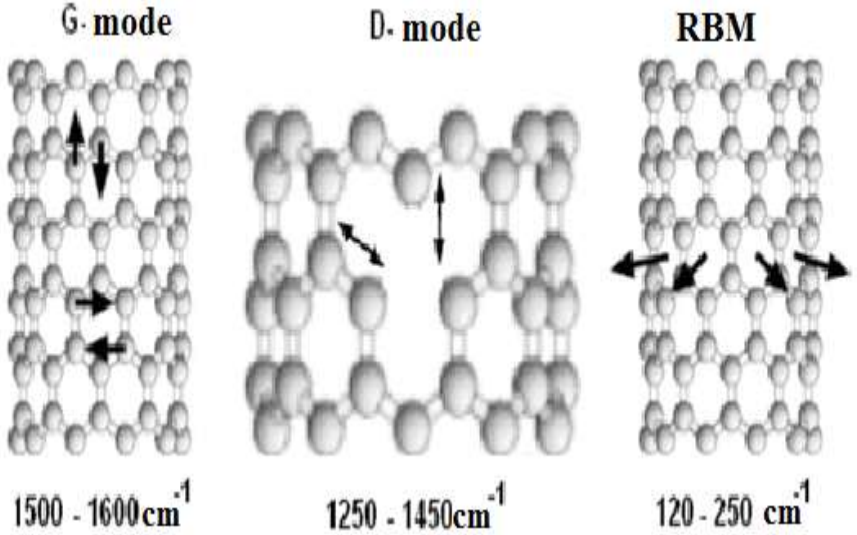
Characterization of SWCNT's



λ_{ex}= 532 nm



Transmission electron microscope (TEM)

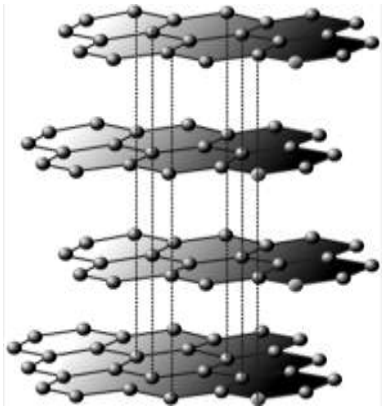


$$\nu\ (cm^{-1}) = \frac{223.75}{D_1\ (nm)}$$ → one nanotube

bundle of nanotubes ← $$\nu\ (cm^{-1}) = \frac{234}{D_2\ (nm)} + 10$$

Graphene nanosheets

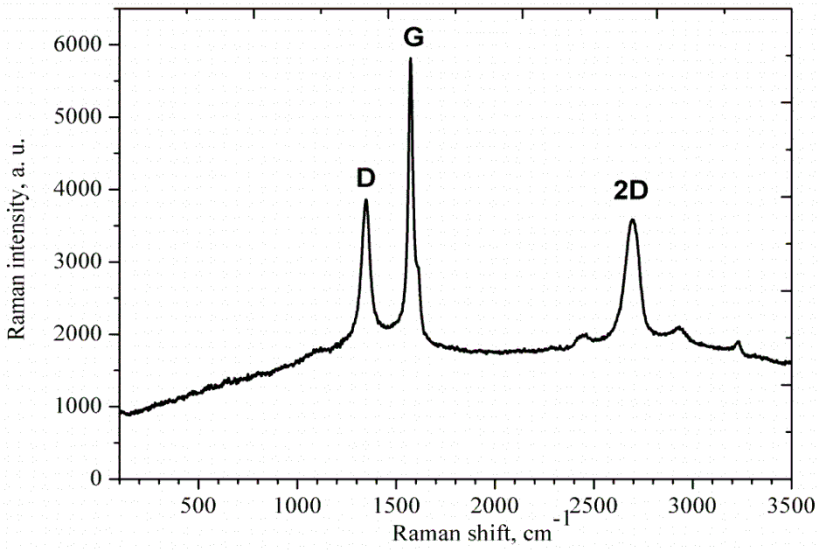
Graphene is a monolayer of carbon atoms packed into a two-dimensional (2D) honeycomb crystal structure.



