

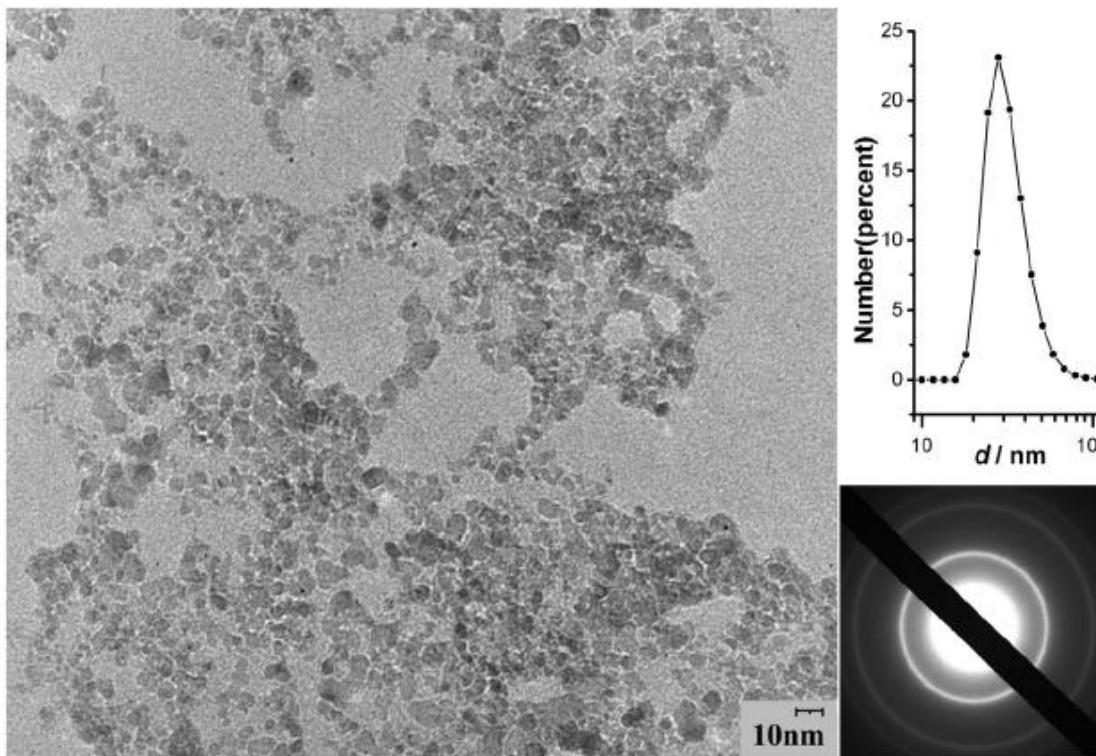
# **MOLECULAR PROBES ON DIFFERENT SURFACES: SPECIAL CASES**

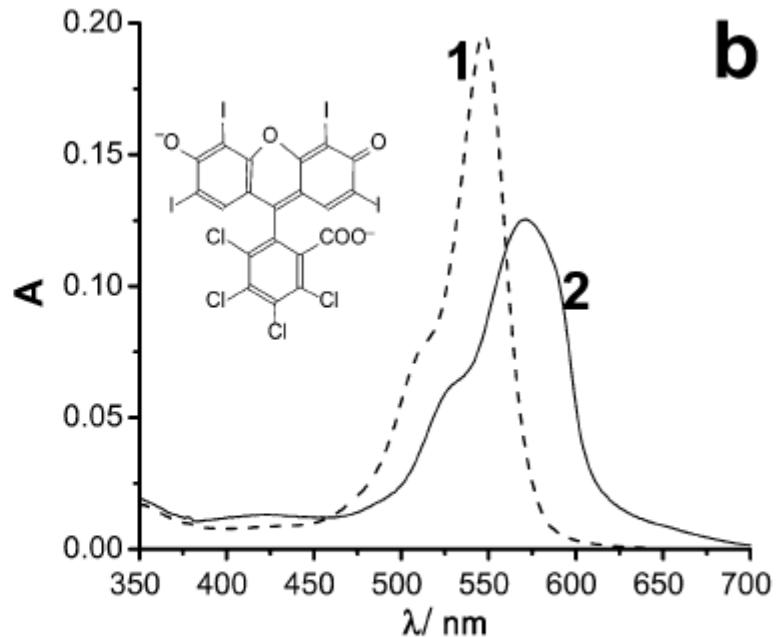
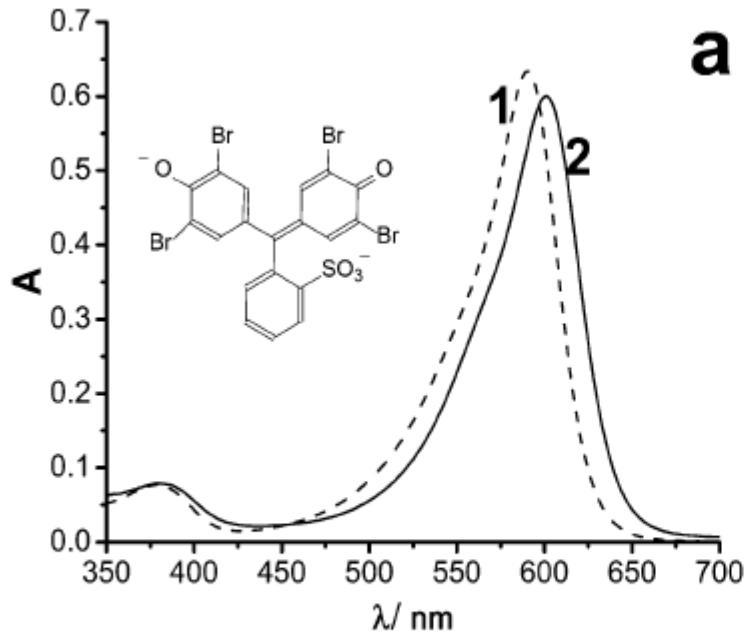


Cite this: *Phys. Chem. Chem. Phys.*,  
2015, 17, 16186

## Colloidal properties and behaviors of 3 nm primary particles of detonation nanodiamonds in aqueous media†

N. O. Mchedlov-Petrossyan,<sup>\*a</sup> N. N. Kamneva,<sup>a</sup> A. I. Marynin,<sup>b</sup> A. P. Kryshtal<sup>c</sup> and E. Ōsawa<sup>d</sup>





Bromophenol blue (a) and rose Bengal B (b) in water (1) and in ND 0.048% solution (2).

**Table 2** The coagulation points, CCC/mM, of the 0.19% ND hydrosol

Electrolyte	CCC	<i>z</i> of the anion	CCC <sub>NaCl</sub> /CCC
NaCl	2.8	-1	1.00
HCl	5.7	-1	0.49
1/2CaCl <sub>2</sub>	2.4	-1	1.2
NaBr	2.5	-1	1.1
C <sub>16</sub> H <sub>33</sub> N(CH <sub>3</sub> ) <sub>3</sub> Br	1.6	-1	1.75
NaClO <sub>4</sub>	1.8	-1	1.6
KI	0.76	-1	3.7
NaOH	0.27	-1	10
C <sub>8</sub> H <sub>17</sub> SO <sub>3</sub> Na	0.15	-1	19
C <sub>12</sub> H <sub>25</sub> OSO <sub>3</sub> Na	0.039	-1	72
C <sub>14</sub> H <sub>29</sub> OSO <sub>3</sub> Na	0.031	-1	90
C <sub>16</sub> H <sub>33</sub> OSO <sub>3</sub> Na	0.041	-1	68
Na <sub>2</sub> SO <sub>4</sub>	0.17	-2	16
K <sub>3</sub> Fe(CN) <sub>6</sub>	0.014	-3	200
K <sub>4</sub> Fe(CN) <sub>6</sub>	0.0048	-4	583

