

Ultrafast Dynamics in Aromatic Cation Based Ionic Liquids: A Femtosecond Raman-Induced Kerr Effect Spectroscopic Study

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Abstract

We studied the ultrafast dynamics of 40 aromatic cation based ionic liquids (ILs) by means of femtosecond Ramaninduced Kerr effect spectroscopy. The low-frequency Kerr spectra (ca. $0.3-700 \text{ cm}^{-1}$) of the ILs were obtained from the Kerr transients by Fourier-transform deconvolution analysis. The low-frequency Kerr spectra in the frequency range less than 200 cm⁻¹ coming mainly from the intermolecular vibrations for the ILs were discussed in terms of (i) anion dependence, (ii) imidazolium cations vs. pyridinium cations, (iii) alkyl group dependence, and (iv) effect of methylation in aromatic cations. Several liquid properties, such as density, viscosity, electrical conductivity, and surface tension, of the present sample ILs at 293 K were also estimated in this study. We clarified that the aromatic cation based ILs show a different relation of the first moment of the low-frequency spectral band to the bulk liquid parameter, which is the square root of surface tension divided by liquid density, from aprotic molecular liquids. The slope of the first moment to the bulk parameter for the aromatic cation based ILs is gentler than that for aprotic molecular liquids.

1. Introduction

Because the intermolecular dynamics of solvents influences the barrier-crossing processes in chemical reactions, biological processes, and relaxations in solutions, such as electron transfer, proton transfer, isomerization, protein folding, and phase transition dynamics, studies on the ultrafast dynamics in liquids and solutions are very important to understand these processes in detail and at molecular level. Accordingly, the intermolecular dynamics in liquids and solutions are of long interest in chemistry, biology, and physics.¹

Progress in laser technology has made it possible to use femtosecond lasers as a light source for molecular spectroscopy.²⁻⁴ To probe liquid dynamics, a wide variety of spectroscopic techniques using femtosecond lasers including lowfrequency (less than ca. $200 \,\mathrm{cm}^{-1}$) spectroscopies such as femtosecond Raman-induced Kerr effect spectroscopy (fs-RIKES) and terahertz time domain spectroscopy (THz-TDS) have been developed. Molecular motions in the low-frequency region for solutions and liquids include intermolecular dynamics such as intermolecular vibrational dynamics and collective orientational dynamics. As well as conventional Raman and FT-IR spectroscopies, fs-RIKES and THz-TDS are complementary spectroscopic techniques but they are specialized for the lowfrequency region below 200 cm^{-1} . There are several review and instructive articles on the ultrafast dynamics in liquids and solutions studied by fs-RIKES⁵⁻¹⁶ and THz-TDS.^{17,18}

fs-RIKES probes the polarizability response function that is described in terms of the polarizability time-correlation function:

$$R_{\rm RIKES}(t) \propto \frac{\rm d}{{\rm d}t} \langle \alpha(0)\alpha(t) \rangle$$
 (1)

where α is the collective polarizability. Because fs-RIKES is a polarization-controlled third-order nonlinear spectroscopy, it can detect isotropic and anisotropic (depolarized) signals, as well as other Raman active signals, by controlling the polarizations of pump and probe lights and analyzer.^{19–22} The isotropic and anisotropic responses can be described by,^{19,23,24}

$$R_{Iso}(t) = \frac{1}{3} \left[R_{zzzz}(t) + 2R_{yyzz}(t) \right] \propto \frac{d}{dt} \left\langle \alpha_{Iso}(0) \alpha_{Iso}(t) \right\rangle$$
(2)

$$R_{Aniso}(t) = \frac{1}{2} \left[R_{zzzz}(t) - R_{yyzz}(t) \right] \propto \frac{d}{dt} \left\langle \alpha_{Aniso}(0) \alpha_{Aniso}(t) \right\rangle \quad (3)$$

where $R_{ijkl}(t)$ is the description of the third-order response and α_{Iso} and α_{Aniso} are the collective polarizabilities for the isotropic and anisotropic components. Common and traditional polarization condition for fs-RIKES measurements is the anisotropic condition (eq 3). In contrast to fs-RIKES, THz-TDS probes a dipole moment time-correlation function:

$$R_{\text{THz-TDS}}(t) \propto \frac{\mathrm{d}}{\mathrm{d}t} \left\langle \mu(0)\mu(t) \right\rangle$$
 (4)

where μ is the dipole moment. Thus the THz-TDS (and dielectric) spectrum is related to the solvation dynamics measured by the time-dependent fluorescence Stokes shift^{25–27} that has been extensively used in the study of ionic liquid (IL) dynamics^{28–37} that is also probed by fs-RIKES.

ILs are purely composed of ions, but they are molten at ambient temperatures (or often defined as below 373 K, that is, the boiling point of water). Therefore ILs possess both the natures of salt and liquid, and they are referred to as Janus materials. Indeed, the earliest "exact" or "real" IL, ethylammonium nitrate (the melting point is 285 K), was reported by Walden as long ago as 1914³⁸ (but it may be ethanolammonium nitrate whose melting point is 325-328 K reported by Gabriel and Weiner in 1888³⁹ if the definition of the melting point of less than 373 K for IL is applicable rather than *real* room temperature). After this discovery, however, ILs did not receive much attention for a while. A milestone of research on ILs is probably the report on water- and air-stable imidazolium salts by Wilkes and Zawarotko in 1992.40 Since then, ILs have become more popular research targets in chemistry, physics, materials engineering, biochemical engineering, and so on.41-53

The reason why ILs are getting more attention recently is probably their unique properties.⁴¹ Of course, the low melting points for the ILs themselves are a purely interesting subject in science. The low (or negligible) volatility, and thus low flammability, for these liquids at ambient conditions is also fascinating for safe and eco-friendly materials and solvents. The high electrical conductivity is an attractive property for application to electrolytes in batteries. The high dissolving power for a wide variety of solutes can provide good solvents. In addition, ILs show microsegregation structure that is not observed in simple and conventional solvents.^{54–58} These unique features and properties of ILs often come from the amphiphilic nature of cations and the complicated and subtle balance of intermolecular interactions and forces. It is thus important to investigate the molecular-level aspects including microscopic structure and interaction of ILs. It is expected that the low-frequency vibrational spectroscopic techniques are very useful to investigate such microscopic structure, interaction, and dynamics in ILs.

Using low-frequency vibrational spectroscopies based on modern time-domain spectroscopic techniques such as fs-RIKES^{30,59,60} and THz-TDS,⁶¹⁻⁶⁷ as well as traditional steadystate Raman⁶⁸⁻⁷⁰ and far-IR spectroscopies,⁷¹⁻⁷⁵ the microscopic structures, interactions, and dynamics of different kinds of ILs have been investigated. Among these spectroscopic techniques, fs-RIKES, which has the advantage of access to the lowest frequency region that is less than 1 cm^{-1} , has been extensively used to investigate ILs. The first fs-RIKES study of imidazolium-based ILs was reported by Quitevis and coworkers in 2002.⁷⁶ So far, various kinds of ILs, e.g., imid-azolium-,^{65,66,77–89} pyridinium-,^{86,89,90} pyrrolidinium-,^{66,86,89,91} ammonium-,^{66,67,86,92,93} and phosphonium-based ILs⁹² were investigated using fs-RIKES by several groups. Currently dicationic imidazolium-based ILs were also investigated by fs-RIKES.^{88,94} Furthermore, fs-RIKES has also been applied for not only neat ILs, but also IL-IL mixtures^{95,96} and ILmolecular liquid mixtures.97-106

Although the low-frequency spectra of ILs have been actively studied, it is still not enough to fully understand the natures of low-frequency spectra or intermolecular vibrational dynamics in ILs. Previously, we collected the low-frequency spectra of as many as 40 aprotic molecular liquids measured by fs-RIKES.¹² In the previous work,¹² we clarified that aromatic molecular liquids, except for hexafluorobenzene, show bimodal line shapes in the low-frequency spectra. We also found the linear relationship between the first moment M_1 of the low-frequency spectral band and bulk parameters which are the square root of surface tension divided by density $(\gamma/\rho)^{1/2}$ and the square root of surface tension divided by formula weight $(\gamma/FW)^{1/2}$. It is thus no doubt that the large number of data gives better and deeper understanding in science. Therefore, like the previous study on aprotic molecular liquids,¹² we have collected the lowfrequency spectra of 40 aromatic cation based ILs measured by fs-RIKES. As far as we know, there is no report of this kind of database of low-frequency spectra for aromatic cation based ILs of as many as or even more than 40 samples. The purpose of this study includes not only collecting the low-frequency spectra of 40 aromatic cation based ILs, but also overviewing the lowfrequency spectra of aromatic cation based ILs, understanding the general and specific features of the spectra dependent on the constituent ion species, and trying to find/understand the relation between the intermolecular vibrational band and the bulk properties. Thus, some bulk properties, such as density ρ , shear viscosity η , electrical conductivity σ , and surface tension ν of the ILs were also measured to investigate a correlation with the low-frequency spectra in this study.