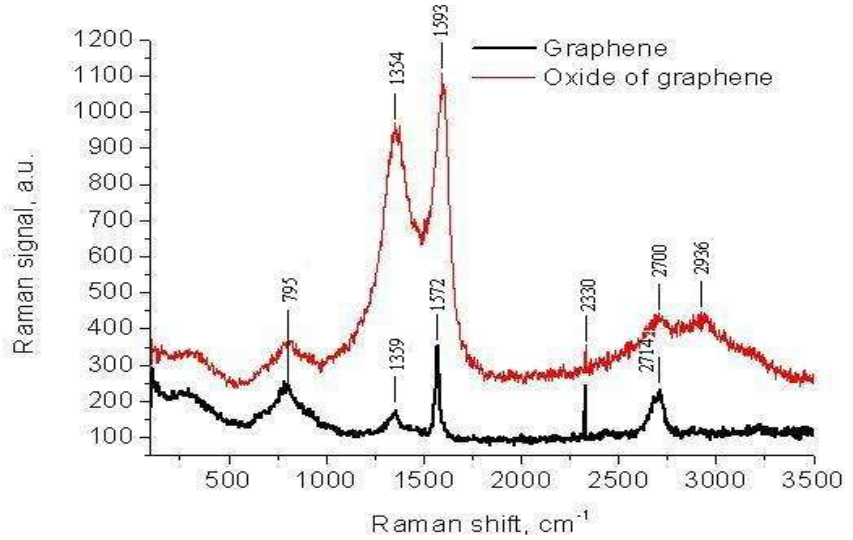
Our samples :

