Strong Quadrupole Light-Molecule Interaction and Surface Enhanced Optical Processes

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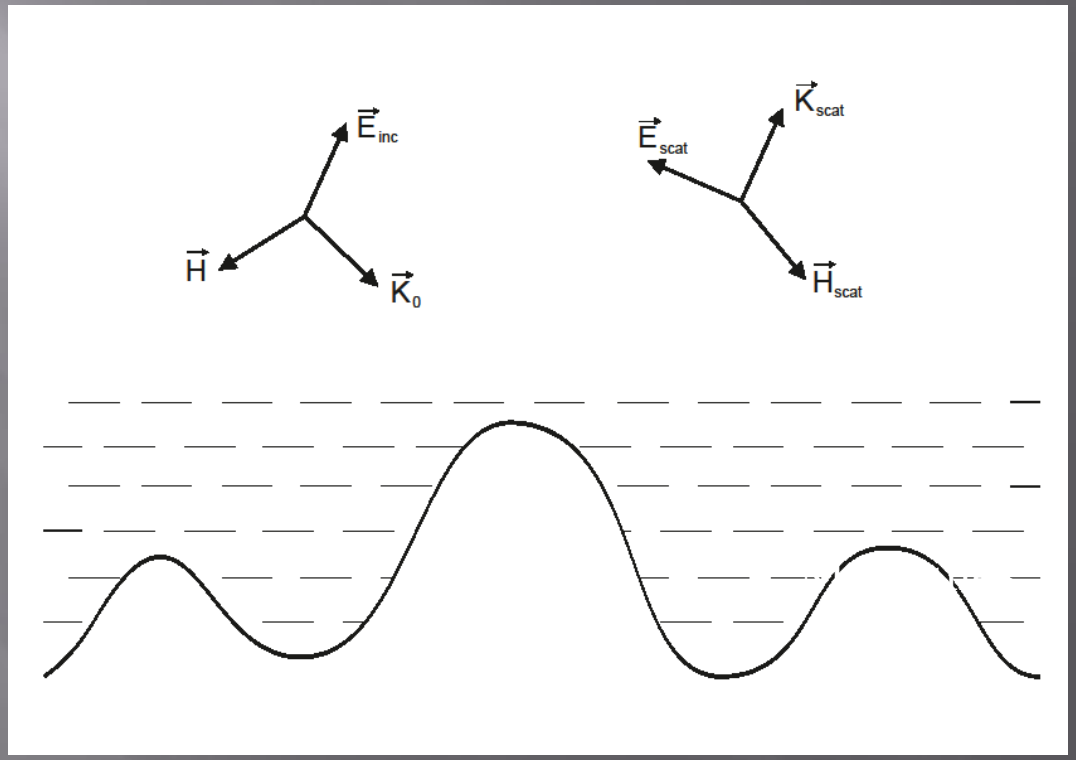
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Spectroscopy is a powerful tool for investigation of molecules and can be very useful in physics chemistry, biology and medicine

SERS-Surface Enhancement of Raman Scattering

$$G = \frac{d\sigma_{surf}}{d\sigma_{vol}} \sim 10^6$$



Metal-(silver, copper, gold)

Discovery of Surface Enhanced Raman Scattering, SERS, is a great achievement, because it allows to rise the sensitivity of this method