2. Experiments

Most ILs used in this study were commercially available, but some of them were synthesized in our laboratory.^{59,87,107,108} The sample ILs and their abbreviations are listed in Table 1. Some ILs obtained from companies which showed brownish color were purified by activated charcoal treatment that is commonly used in acetonitrile.⁴¹ The newly synthesized ILs in our laboratory for this study were confirmed by ¹H NMR and elemental analysis. In the elemental analysis, the estimated values of carbon, hydrogen, and nitrogen for the ILs agreed with their calculated values within $\pm 0.4\%$, the criteria for the Journal of

Table 1. Abbreviations and supplier sources of ionic liquids used in this study

Entry Number	Abbreviation	Name	Source
1	[C ₂ MIm][NTf ₂]	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide	Ref. 107
2	$[C_2MIm][BF_4]$	1-ethyl-3-methylimidazolium tetrafluoroborate	Ref. 108
3	$[C_2MIm][OTf]$	1-ethyl-3-methylimidazolium trifluoromethanesulfonate	This work
4	$[C_2MIm][NPf_2]$	1-ethyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)amide	Ref. 107
5	[C ₂ MIm][TCNB]	1-ethyl-3-methylimidazolium tetracyanoborate	Merck
6	[C ₂ MIm][FAP]	1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	Merck
7	[C ₂ MIm][EtSO ₄]	1-ethyl-3-methylimidazolium ethylsulfate	Iolitec
8	[C ₃ MIm][NTf ₂]	1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)amide	Ref. 107
9	[C ₃ MIm][BF ₄]	1-methyl-3-propylimidazolium tetrafluoroborate	Ref. 107
10	[C ₄ MIm][NTf ₂]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide	Ref. 87
11	$[C_4MIm][BF_4]$	1-butyl-3-methylimidazolium tetrafluoroborate	Ref. 107
12	[C ₄ MIm][OTf]	1-butyl-3-methylimidazolium trifluoromethanesulfonate	Ref. 87
13	[C ₄ MIm][NPf ₂]	1-butyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)amide	This work
14	$[C_4MIm][PF_6]$	1-butyl-3-methylimidazolium hexafluorophosphate	Fluka
15	[C ₄ MIm]I	1-butyl-3-methylimidazolium iodide	Kanto
16	[C ₄ MIm][DCA]	1-butyl-3-methylimidazolium dicyanamide	Merck
17	[C ₄ MIm][NO ₃]	1-butyl-3-methylimidazolium nitrate	Ref. 107
18	[C ₄ MIm][SCN]	1-butyl-3-methylimidazolium thiocyanate	Aldrich ^{a)}
19	$[C_4MIm][NF_2]$	1-butyl-3-methylimidazolium bis(fluorosulfonyl)amide	Kanto
20	[C ₄ DMIm][NTf ₂]	1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)amide	Iolitec
21	$[C_6MIm][NTf_2]$	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide	Ref. 107
22	$[C_6MIm][BF_4]$	1-hexyl-3-methylimidazolium tetrafluoroborate	Ref. 108
23	$[C_6MIm][PF_6]$	1-hexyl-3-methylimidazolium hexafluorophosphate	This work
24	$[C_8MIm][NTf_2]$	1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)amide	Ref. 108
25	$[C_8MIm][BF_4]$	1-methyl-3-octylimidazolium tetrafluoroborate	Iolitec
26	[C ₁₀ MIm][NTf ₂]	1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide	Ref. 108
27	$[C_{10}MIm][BF_4]$	1-decyl-3-methylimidazolium tetrafluoroborate	Iolitec
28	[SiMIm][NTf ₂]	1-methyl-3-trimethylsilylmethylimidazolium bis(trifluoromethylsulfonyl)amide	Ref. 59
29	$[C_4Py][NTf_2]$	1-butylpyridinium bis(trifluoromethylsulfonyl)amide	Ref. 86
30	$[C_4Py][BF_4]$	1-butylpyridinium tetrafluoroborate	Iolitec
31	[1C ₄ 2MPy][NTf ₂]	1-butyl-2-methylpyridinium bis(trifluoromethylsulfonyl)amide	Iolitec ^{a)}
32	$[1C_43MPy][NTf_2]$	1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)amide	Iolitec ^{a)}
33	$[1C_43MPy][BF_4]$	1-butyl-3-methylpyridinium tetrafluoroborate	Iolitec ^{a)}
34	$[1C_44MPy][NTf_2]$	1-butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)amide	Iolitec ^{a)}
35	$[1C_44MPy][BF_4]$	1-butyl-4-methylpyridinium tetrafluoroborate	Iolitec ^{a)}
36	$[C_6Py][NTf_2]$	1-hexylpyridinium bis(trifluoromethylsulfonyl)amide	This work
37	$[C_6Py][BF_4]$	1-hexylpyridinium tetrafluoroborate	Iolitec
38	$[C_8Py][NTf_2]$	1-octylpyridinium bis(trifluoromethylsulfonyl)amide	This work
39	$[C_{10}Py][NTf_2]$	1-decylpyridinium bis(trifluoromethylsulfonyl)amide	This work
40	$[C_{12}Py][NTf_2]$	1-dodecylpyridinium bis(trifluoromethylsulfonyl)amide	This work

a) Purified by activated charcoal treatment.

Organic Chemistry published by the American Chemical Society. The details of the preparation procedures and analytical data of the synthesized ILs for this study are summarized in Supporting Information. The sample ILs were dried in a vacuum oven at 313 K for more than 36 h before experiments.

 ρ of the ILs were obtained at 293.0 ± 0.5 K using a 2 mL volumetric flask. η of the ILs were measured using a reciprocating electromagnetic piston viscometer (Cambridge Viscosity, ViscoLab 4100) equipped with a circulating water bath (Yamato, BB300) at 293.0 ± 0.2 K. σ of the ILs were measured by an electrical conductivity meter (Mettler Toledo, S470 SevenExcellence) at 293.0 ± 0.5 K. γ of the samples were measured using a duNouy tensiometer (Yoshida Seisakusho) at 293.0 ± 0.5 K. The water contents of the ILs were estimated from Karl Fischer titrations using a coulometer (Hiranuma,

AQ-300). The values of the water contents of the ILs are summarized in Table 2.

The details of the fs optical heterodyne detected (OHD) RIKES setup used in this study were reported in previous publications.^{12,109} Optical heterodyne detection is well used in nonlinear spectroscopy including fs-RIKES to enhance the signal.^{3,4} In the current fs-OHD-RIKES setup, the light source was a titanium sapphire laser (KMLabs, Griffin) pumped by a Nd:YVO₄ diode laser (Spectra Physics, Millennia Pro 5sJ).¹¹⁰ The output power of the titanium sapphire laser was approximately 390–440 mW. The temporal response, which is the cross-correlation between the pump and probe pulses measured using a 200 µm thick KDP crystal (type I), of the fs-RIKES setup was typically ca. 36 fs (full-width at half-maximum, FWHM). In the fs-RIKES experiments, scans with a high time