L.V. Pisarzhevsky Institute of Physical Chemistry of the NASU, Ukraine

Cheap Tubes Company, USA

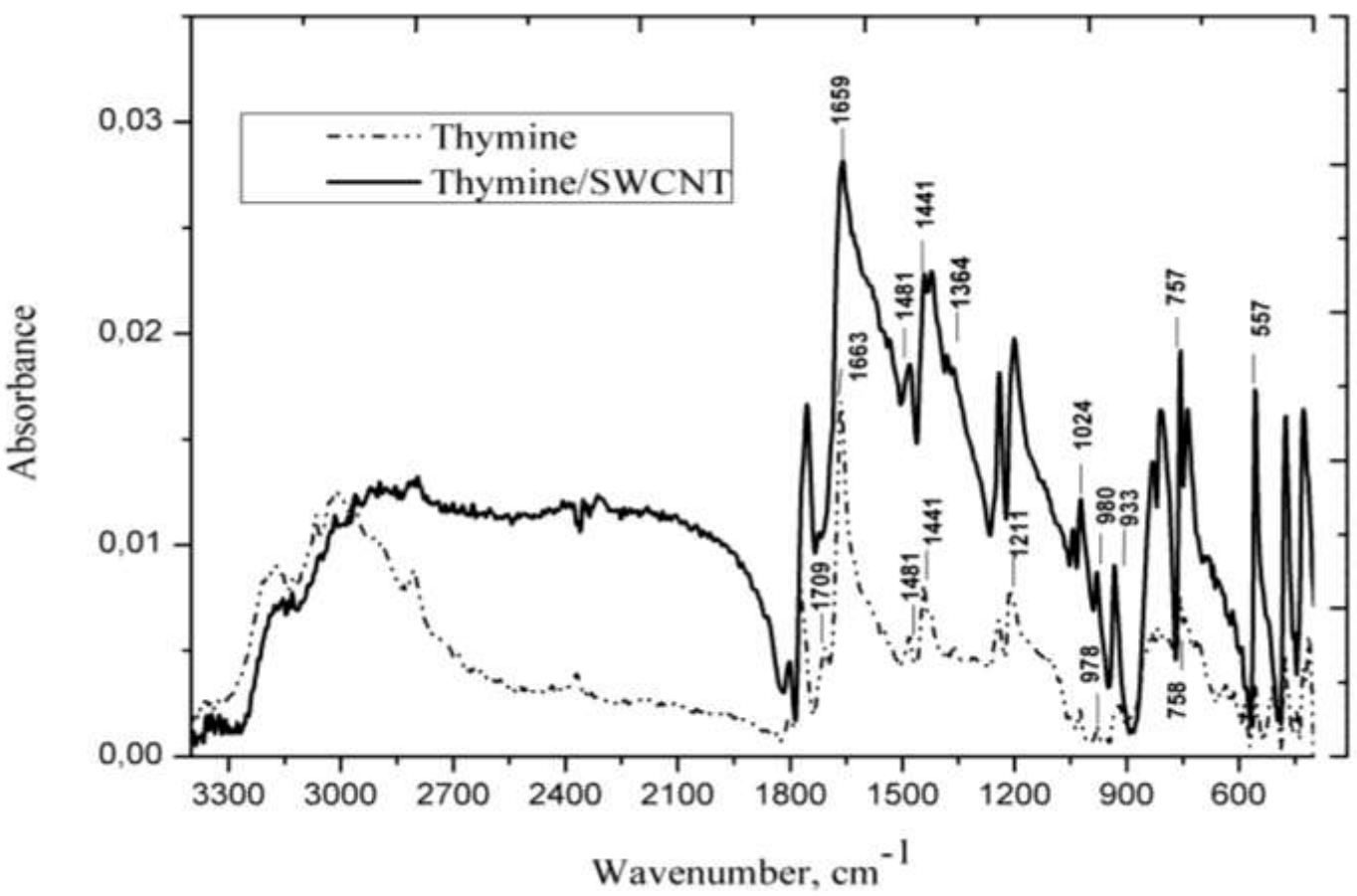


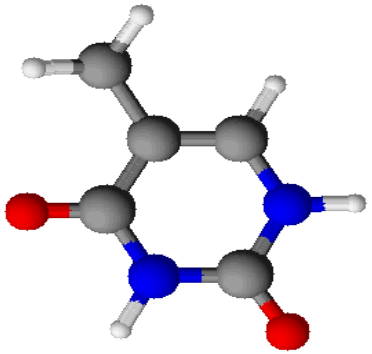
Raman spectrum of the graphene film (λ_{ex}= 532 nm).



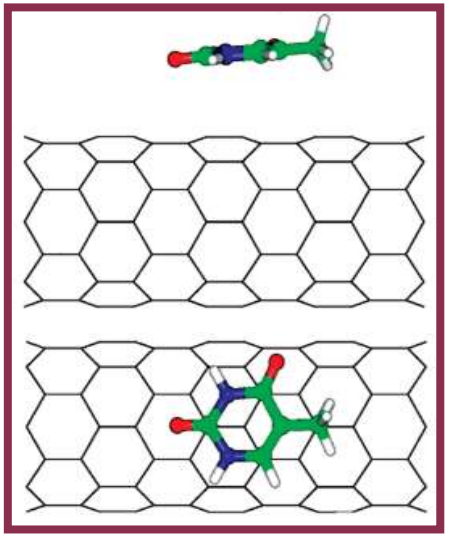
Raman spectra of the graphene & graphene oxide (λ_{ex}= 514,5 nm).