There are another Surface Enhanced optical processes

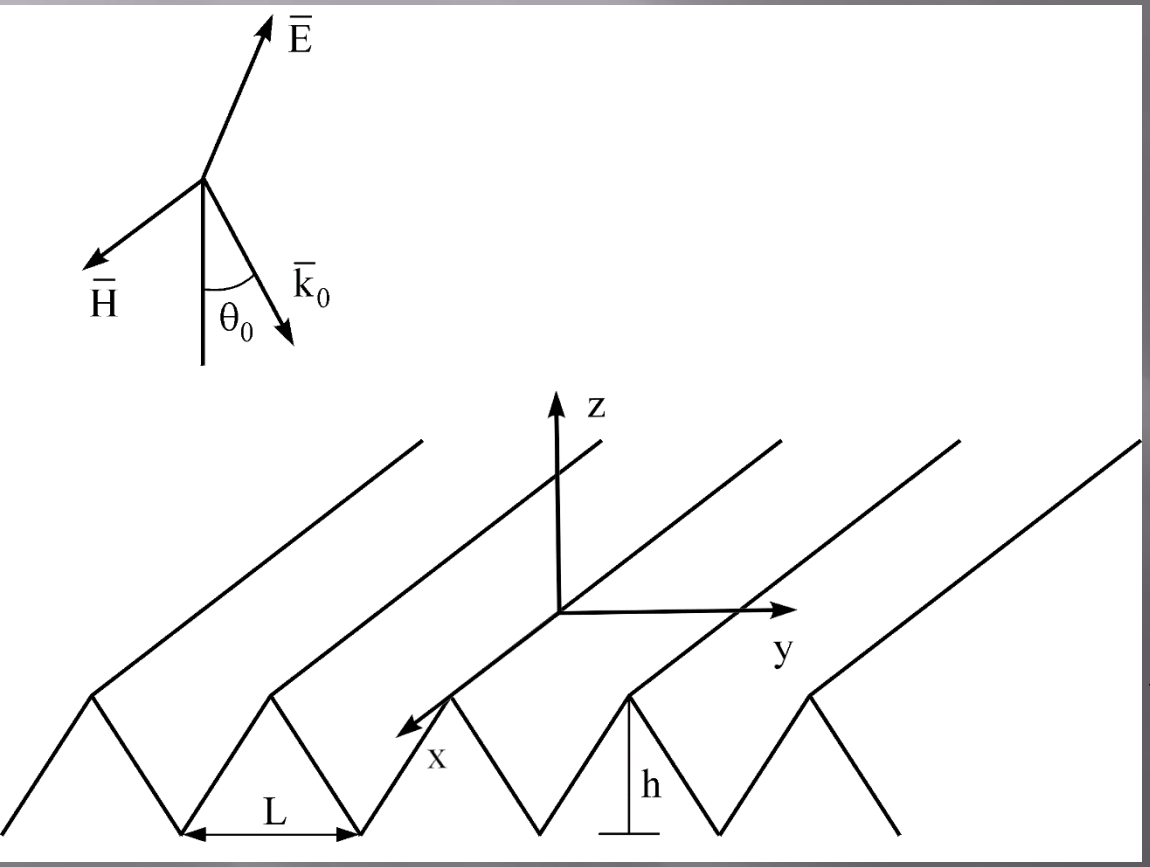
Surface Enhanced Infrared Absorption (SEIRA)

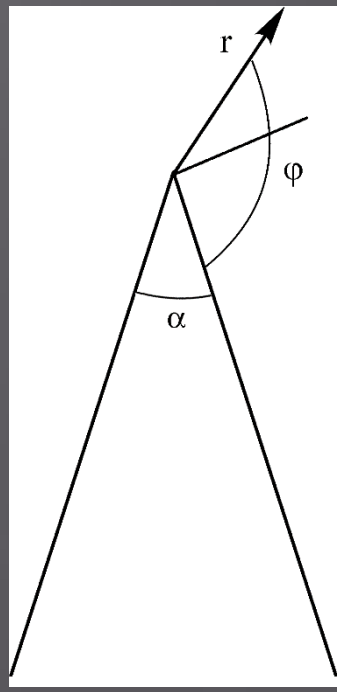
$$G_{SEIRA} = \frac{d\sigma_{surf}}{d\sigma_{vol}} \sim 10^{2}$$