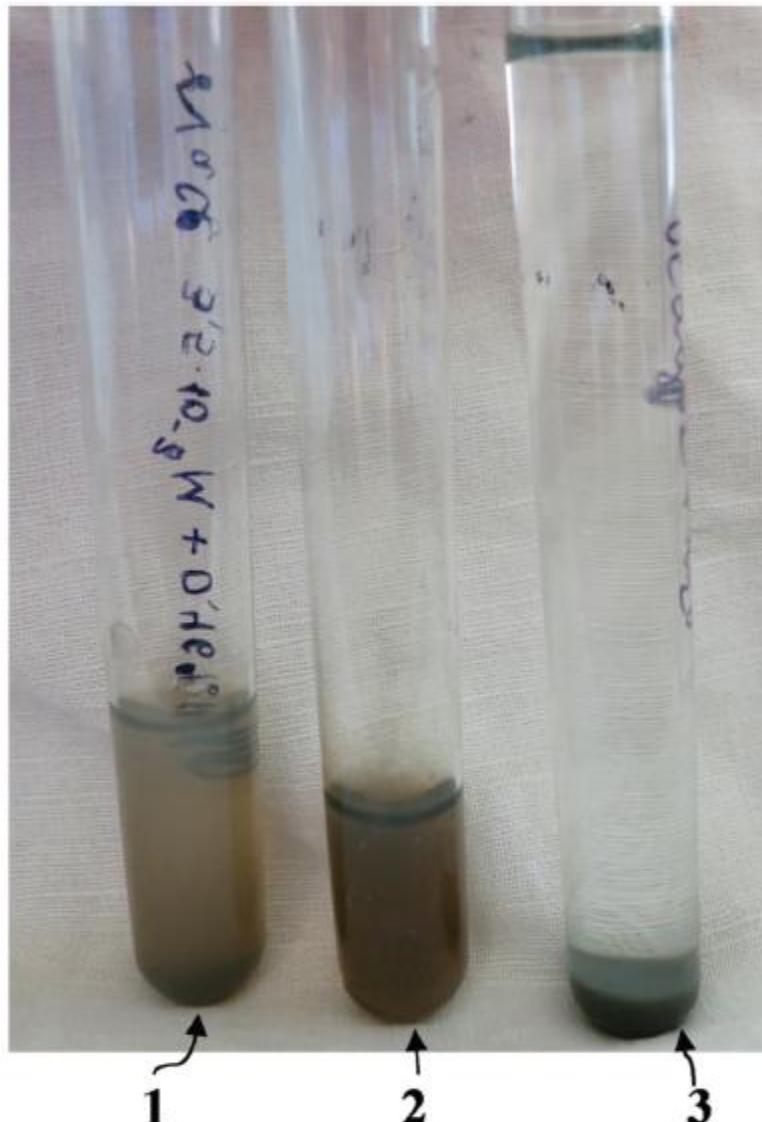


Fig. 10 The results of the peptization procedure: the 0.19% ND hydro-sol, coagulated by NaCl ( $3.5 \times 10^{-3}$  M) and then diluted by water (1); the initial hydrosol of the 0.19% ND (2); the same sol coagulated by NaOH ( $4.0 \times 10^{-4}$  M) and diluted by an even larger portion of water (3). The samples (1) and (3) were shaken after dilution and left to remain 15 min before being photographed; after several days the picture remains unchanged.

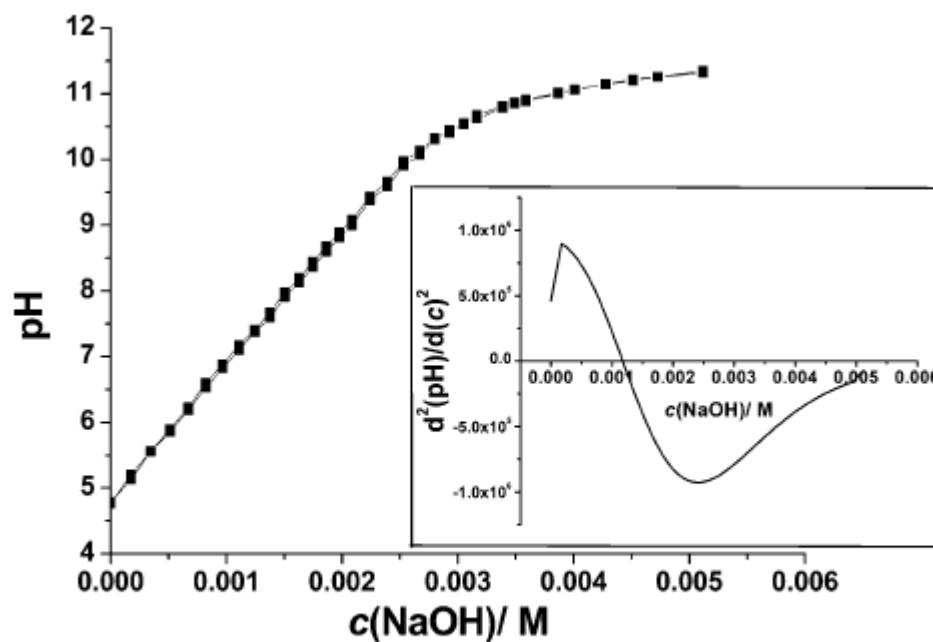
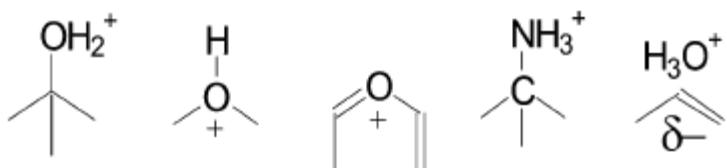