IR spectra of thymine with SWCNT's





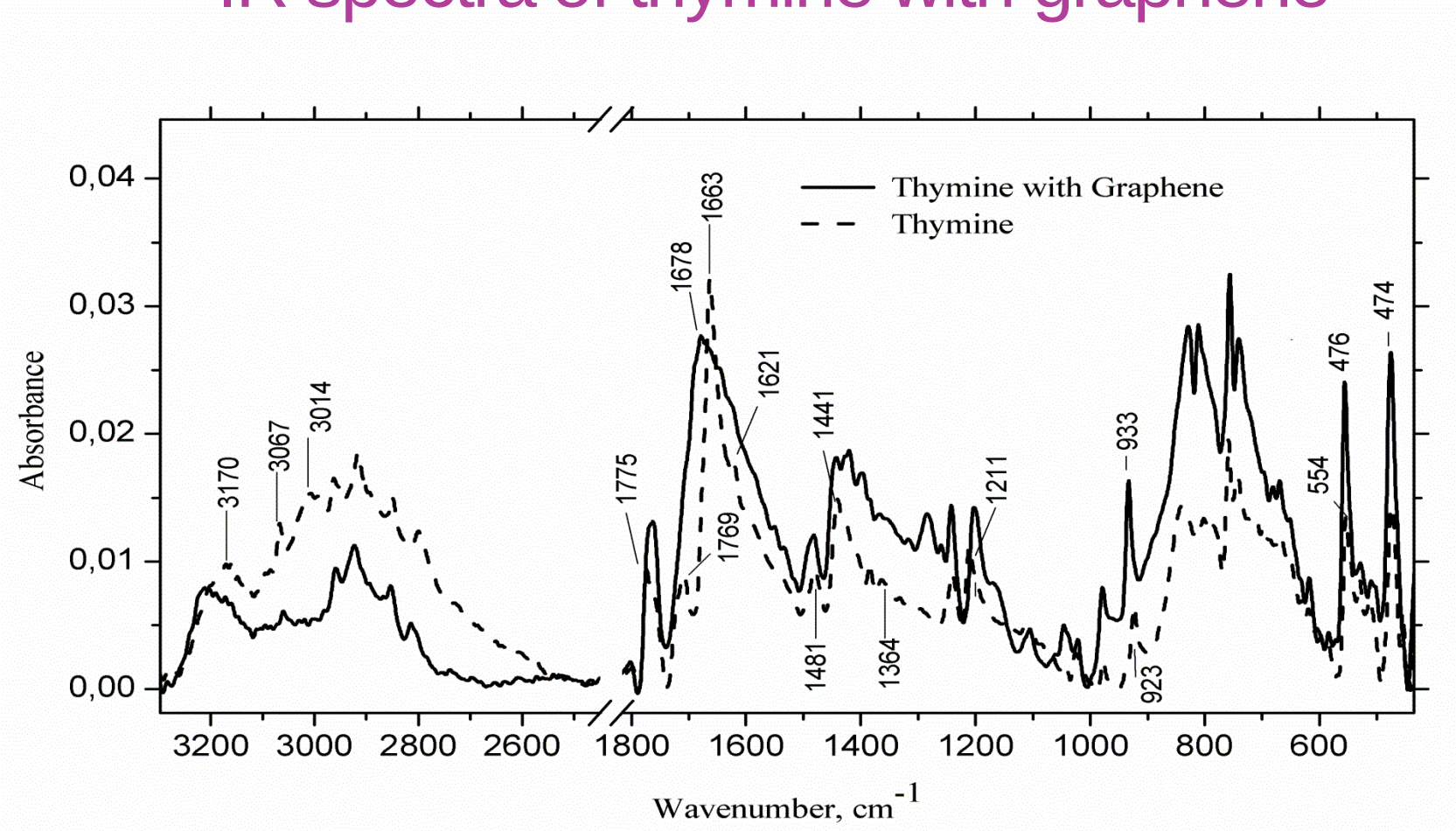
$C_5H_6N_2O_2$



G. Dovbeshko, O. Gnatuyk, O. Fesenko, A. Rynder, O. Posudievsky *Enhancement of IR absorption of biomolecules adsorbed on single wall carbon nanotubes and graphene nanosheets// Journal of Nanophotonics (2012)* ***in print***

Ya. Shtogun, L. Woods, G. Dovbeshko "Adsorption of Adenine and Thymine and Their Radicals on Single-Wall Carbon Nanotubes" J. Phys. Chem. ***2007, 111, p.18174-18181***

