Theoretical Study on SERS of Wagging Vibrations of Benzyl Radical Adsorbed on Silver Electrodes

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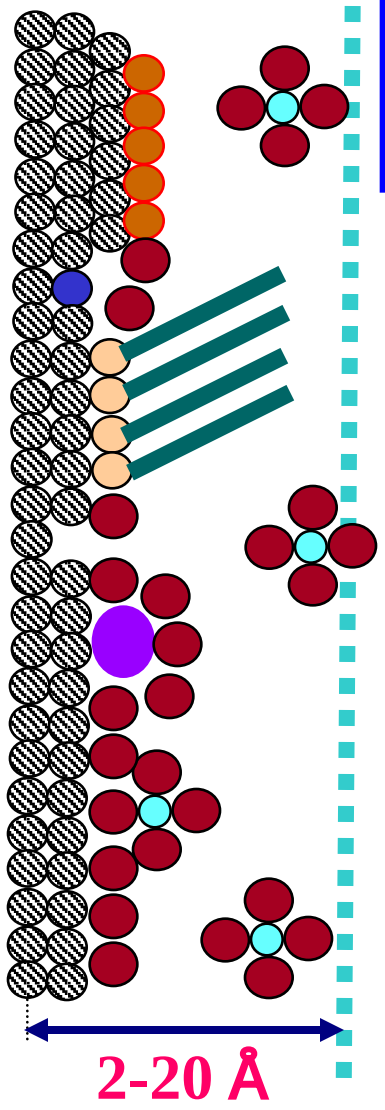
2016.6.23

Studies on solution/metal electrodes



Surface-enhanced Raman spectroscopy：SERS

Surface plasmon resonance

High Resolution

Energy

Space

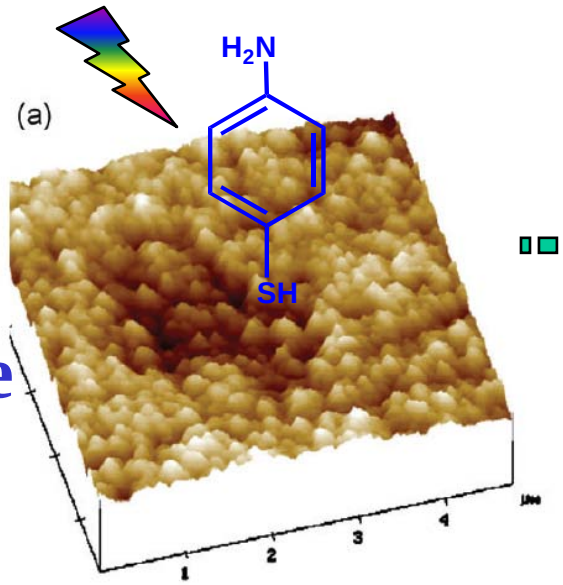
Time

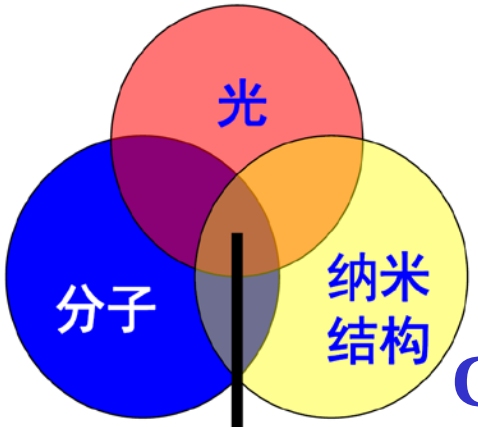
Chemical property

High detection sensitivity

EC-SERS (Metal NPs + Molecule + Light)