Fig. 11 The titration curve for 2.5% ND hydrosol with 0.00899 M NaOH solution; inset: the second derivative differential curve.

$$pK_a^{\text{app}} = pK_a^i - \frac{\Psi F}{2.303RT}$$

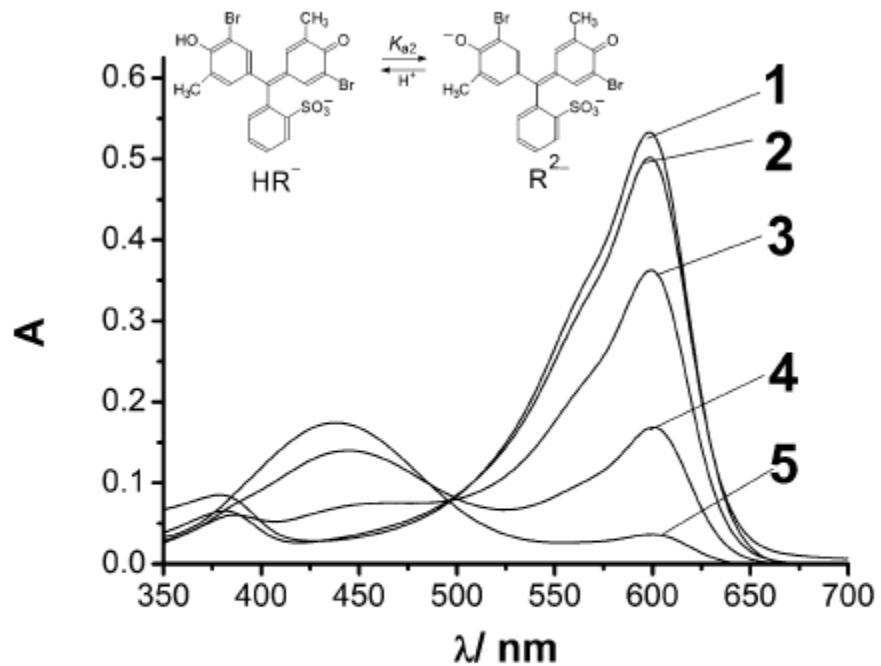


Fig. 12 The spectra of the indicator bromocresol purple at different pH values in 0.024% ND: the spectrum of  $R^{2-}$  with small NaOH addition, well below CCC (1); without HCl additives (2); with HCl additives, pH = 4.10 (3), 3.59 (4), and 3.04 (5).