IR spectra of thymine with graphene



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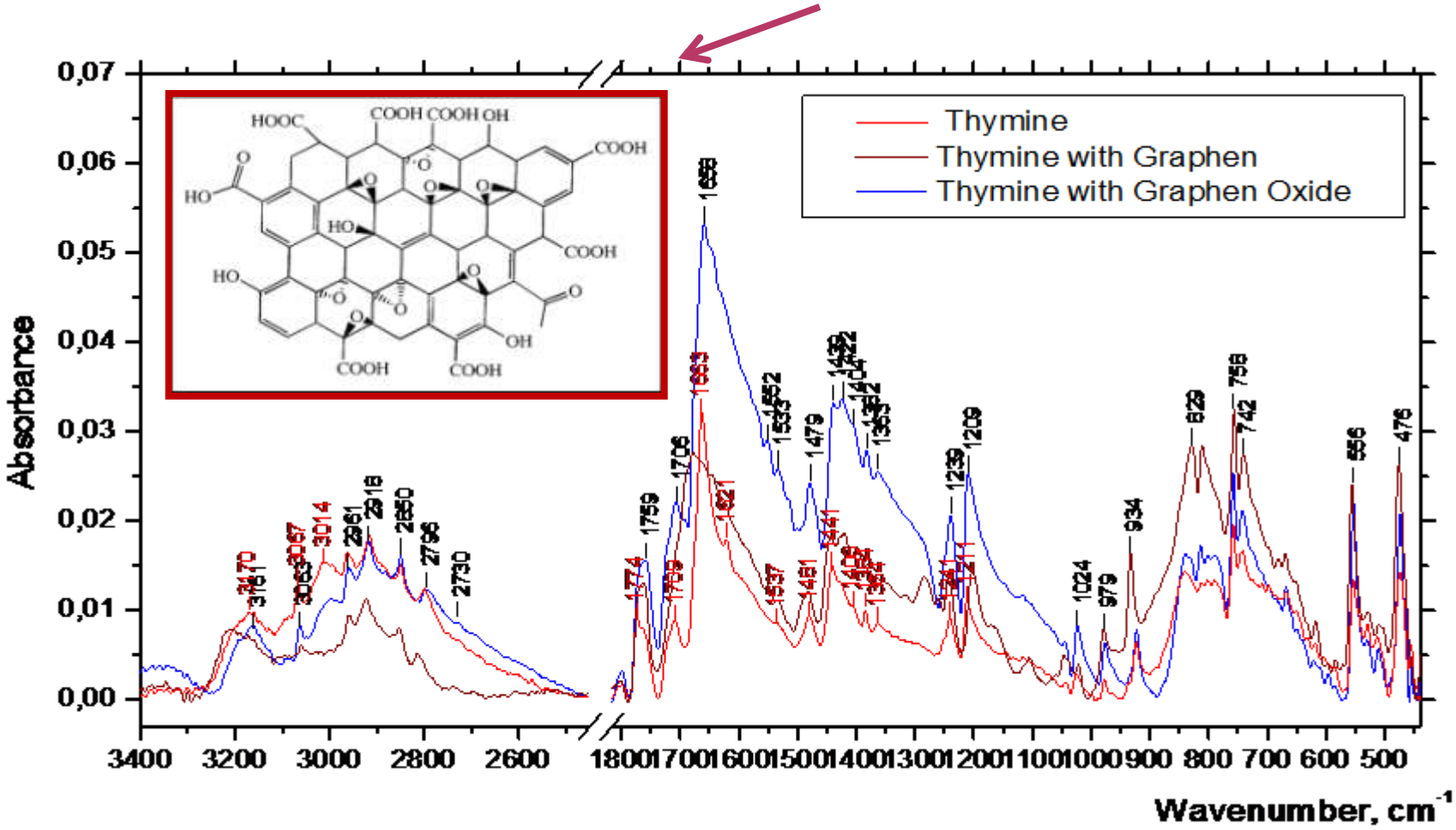
Calculated enhancement factor

Thy (on the Au)	Thy+Graphene		Assignment	Thy+SWCNT		Assignment
	Wavenumber, cm^{-1}	$g^{2(*)}$		Wavenumber, cm^{-1}	$g^{2(*)}$	
1709	1706	1,9	C_2=O	1709	1,8	C_2=O
1663	1678	0,9	C_4=O	1659	1,4	C_4=O
1550	1550	1,4	C=C	1550	2,3	C=C
1481	1482	1,3	N_1-H def	1481	2,7	C-H_3 def
1440	1443	1,2	N_1-H def, C_3-H def	1441	4,0	N_1-H def
1427	1420	1,4	C_3-H def	1421	5,3	N_1-H def, C_3-H
1364	1366	3,0	N_3-H def	1364	4,0	N_3-H def.
1241	1241	1,7	C-C	1241	1,7	C-C
1212	1202	1,3	C_6-H def , C_2-N_3 str.	1201	2,3	C_6-H def, C_2-N_3 str.
1025	1022	1,5	CH, C-OH	1024	4,2	C-H, C-OH
978	979	3,7	N-C_2 ring-bending	980	4,1	N-C_2 ring-bending
920	934	2,6	γ-CH	933	5,0	γ-CH
842	829	2,0	N_3-H, γ-C_2=O	831	2,6	N_3-H, γ-C_2=O
812	811	2,2	N_1-H, γ-C_2=O, C_4=O	810	2,7	N_1-H, γ-C_2=O, C_4=O
758	757	1,7	Skeletal ring mode	757	2,5	Skeletal ring mode
743	741	1,7	C_4=O			
				617	2,3	γ- C_4=O
554	556	2,0	N-H	557	4,2	β- C_4=O
474	476	1,9	N-H	475	2,8	α-ring-bending

