Surface Structure at the Ionic Liquid-Electrified Metal Interface

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Introduction

1. the structure of room-temperature ionic liquids at the electrified interface

2. Demonstrate that the interfacial region is one ion layer thick.

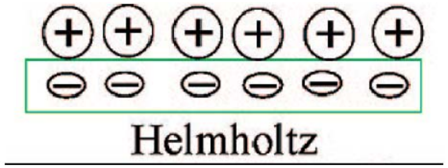
   - The interfacial capacitance
   - The vibrational Stark shift of CO at the interface.

3. Sum frequency generation (SFG) demonstrate

   - An oriented layer of ions does exist at the electrode interface
   - The orientation depends on the surface charge

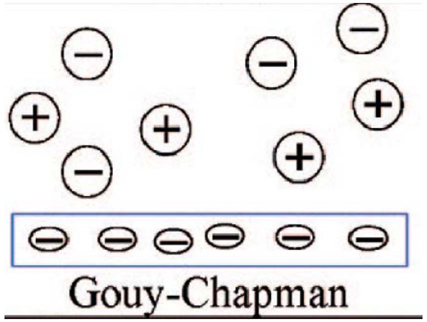
Theory

1. Three common models for the electrochemical interface



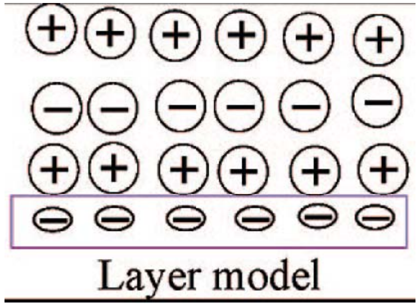
$$\frac{1}{C_\mathrm{d}} = \frac{d}{\epsilon\epsilon_0}$$

C_d : double layer capacitance
ε_0 : permittivity of vacuum
ε : relative permittivity
d: distance



$$\frac{1}{C_\mathrm{d}} = \left(\frac{2\epsilon\epsilon_0 z^2 e^2 n^0}{kT}\right)^{-1/2} \frac{1}{\cosh\left(\frac{ze\varphi_0}{2kT}\right)}$$

φ_0 : potential
n^0 : ion number density



$$\frac{1}{C_\mathrm{d}} = \frac{1}{C_\mathrm{k}} - \frac{\delta}{\epsilon_0\left(1 - \frac{\delta\beta|\xi|}{\epsilon_0}\right)}$$

ξ: charge density on the metal,
$C_\mathrm{k} = \varepsilon\,\varepsilon_0/d$: capacitance of a parallel plate capacitor ;
d: the cation radius,
$\delta^2 = (2\,\varepsilon_0\, kT)/(q^2 c_0(z - 2))$ and $\beta = (\alpha q c_0\,(z - 1))/(2\,\varepsilon_0\, kT)$: functions of the concentration of vacancies c_0,
z: coordination number, q: charge of vacancy, R: polarizability.

2. Sum frequency generation (SFG)

- The chemical information on the functional groups at the surface and how they are oriented.

- A vibrational spectrum of the interfacial molecules of a molecular-level

$$I_{\mathrm{SF}} \propto |\overleftrightarrow{\chi}^{(2)}:E_{\mathrm{vis}}E_{\mathrm{IR}}|^2$$

$$\chi^{(2)} = \chi_{\mathrm{R}}^{(2)} + \chi_{\mathrm{NR}}^{(2)} = \sum_q \frac{NA_q}{\omega\mathrm{IR} - \omega q + i\Gamma} + \chi_{\mathrm{NR}}^{(2)}$$

3. Electrochemistry

(1) Electrochemical impedance spectroscopy (EIS) :

- measure the capacitance →“double layer” thickness

- the potential of zero charge (PZC).

(2) Cyclic voltammetry(CV) :

used to ensure that there are no electrochemical reactions occurring in the potential window of the experiment.