Rough electrode surfaces



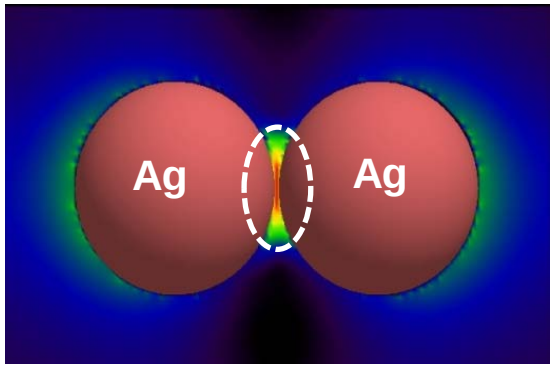


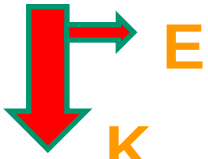
Silver
Gold
Copper

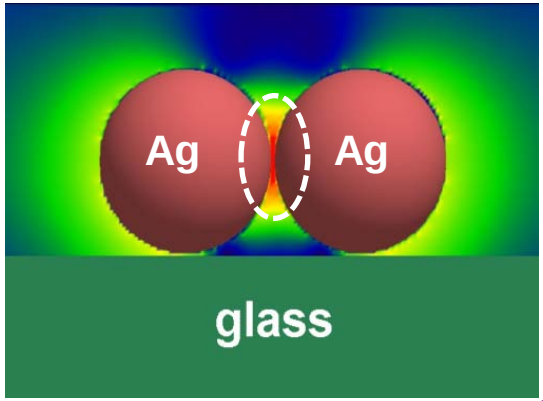
表面光化学

Nanostructures

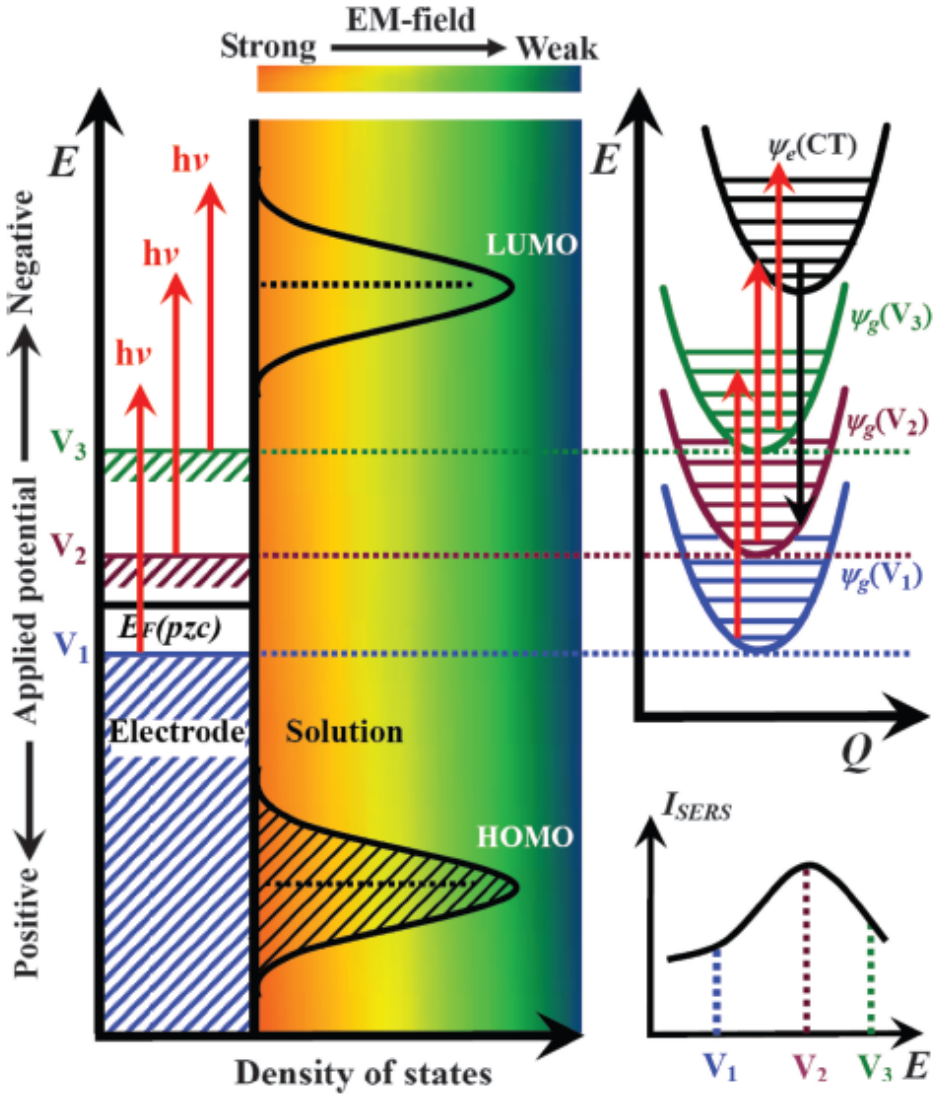
633 nm laser

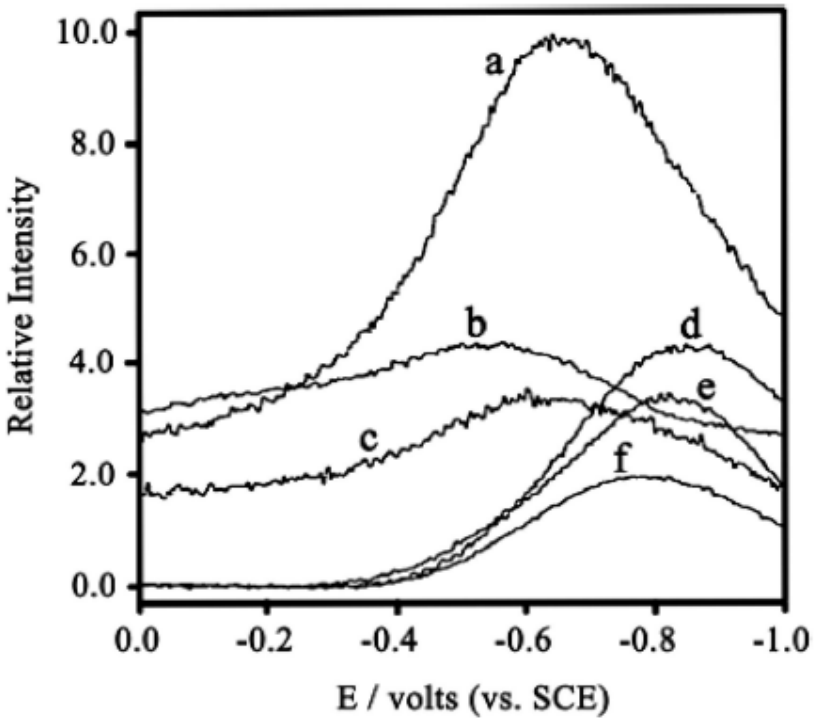






Potential-Intensity Profiles dependent on Laser Lines





a. 1010 cm^{-1}; d. 1215 cm^{-1}

b. 1036 cm^{-1}; e. 1594 cm^{-1}

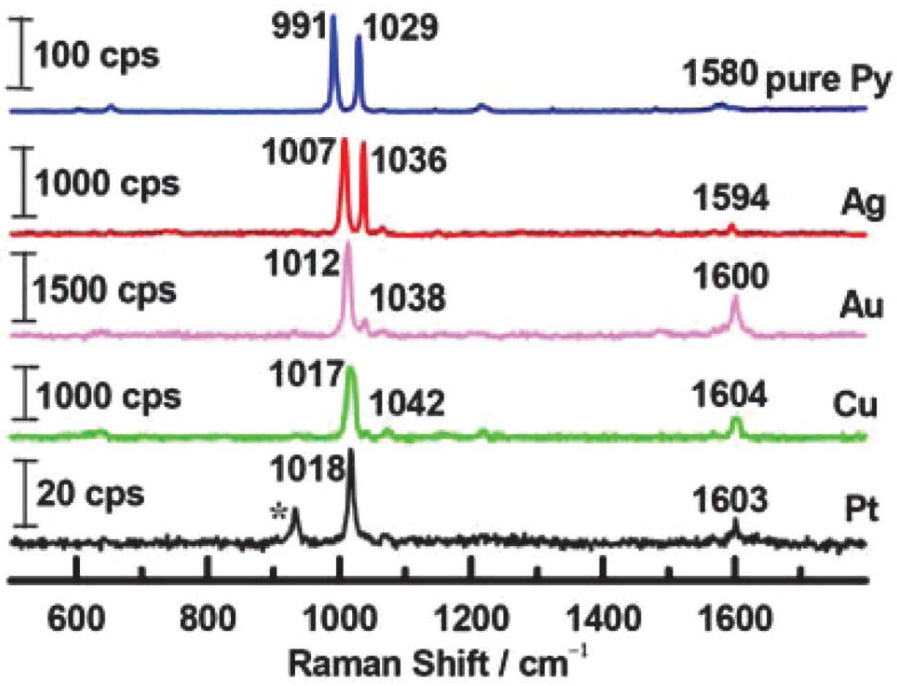
c. 3056 cm^{-1}; f. 623 cm^{-1}

DY Wu, JF Li, B Ren, ZQ Tian, Chem. Soc. Rev. 2008, 37, 1025

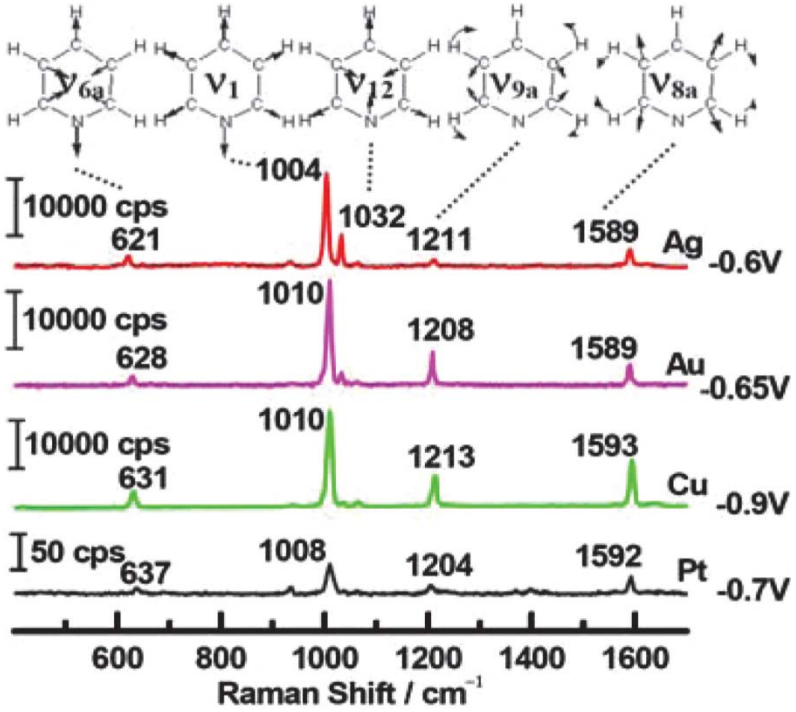
Electrochemical Surface-Enhanced Raman Spectroscopy of Pyridine

Pyridine N-Metal Interaction:

Pt > Au, Cu > Ag



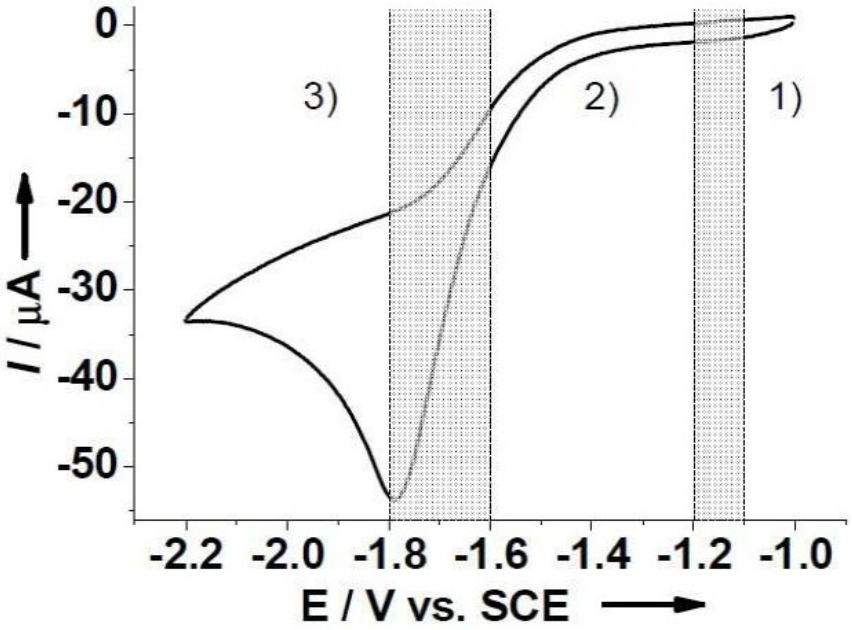
At the open circuit potential



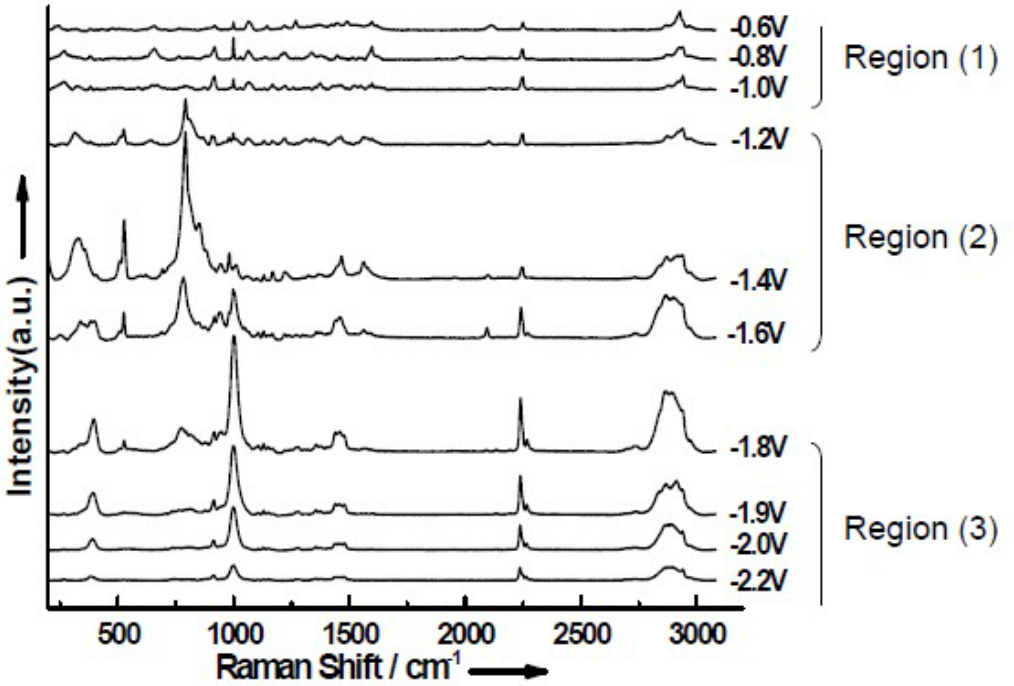
At the peak potential of the ring breathing mode

DY Wu, JF Li, B Ren, ZQ Tian, Chem. Soc. Rev. 2008, 37, 1025

Electrochemical CV and SERS of Benzyl Chloride on Silver Electrodes



Cyclic voltammetry of PhCH2Cl, 5 mM in 0.1 M TEAP + CH3CN, at a Ag electrode (2 mm diameter) and a scan rate of 0.2 Vs^{-1}.