$$pK_a^{\text{app}} = \text{pH} + \log \frac{[\text{acidic form}]}{[\text{basic form}]}$$

$$\Psi/\text{mV} = 59.16 (\text{p}K_a^i - \text{p}K_a^{\text{app}})$$

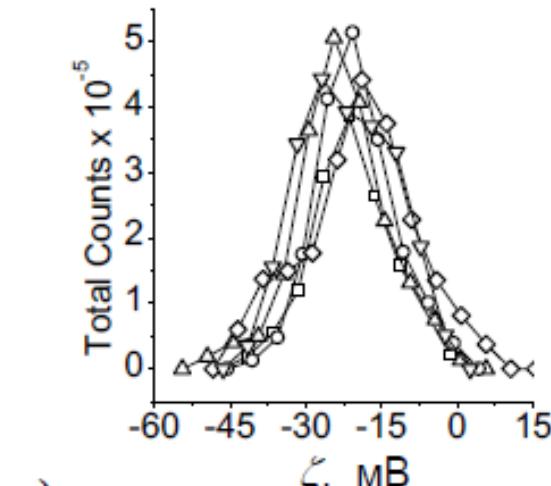
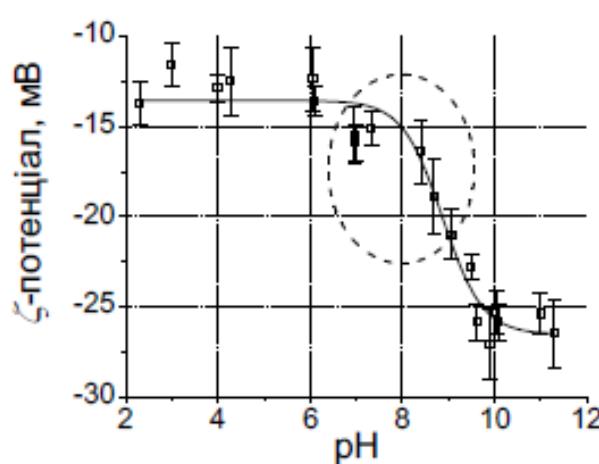
**Table 3** The indices of the apparent ionization constants of the acid–base indicators,  $pK_a^{\text{app}}$ , and the estimates of the interfacial electrical potential,  $\Psi$ , in 0.024% ND sol

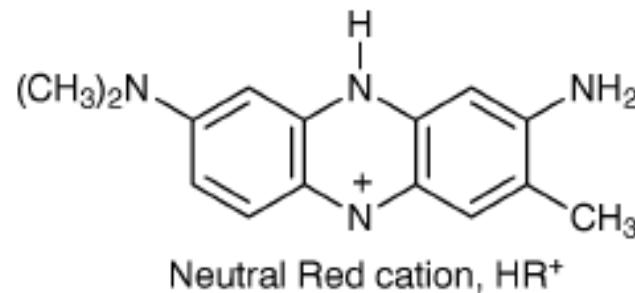
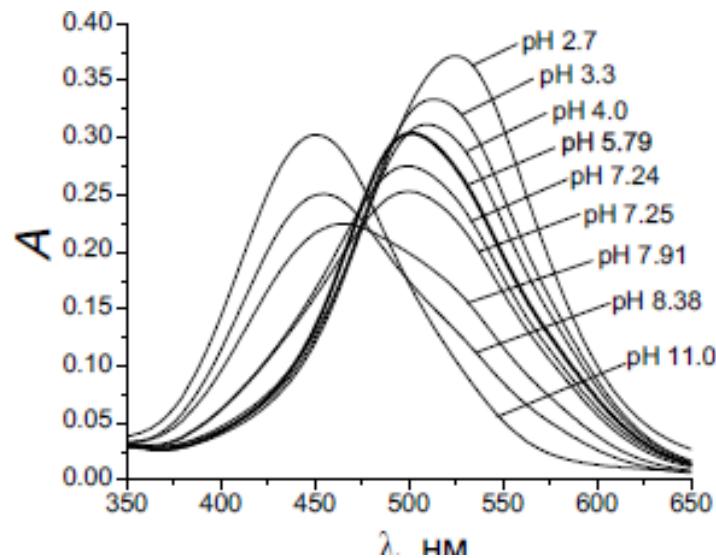
Indicators	$c(\text{HCl}) \times 10^4/\text{M}$				
	10.00	5.01	3.16	2.00	1.00
	$pK_a^{\text{app}}{}^a (\Psi/\text{mV})$				
Bromophenol blue [4.20] <sup>b</sup>	2.35 (109)	—	—	—	—
Bromocresol green [4.90] <sup>b</sup>	3.38 (90)	3.37 (90)	3.34 (92)	3.27 (96)	—
Bromocresol purple [6.40] <sup>b</sup>	4.13 (134)	—	3.81 (153)	—	3.58 (167)
Sulfonefluorescein [6.76] <sup>b</sup>	—	3.96 (166)	3.54 (190)	3.56 (189)	3.62 (186)
Average $\Psi/\text{mV}$	111	128	145	142	176

<sup>a</sup> 25 °C. <sup>b</sup> In the brackets, the  $pK_a^w$  values in water are given.