The IR spectra of thymine, thymine with *graphene and graphene oxide*



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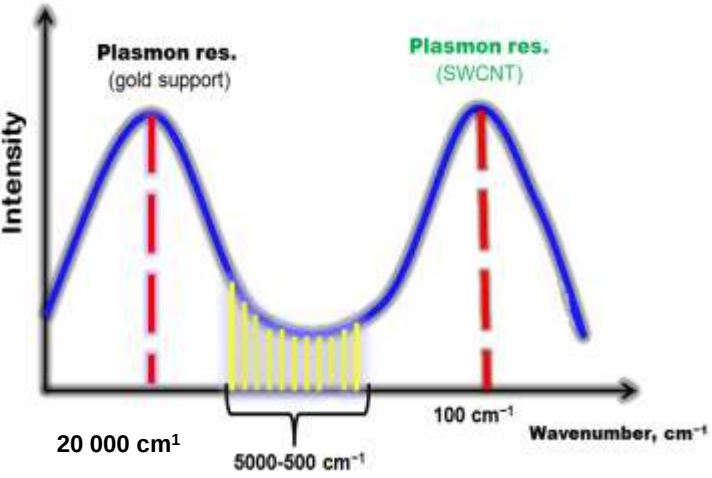
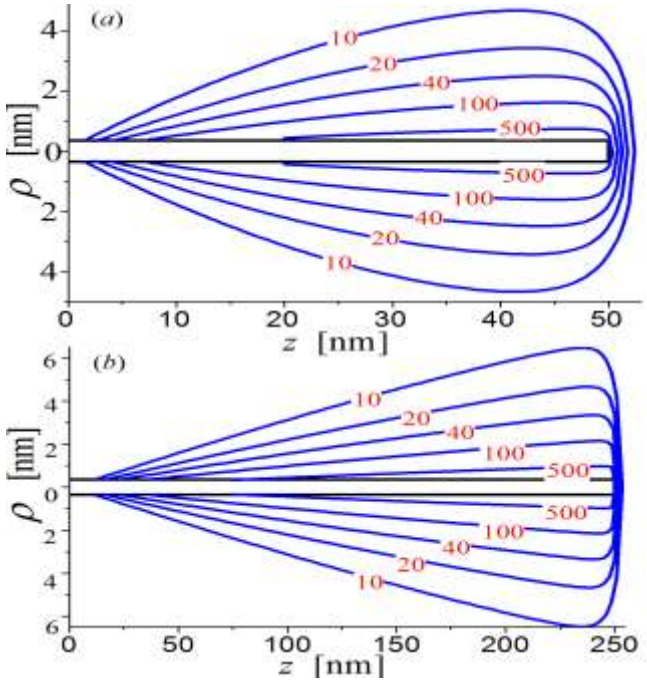
Factor of enhancement of Thy on *graphene* and *graphene oxide*

Thymine	Thy+Graphene Oxide		Thy+Graphene		Assignment
	position	Enh. factor	position	Enh. factor	
1798	1799	2,0	1802	1.4	C_4=O for isolated Thy molecules
1709	1706	2.4	1706	1.9	C_2=O
1550	1553	3,2	1550	1.4	C=C
1481	1480	2,6	1482	1.3	N_1-H def
1406	1405	3,0	1397	1.6	C-N str.
1364	1363	3,0	1366	1.5	N_3-H def
1296	1287	3,0	1284	2.2	C_6-H def
1212	1210	2,3	1202	1.4	C_6-H def , C_2-N_3 str.
1025	1023	3,0	1022	1.5	CH, C-OH
978	977	3,0	979	3.6	N-C_2
924	923	1.2	933	2.6	γ-CH

Possible mechanism of SEIRA effect

- Local field enhancement in the near-field zone of the finite-length metallic SWCNTs.