Potential dependent SERS spectra of $PhCH_2Cl$ on Ag electrode, excited by 633 nm

J. Am. Chem. Soc. 2010, 132, 9534-9536.

Computational details

Cluster Model: Molecule-M_n; M_n – Molecule – M_n (M = TM)

DFT: B3LYP, PW91PW91, …

Basis set: LANL2DZ (Ag)/

6-311+G(d,p)(C,N,H,S)

→ Optimized structure

→ Bonding analysis

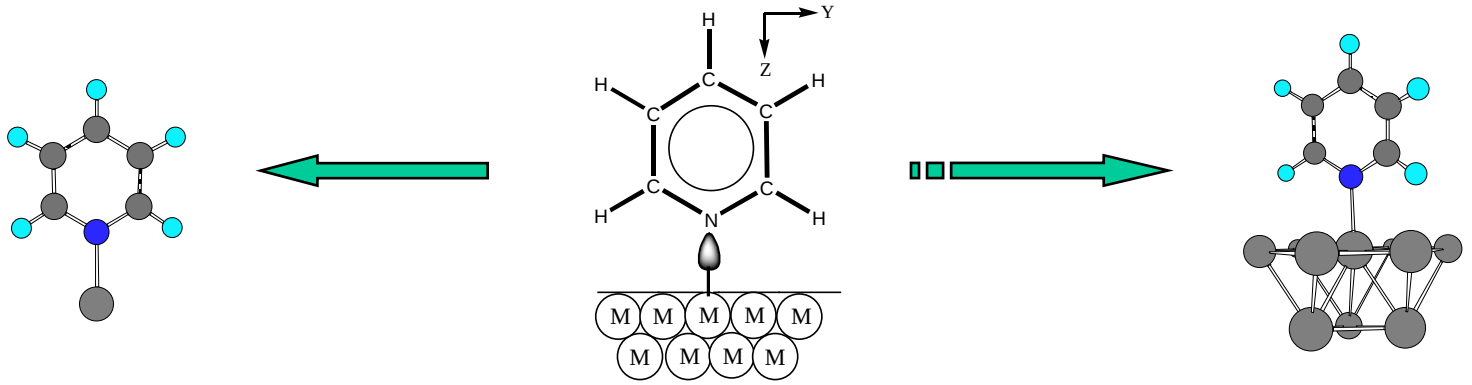
Scaled Quantum Mechanics force field method (SQMF)]

Calculations of Raman Intensity:

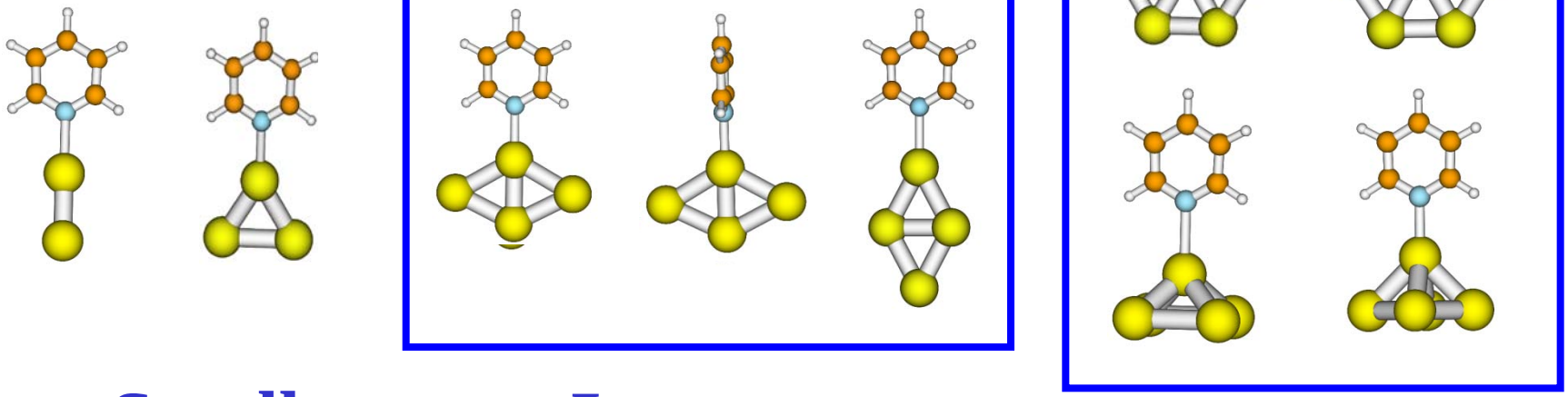
$$I_i^R = \frac{h}{8\pi^2 c\tilde{\nu}_i} \cdot \frac{\left(\tilde{\nu}_0 - \tilde{\nu}_i\right)^4}{45\left[1 - \exp\left(-hc\tilde{\nu}_i / k_B T\right)\right]} \left(45\bar{\alpha}_i'^2 + 7\gamma_i'^2\right)$$

Non-resonance, pre-resonance, and resonance cases

Metallic Cluster Modeling: Size effect



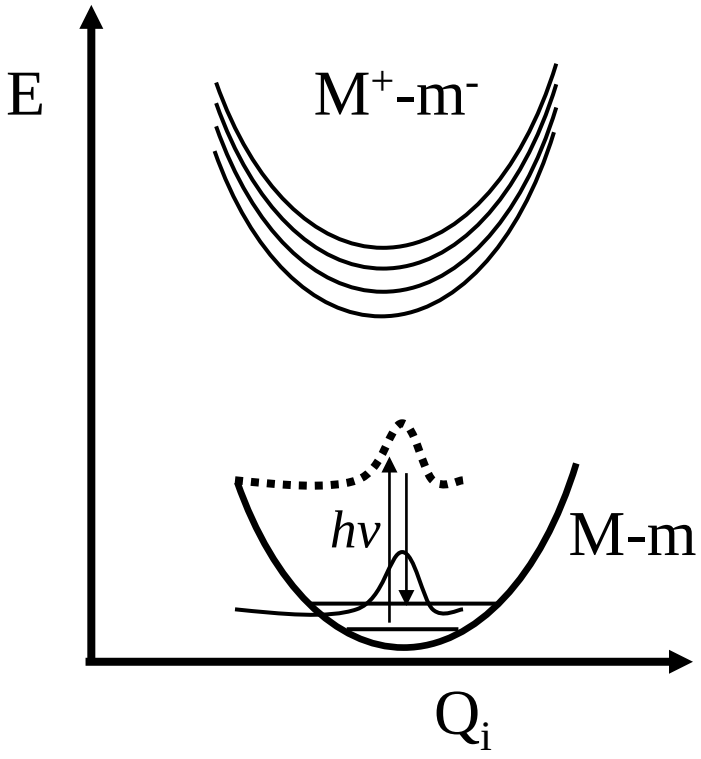
M = Cu, Ag, Au, TM



Small → **Large**

SERS Intensity: Raman scattering processes

Schrödinger Equation: H = T + V, V=V(R) **Vibrational peaks**



Raman Intensity:

$$I_{Raman} \propto \left(\frac{d\sigma}{d\Omega}\right)_k$$

$$= \frac{h}{8\pi^2 c\tilde{\nu}_k} \frac{2\pi^4(\tilde{\nu}_i - \tilde{\nu}_k)^4}{45} S_k \left[1 - \exp\left(-\frac{hc\tilde{\nu}_k}{kT}\right)\right]^{-1}$$

$$S_k = 45\left(\frac{d\alpha}{dQ_k}\right)^2 + 7\left(\frac{d\gamma}{dQ_k}\right)^2$$

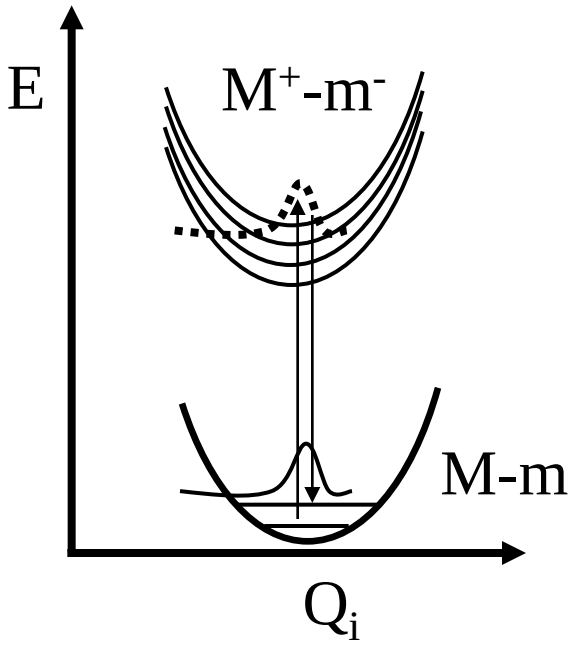
$$\bar{\alpha}' = \frac{1}{3}\left[\left(\frac{\partial\alpha_{xx}}{\partial Q}\right)_0 + \left(\frac{\partial\alpha_{yy}}{\partial Q}\right)_0 + \left(\frac{\partial\alpha_{zz}}{\partial Q}\right)_0\right]$$

$$\gamma'^2 = \frac{1}{2}\left\{\left[\left(\frac{\partial\alpha_{xx}}{\partial Q}\right)_0 - \left(\frac{\partial\alpha_{yy}}{\partial Q}\right)_0\right]^2 + \left[\left(\frac{\partial\alpha_{yy}}{\partial Q}\right)_0 - \left(\frac{\partial\alpha_{zz}}{\partial Q}\right)_0\right]^2 + \left[\left(\frac{\partial\alpha_{xx}}{\partial Q}\right)_0 - \left(\frac{\partial\alpha_{zz}}{\partial Q}\right)_0\right]^2 + 6\left[\left(\frac{\partial\alpha_{xz}}{\partial Q}\right)_0^2 + \left(\frac{\partial\alpha_{yz}}{\partial Q}\right)_0^2 + \left(\frac{\partial\alpha_{xy}}{\partial Q}\right)_0^2\right]\right\}$$