4. Stark Shift

Carbon monoxide displays a dramatic shift in its vibrational frequency as a function of the external electric field known as the vibrational Stark effect

Setup

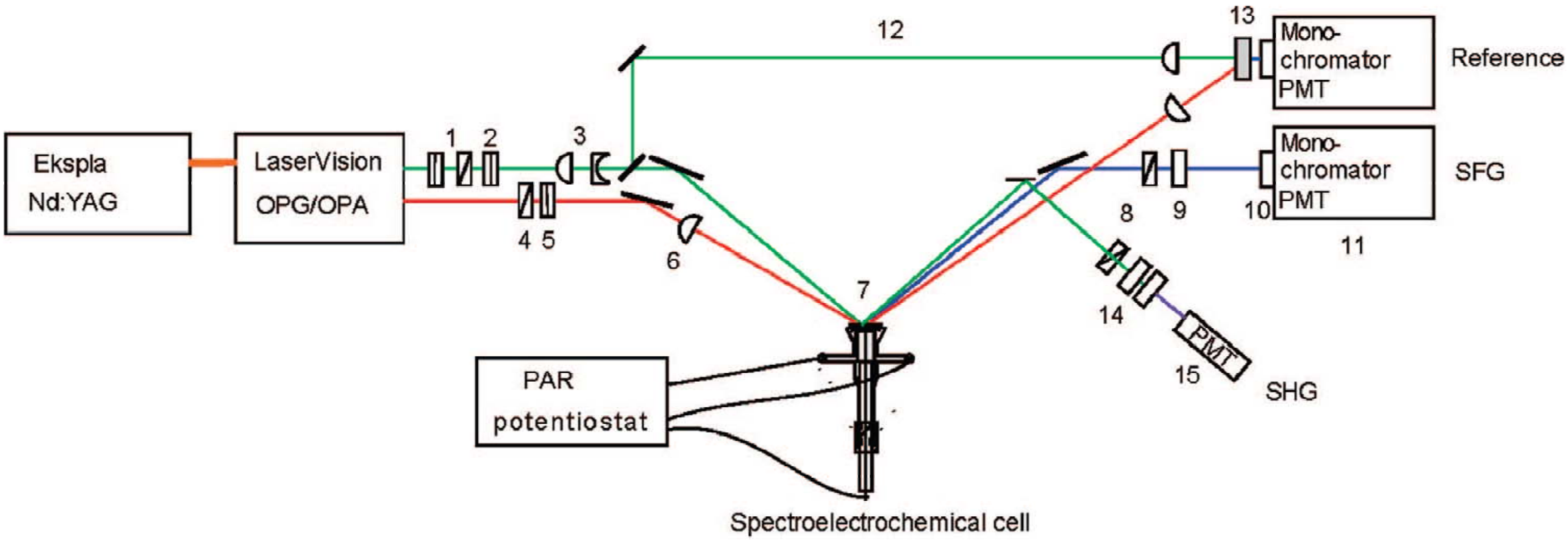


FIGURE 3. Diagram of the picosecond-scanning SFG spectrometer. One part is frequency-doubled to 532 nm. The other part generates infrared light (IR) : (1) attenuator (half-wave plates/polarizer); (2) $\lambda/2$ plate(polarization control); (3) collimating reducing telescope; (4, 5) polarizer/half-wave plate (polarization control); (6) long focal length BaF2 lens (8) analysis polarizer; (9) Kaiser Notch Plus filter; (10) 515 nm short pass filter; (12) reference arm; (13) single-crystal quartz (nonlinear signal reference); (14) 532 nm filters;

Sample & Cell

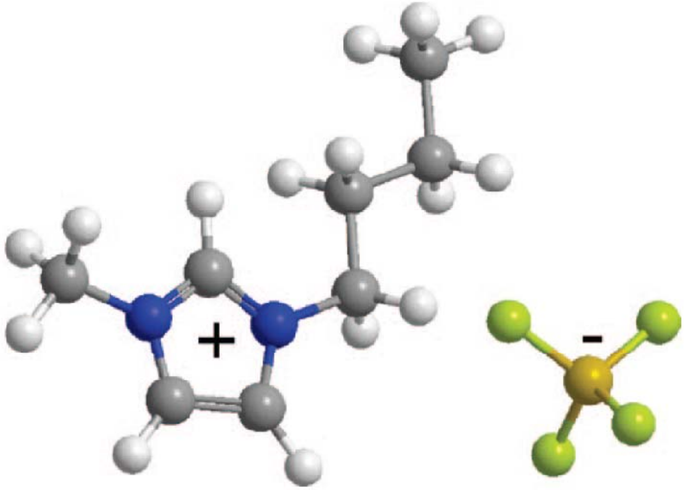


FIGURE 1. Structure of 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF4].