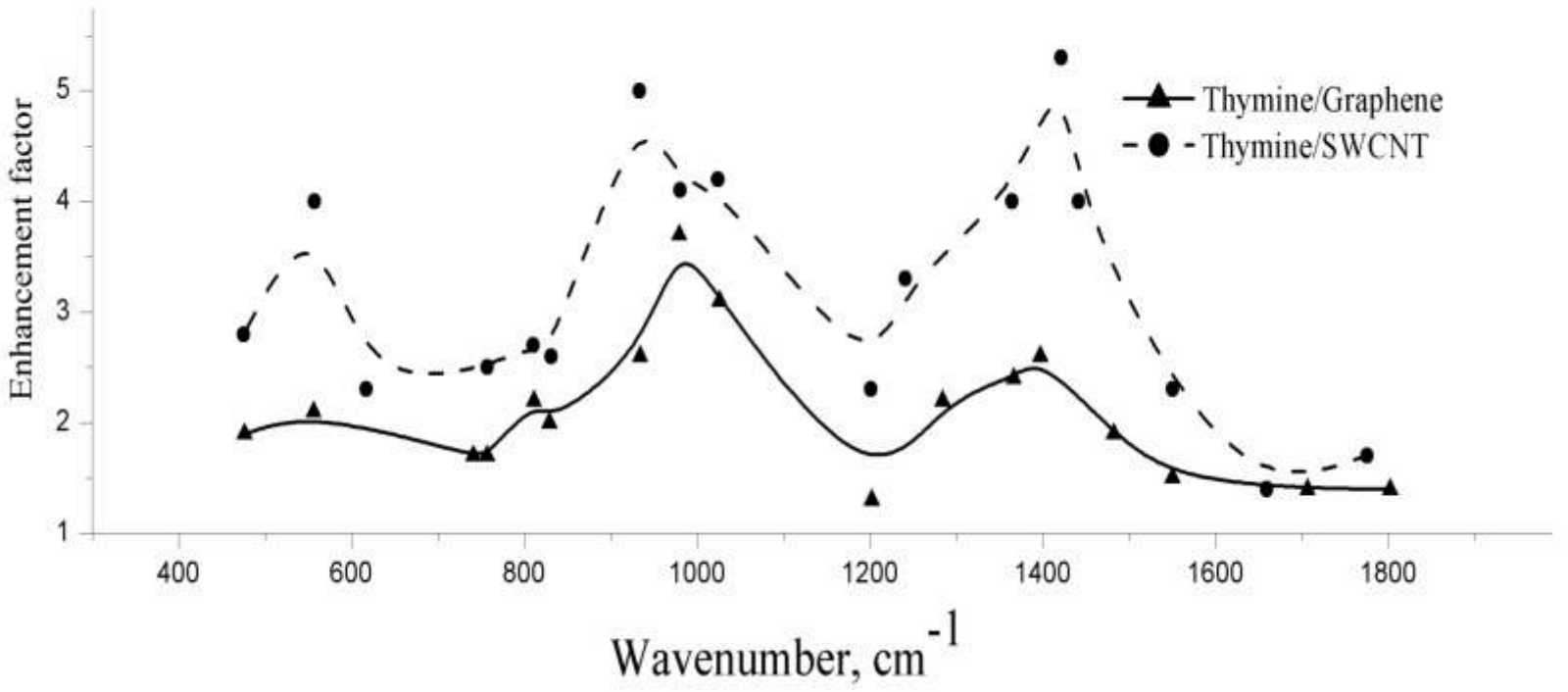
Plasmon resonance frequencies for different length of nanotube

L, μm	***W_p/c, cm^{-1}***
1,08	150
0,61	170
0,24	600
0,18	1020

G.Ya. Slepyan, M.V. Shuba, S.A. Maksimenko, C. Thomsen, A. Lakhtakia et. al *Experimental evidence of localized plasmon resonance in composite materials containing single-wall carbon nanotubes// Phys. Rev. B,* ***2012****. Vol.85.P. 165435.*

G.Ya. Slepyan, M.V. Shuba S.A. Maksimenko, C. Thomsen, A. Lakhtakia *. Terahertz conductivity peak in composite materials containing carbon nanotubes: Theory and interpretation of experiment // Phys. Rev. B,* ***2010****. Vol. 81. P. 205423.*

