

Electronic Supplementary Information

Bi-layering at Ionic Liquid Surfaces: A Sum-Frequency Generation Vibrational Spectroscopy- and Molecular Dynamics Simulation-based Study

Takashi Iwahashi,^a Tatsuya Ishiyama,^b Yasunari Sakai,^a Akihiro Morita,^{c,d} Doseok Kim^e
,and Yukio Ouchi*^a

^aDepartment of Materials Science and Engineering, School of Materials and Chemical Technology,
Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo, 152-8552, Japan

^bDepartment of Environmental Applied Chemistry, Faculty of Engineering,
University of Toyama, Gofuku, Toyama-shi, Toyama 930-8555, Japan,

^cDepartment of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai, 980-8578, Japan,

^dElements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, Kyoto 615-8520, Japan

^eDepartment of Physics, Sogang University, Seoul, 04107, Republic of Korea

*To whom correspondence should be addressed.

E-mail: ouchi.y.ab@m.titech.ac.jp Phone: +81-3-5734-2436 Fax: +81-3-5734-2876

Introduction

In this electronic supplementary information, the fitting parameters for all the SFG spectra discussed in the manuscript are given in the tables below.

Mode	Chain length n	Frequency / cm^{-1}	Width / cm^{-1}	Amplitude, A_q / arb. units	
				ssp	ppp
r^+ mode	4	2886.8	5.8	16.63	7.76
	8	2879.3	6.0	17.08	8.01
	12	2878.7	6.4	16.61	7.42
r^- mode	4	2977.6	6.3	-7.64	38.87
	8	2969.5	6.9	-6.88	38.46
	12	2969.1	7.1	-7.29	39.37
r^+_{FR} mode	4	2945.6	8.9	22.76	11.03
	8	2938.4	8.1	22.89	9.34
	12	2936.1	7.9	22.59	10.08
d^+ mode	4	2874.2	6.3	-1.74	-1.36
	8	2860.0	8.1	13.48	6.47
	12	2856.7	6.0	20.40	9.34
d^- mode and/or $r^+(\text{NCH}_3)$ mode	4	2916.2	8.4	3.77	0.11
	8	2913.4	10.2	10.30	7.02
	12	2903.7	12.2	3.90	25.64
d^- mode and/or $r^+(\text{NCH}_3)$ mode	4	2925.9	10.5	2.90	9.14
	8	2926.7	10.5	10.53	15.65
	12	2926.0	13.0	23.48	31.70

Table 1. Fitting parameters for SFG spectra taken within the CH stretch mode region of air/[C_n mim][TFSA] interfaces ($n = 4, 8$ and 12) shown in Fig. 2 of the manuscript.

Mode	Chain length n	Frequency / cm^{-1}	Width / cm^{-1}	Amplitude, A_q / arb. units	
				ssp	ppp
SO ₂ -ss mode	4	1139.3	8.1	6.13	0.20
	6	1138.7	6.7	4.48	0.16
	8	1138.5	7.0	4.03	0.12
	10	1138.5	7.0	3.51	0.08
	12	1138.4	9.3	3.11	0.08
CF ₃ -as mode	4	1207.9	12.4	0.08	1.76
	6	1207.9	12.4	N.D.	1.08
	8	1207.9	12.4	N.D.	0.96
	10	1207.9	12.4	N.D.	0.94
	12	1195.1	12.4	N.D.	0.97
CF ₃ -ss mode	4	1239.9	8.2	-2.86	0.56
	6	1240.7	8.6	-2.01	-0.10
	8	1240.2	10.1	-1.81	0.01
	10	1240.2	10.1	-1.21	-0.13
	12	1239.9	10.2	-1.00	-0.14

Table 2. Fitting parameters for SFG spectra taken within the SO and CF stretch region of the air/[C_{*n*}mim][TFSA] interfaces ($n = 4, 6, 8, 10,$ and 12) shown in Fig. 5 of the manuscript. The amplitudes of the CF₃-as mode at the air/[C_{*n*}mim][TFSA] interfaces ($n = 6, 8, 10$ and 12) with the ssp polarization combination could not be obtained because of the low SF signal below noise.