No.	Ionic Liquid	FW /a mol ⁻¹	ρ /a mI $^{-1}$	$V_{ m m}$ /mI_mol^{-1}	η_{cP}	σ /mS cm ⁻¹	$A/\mathrm{Scm}^2 \mathrm{mol}^{-1}$	$\gamma^{/{ m mNm}^{-1}}$	$M_1^{/\mathrm{cm}^{-1}}$	H ₂ O Cont.
-	[C ₂ MIm][NTf ₂]	391.29	1.51	259	35.7	7.83	2.03	37.0	61.3	16
7	$[C_2MIm][BF_4]$	197.97	(1.52, ^{diver} 1.52 ^{c)1.2}) 1.27 71 30 dil07 1 30133	156	(30.7, 42.7 42.7 730 el155 AF E 1332	(9.2, 571 9.50 9.00) 13.8 713 £ 8155 15 28161	2.15	(38.0, ^{0,107} 36.9 ¹⁰⁷) 54.2 754 A d)107 54 Ae)1557	62.1	64
б	[C ₂ MIm][OTf]	260.24	(1.20, 1.20) 1.38 (1.20)134	189	(c	(2.01 2.0.01) 7.80 7.02 eAt e 24167	1.48	(+++,	64.2	80
4	$[C_2MIm][NPf_2]$	491.32	(1.59 1.59 1.50 d)107 1, 60 ¹³⁵	309	(7.1.5) 98.1 (81 0 ^{d)107} 08 ¹³⁵)	(0.816	(32.2c) 32.1 (72.0d)107)	55.1	51
5	[C ₂ MIm][TCNB]	226.05	(1.00) 1.00 1.03 (1.04 ¹³⁶)	219	(01.3, 0.30) 19.9 (71.8 136 77157)	(00.2 2.00 13.2 (13.157)	2.89	(48.2)	63.8	40
9	[C ₂ MIm][FAP]	556.18	(1.70)	327	(21:0, 22) 72.5 (60e)158)	(4.38)	1.43	35.0 34 9 ¹³⁷)	57.1	41
L	[C ₂ MIm][EtSO ₄]	236.29	(1.24)	191	(97.6°)	$(\frac{1.1}{2.72})$ 2.72 (2.91 ¹⁶⁹ 3.1 ¹⁶⁷)	0.520	(27.2) 47.7 (47.3 ¹³⁸ 46 1 ¹³⁹)	67.8	47
~	[C ₃ MIm][NTf ₂]	405.32	(1.47 1.47 (1.48 ^{d)107})	276	51.8 51.8 (42 8 d)107 53159)	4.80 (4.24 ¹⁷⁰)	1.32	(35.9 d)107 34.9 ¹⁸⁴)	68.1	21
6	$[C_3MIm][BF_4]$	212.00	(1 24 ^{d)107} 1 24 ¹³³)	171	97.1 97.1 (73.d) ¹⁰⁷ 95.4 ¹³³)	4.46 $(5 9^{171})$	0.763	50.0 50.0 51.1 ^{d)107})	75.7	39
10	[C4MIm][NTf2]	419.35	(1.24, 1.43 1.43 (1.44 d) ⁸⁷ 1.44e) ¹⁴⁰)	293	59.3 59.3 (63 ¹⁴¹ 50 ^{1e)} ¹⁴⁰	(2.0) 3.40 (4.0 e) ¹⁴⁰ .4.73e) ¹⁶¹	0.996	(32.0 (34.1 d)87 33.6 ¹⁸⁴)	65.2	59
11	$[C_4MIm][BF_4]$	226.03	$(1.20^{0})^{0.07}$	190	$(101 \text{ d})^{107} 103^{\text{e}}^{160}$	$(3.7)^{172} 4.36^{(0)161}$	0.676	(44.4 (46.9 d)107 44 3 ¹³⁹)	71.7	78
12	[C4MIm][OTf]	288.29	(130)	222	104 104 (83 ^{d)87})	2.52 2.60 ⁰¹⁷³)	0.559	34.4 35.7 ^{d)87}	70.9	77
13	[C4MIm][NPf ₂]	519.37	$(151 \text{ d})^{107} (152 \text{ d})^{107}$	344	147 147 1115 d)107 151 ¹⁴¹)	1.141 1.141	0.495	29.4 29.4 (31 7 d) ¹⁰⁷ 37 6 ¹⁸⁵)	62.6	15
14	$[C_4MIm][PF_6]$	284.19	(137 1.37 (137 ^{d)85})	207	(110, 121) 340 (789 6 ^{d)85} 354 ¹⁴¹)	(115 e)41 1 65e)161)	0.271	(2111, 2110) 43.7 (43.7 ^{d)59})	69.7	61
15	[C ₄ MIm]I	266.13	(1.49)	179	(1110 ^{e)142})	0.538 0.538 0.28 ¹⁷²)	0.0963	52.3 52.3 (54.7 ^{e)142})	73.2	51
16	[C4MIm][DCA]	205.26	$(1.06^{0.87})$	194	32.0 (28.2 ^{d)87})	9.42 9.42 $(9.4^{172} 10.5^{e)173})$	1.83	45.5 45.5 (46.4 ^{d)87})	71.0	83
17	[C4MIm][NO ₃]	201.23	1.16	173	$(166^{d})^{107})$	1.75	0.303	47.5 $(50.5^{d})^{107}$	72.2	79
18	[C4MIm][SCN]	197.30	$(1.07^{d)87})$	184	$(56^{d)87})$	4.47 (4.2 ¹⁷²)	0.822	47.5 (48 ^{d)87})	72.3	68
19	$[C_4MIm][NF_2]$	319.35	$(1.36,^{143}, 1.36^{\circ})^{144})$	235	(39.7^{143})	(6.80)	1.60	43.8	64.6	22
20	[C4DMIm][NTf2]	433.40	$(1.42^{\circ})^{145}$ 1.42 $^{\circ})^{140}$	307	$(118,^{b)159}$ 89.5 $^{e)140}$)	$(2.20,e^{0159} 2.14e^{0140})$	0.583	34.3 (37.4, ¹⁸⁶ 32.5 ^{e)145})	65.2	37
								Cc	ontinued a	n next page.

Contu	nued.									
No.	Ionic Liauid	FW	θ	$V_{\rm m}$	h	α	V	Z	M_1	H_2O Cont.
		/g mol ⁻¹	$/\text{gmL}^{-1}$	/mL mol ⁻¹	/cP	$/\mathrm{mS}\mathrm{cm}^{-1}$	/Scm ² mol ⁻¹	/mNm ⁻¹	/cm ⁻¹	(mdd)
21	[C ₆ MIm][NTf ₂]	447.42	1.37 (1 37 ^{d)107})	348	82.7 (69 3 d)107 74 ge)161)	1.99 (2.26 ^{e)161})	0.693	30.8 (33 8 ^{d)107} 32 3 ¹⁸⁴)	67.4	21
22	$[C_6MIm][BF_4]$	254.08	1.14 1.14 1.15 d)107 1 15 133	223	256 256 257 d)107 260133	1.30 1.30	0.290	38.2 38.2 20 £d)1075	75.3	99
23	[C ₆ MIm][PF ₆]	312.24	(1.10, 7.1.1) 1.28 7.306/133	244	(227, 200) 713 7705 165 5056)133	0.661 0.661	0.149	(2.20) 39.1 778 Table7	73.1	40
24	[C ₈ MIm][NTf ₂]	475.46	(1.29 ⁻⁷⁻¹) 1.32	347	((0.020-0) 1.31	0.455	30.8 30.8	65.2	71
25	$[C_8MIm][BF_4]$	282.13	$(1.34,^{1.27} 1.31^{1.01+0})$ 1.09 $(1 10 e)^{132} 1.08 ^{139}$	259	(115, ^{11,1} 122, ¹⁴⁰) 389 7357 e)160 241 e)132)	(1.37°) 0.711 $(0.752^{\circ})^{161}$	0.184	$(30.6, 127 31.9^{107})$ 33.4 $(32.7)^{139}$	69.4	33
26	$[C_{10}MIm][NTf_2]$	503.51	(1.10, 1.00, 1.00, 1.27 $(1.27h)^{1.46}$	396	(552, 541) 151 (154 ¹⁴⁶ 150 ⁶⁾¹⁶²)	(0.52) 0.950 $(0.831^{e)162}$	0.376	30.7	62.9	73
27	$[C_{10}MIm][BF_4]$	310.19	(1.06)	293	767 767 (630 ⁰) ¹⁶⁰)	0.603 0.603 0.37 ¹⁷⁴)	0.177	29.2 29.2 $(30 3^{188})$	70.1	83
28	[SiMIm][NTf ₂]	449.45	1.38	326	(000) 107 (90 7 ^{d)59})	1.69	0.551	29.9 29.9 (30.1 ^{d)59})	58.2	21
29	[C4Py][NTf2]	416.37	(1.145 1.45 (1.46 ¹⁴⁷ 1.45 ¹⁴⁸)	287	75.2 75.2 775 6 147 76 2148)	2.78	0.798	(33.1 33.1 (35.0 ¹⁴⁷)	67.6	76
30	$[C_4Py][BF_4]$	223.02	(1.70, 1.70) 1.22 (1.316)1495	183	(2.0, 2.0.2) 200 715001149	(2:2) 1.96 (1 01175)	0.359	46.2 46.2	73.8	44
31	[1C42MPy][NTf2]	430.39	$(1.21^{-9.16})$ 1.43 (1.40^{147})	301	(1007-1) 122 7143 01147	(1.81 - 1)	0.572	(40.90~~) 34.6 136 5147	67.9	60
32	$[1C_43MPy][NTf_2]$	430.39	(1.46 - 1) 1.42 (1.43 + 1.42	301	(142.91-1) 80.6 (81 71 ¹⁴⁷ 70 9 ¹⁵⁰)	2.23 (7.17 ¹⁵⁰)	0.671	(63.5	45
33	$[1C_43MPy][BF_4]$	237.05	(27.1 , 27.1) 1.18 71 10 ¹⁴⁷	201	(01.71, 7.7.7) 214 7376 15 ¹⁴⁷	(-1.7) 1.67 (1.55 ¹⁷⁵)	0.336	(100, 200, 000) 45.8 (175, 147, 15, 2189)	67.6	78
34	$[1C_44MPy][NTf_2]$	430.39	(1.12) 1.42 $(7)^{147}$	303	(210.12) 70.2 (65 2147)	2.98	0.903	(7.5, 7.5.5) 33.0 (35.0147)	65.0	25
35	$[1C_44MPy][BF_4]$	237.05	(1.72) 1.20 (1.10^{151})	198	223 223 203e)151)	1.46 (1 32 ¹⁷⁵)	0.289	45.5 45.5 (45 8189)	69.1	39
36	[C ₆ Py][NTf ₂]	444.42	(1.1) 1.38 (1.20^{152})	322	(202) 104 (84 5 e)152 53 8e)163)	1.61	0.518	31.3 31.3 (22,0152)	6.69	65
37	$[C_6Py][BF_4]$	251.08	(1.16^{153})	213	(241 ^{e)163} 212 ^g) ¹⁶⁴)	0.835	0.178	39.2	76.1	70
38	[C ₈ Py][NTf ₂]	472.47	(1.33^{148})	353	$(134^{\circ})^{163}$ 150 ¹⁴⁸)	1.07 (1.18 ¹⁷⁶)	0.378	30.4	67.7	63
39	$[C_{10}Py][NTf_2]$	500.53	(1.29^{148})	391	$(160, ^{\circ)163} 201^{148})$	0.779	0.305	30.4	68.3	65
40	[C ₁₂ Py][NTf ₂]	528.58	(1.24) (1.25 ¹⁴⁸)	426	245 (270 ¹⁴⁸)	0.629	0.268	30.9	67.6	24
Data Data	in parentheses are fro at 295–298 K.	m the literatu	re. a) Data at 294 K. b)	Data at 295 K.	. c) Data at 296 K. d) Dat	a at 297 K. e) Data	at 298 K. f) Data at	299 K. g) Data at 303	3 K. h) Dat	t at 308K. i)