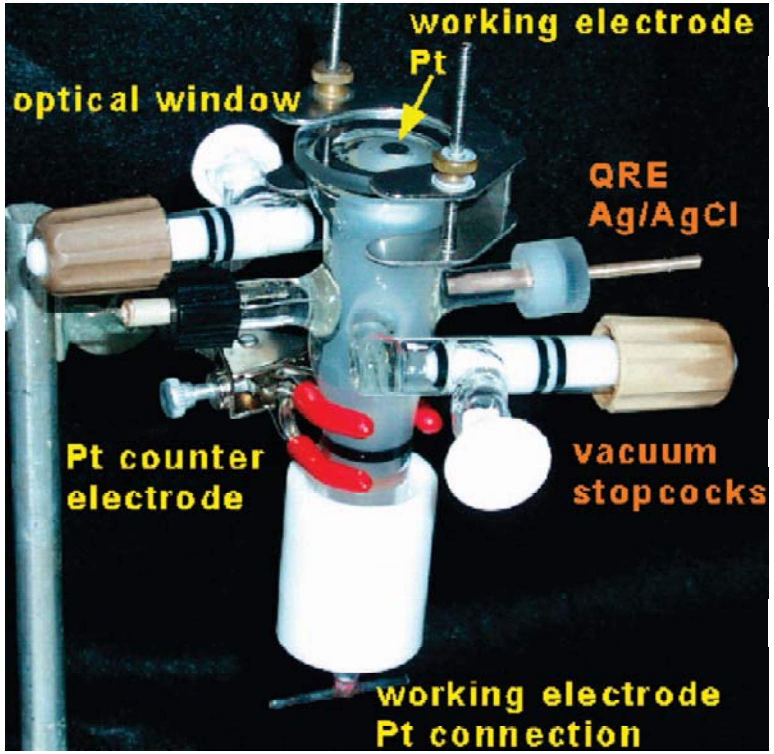
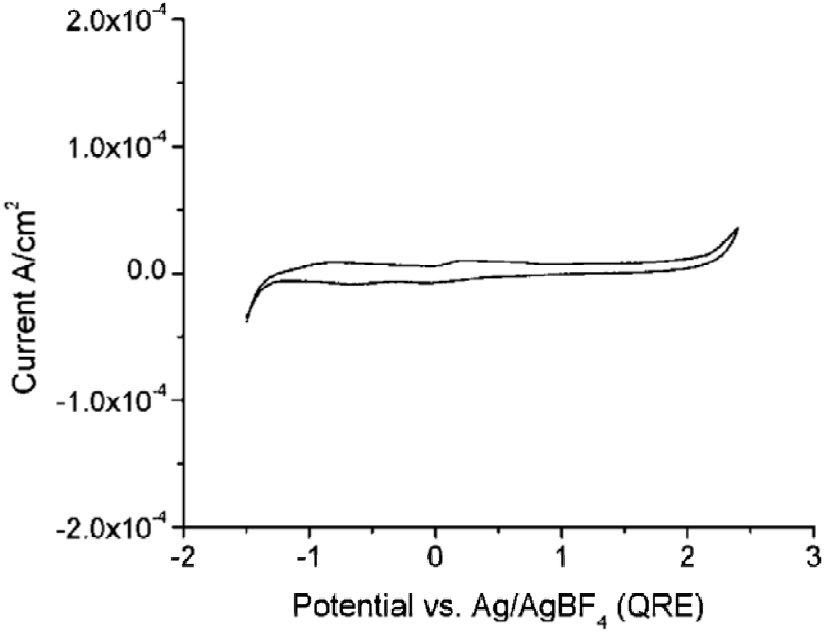
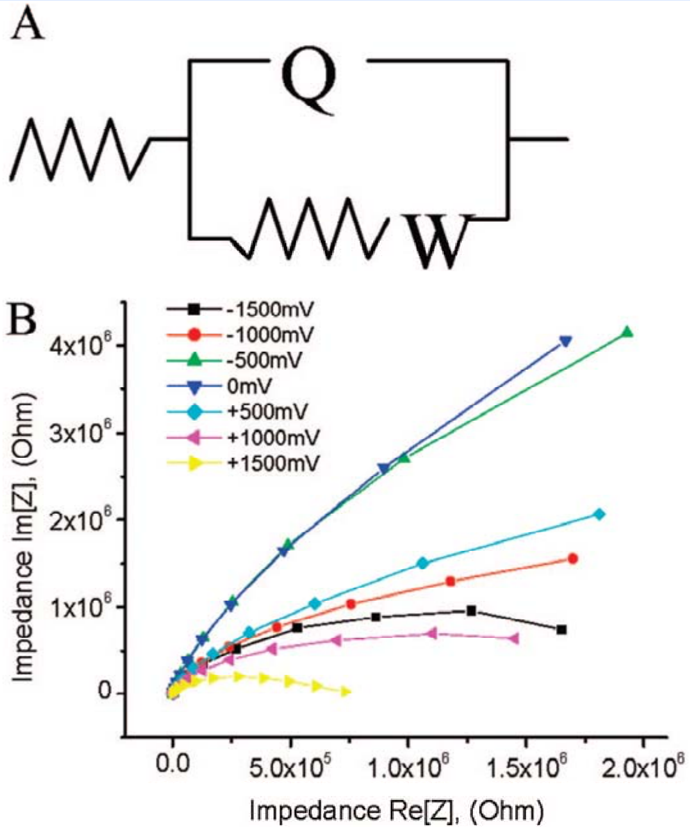