Surface Enhanced Hyper Raman Scattering (SEHRS)

$$G_{SEHRS} = \frac{d\sigma_{surf}}{d\sigma_{vol}} \sim 10^{12}$$

Models of roughness and a rough surface



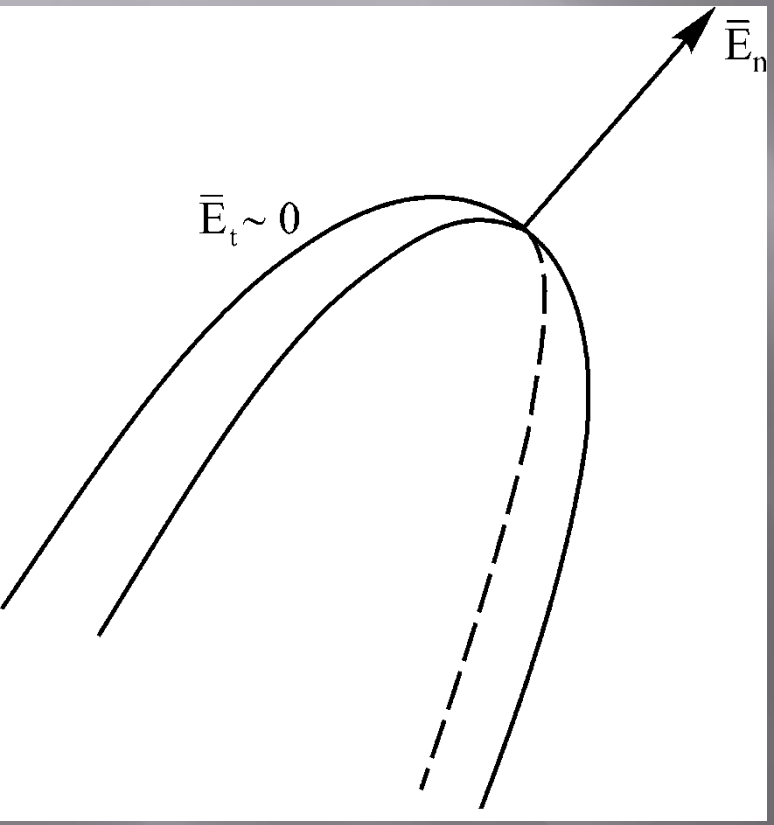


$$E_r \sim \left|\bar{E}inc\right| C_0 \left(\frac{l_1}{r}\right)^{\beta} \qquad 0 < \beta < 1$$

$$E_r \to \infty$$

$$r \to 0$$

For more real model of the roughness there is the enhancement both the component of the electric field, which is perpendicular to the surface and the enhancement of its derivatives



$$E_r \sim \left|\overline{E}_{inc}\right| C_0 \left(\frac{l_1}{r}\right)^{\beta}$$

$$\frac{1}{E_r}\frac{\partial E_r}{\partial r} \sim -\left(\frac{\beta}{r}\right)$$

This results in the necessity to take into account not only the dipole but the quadrupole light-molecule interaction, because of the increase of the electric field derivatives.

Thus the light molecule interaction Hamiltonian must be in a form, when the quadrupole interaction is taken into account

$$\hat{H}_{e-r}^{inc} = \left|\overline{E}_{inc}\right| \frac{(\overline{\overline{e}}^{*}\overline{\overline{f}}_{e}^{*})_{inc} e^{i\omega_{inc}t} + (\overline{\overline{e}}\,\overline{\overline{f}}_{e})_{inc} e^{-i\omega_{inc}t}}{2}$$