resolution of 3072 points at 0.5 µm per step that corresponds to 3.34 fs per step were made for a short time window (ca. 10.2 ps). Longer time window transients (ca. 300 ps) of 2000 points at 25.0 µm per step that correspond to 167 fs per step were also measured. A pure heterodyne signal was obtained by recording scans for both plus and minus ca. 1.5° rotations of the input probe beam polarization using a quarter wave plate; these signals were then combined to eliminate the residual homodyne signal. The rotations by the quarter wave plate were done with monitoring the intensity of the local oscillator. The numbers of scans for the short and long time window transients were 3 and 5 in each polarization, respectively. The ILs were injected into a quartz cell (Tosoh Quartz, 3 mm optical path length) via a 0.2 µm or 0.02 µm Anotop filter (Whatman). During the fs-RIKES experiments the temperatures of the samples were kept at 293.0 ± 0.2 K by a laboratory-built temperature controller based on a Peltier temperature controller (VICS, VPE35-5-20TS).

Ab initio quantum chemistry calculations were performed for some ion species to obtain the stable structures and the Raman spectra using the Gaussian 09 program suite.¹¹¹ The B3LYP/6-31+G(d,p) level of theory was used for the calculations in this study.

3. Data Analysis

The Kerr transients of the ILs obtained by fs-RIKES were analyzed by the Fourier-transform deconvolution method to provide their low-frequency spectra, because the Kerr transients include many underdamped and overdamped motions and thus they are overlapped in time domain and complicated. The method of the Fourier-transform deconvolution analysis for Kerr transients was extensively developed by Lotshaw and McMorrow,^{112,113} and the details of the analysis procedure used in this study were reported elsewhere.^{59,60}

Figure 1a shows the logarithmic plots for the Kerr transient of $[C_2MIm][OTf]$ with the time window of 300 ps and Figure 1b shows the short time range from -0.5 to 3.0 ps. The intensity of the Kerr transient is normalized at the intensity at t = 0 that is the electronic response. Figure 1a also shows the fit to the Kerr transient from 3 to 300 ps by a triexponential function,

$$a_0 + \sum_{i=1}^3 a_i \exp(-t/\tau_i)$$
 (5)

where a_0 is the offset amplitude, a_i is the amplitude of the *i*-th component, and τ_i is the time constant of the *i*-th component. In this study, a triexponential function was used for all the Kerr transients. The fit parameters obtained for all the present 40 ILs are given in Supporting Information. In fact, the time scale of the slowest relaxation component for ILs is typically nanoseconds though it depends on the IL.^{65–67,114–116} The present fs-RIKES apparatus whose light source is a titanium sapphire oscillator, not an amplifier, and the delay stage is the length of 5 cm, can obtain reliable data in the time range of less than approximately 300 ps.¹⁰⁹ Thus the slow relaxation components over subnanoseconds are treated as the amplitude a_0 in this study. Note that even if the slow relaxation component cannot be captured completely in the present setup, the line shape of the low-frequency spectrum without the component of the



Figure 1. (a) Logarithmic plots of the normalized Kerr transient (red curve) together with its triexponential function (blue curve) and (b) short time window transient from -0.5 to 3.0 ps for [C₂MIm][OTf]. (c) Fourier-transform Kerr spectra: entire spectrum (black curve); picosecond overdamped relaxation component (blue curve); entire spectrum minus picosecond overdamped relaxation component (red curve).

slow relaxation component in the frequency region as low as ca. 0.6 cm^{-1} (or probably even low frequency region) can be discussed adequately.⁹⁴ The Fourier-transform Kerr spectrum of [C₂MIm][OTf] is shown in Figure 1c. This figure also shows the decompositions of the spectra: the overdamped component (triexponential fit excluded the fast component: $a_0 + a_2 \exp(-t/\tau_2) + a_3 \exp(-t/\tau_3)$) and the spectrum produced by the subtraction of the overdamped relaxation component. Because the relaxation time constants of the first exponential components ($a_1 \exp(-t/\tau_1)$) were a few picoseconds, which is competitive to the dephasing time in intramolecular vibrations and the characteristic time in collision-induced intermolecular motions, this component was included in the low-frequency spectra for all the present ILs (Supporting Information).

The low-frequency Kerr spectra after subtractions of the slow overdamped relaxation components were further analyzed for their line shapes. The primary purpose of the line shape analyses of the low-frequency spectra includes (i) distinguishing clear intramolecular vibrational modes from low-frequency broad bands, (ii) estimations of the first moments (M_1) of spectra which excluded clear intramolecular vibrational modes, and (iii) representing the low-frequency spectra numerically. There are two major line shape models for low-frequency spectra of liquids and solutions measured by fs-RIKES. One is the sum of Ohmic (or Bucaro–Litovitz)¹¹⁷ and antisymmetrized Gaussian functions,¹¹⁸ and the other is the multimode Brownian oscillator model.^{119,120} There are small differences in the line shape fits especially in the high-frequency side of the low-frequency spectra of aromatic molecular liquids,^{12,109} but both the former^{59,60} and latter models^{82,91} seem to work equally well for ILs. In this study, we used the former model. The Ohmic component is given by,

$$I_{\rm O,i}(\omega) = \sum_{i=1}^{2} a_{\rm O,i} \omega \exp(-\omega/\omega_{\rm O,i}),$$
 (6)

where $a_{\text{O},i}$ and $\omega_{\text{O},i}$ are the amplitude and characteristic frequency parameters for the *i*-th Ohmic function, respectively. The antisymmetrized Gaussian component is¹¹⁸

$$I_{G,i}(\omega) = \sum_{i=1}^{n} \left\{ a_{G,i} \exp\left[\frac{-2(\omega - \omega_{G,i})^2}{\Delta \omega_{G,i}^2}\right] - a_{G,i} \exp\left[\frac{-2(\omega + \omega_{G,i})^2}{\Delta \omega_{G,i}^2}\right] \right\},$$
(7)

where $a_{G,i}$, $\omega_{G,i}$, and $\Delta \omega_{G,i}$ are the amplitude, characteristic frequency, and bandwidth parameters for the *i*-th antisymmetrized Gaussian function, respectively. For a clear intramolecular vibrational mode, a Lorentzian function,

$$I_{\rm L}(\omega) = \frac{a_{\rm L}}{(\omega - \omega_{\rm L})^2 + \Delta \omega_{\rm L}^2},\tag{8}$$

where a_L , ω_L , and $\Delta \omega_L$ are the amplitude, peak frequency, and bandwidth parameters, respectively, has been used to fit an intramolecular vibrational band. Figure 2 shows the line shape analysis results for the low-frequency spectra of [C₄MIm][DCA] and [C₄Py][NTf₂], as examples. All the Fourier-transform Kerr spectra of the present ILs and the line shape analysis results are summarized together with the normalized Kerr transients and their triexponential fits in Supporting Information. The M_1 values of the low-frequency spectra for the ILs are listed in Table 2. M_1 is defined as,

$$M_1 = \int \omega I(\omega) d\omega / \int I(\omega) d\omega$$
(9)

where $I(\omega)$ is the frequency-dependent intensity of the spectra from which the contributions of the picosecond overdamped relaxation process and clear intramolecular vibrational bands are subtracted (red areas in Figure 2, for example). The integration was made from 0 to 1000 cm⁻¹.