SERS Intensity: Resonance Raman Scattering

Kramers-Heisenberg-Dirac Dispersion Equation

$$\alpha_{\rho,\sigma} = \sum_{K \neq I,F} \left[\frac{\langle I|\mu_\sigma|K\rangle\langle K|\mu_\rho|F\rangle}{E_K - E_I - \hbar\omega_0 + i\Gamma_K} + \frac{\langle I|\mu_\rho|K\rangle\langle K|\mu_\sigma|F\rangle}{E_K - E_F + \hbar\omega_0 + i\Gamma_K} \right]$$



$$I_{a1_i,a0_i}(V_{app}) = s_i \left(\frac{2\beta_i'}{\beta_i + \beta_i'} \right)^2 \left| M_{am}(2) M_{ma}(1) \right|^2$$

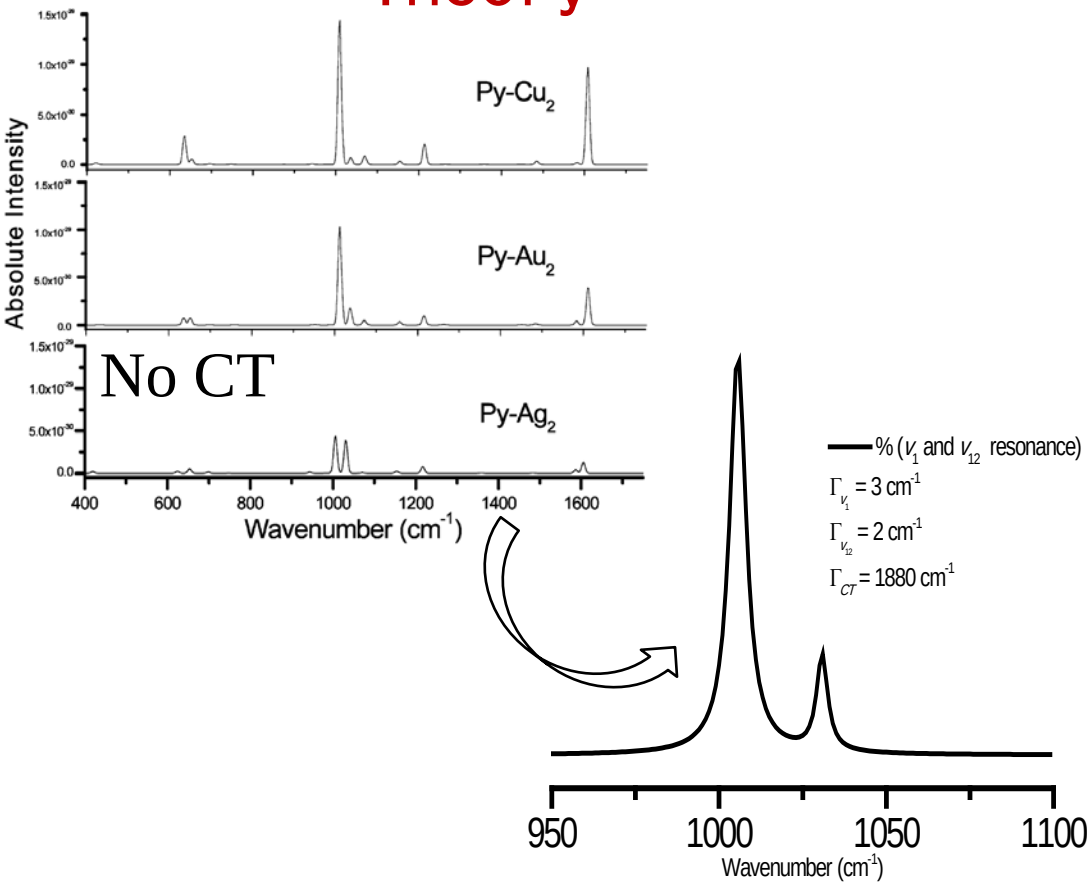
$$\times \left| \int_0^\infty dt \frac{\left(e^{-\lambda_i'} - 1\right)}{1 + e^{-\lambda_i'} \left(\beta_i - \beta_i'\right)/\left(\beta_i + \beta_i'\right)} \times \exp\left[-\Gamma_{m,n} t + it \left(\omega_1 + a\left(\omega_{m,n}(0) + \frac{e}{h} V_{app} \right) + \frac{1}{2} \sum_i \omega_i \right) \right] \prod_i G_i(t) \right|^2$$

$$f_{CE} = \frac{\sum_{n=1}^{2} \sum_{\rho,\sigma} \left| \alpha_{\rho\sigma,n} \right|^2}{b^2 (v+1) \left(\frac{\partial \alpha}{\partial Q} \right)^2} \sim 10 - 10^3 \qquad b^2 = \frac{h}{8\pi^2 \omega}$$

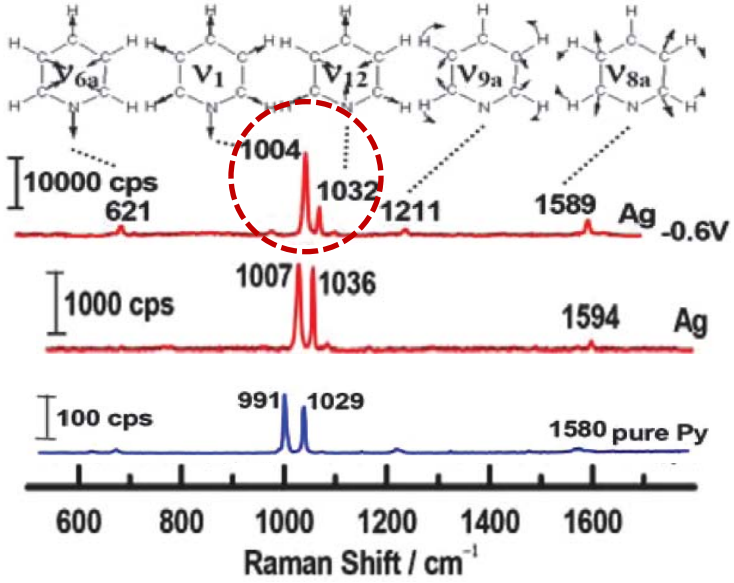
D. Wu, et al., Spectrochim. Acta A, 2004, 60, 137;J. Chem, Phys. 2005, 122, 094719

Charge transfer mechanism of pyridine/Ag

Theory



Experiments



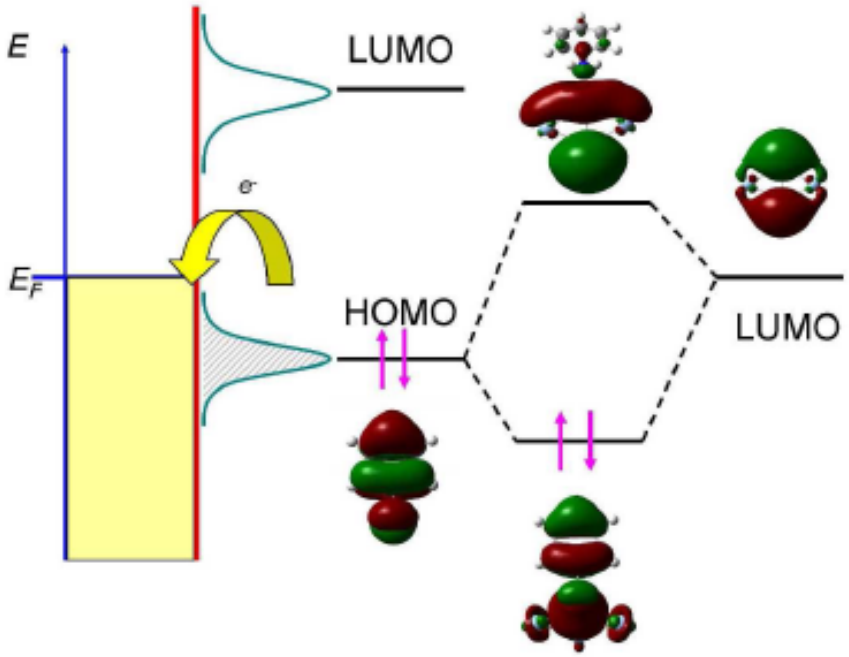
Energy matching between photon and the CT state

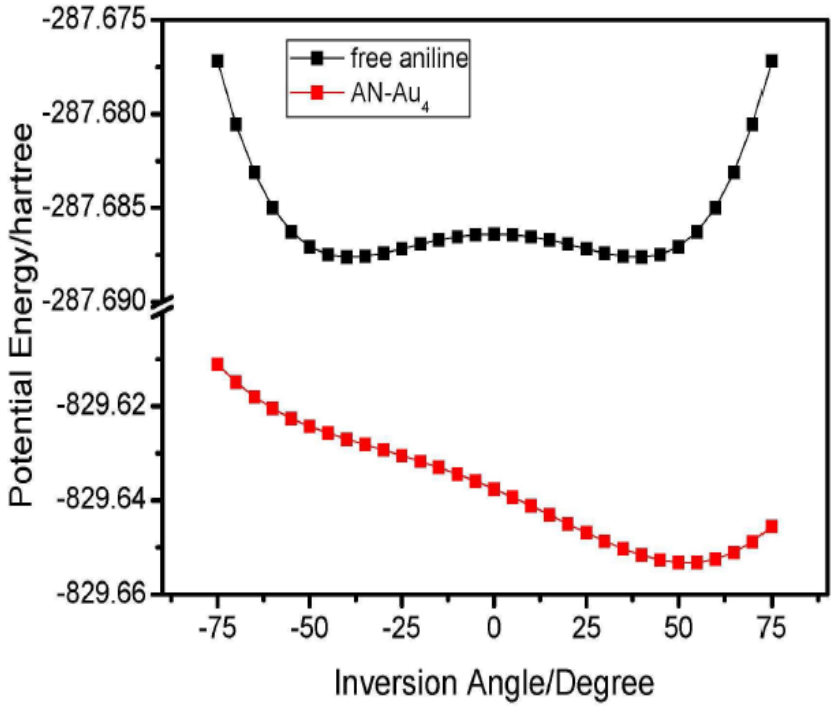
D.Y. Wu*, et al., *Spectrochim. Acta. A*, 2004, 60, 137.