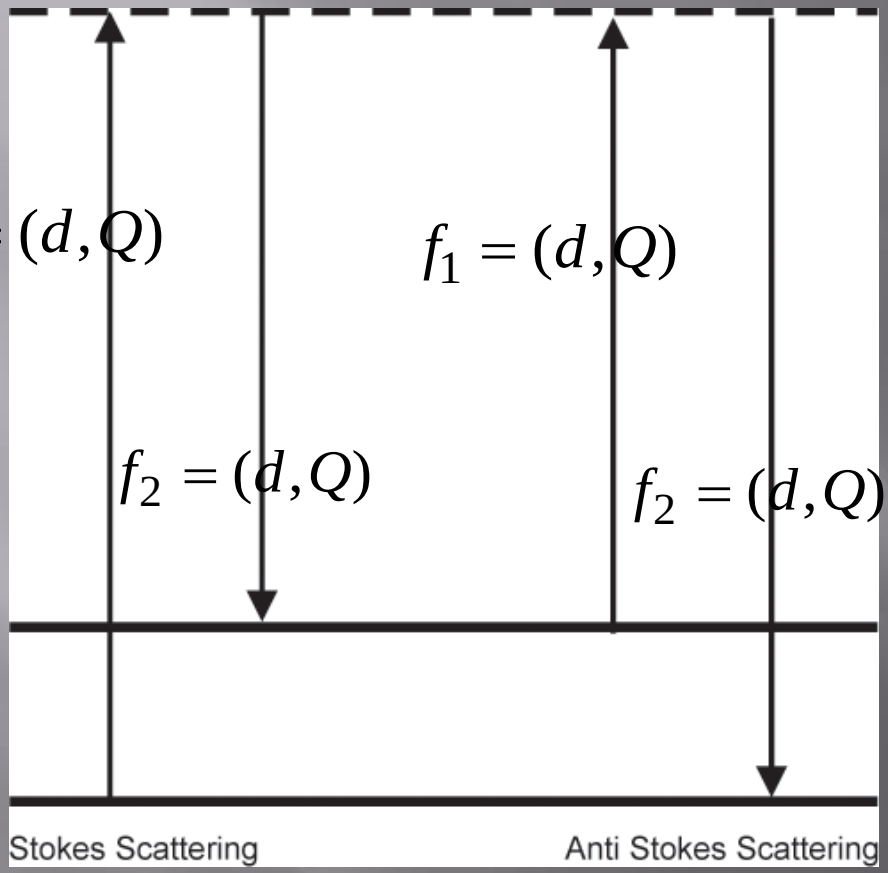
$$\hat{H}_{e-r}^{scat} = \left|\overline{E}_{scat}\right| \frac{(\overline{\overline{e}}^{*}\overline{\overline{f}}_{e}^{*})_{scat} e^{i\omega_{scat}t} + (\overline{\overline{e}}\,\overline{\overline{f}}_{e})_{scat} e^{-i\omega_{scat}t}}{2}$$

$$f_{e\alpha} = d_{e\alpha} + \frac{1}{2E_{\alpha}} \sum_{\beta} \frac{\partial E_{\alpha}}{\partial x_{\beta}} Q_{e\alpha\beta}$$

The second factor is that the quadrupole interaction with a constant sign Q_{xx}, Q_{yy}, Q_{zz} are responsible for the strong additional enhancement, while the moments Q_{xy}, Q_{xz}, Q_{yz} are not essential

The moments, Q_{xx}, Q_{yy}, Q_{zz} are designated as Q_{main}

The Raman process with the dipole and quadrupole interactions taken into account is presented on the diagram



In SERS it takes place via various combinations of the dipole and quadrupole moments, for example $(Q_{main} - Q_{main})$ $(Q_{main} - d_z)$

It can be demonstrated that the quadrupole interaction with the moments

Q_{main} can be more than the dipole interaction with the moment d_z

The quadrupole interaction and the increase of the number of moments, responsible for the scattering results in the change of the SERS, SEHRS and SEIRA spectra of molecules of symmetrical molecules **and appearance of forbidden lines**.