We should notice an important issue in the line shape analysis of the low-frequency spectra of solutions and liquids including ILs. The simple assignments of *intermolecular* vibrational modes in the low-frequency spectra of liquids based on the line shape analysis are often beyond safe discussion: the nature of intermolecular vibrations that is strongly coupled between them is neglected. It is known that the intermolecular vibrational motions are coupled with each other and their cross



Figure 2. Line shape analysis results for the low-frequency Kerr spectra of (a) $[C_4MIm][DCA]$ and (b) $[C_4Py][NTf_2]$. Black dots denote the experimental data, red lines denote the entire fits, blue areas denote the Ohmic functions, green areas denote the antisymmetrized Gaussian functions, brown areas denote the Lorentz functions, and red areas denote the sums of the Ohmic and antisymmetrized Gaussian functions.

correlation can contribute to the spectral intensity sometimes positively and sometimes negatively not only for molecular liquids,^{121–126} but also ILs.^{127–129} The above line shape analysis never models such a contribution in the low-frequency spectrum. Exceptions are fixed intermolecular systems, such as hydrogen-bonded complex systems including 7-azaindole dimer that show clear intermolecular vibrational modes.^{130,131} However, the present ILs are not such rigid intermolecular systems and thus are not this type of research target. Nonetheless, as mentioned above, the line shape analysis is useful for the purposes of resolving clear intramolecular vibrational modes from broad spectra, estimating M_1 of spectrum, and representing the low-frequency spectra numerically.

4. Results and Discussion

4.1 Bulk Properties. 4.1.1 Density ρ : Table 2 lists the ρ values of the ILs at 293 K measured in this study. The values of ρ for all the ILs at 293 K and/or near temperatures were reported in other literature. In Table 2, we can find reports on the ρ of the ILs that agree with that estimated in this study within \pm ca. 1-2%, ^{59,85,87,107,132-153} except for $[1C_42MPy][NTf_2]$,¹⁴⁷ if we take the temperature effect on the ρ in ILs into consideration. Note that the ρ values of ILs slightly decrease with increasing temperature.¹⁵⁴ As far as we know, there is only one report on the ρ of $[1C_42MPy][NTf_2]$ by Bittner et al.¹⁴⁷ The difference in the ρ of $[1C_42MPy][NTf_2]$ between the value estimated in this study and that reported by Bittner et al. is



Figure 3. Dependence of carbon number of alkyl group of the cations on the density ρ for $[C_nMIm][NTf_2]$ (open circles), $[C_nMIm][BF_4]$ (open squares), and $[C_nPy][NTf_2]$ (filled circles). Linear fits are also shown.

as large as 3.5%, but the ρ value of $[1C_42MPy][NTf_2]$ estimated in this study is quite similar to those of the isomeric cation based ILs, $[1C_43MPy][NTf_2]$ and $[1C_44MPy][NTf_2]$ (see Table 2). The values of the molar volume $V_{\rm m}$ estimated from the ρ and FW ($V_{\rm m} = FW/\rho$) for the ILs are also summarized in Table 2.

As seen in Table 2, the ρ values of the ILs are variable with the different anion species. On the basis of the data of the ILs of [C₂MIm]⁺ and [C₄MIm]⁺ cations, the tendency of the ρ with variation of the anion species is found as,

$$\begin{split} [FAP]^- &> [NPf_2]^- > I^- > [NTf_2]^- > [PF_6]^- \approx [NF_2]^- \\ &> [OTf]^- > [BF_4]^- \approx [NO_3]^- \approx [EtSO_4]^- \\ &> [SCN]^- \approx [DCA]^- > [TCNB]^-. \end{split}$$

Overall, the anions having the larger number of fluorine atoms provide the more dense ILs.

Alkyl group dependence of the ρ for the [C_nMIm][NTf₂], $[C_nMIm][BF_4]$, and $[C_nPv][NTf_2]$ is shown in Figure 3. Previously, the linear dependence of the carbon number of the alkyl group on the ρ for [C_nMIm][BF₄] and [C_nMIm][PF₆] was reported by Seddon and coworkers.¹⁵⁴ It is clear from the figure that the ρ values of the [C_nMIm][NTf₂] are quite similar to those for the $[C_n Py][NTf_2]$ when we compare the ILs having the same alkyl group (and also the alkyl group dependence of ρ). This is most likely attributed to the structural similarity: (i) the molecular weights of the two cation moieties are quite similar (-MIm⁺: 82.1 and -Py⁺: 79.1) and (ii) the both are aromatic. Furthermore, the ρ values for the three series of the ILs, [C_nMIm][NTf₂], [C_nMIm][BF₄], and [C_nPy][NTf₂], decrease almost monotonically with increasing the alkyl groups of the cations: $\rho = 1.557 - 0.02954$ for the [C_nMIm][NTf₂]; $\rho = 1.313 - 0.02641$ for the [C_nMIm][BF₄]; $\rho = 1.543 - 0.02641$ 0.02545n for the $[C_n Py][NTf_2]$. This indicates that the intrinsic density ρ (n = 0) is determined by the combination of the cation and anion, but the alkyl group length dependent feature is mainly due to the increment ratio of the CH₂ volume to the sum of the anion and cation volumes.

4.1.2 Viscosity η : As well as ρ , η is probably one of the most well characterized physical properties of ILs.⁴¹ The η values of the present ILs at 293 K measured in this study are summarized in Table 2. The η values of all the ILs at 293 K



Figure 4. Semi-logarithmic plots of viscosity η vs. carbon number of alkyl group for $[C_nMIm][NTf_2]$ (open circles), $[C_nMIm][BF_4]$ (open squares), and $[C_nPy][NTf_2]$ (filled circles). Linear fits in the plots (exponential fits) are also shown.

and/or its near temperatures were also reported. As seen in Table 2, we can find similar values of the η for the present ILs within approximately $\pm 20\%$ in a handbook¹³² and reported literature^{59,85,87,107,133,135,136,138,140–143,146–152,155–165} if the temperature effect is accounted for. Note that the temperature effects on the η values of ILs are quite large compared to common molecular liquids: Increasing temperature lowers η in ILs as in most liquids (again the temperature effect on η is much larger in ILs than in molecular liquids).¹⁵⁴

It is well-known that the η of IL depends strongly on the anion species, as seen in Table 2. The anion species dependence of η appears to change with the counter cations for the present ILs: Even the [C₂MIm]⁺- and [C₄MIm]⁺-based ILs show different trends (42.7 cP for [C₂MIm][BF₄] and 54.4 cP for [C₂MIm][OTf], but 116 cP for [C₄MIm][BF₄] and 104 cP for [C₄MIm][OTf]). The following tendency of η with the variation of anion species is found for the present [C₄MIm]⁺-based ILs.

$$I^- > [PF_6]^- > [NO_3]^- > [NPf_2]^- > [BF_4]^- \approx [OTf]^- > [SCN]^- > [NTf_2]^- > [NF_2]^- \approx [DCA]^-.$$

For the $[C_2MIm]^+$ -based ILs, the tendency of the η with the variation of anion species is following:

$$[EtSO_4]^- > [NPf_2]^- > [FAP]^- > [OTf]^- > [BF_4]^- > [NTf_2]^- > [TCNB]^-.$$

The η values of the ILs increase with the longer alkyl group of the cations. Figure 4 shows the semi-logarithmic plots of η vs. the carbon number of the alkyl group for the $[C_nMIm][NTf_2]$, $[C_nMIm][BF_4]$, and $[C_nPy][NTf_2]$. As displayed in Figure 4, the η value is roughly exponentially proportional to the number of carbon of alkyl group n: $\log(\eta) = 1.457 + 0.07404n$ for the $[C_nMIm][NTf_2]$; $\log(\eta) = 1.463 + 0.1450n$ for the $[C_nMIm][BF_4]$; $\log(\eta) = 1.628 + 0.06392n$ for the $[C_nPy][NTf_2]$. The slope of the plots for the $[C_nMIm][BF_4]$ is steeper than those for the $[C_nMIm][NTf_2]$ and $[C_nPy][NTf_2]$, and the slopes for the $[C_nMIm][NTf_2]$ and $[C_nPy][NTf_2]$ are quite similar. Therefore, the alkyl group length dependence of the η values for the ILs is varied with the anion species, but the difference between imidazolium and pyridinium cations is not significant.