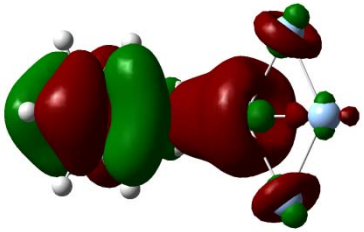
D. Y. Wu*, et al., *J. Phys. Chem. C*, 2008, 112, 4195.

Wagging Vibrations of Amino Group in Adsorbed Aniline

Aniline ⟶ **Benzyl species**



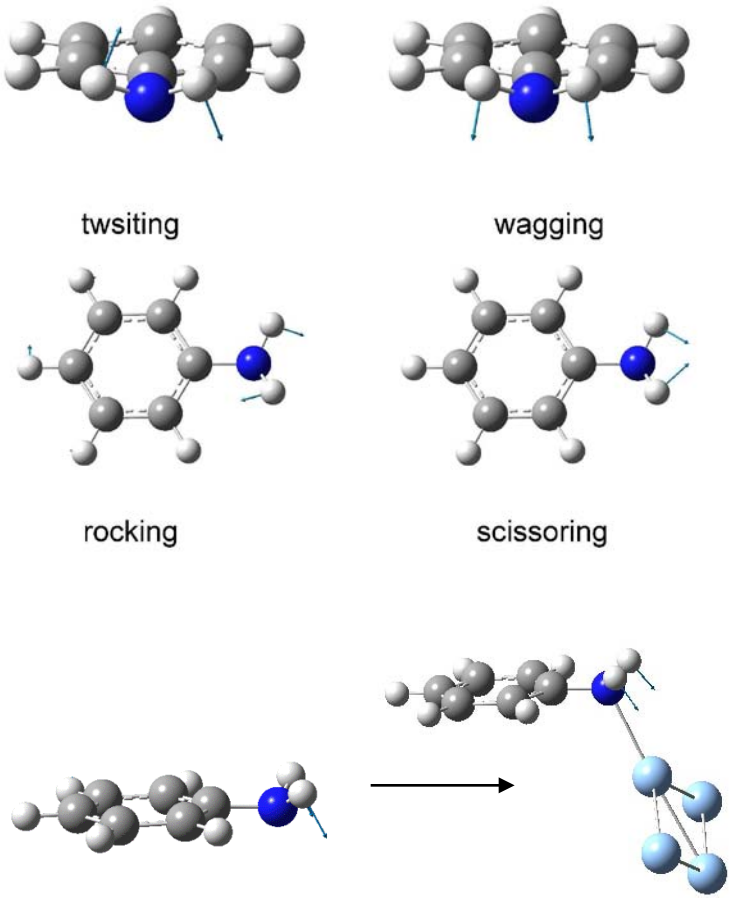


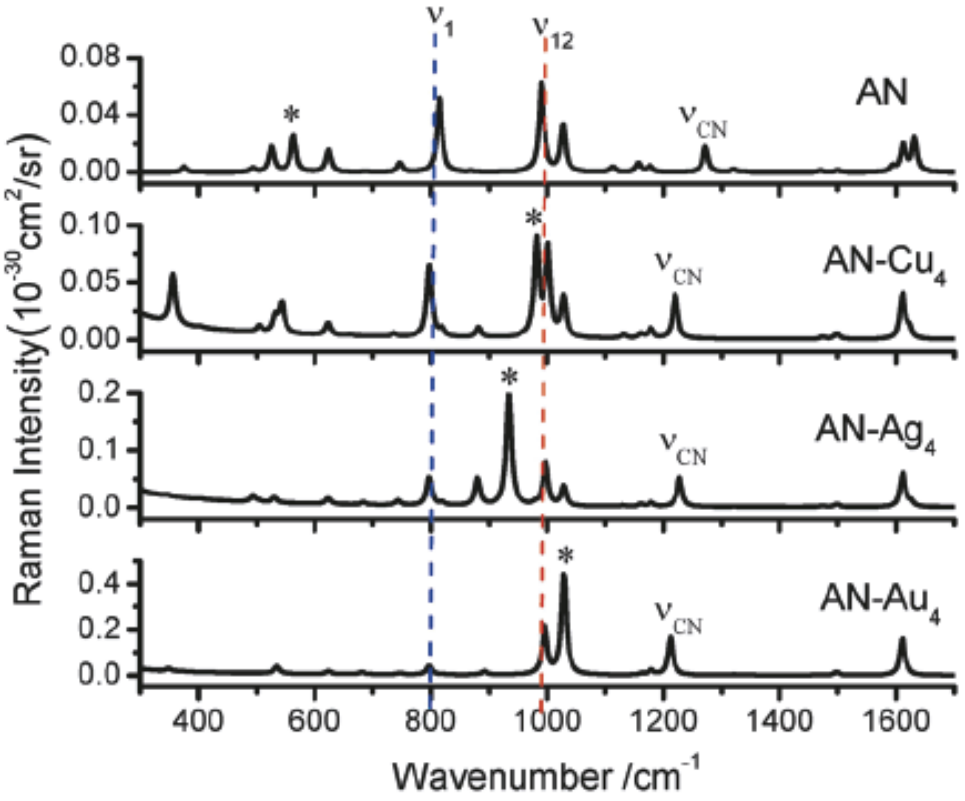


sp^2 – sp^3 hybridization

J. Phys. Chem. C, 2011,115, 4174

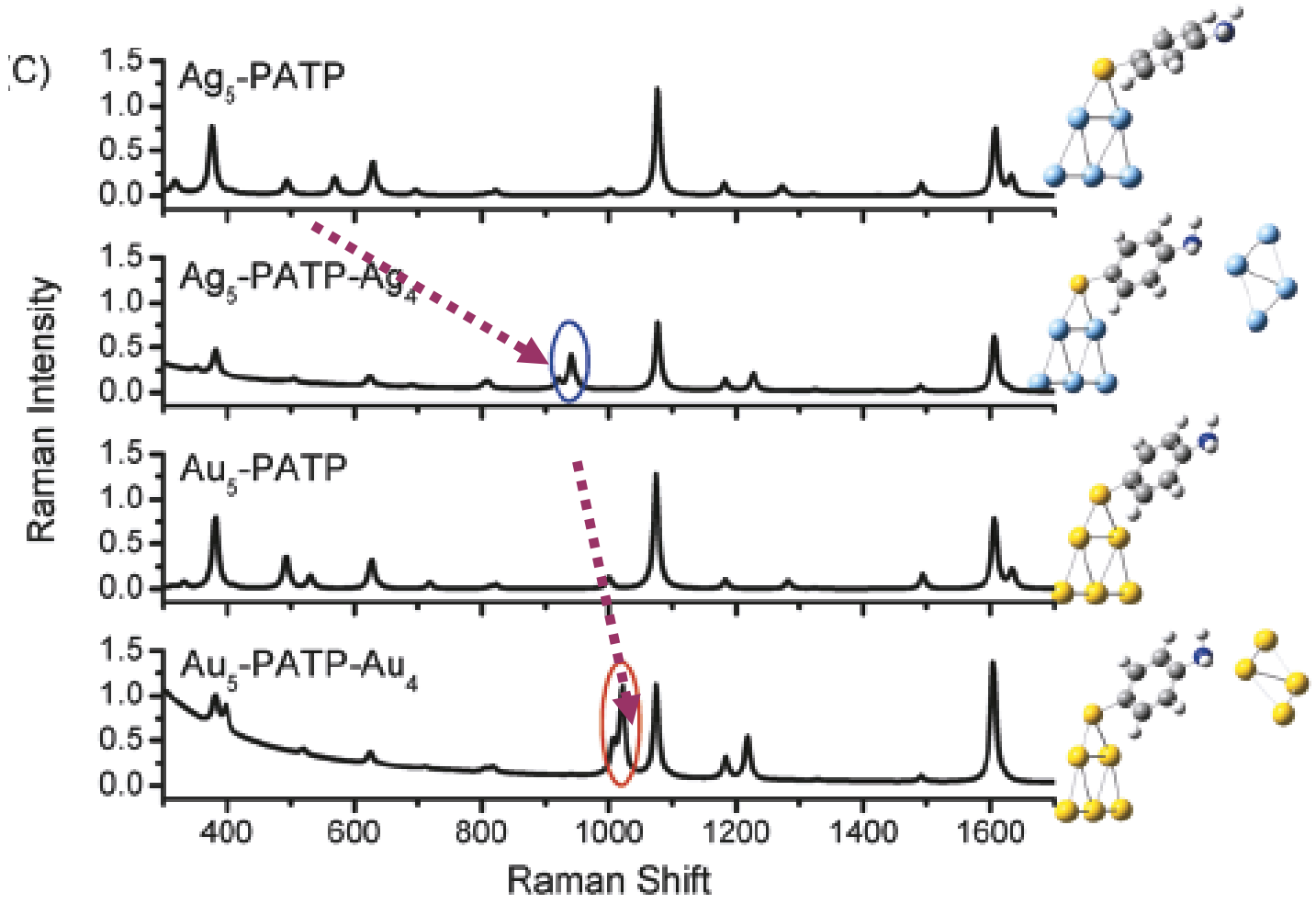
Wagging Vibrations of Amino group in Adsorbed Aniline