FIGURE 5. Thin layer SFG electrochemistry cell. Cell is able to hold vacuum down to 10-6 Torr.

Result(Electrochemistry)

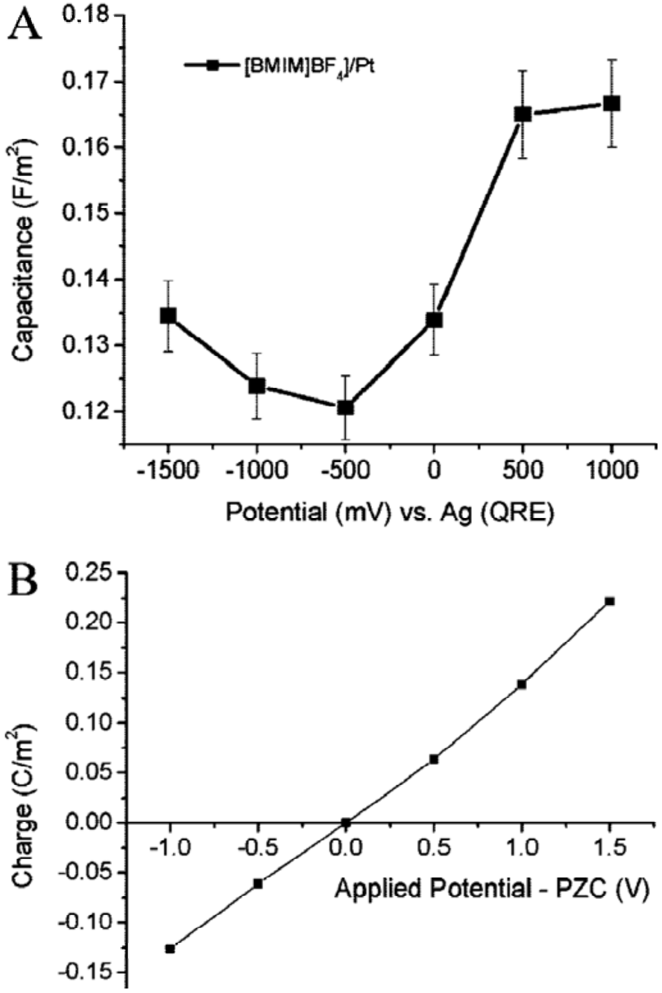




The first resistor corresponds to the solution resistance
Q : the dispersive capacitance related to the double layer
W : the Warburg element for solution diffusion processes

FIGURE 4. Cyclic voltammogram of neat [BMIM][BF4] at 5 × 10-5 Torr. Scan rate 100 mV/s.