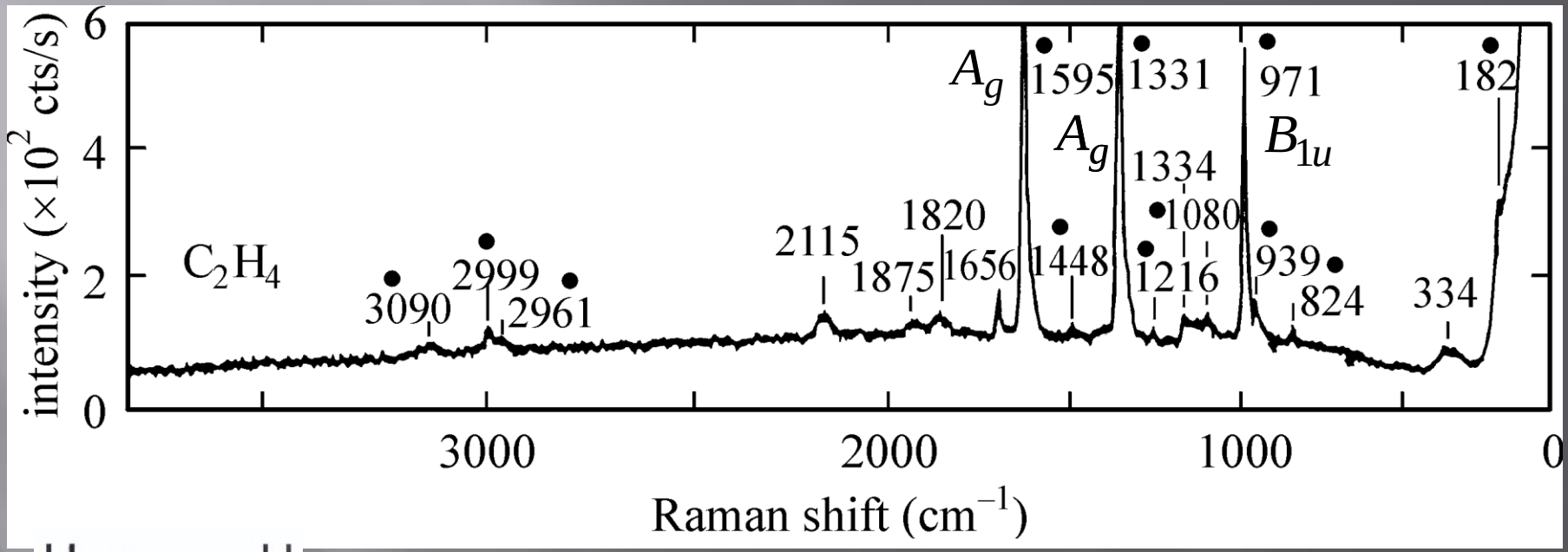
The most enhanced scattering arise from the scattering via the moments Q_{xx}, Q_{yy}, Q_{zz} and d_z

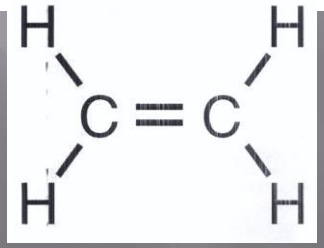
In SERS the most enhanced scattering occur via $(Q_{main} - Q_{main})$

$(Q_{main} - d_z)$

The quadrupole interaction changes main regularities of these spectra and results in appearance of strong forbidden lines