J. Phys. Chem. C, 2011,115, 4174

Simulated Raman Spectra of PATP/Ag or Au

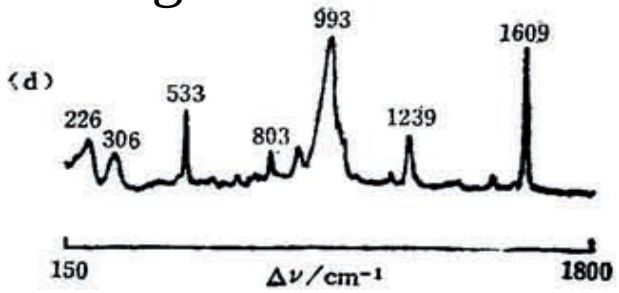


J. Phys. Chem. C, 2011,115,4174-4183

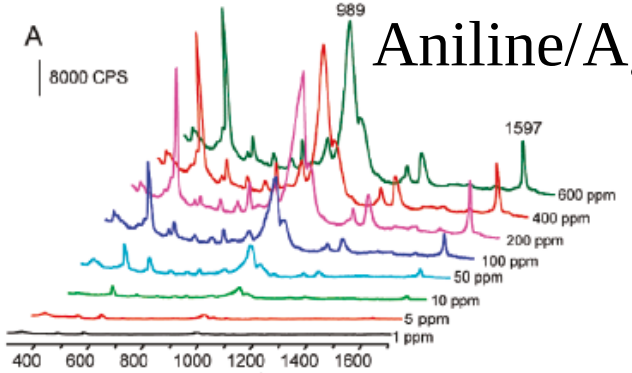
J. Phys. Chem. C, 2009,113,18212-182212

Wagging Vibrations of Aniline and its derivatives/Ag

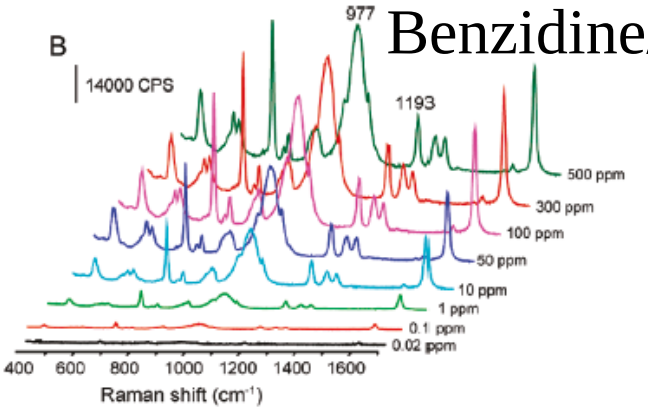
Aniline/Ag Electrode

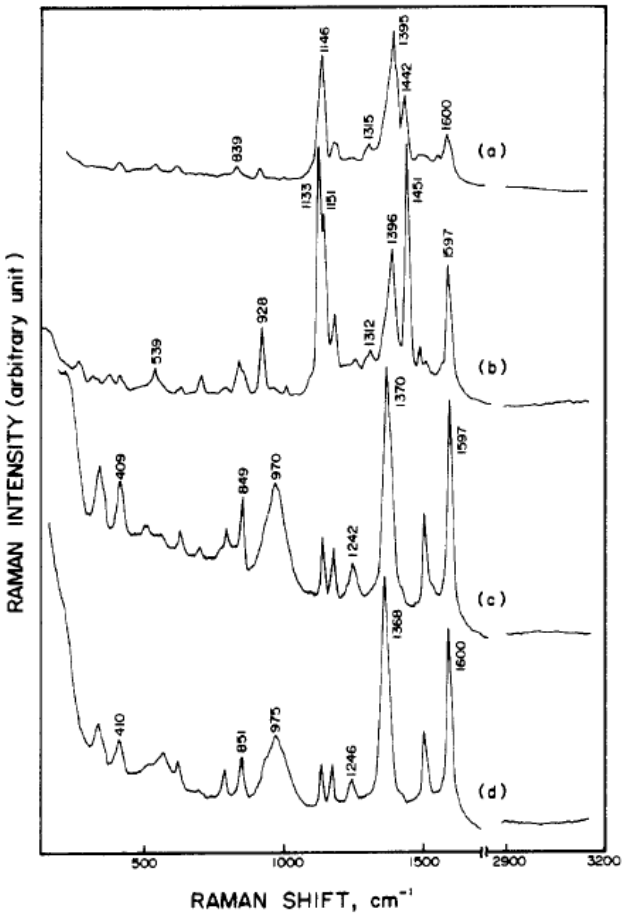


Aniline/AgNP



Benzidine/Ag

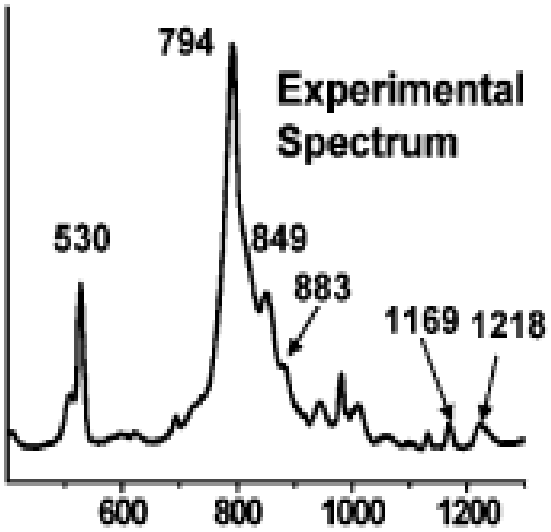


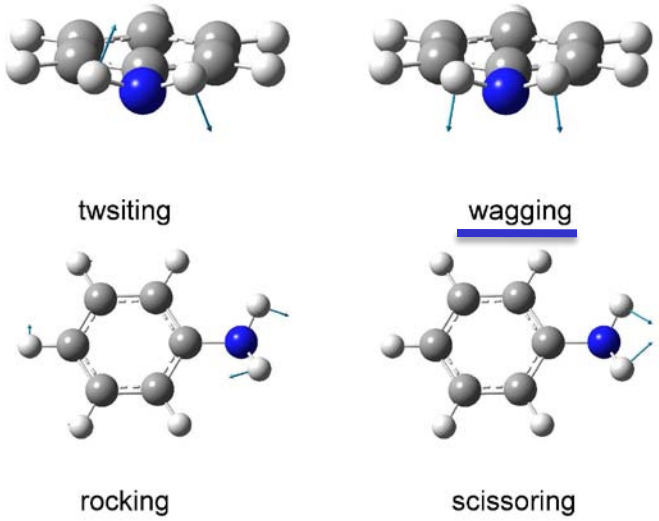


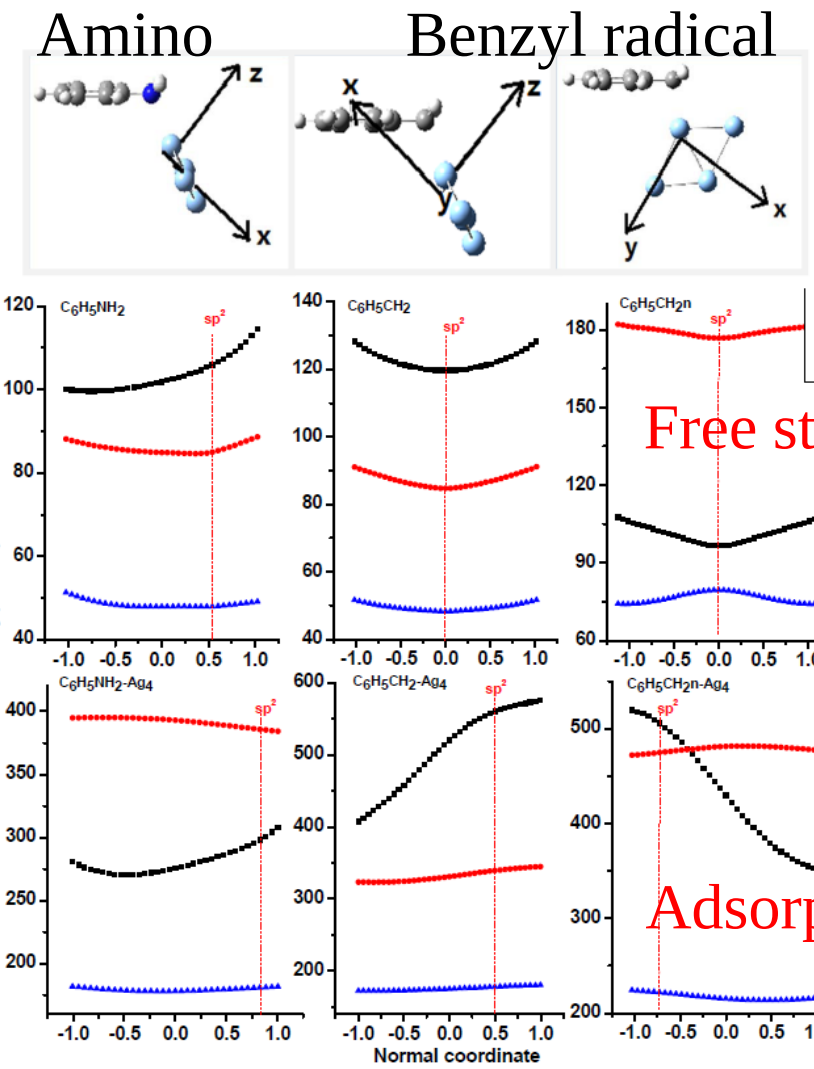
p -Aminobenzoic acid at Ag electrode

Tian, et al, Acta Phys. Chem. Sinica, 1987, 3, 178.
Li, et al, Environment Sci. & Tech., 2011, 45,4046
Kim, et al., J. Phys. Chem., 1990, 94,7576