FIGURE 6. (A) The equivalent circuit used to model the EIS data and (B) electrochemical impedance spectra of [BMIM][BF4] at the Pt electrode.



$$\frac{1}{C_d} = \frac{d}{\epsilon\epsilon_0}$$

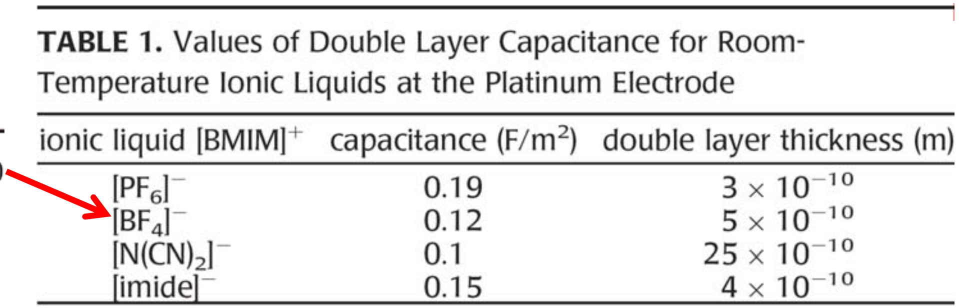


TABLE 1. Values of Double Layer Capacitance for Room-Temperature Ionic Liquids at the Platinum Electrode

ionic liquid $[BMIM]^+$	capacitance (F/m^2)	double layer thickness (m)
$[PF_6]^-$	0.19	3×10^{-10}
$[BF_4]^-$	0.12	5×10^{-10}
$[N(CN)_2]^-$	0.1	25×10^{-10}
$[imide]^-$	0.15	4×10^{-10}

FIGURE 7. (A) Interfacial capacitance vs applied potential for ionic liquid [BMIM][BF4] at 10-5 Torr pressure and (B) Interfacial charge vs potential from PZC.

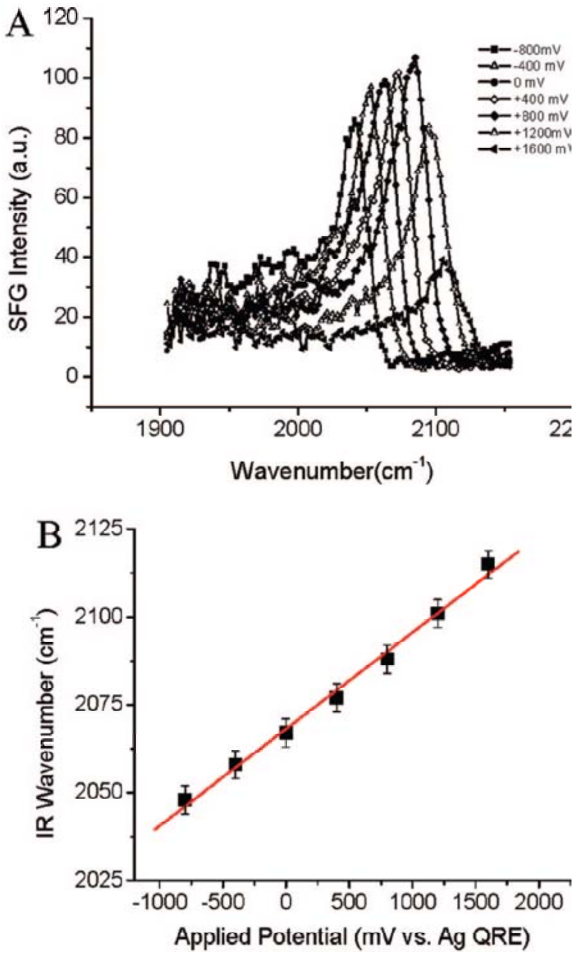


FIGURE 8. (A) SFG spectra of CO on Pt electrode as a function of potential, taken with ppp polarization, and (B) plot of CO peak position vs applied potential.

TABLE 2. Stark Shift for CO on Pt in Ionic Liquid Electrolyte

ionic liquid $[BMIM]^+$	Stark effect (cm^{-1}/V)	double layer width (m)
$[PF_6]^-$	26	3.8×10^{-10}
$[BF_4]^-$	33	3.3×10^{-10}
$[imide]^-$	24	4.2×10^{-10}
[DCA]-	<10	25×10^{-10}