The SERS spectrum of ethylene



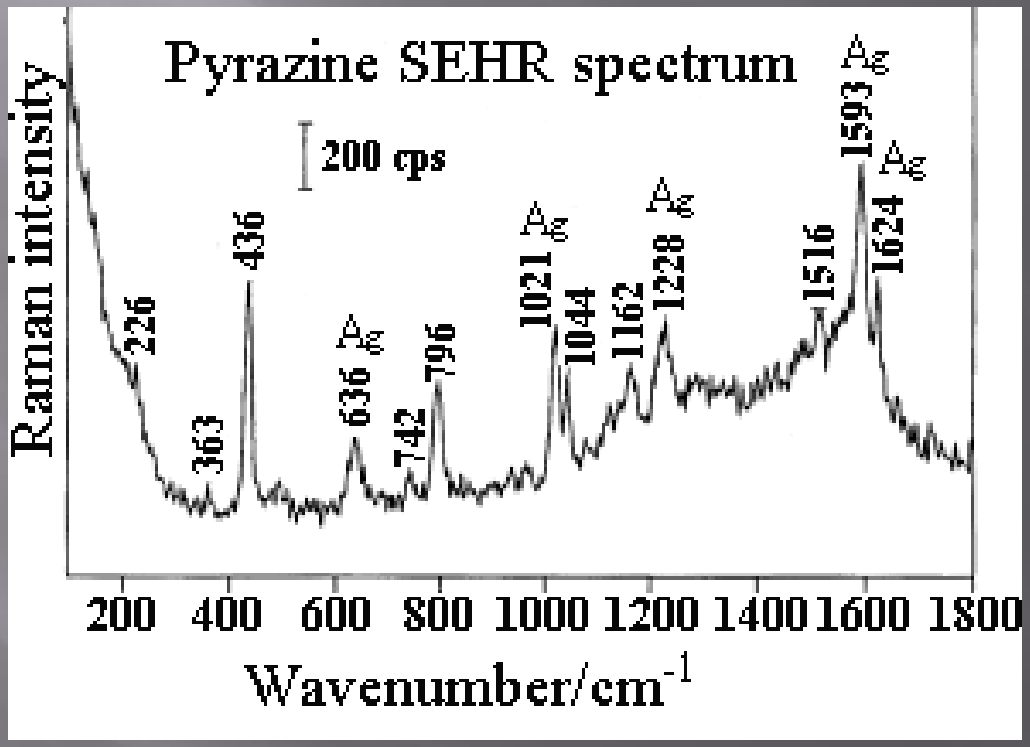


$1595cm^{-1}$ A_g allowed $(Q_{main} - Q_{main})$

$1331cm^{-1}$ A_g allowed

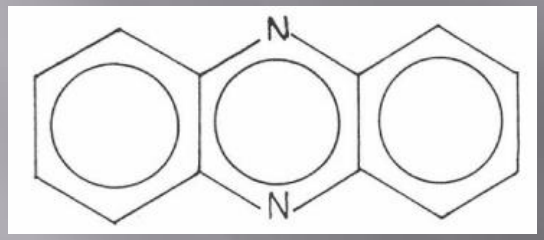
$971cm^{-1}$ B_{1u} forbidden $(Q_{main} - d_z)$

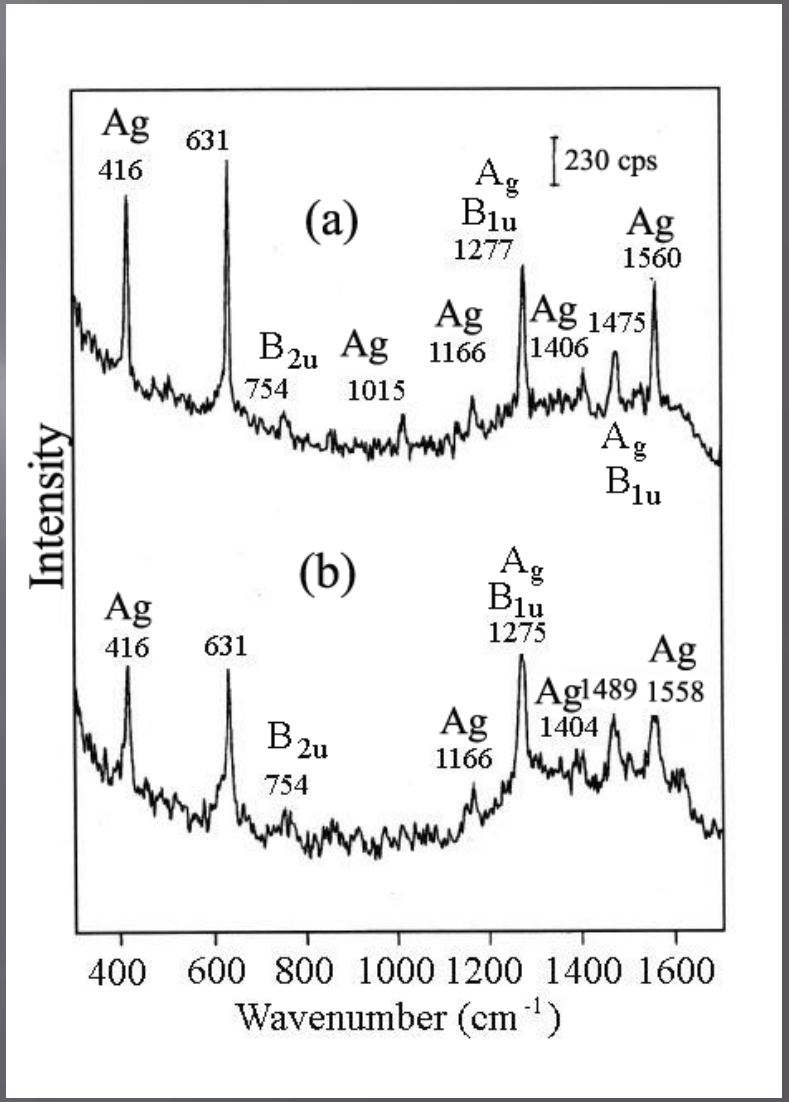
The SEHRS spectrum of pyrazine with D2h symmetry group



Wu-Hu Li, Xiao-Yuan Li, Nai-Teng Yu // Chem. Phys. Lett. 1999, V. 305, P. 303.