Benzyl and Amino Groups Adsorbed on Silver Electrodes

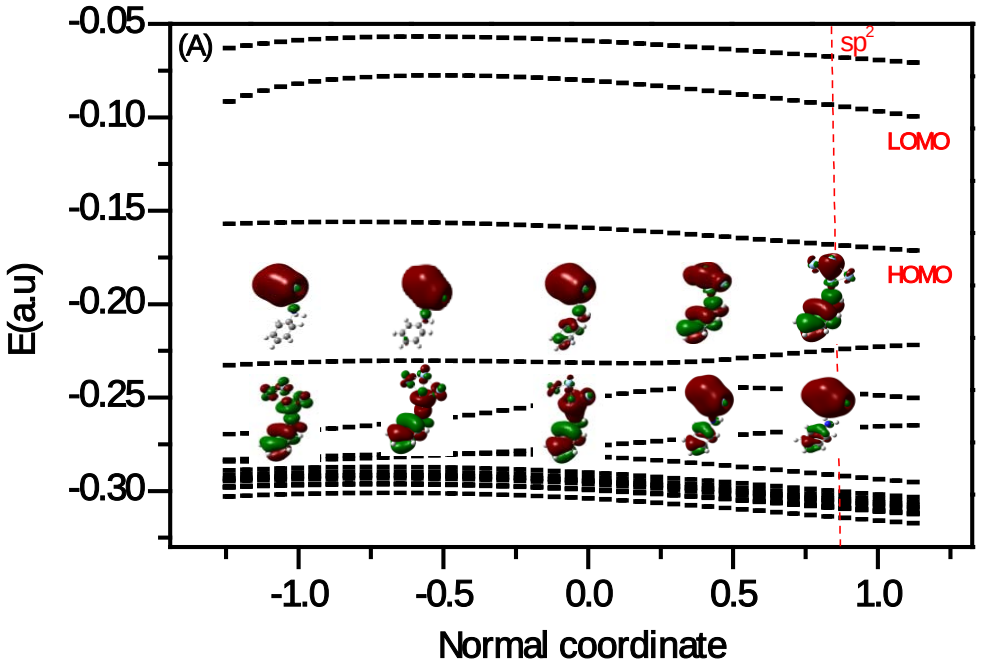


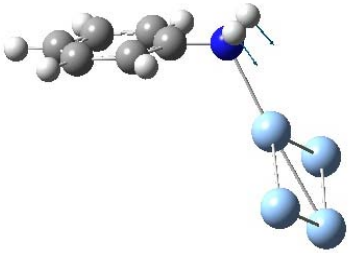


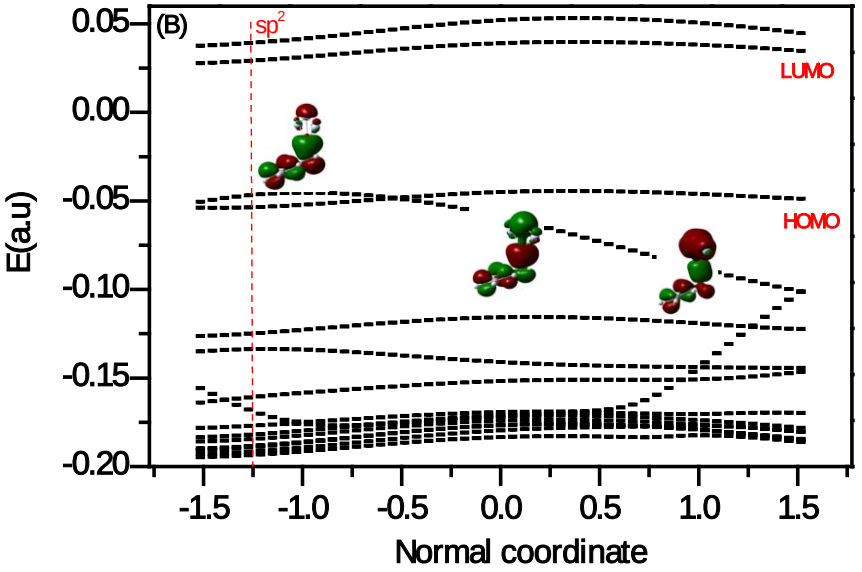


S. Tao, et al., J. Phys. Chem. C., 2013, 117, 18891

Wagging Vibrations of Aniline and Benzyl/Ag





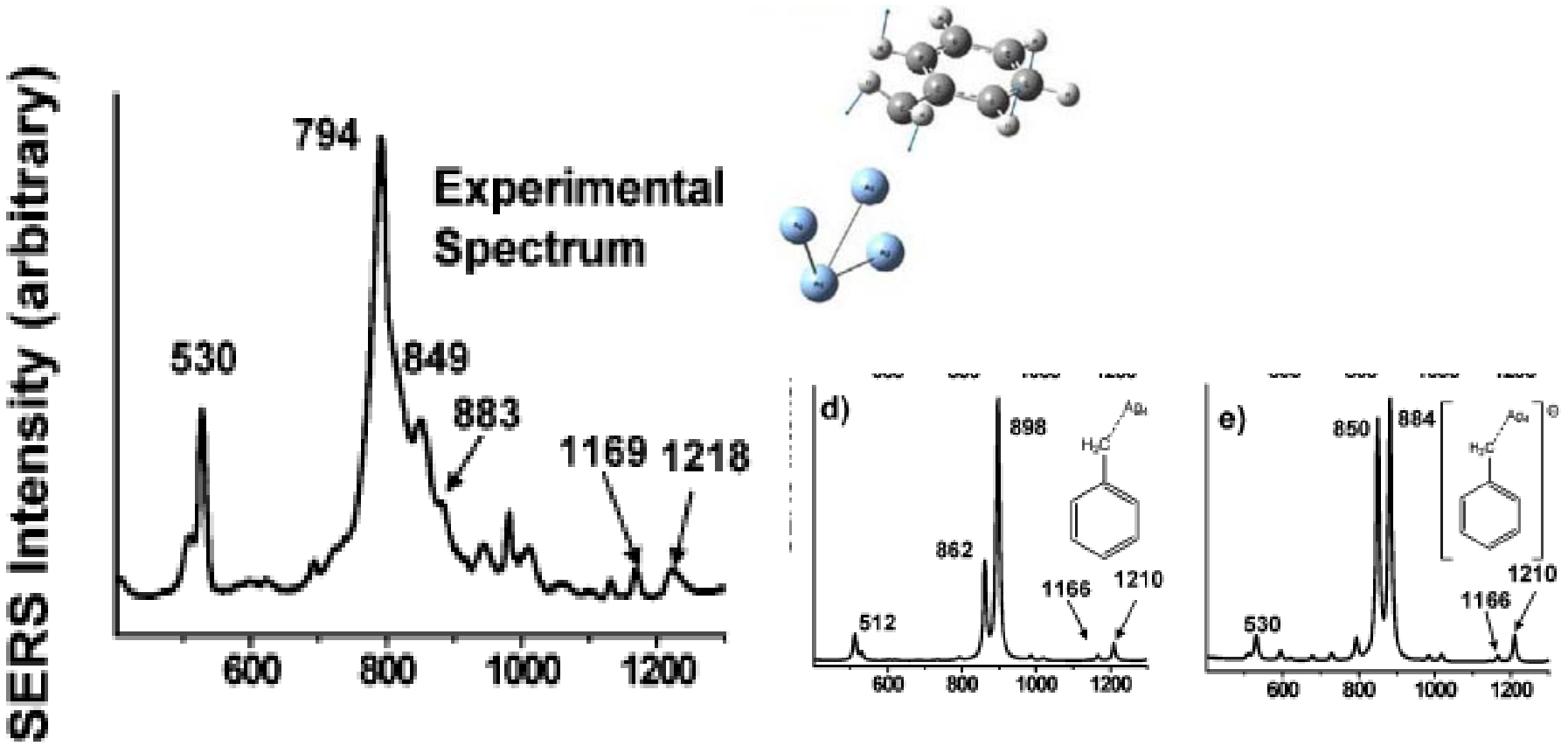


Three factors:

1. Binding strength
2. p-π
3. sp^2-sp^3

J. Phys. Chem. C, 2013,117,18891

Wagging Vibrations of Benzyl/Ag and Aniline/Ag Nanopart.