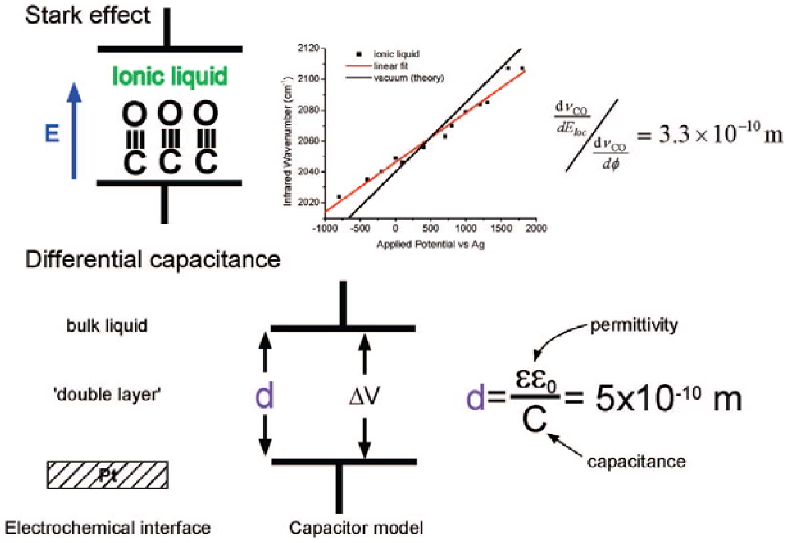


FIGURE 9. A summary of two different views on the thickness of the interfacial layer between ionic liquid and metal electrode: top, vibrational Stark shift measurement; bottom, double layer capacitance.

Result(SFG)

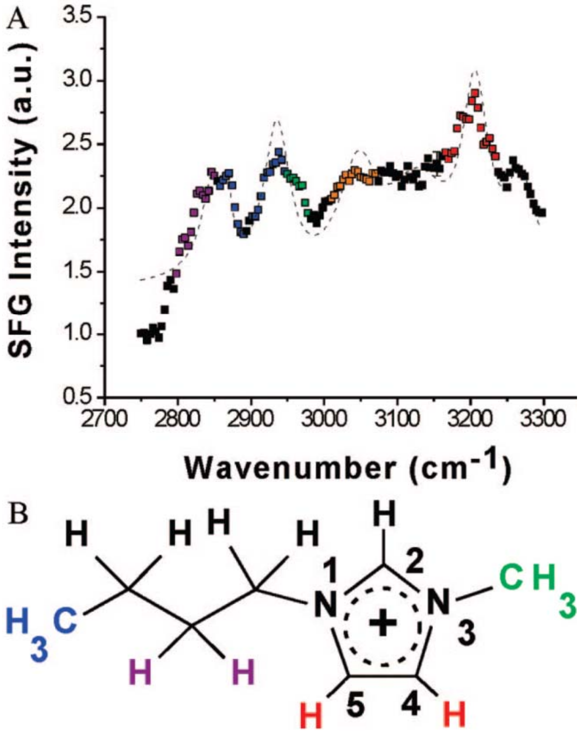


FIGURE 10. (A) SFG spectrum of [BMIM]+ at the Pt electrode with ppp polarization and (B) Structure of [BMIM]+ cation with color code and number scheme. Color corresponds to the colored region in the SFG spectrum in part A.