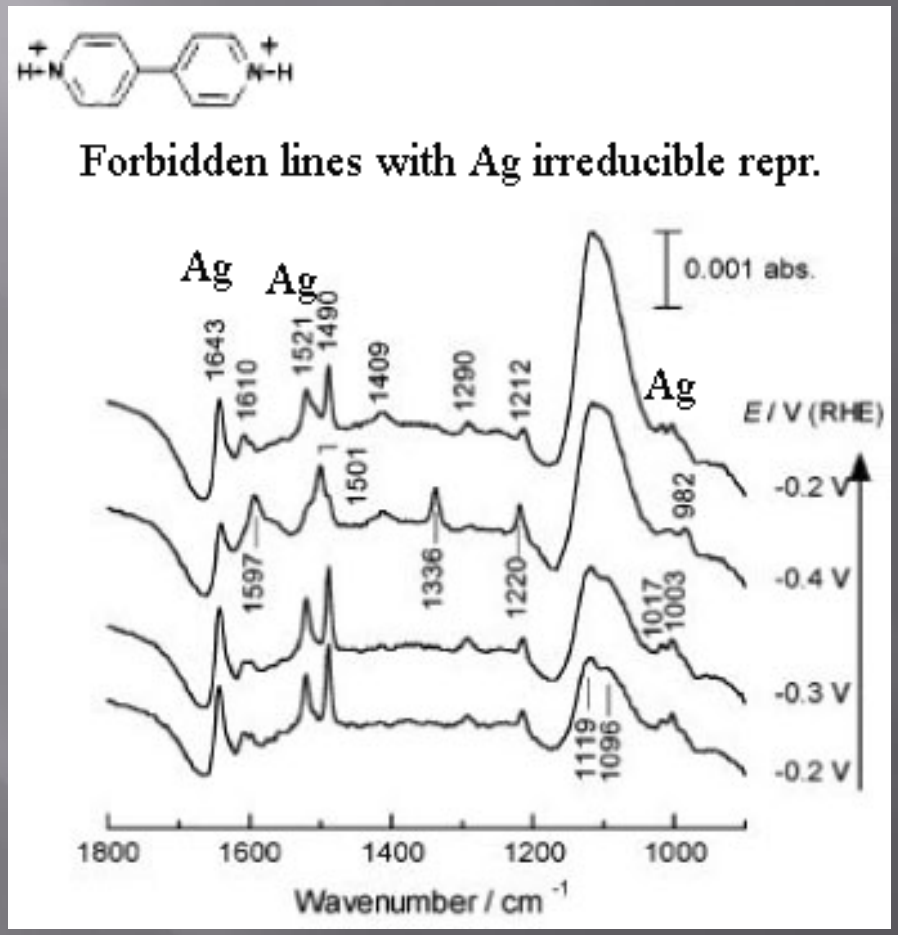
The SEHRS spectrum of phenazine with D2h symmetry group





Wu-Hu Li, Xiao-Yuan Li, Nai-Teng Yu, Chem. Phys. Lett. **327**, 153, (2000)

The SEIRA spectrum of $BiPyH_2^{2+}$ with D2h symmetry group



Yu-Xia Diao, Mei-Juan Han, Li-Jun Wan, Kingo Itaya, Taro Uchida, Hiroto Miyake, Akira Yamakata and Masatoshi Osawa, Langmuir **22,** 3640, (2006).

CONCLUSION

Thus the theory, which is based on the conception of the strong quadrupole light-molecule interaction successfully explains all features of the spectra of Surface Enhanced Optical processes. It can be demonstrated that it explains all accompanying phenomena.

Thank You for Your attention