It is clearly shown in Table 2 that the methylation on the aromatic cations has a significant influence on η although it is not straightforward. The η value of $[C_4MIm][NTf_2]$ at 293 K is approximately doubled by the methylation ($[C_4DMIm][NTf_2]$). This feature is actually known.¹⁶⁶ The pyridinium-based ILs show more complicated methylation effect on η . The η for the pyridinium-based ILs slightly increases by the methylation in most cases, as the η of $[1C_44MPy][BF_4]$ is higher than that of $[C_4Py][BF_4]$. However, it is noteworthy that $[1C_44MPy][NTf_2]$ is slightly less viscous than $[C_4Py][NTf_2]$. This indicates that the methylation on the aromatic cations not only modifies the cation's nature itself but can also change the intermolecular nature of cation and anion appreciably.

4.1.3 Electrical Conductivity σ : The σ value is probably one of the most important physical properties of ILs, because the use of ILs as electrolyte in capacitors, batteries, solar cells, and so forth, is a major industrial application. The σ values of the present ILs at 293 K measured in this study are tabulated in Table 2. The σ values of most of those ILs can be found in the literature, and some reported data at 293 K and/or near temperatures are in good agreement with the present data within approximately $\pm 20\%$ if we take the temperature effect into account. 41,135,140,141,143,150,152,155,157,159,161,162,167–176 As well as the temperature effect on η , the σ values of ILs are quite temperature dependent: the σ value increases with increasing temperature. According to our survey, the σ values of [C₄MIm]-[NO₃], [SiMIm][NTf₂], [1C₄2MPy][NTf₂], [1C₄4MPy][NTf₂], $[C_6Py][BF_4]$, $[C_{10}Py][NTf_2]$, and $[C_{12}Py][NTf_2]$ studied here are the first report.

When we look at the σ values of [C₂MIm]⁺- and [C₄MIm]⁺based ILs, they are variable with the different anion species, as the η values discussed above. In addition, the change in the σ for the ILs by an exchange of the anion species looks dependent on the cation, as well as the η values. The tendency of the σ with the exchange of the anion species for the present [C₄MIm]⁺-based ILs is as follows:

$$[DCA]^- > [NF_2]^- > [SCN]^- > [BF_4]^- \approx [NTf_2]^- > [OTf]^- > [NO_3]^- > [NPf_2]^- \approx [PF_6]^- > I^-.$$

The following tendency is for the $[C_2MIm]^+$ -based ILs.

$$[BF_4]^- \approx [TCNB]^- > [NTf_2]^- \approx [OTf]^- > [FAP]^- > [EtSO_4]^- \approx [NPf_2]^-.$$

These orders in the σ are roughly related to the opposite trends in the η , though that correlation is not perfect. In particular, the ILs with the anions of $[NTf_2]^-$ and $[NPf_2]^-$ show the lower σ values than the values expected from the η .

We also estimated the molar electrical conductivity Λ from the σ and $V_{\rm m}$ ($\Lambda = \sigma/V_{\rm m}$). The Λ values of the present ILs are also listed in Table 2. The trend of the Λ with the replacement of the anion species for the present [C₄MIm]⁺-based ILs is the following:

$$\begin{split} [DCA]^- > [NF_2]^- > [NTf_2]^- > [SCN]^- > [BF_4]^- \\ > [OTf]^- > [NPf_2]^- > [NO_3]^- > [PF_6]^- > I^-. \end{split}$$

The following trend is for the $[C_2MIm]^+$ -based ILs.

$$[TCNB]^- > [BF_4]^- > [NTf_2]^- > [OTf]^- \approx [FAP]^- > [NPf_2]^- > [EtSO_4]^-.$$



Figure 5. Plots of (a) electrical conductivity σ vs. inverse of viscosity η^{-1} and (b) molar electrical conductivity Λ vs. η^{-1} for the present ILs. The linear fits are also shown.

The trends for the Λ are better correlated to those for the η rather than those for the σ . Figure 5 shows the plots of σ vs. $1/\eta$ and Λ vs. $1/\eta$. It is obvious that the Λ is more clearly inversely proportional to the η than the σ is. It is reported that the ionicity is an important factor for electrical conductivity.¹⁷⁷ Angell and coworkers pointed out that the different fragilities show the different correlations in the Walden plots.¹⁷⁸ While a few data points are scattered from the correlation between σ vs. $1/\eta$ and Λ vs. $1/\eta$ in the present results (Figure 5), which are likely coming from such natures of cation and anion combinations and liquids, the electrical conductivities of the present ILs at 293 K roughly obey the Walden rule overall.

It is also clear from the data for $[C_nMIm][NTf_2]$, $[C_nMIm][BF_4]$, and $[C_nPy][NTf_2]$ in Table 2 that the σ value depends greatly on the alkyl group of the cations. Watanabe and coworkers reported that the σ value decreases with the longer alkyl group of cation in ILs.¹⁷⁹ They pointed out that the variation in the alkyl chain length causes change in not only the ionic concentration, but also the van der Waals interactions. Figure 6 shows the semi-logarithmic plots of σ vs. carbon number of alkyl group n, as well as the semi-logarithmic plots of Λ vs. n, for the $[C_nMIm][NTf_2]$, $[C_nMIm][BF_4]$, and $[C_nPy][NTf_2]$. As seen in the figure, the σ and Λ values do not simply express an exponential feature unlike the η . Instead, the Vogel–Tammann–Fulcher function,^{180–183} which is used to express the temperature dependent η of liquids including ILs, fits well to each series.

$$\sigma = \sigma_0 \exp(B/(n - n_0)) \tag{10}$$

where σ_0 is the limiting conductivity, *B* is a constant that could be related to a parameter of the carbon number sensitivity to σ , and n₀ is a constant that could be the critical carbon number of the alkyl group that the conductivity diverges at. Also,



Figure 6. Semi-logarithmic plots of (a) electrical conductivity σ vs. carbon number of alkyl group and (b) molar electrical conductivity Λ vs. n for [C_nMIm][NTf₂] (open circles), [C_nMIm][BF₄] (open squares), and [C_nPy][NTf₂] (filled circles). Fits by the Vogel–Tammann–Fulcher equation are also shown.

Table 3. Fit parameters for the alkyl group dependence of electrical conductivity and molar electrical conductivity for [C_nMIm][NTf₂], [C_nMIm][BF₄], and [C_nPy][NTf₂]

	$\sigma_0 \ /{ m mScm^{-1}}$	В	n ₀	$\frac{\varLambda_0}{/\mathrm{Scm}^2\mathrm{mol}^{-1}}$	Β'	n_0'
[C _n MIm][NTf ₂]	0.103	16.1	-6.56	0.094	8.95	-4.72
[C _n MIm][BF ₄]	0.097	9.61	-2.50	0.055	5.42	-1.45
[C _n Py][NTf ₂]	0.090	15.4	-6.33	0.093	7.12	-3.60

$$\Lambda = \Lambda_0 \exp(B'/(n - n_0')) \tag{11}$$

where Λ_0 is the limiting molar conductivity, B' is a constant that could be related to a parameter of the carbon number sensitivity to Λ , and n_0' is a constant that could be the critical carbon number of the alkyl group. Note that the fits using eqs 10 and 11 to the σ and Λ data here are just empirical, not based on a theory or an authority. The fit parameters for σ (eq 10) and Λ (eq 11) are summarized in Table 3. Therefore the alkyl group dependence of the σ and Λ for the [C_nMIm][NTf₂] is quite similar to that of the [C_nPy][NTf₂]. These results suggest that the alkyl group dependence of the σ and Λ is critically influenced by the anion species, but not much affected by the cation moiety.

4.1.4 Surface Tension \gamma: The γ values of the present ILs at 293 K measured in this study are listed in Table 2. The γ values at 293 K and/or the near temperatures for the present ILs, except for [C₄MIm][NF₂], [C₆Py][BF₄], [C₁₀Py][NTf₂], and [C₁₂Py]-



Figure 7. Plots of surface tension γ vs. carbon number of alkyl group for [C_nMIm][NTf₂] (open circles), [C_nMIm]-[BF₄] (open squares), and [C_nPy][NTf₂] (filled circles).