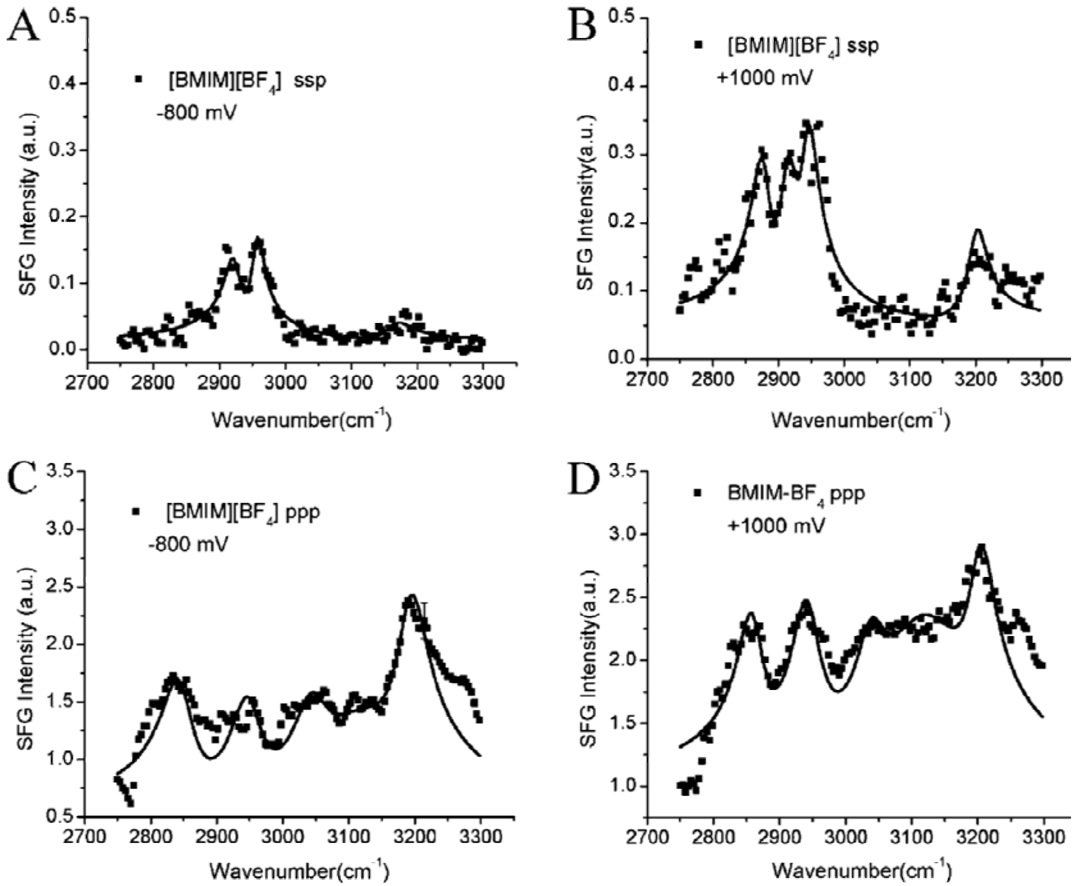


FIGURE 11. SFG spectra of [BMIM]+ at the Pt electrode taken at two different polarization combinations and two potentials: (A) ssp at -800 mV; (B) ssp at +1000 mV; (C) ppp at -800 mV; (D) ppp at +1000 mV.

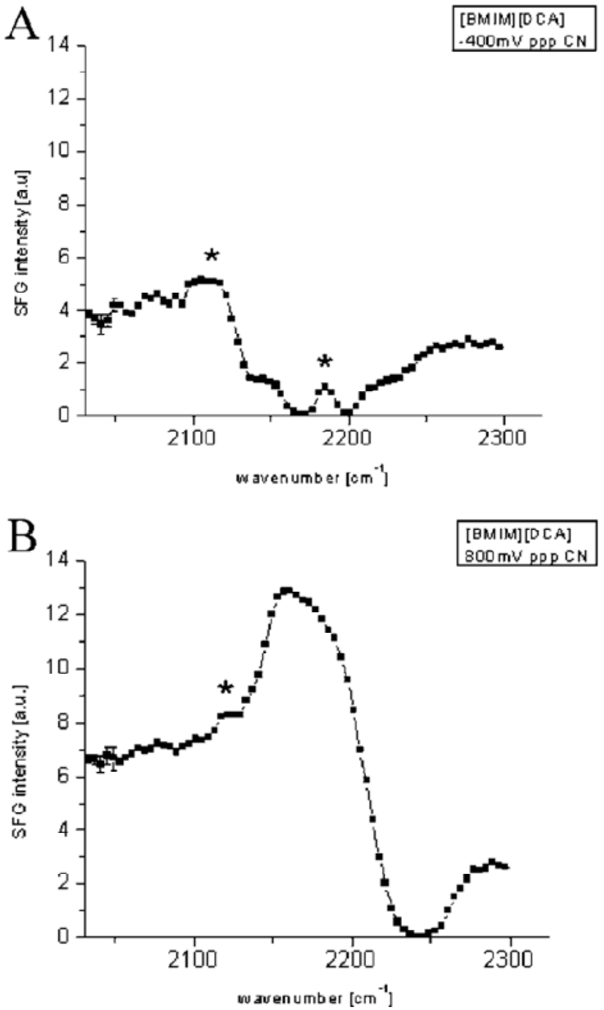


FIGURE 12. SFG spectra of [DCA]- at the Pt electrode taken at ppp polarization and two potentials: (A) -400 mV; (B) +800 mV.