SERS spectra of Benzyl adsorbed on silver electrodes

J. Am. Chem. Soc. 2010, 132, 9534-9536.

Table 6. Six Derivatives of Polarizability Components α'_{xx}, α'_{yx}, α'_{yy}, α'_{zx}, α'_{zy}, and α'_{zz}, Isotropous Polarizability ($Å^2/amu^{1/2}$), Anisotropic Polarizability, and Raman Scattering Factor (S^R, $Å^4/amu$) of Wagging Mode for Aniline, Benzyl, and Their Metallic Complexes

species	α'_{xx}	α'_{yx}	α'_{yy}	α'_{zx}	α'_{zy}	α'_{zz}	$\bar{\alpha}'$	γ'^2	S^R
C_6NH_2	0.75	0.00	−0.13	−0.10	0.00	0.04	0.22	0.68	6.88
C_6NH_2–Ag_4	2.83	0.00	−0.94	0.02	0.00	0.18	0.69	11.26	100.39
C_6CH_2·	0.00	0.00	0.00	0.57	0.00	0.00	0.00	0.97	6.76
C_6CH_2··Ag_4	16.84	1.25	2.46	0.00	0.00	0.77	6.69	238.72	3686.34
$C_6CH_2^-$	0.00	0.00	0.00	−0.03	2.73	0.00	0.00	22.29	156.01
$C_6CH_2^-$-Ag_4	−17.66	1.06	0.60	−0.35	0.15	−1.00	−6.02	310.71	3806.80

Chemical enhancement factor from chemical bonding 10~500 fold

Summary

(1) Chemical enhancement effect is significantly influenced by charge transfer and chemical binding interaction on metal electrode surfaces.

(2) The p-π conjugation effect, hybridization effect, and the strength of the binding interaction influence on the surface Raman bands of wagging vibrations (Vibrational frequency and Raman intensity).

(3) Quantum chemical calculation is helpful to understand the observed phenomena in surface Raman spectra in Electrochemical interfaces. EC-SERS + QC

Acknowledgements：

Collaborators:

Prof. Zhong-Qun Tian (Xiamen University) EC-SERS Expt

Prof. Bin Ren (Xiamen University) EC-SERS Expt

Prof. Zhi-Lin Yang (Xiamen University) SERS-Surface Plasmon

Prof. S. H. Lin (IAMS, Taipei) Molecular Spectroscopy

Students：

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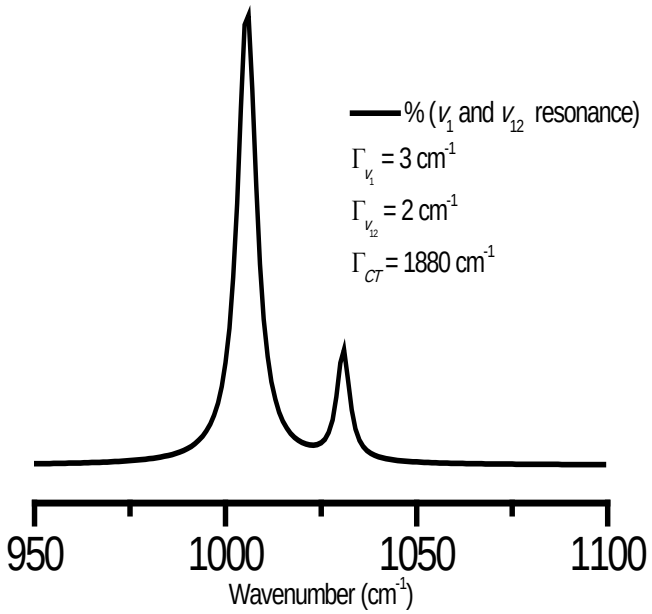
Fund: NSF of China, Basic Research Project of MOST

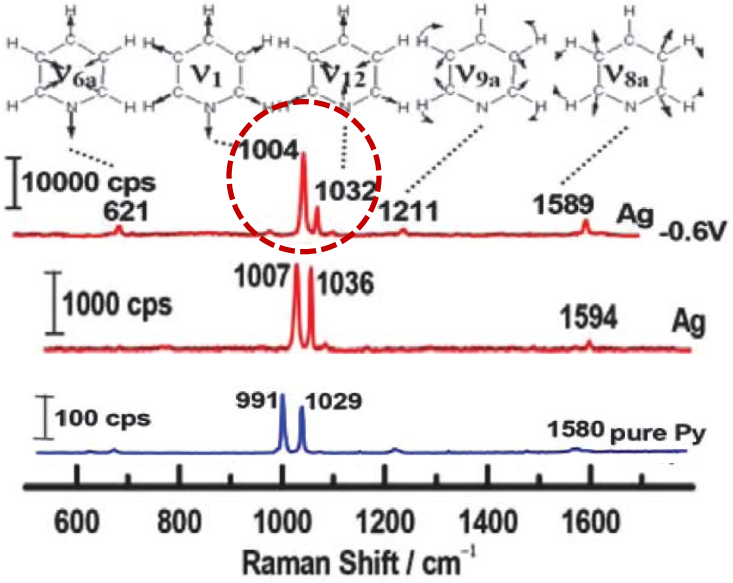
Thanks for your attention!

Charge transfer mechanism of pyridine/Ag

Theory



Experiments

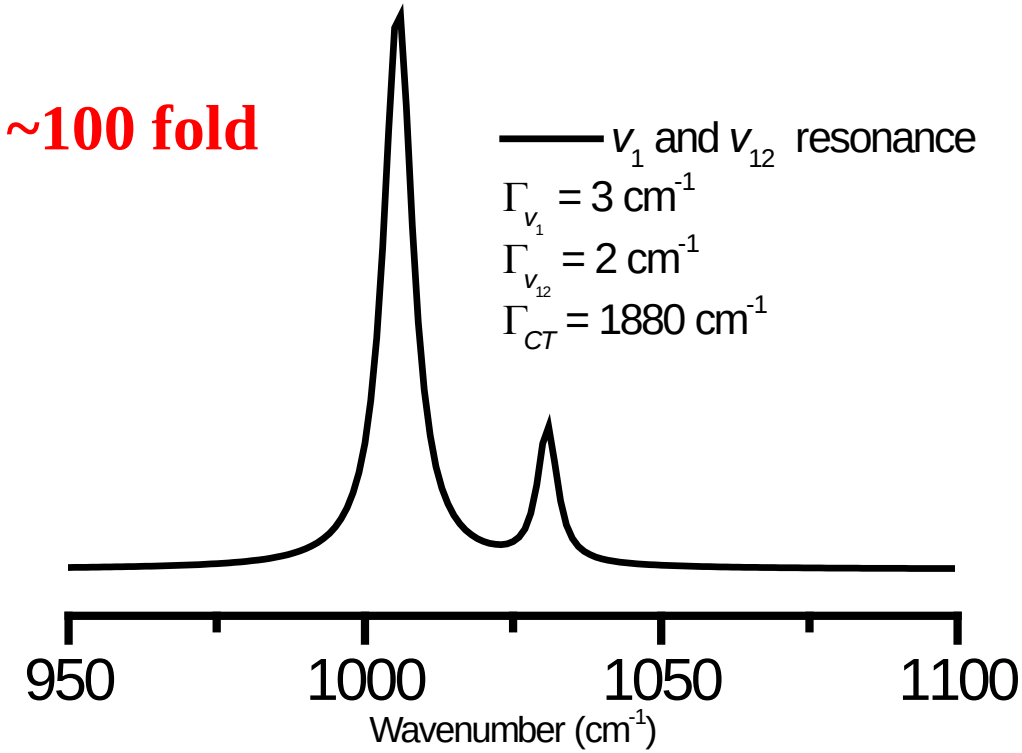


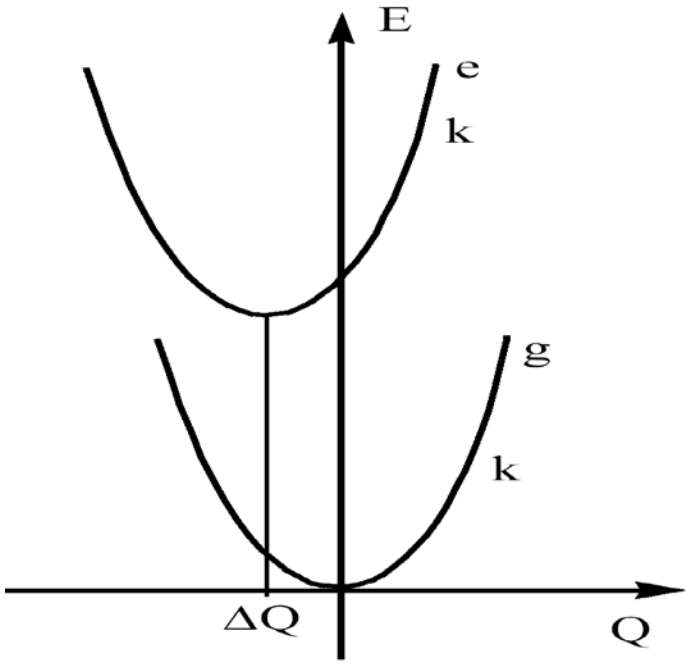
Energy matching between photon and charge transfer state

D.Y. Wu*, et al., *Spectrochim. Acta. A*, 2004, 60, 137.

D. Y. Wu*, et al., *J. Phys. Chem. C*, 2008, 112, 4195.

Charge Transfer Enhancement for Pyridine/Ag





Mode	ν_2	ν_{13}	ν_{20a}	ν_{8a}	ν_{19a}	ν_{9a}	ν_{18a}	ν_{12}	ν_1	ν_{6a}
s	0.000	0.000	0.001	0.288	0.021	0.339	0.052	0.035	0.309	0.152
Ground state	3097.2	3076.5	3067.2	1605.4	1485.4	1217.2	1071.7	1030.8	1005.6	623.9
Excited state	3054.8	3100.5	3077.9	1579.0	1435.3	1189.0	985.2	1019.4	937.6	613.8