**Залежність  $\zeta$ -потенціалу агрегатів фулеренолу від pH  
при  $c (C_{60}OH_{(18-22)}) = 0,013$  г/л та  $I = 0,005$  М**

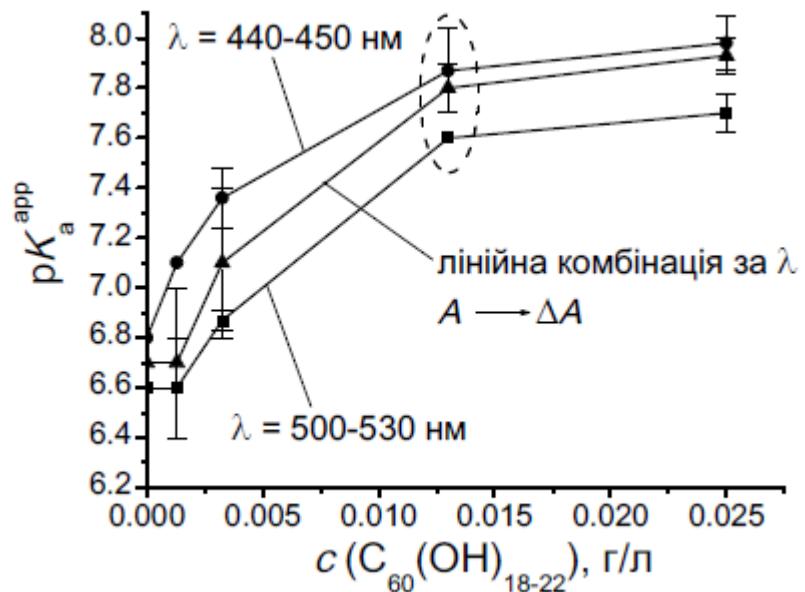
pH	$\zeta$ -потенціал, мВ	pH	$\zeta$ -потенціал, мВ
2,3	$-13,7 \pm 1,2$		<i>продовження</i>
3,0	$-11,6 \pm 1,2$	8,69	$-18,9 \pm 2,1$
4,0	$-12,9 \pm 0,8$	9,07	$-21,0 \pm 1,4$
4,27	$-12,5 \pm 1,9$	9,5	$-22,8 \pm 0,7$
6,07	$-12,4 \pm 1,8$	9,62	$-25,9 \pm 1,0$
6,1	$-13,6 \pm 0,8$	9,91	$-27,1 \pm 2,0$
6,97	$-15,5 \pm 1,6$	10,05	$-25,3 \pm 1,2$
6,99	$-15,9 \pm 1,0$	10,1	$-25,9 \pm 1,0$
7,34	$-15,1 \pm 1,0$	11,0	$-25,4 \pm 1,1$
8,40	$-16,4 \pm 1,8$	11,3	$-26,5 \pm 1,9$





$c(\text{C}_60\text{OH}_{(18-22)})$ , г/л	$pK_a^{\text{app}}$ ( $\lambda$ , нм)	$pK_a^{\text{app}}$ ( $\lambda$ , нм)	$pK_a^{\text{app}}$ за $\Delta A$
0	6,6 (530)	6,8 (450)	6,7
0,0013	6,6±0,2 (530)	7,1 (450)	6,7±0,3
0,0033	6,87±0,04 (528)	7,36±0,12 (450)	7,1±0,3
0,013	7,6 (504)	7,87±0,17 (450)	7,8±0,1
0,025	7,7±0,08 (510)	7,98±0,11 (440)	7,93±0,07