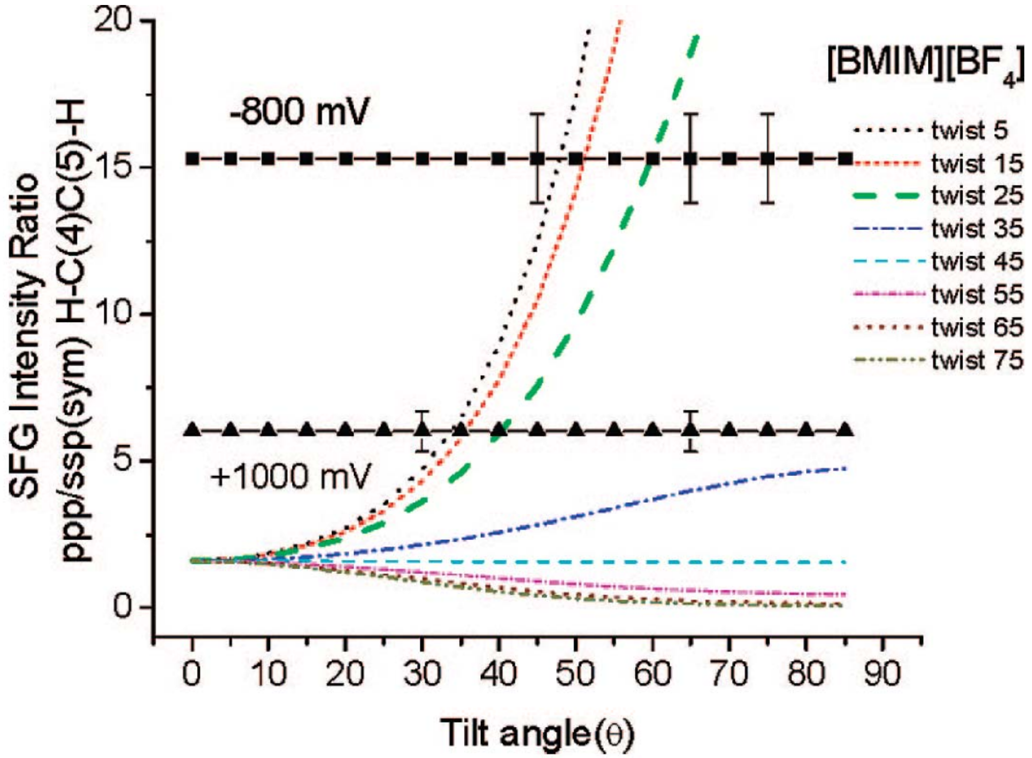
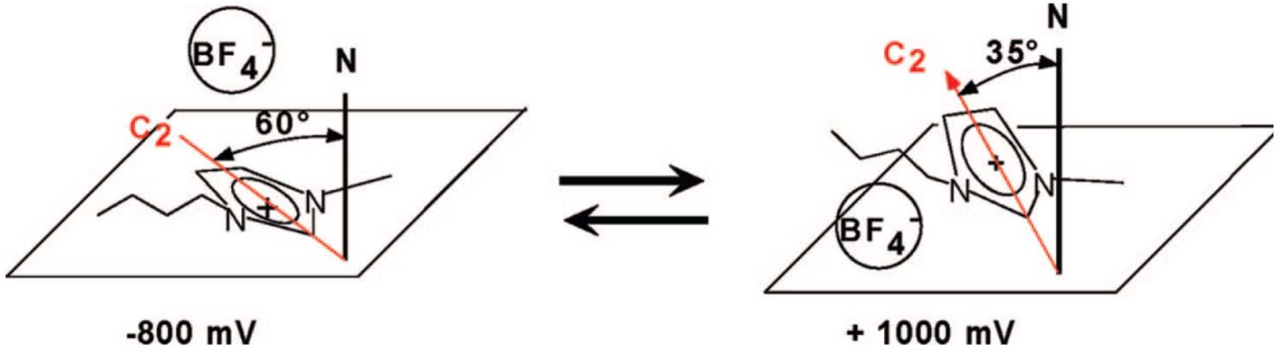


FIGURE 13. Orientation plots for the H-C(4)C(5)-H symmetric stretch as orientation tilt angle vs SFG intensity ratio. Each curve is for a different twist angle about the *C*2 axis.

Representation of the orientation of [BMIM]+ on the surface of the Pt electrode.



Concluse

1. the interfacial region is one ion layer thick

    - the interfacial capacitance
    - the vibrational Stark shift of CO at the interface.

2. SFG

The surface charge is made negative charged
→ imidazolium ring lies more parallel to the surface to maximize attractive interaction.

The surface charge is made positively charged,
→imidazolium ring is repelled from the surface,
→anion is interacting with the Pt surface to screen the positive charge.