[NTf₂], were already reported. As seen in Table 2, we can find similar values of the γ for the present ILs within approximately $\pm 20\%$ in reported literature when the temperature effect is taken into consideration.^{59,87,107,134,136–139,142,145,147,150,152,155,184–189} Note that the γ values of ILs decrease with increasing temperature.^{184,186,187}

It is clear from Table 2 that the γ of the ILs is strongly influenced by the anion species. When we compare the γ values of the [C₂MIm]⁺- and [C₄MIm]⁺-based ILs in Table 2, it is found that the tendency of the γ for the anion species of the aromatic cation based ILs is as follows:

$$\begin{split} I^{-} &> [NO_3]^{-} \approx [SCN]^{-} > [DCA]^{-} > [BF_4]^{-} \approx [NF_2]^{-} \\ &\approx [PF_6]^{-} > [TCNB]^{-} \approx [EtSO_4]^{-} > [OTf]^{-} > [NTf_2]^{-} \\ &> [FAP]^{-} > [NPf_2]^{-}. \end{split}$$

It seems that γ depends on the ionic volume of the anion species. We will see the relation between the γ and $V_{\rm m}$ for the ILs (vide infra).

Besides the anion effect, the length of the alkyl group for the 1-alkyl-3-methylimidazolium and 1-alkylpyridinium cations, $[C_nMIm]^+$ and $[C_nPy]^+$, affects γ too. For example, Kolbeck et al. reported that the γ of [C_nMIm][NTf₂] at 298 K decreases to the value of 29.5 mN m^{-1} with the longer alkyl group up to octyl, but the longer alkyl groups than octyl do not influence greatly the γ value.¹⁹⁰ Figure 7 shows the carbon number dependences of γ for the [C_nMIm][NTf₂], [C_nMIm][BF₄], and $[C_n Py][NTf_2]$. As shown in the figure, γ decreases with the longer alkyl group of the cations for the [C_nMIm][BF₄] within the ethyl group and the decyl group. On the other hand, the $[C_nMIm][NTf_2]$ and $[C_nPy][NTf_2]$ show that the γ becomes low with increasing length of the alkyl group up to the octyl group but it becomes a constant at ca. 30.5 mN m^{-1} with further lengthening the alkyl group. In addition, the carbon number dependence of γ for the [C_nMIm][NTf₂] is almost the same as that for the $[C_n Py][NTf_2]$. This indicates that the anion species critically affects the alkyl group dependence of the γ for the imidazolium- and pyridinium-based ILs, but the difference in the cations, imidazolium and pyridinium, is not crucial for the alkyl group dependence of γ .

Maroncelli and coworkers previously reported a single relation between γ and $V_{\rm m}$ in alkali halides at their melting points and ILs at room temperature.¹⁹¹ Figure 8 shows the plots of γ



Figure 8. Plots of surface tension γ vs. molar volume $V_{\rm m}$ for aromatic cation based ILs. Exponential fit is also shown. Empirical correlation for molten salts including ILs reported by Maroncelli and coworkers is also shown.¹⁹¹

vs. $V_{\rm m}$ for the present ILs. In the figure, the empirical correlation curve reported by Maroncelli and coworkers¹⁹¹ and the fit to the present data by an exponential function ($\gamma =$ 178.52 exp($-0.0124V_{\rm m}$) + 28.705) are also given. When we carefully look at Figure 8, it is found that the present data depart slightly from the empirical correlation reported by Maroncelli and coworkers especially in the smaller $V_{\rm m}$ region: the empirical correlation underestimates the γ values for compact ILs. This is probably because the γ data for the alkali halides, which are smaller $V_{\rm m}$ than the ILs, are at the melting points but those for the ILs are at 298 K.¹⁹¹ Because the γ in most liquids decreases with increasing temperature,¹³² the γ values in the ILs with smaller $V_{\rm m}$ are likely underestimated in the single correlation for alkali halides and ILs.¹⁹¹

4.2 Ultrafast Dynamics: Low-Frequency Spectra. 4.2.1 General Features of Aromatic Cation Based ILs: Prior to discussing each subject regarding the low-frequency Kerr spectra of the aromatic cation based ILs in this section, let us summarize some unique spectral features of aromatic cation based ILs.⁶⁰ First, the Kerr intensities due to the nuclear response relative to the signal intensities of electronic responses are much higher for aromatic cation based ILs than nonaromatic cationbased ILs when the same anions are compared. Second, the spectral density in the frequency region higher than $50 \,\mathrm{cm}^{-1}$ is large for aromatic cation based ILs because of the ring librational motion. The maxima in the low-frequency spectra for aromatic cation based ILs usually appear at approximately $80-100 \text{ cm}^{-1}$. Conversely, the spectral intensity responsible for cation motion is very small for nonaromatic cation based ILs. These differences in the intensities of the Kerr transients and the low-frequency spectra between aromatic and nonaromatic ILs are commonly observed in molecular liquids as well.^{192–195} The third one is unique for ILs. There is a correlation between the characteristic frequency of low-frequency spectral band (M_1) and the bulk parameter $((\gamma/\rho)^{1/2})$ for a protic molecular liquids whether they are aromatic or nonaromatic, but the correlations seem to be different between aromatic and nonaromatic cation based ILs, although the number of data is not extensive. Keeping these general features for aromatic cation based ILs in mind, we see the following four topics of the low-frequency Kerr spectra for aromatic cation based ILs: (i) anion depend-



Figure 9. Low-frequency Kerr spectra of (a) [C₄MIm]I, (b) [C₄MIm][BF₄], and (c) [C₄MIm][PF₆]. Spherical top anions are compared.

ence, (ii) imidazolium cations vs. pyridinium cations, (iii) alkyl group dependence, and (iv) effect of methylation in aromatic cations. The correlation between the low-frequency spectral band and the bulk parameter will be discussed after this section.

4.2.2 Anion Dependence: It is well-known that the line shape of the low-frequency Kerr spectrum in ILs depends on the anion species. For example, $[NTf_2]^-$ anion was compared to spherical top anions, Br⁻,^{78,96} [PF₆]⁻,^{78,82,92,96} and [BF₄]⁻,⁸³ and a simpler anion [OTf]⁻,^{82,96} [XF₆]⁻ anions with different center elements, P, As, and Sb, were compared,⁸⁵ and some systematically differently branched anions, [SCN]⁻, [DCA]⁻, [C(CN)₃]⁻, [OTf]⁻, [NTf₂]⁻, and tris(trifluoromethylsulfonyl)-methide [CTf₃]⁻, were studied.⁸⁷ Here, we show the low-frequency spectra of the ILs with 13 different anions (the [C₂MIm]⁺- and [C₄MIm]⁺-based ILs).

First of all, we compare the spherical top anions, I^- , $[BF_4]^-$, and $[PF_6]^-$, in the $[C_4MIm]^+$ -based ILs, as shown in Figure 9. It is well-known that the Kerr signals of spherical top molecular liquids such as carbon tetrachloride are tiny compared to aromatic molecules in the typical fs-RIKES which uses the polarization geometry for the anisotropy detection.^{109,130,131,196,197} As well as such spherical top molecular liquids, it is expected that the contributions of spherical top anions to the low-frequency Kerr spectra of aromatic cationbased ILs are small compared to the cations. Nonetheless, it is clear from Figure 9 that the line shapes of the low-frequency Kerr spectra of $[C_4MIm]I$, $[C_4MIm][BF_4]$, and $[C_4MIm][PF_6]$ are quite different, especially in the low-frequency region below ca. 50 cm^{-1} : The intensity in this low-frequency region relative to the high-frequency region at ca. 100 cm^{-1} is small in [C₄MIm]I but that is close to the intensity at ca. 100 cm^{-1} in [C₄MIm][BF₄].