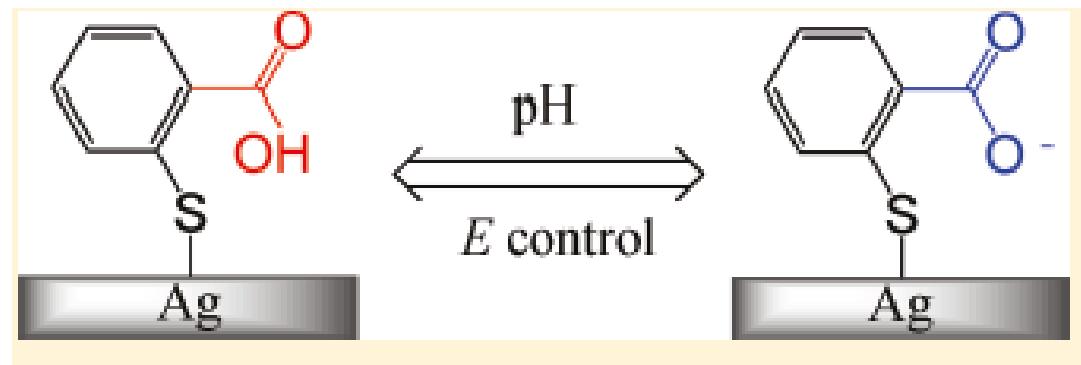
$$\Psi = 59.16(6.7 - 7.9) = -71 \text{ (mV)}$$



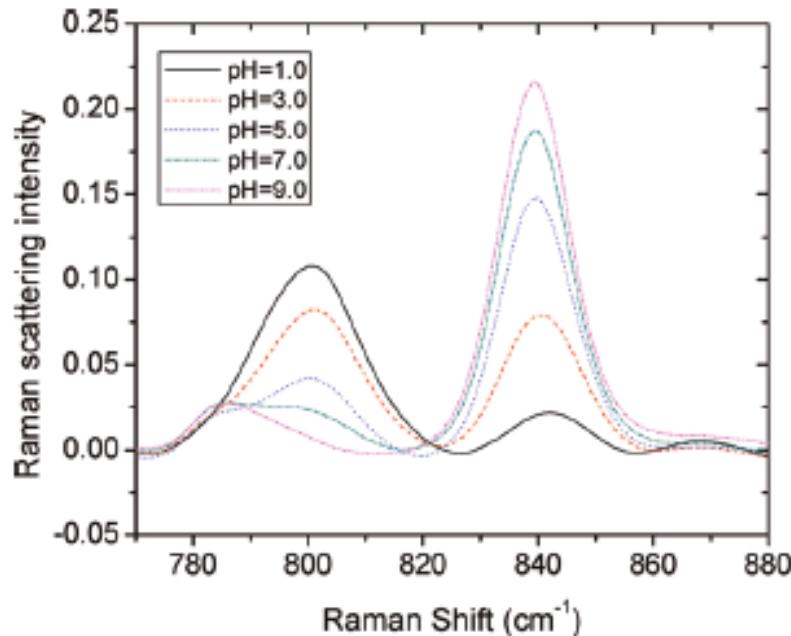
## Surface-Enhanced Raman Spectroscopy Investigation of the Potential-Dependent Acid–Base Chemistry of Silver-Immobilized 2-Mercaptobenzoic Acid

Chaoxiong Ma and Joel M. Harris\*

Department of Chemistry, University of Utah, 315 South 1400 East, Salt Lake City, Utah 84112-0850, United States



$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{\beta}{1 - \beta} + \frac{\overline{E}\beta}{2.303RT}$$



**Figure 3.** SERS spectra of 2-MBA in different solution pH with applied potential =  $-0.4$  V (versus Ag/AgCl).

$$\beta = \frac{[-\text{COO}^-]}{[-\text{COO}^-] + [-\text{COOH}]} = \frac{I_{840}^{\text{rel}}}{I_{840}^{\text{rel}} + I_{800}^{\text{rel}}}$$

$$a_{\text{interface}} = a_{\text{bulk}} \exp(-zF\Phi_0/RT)$$



$$\text{pH}_{\text{interface}} = \text{pH}_{\text{bulk}} + \frac{F}{2.303RT} \Phi_x$$

$$\text{p}K_{\text{a},x} = \text{p}K_{\text{a},0} - \frac{F}{2.303RT} \Phi_x$$