Dependence of the enhancement factor on wavenumbers



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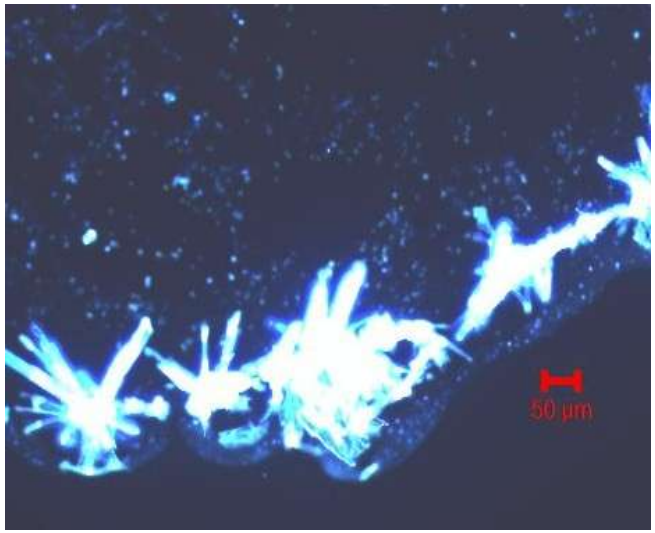
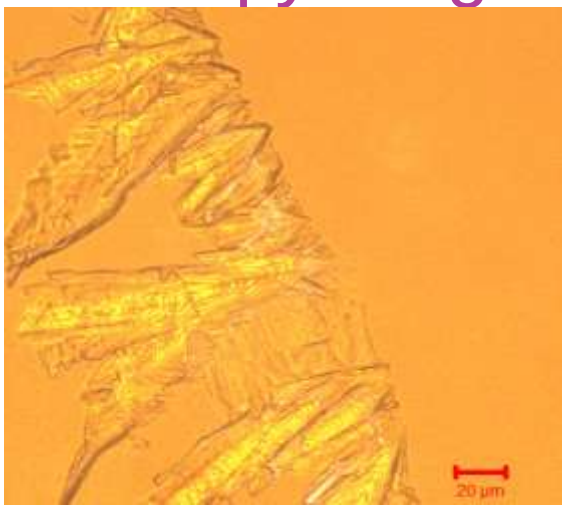
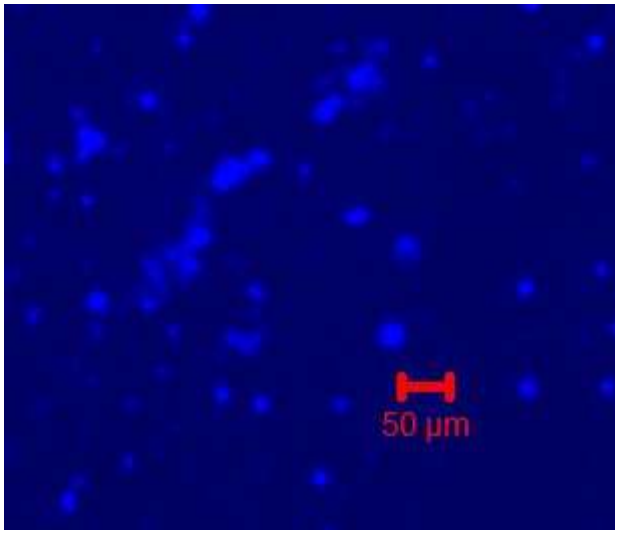
Confocal microscopy images



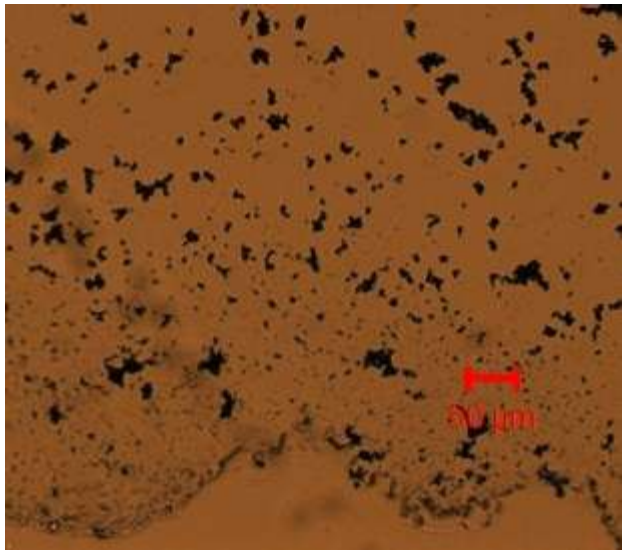
Thymine on Au



Thymine on glass



Thy +graphene on Au support



Graphene on glass

Conclusions

- Graphene and SWCNT could be used as an enhancing substrate for IR spectroscopy;
- The enhancement factor for Thymine adsorbed on SWCNT (6) is greater than that on graphene nanosheets (4);
- Mechanism of enhancement of biological molecules adsorbed on nanostructured carbon substrates seems to have chemical and electromagnetic nature.

.

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Thank You for Attention !

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