In a neat aromatic molecular liquid benzene, it was pointed out that the translational motion (interaction-induced or collision-induced motion) appears in the low-frequency region below $50 \,\mathrm{cm}^{-1}$ but the reorientational motion (libration) contributes to the intermolecular vibrational spectrum entirely, especially the spectral density in the high-frequency region (ca. $75-200 \text{ cm}^{-1}$), by the molecular dynamics (MD) simulation work of Ryu and Stratt.¹²¹ If this consideration is also applicable for these aromatic cation based ILs, the spherical top anions significantly influence the spectral density in the lowfrequency region and the translational motion (and probably the coupling motion with the cation as well) arising from the anion is expected to be suppressed with the order of the masses: $I^- >$ $[PF_6]^- > [BF_4]^-$. Previously, we compared the low-frequency spectra of [C₄MIm][PF₆], [C₄MIm][AsF₆], and [C₄MIm]-[SbF₆].⁸⁵ The intensity in the low-frequency region below $50 \,\mathrm{cm}^{-1}$ relative to that in the high-frequency region at ca. 100 cm^{-1} decreases with the order of $[PF_6]^- > [AsF_6]^- > [SbF_6]^-$. In the present study, however, the low-frequency Kerr spectra of $[C_4MIm]I, [C_4MIm][BF_4], and [C_4MIm][PF_6] do not show such$ a clear correlation with the formula weights (FW) or size of their anions. As shown in the low-frequency Kerr spectra in Figure 9. the intensity at the low-frequency region below 50 cm^{-1} relative to the high-frequency region at ca. $100 \,\mathrm{cm}^{-1}$ increases with the order of $I^- < [BF_4]^- \approx [PF_6]^-$ but FW of the anions changes differently as $[BF_4]^-$ (86.80 g mol⁻¹) < I⁻ (126.90 g mol⁻¹) < $[PF_6]^-$ (144.96 g mol⁻¹) and so does the ion radii (I⁻ (220 Å) < $[BF_4]^-$ (230 Å) < $[PF_6]^-$ (245 Å)).¹⁹⁸ Rather, the relative intensities in this low-frequency region changes in parallel with the fluidity properties (η and σ , see Table 2). This might imply that the intermolecular interaction is a dominant factor for the spectral intensity in the low-frequency region or translational motion (and probably coupling motion too) compared to the effects of the mass and volume. Note that spherical top molecules do not show depolarized Raman intensities arising from their librations. This is an example that shows how complicated the line shape of the low-frequency Kerr spectra of ILs are: even the ILs consisting of spherical top anions do not show a simple trend.

Secondly, the ILs with the series of the bis(fluorosulfonyl)amide and bis(perfluoroalkylsulfonyl)amide anions, i.e., $[NF_2]^-$, $[NTf_2]^-$, and $[NPf_2]^-$, are compared, as shown in Figure 10. In the figure, the spectrum of $[C_4MIm][OTf]$ is also shown for a comparison. The clear characteristic peaks of the spectra for $[C_4MIm][NF_2]$, $[C_4MIm][NTf_2]$, and $[C_4MIm]-[NPf_2]$ are observed at ca. 10–30 cm⁻¹, but the peak at ca. 10– 30 cm⁻¹ is not clear in $[C_4MIm][OTf]$. Indeed, this unique spectral feature is not observed in the ILs with the other anions, except for $[FAP]^-$ (Supporting Information).

Previously, we compared the spectra of $[C_4MIm][OTf]$, $[C_4MIm][NTf_2]$, and 1-butyl-3-methylimidazolium tris(trifluoromethylsulfonyl)methide ($[C_4MIm][CTf_3]$), and found that the peaks at ca. 20 cm⁻¹ were there in $[C_4MIm][NTf_2]$ and $[C_4MIm][CTf_3]$, but that of $[C_4MIm][OTf]$ shows no clear peak at ca. 20 cm⁻¹.⁸⁷ We assigned the characteristic spectral peaks for $[C_4MIm][NTf_2]$ and $[C_4MIm][CTf_3]$ to the libration



Figure 10. Low-frequency Kerr spectra of 1-butyl-3-methylimidazolium-based ILs with the anions of (a) bis-(fluorosulfonyl)amides and bis(perfluoromethylsulfonyl)amides, (b) [C₄MIm][NTf₂], and (c) [C₄MIm][NPf₂]. (d) Spectrum of 1-butyl-3-methylimidazolium trifluoromethanesulfonate [C₄MIm][OTf] is also shown as a reference.

of the $[NTf_2]^-$ or $[CTf_3]^-$ anion and/or the coupling of translational and reorientational motions previously.⁸⁷ The translational motions in molecular liquids and ILs often appear in the low-frequency region below $50 \,\mathrm{cm}^{-1}$. Thus the translational motion can influence the spectral density in the low-frequency region. In polymer solutions, on the other hand, the spectral intensity in this low-frequency region is lower for the heavier polymer and oligomers than the lighter monomer.^{199–201} Furthermore, the intensity in the low-frequency region below 20 cm⁻¹ of the low-frequency Kerr spectra of [C₄MIm]-based ILs with hexafluoropnictogenate anions becomes smaller with the substitution from $[PF_6]^-$ to $[AsF_6]^-$ and $[SbF_6]^{-.85}$ MD simulation results of [C₄MIm][PF₆], [C₄MIm][AsF₆], and $[C_4MIm][SbF_6]$ indicated that the translational motion is clear in [C₄MIm][PF₆] but not active in the other two ILs with heavier anions.¹²⁸ However, the trend observed in [C₄MIm][OTf], [C₄MIm][NTf₂], and [C₄MIm][CTf₃] is opposite to these



Figure 11. Low-frequency Kerr spectra of (a) $[C_4MIm]$ -[DCA], (b) $[C_4MIm][NO_3]$, and (c) $[C_4MIm][SCN]$. Simple symmetric anions $(C_{2\nu}, D_{3h}, C_{\infty\nu})$ are compared.

reported cases. Thus the peak intensities at the low-frequency region at ca. 20 cm^{-1} for [C₄MIm][NTf₂] and [C₄MIm][CTf₃] were assigned to the anion's librations and/or the coupling of translational and reorientational motions.

In the same way as the previous study of $[C_4MIm][NTf_2]$ and $[C_4MIm][CTf_3]$,⁸⁷ we attribute the characteristic peaks at ca. 10–30 cm⁻¹ for $[C_4MIm][NF_2]$ and $[C_4MIm][NPf_2]$ to the anion's libration and/or the coupling of translational and reorientational motions, not mainly due to the translational motion. This is because the chemical structures of anions are quite similar. It is further found from the comparison of $[C_4MIm][NF_2]$, $[C_4MIm][NTf_2]$, and $[C_4MIm][NPf_2]$ shown in Figure 10 that the peak in the low-frequency region shifts to the lower frequency with the larger anion: $[C_4MIm][NF_2]$ (ca. $21 \text{ cm}^{-1}) > [C_4MIm][NTf_2]$ (ca. $18 \text{ cm}^{-1}) > [C_4MIm][NPf_2]$ (ca. 14 cm^{-1}). This is rather reasonable, because the order of the peak frequencies of the three ILs is the inverse of the orders of the masses and the volumes of the anions.

Figure 11 displays the low-frequency Kerr spectra of the $[C_4MIm]^+$ -based ILs with relatively simple and highly symmetrized anions: $[DCA]^-$ (C_{2v}), $[NO_3]^-$ (D_{3h}), and $[SCN]^-$ ($C_{\infty v}$). There is a strong intramolecular band at ca. 182 cm⁻¹ in $[C_4MIm][DCA]$, but the low-frequency bands, which are mainly attributed to the intermolecular vibrations for the three ILs, are quite similar. If we consider the fact that $[DCA]^-$, $[NO_3]^-$, and $[SCN]^-$ anions are not spherical top and their librational motions are most likely active because of their non-zero polarizability anisotropy volumes, they could fairly



Figure 12. Low-frequency Kerr spectra of (a) $[C_2MIm]$ -[TCNB] and (b) $[C_2MIm][FAP]$. Low-frequency spectra of ILs with unique anions are shown as examples. Calculated Raman spectra of (c) $[TCNB]^-$ and (d) $[FAP]^-$ based on the B3LYP/6-31G+(d,p) level of theory are also shown.

contribute to the low-frequency spectra of [C₄MIm][DCA], [C₄MIm][NO₃], and [C₄MIm][SCN], and the line shapes of their low-frequency spectra would be different. However, this is not the case. As seen in Table 2, the three ILs have similar FW values (Table 2) and their bulk properties such as ρ and γ , which are related to the M_1 of the low-frequency spectrum (vide infra), are also similar. Thus, it is not very surprising that the three ILs share the close similarity in the line shapes of their low-frequency spectra.

Figures 12a and 12b displays the low-frequency Kerr spectra of the $[C_2MIm]^+$ -based ILs with relatively complicated anions: $[TCNB]^-$ and $[FAP]^-$. In contrast to the simple anions that consist of relatively small number of light atoms as shown in Figures 9 and 11, the line shapes of the low-frequency Kerr spectra of $[C_2MIm][TCNB]$ and $[C_2MIm][FAP]$ are complicated and unique: $[C_2MIm][TCNB]$ shows the strong bands at ca. 120 and 145 cm⁻¹ and $[C_2MIm][FAP]$ shows a bimodal line shape. Figures 12c and 12d show the calculated Raman spectra

of [TCNB]⁻ and [FAP]⁻ anions based on ab initio quantum chemistry calculations. As seen in the figure, the strong bands at 124 and 147 cm⁻¹ for [C₂MIm][TCNB] are assigned to the anion's intramolecular vibrational modes based on the calculated Raman spectrum. The first band includes two modes (NC-B-CN twisting and scissoring) and the latter one is triple degeneracy mode (combination of rocking and wagging or scissoring and scissoring). On the other hand, [FAP]⁻ anion shows many Raman active intramolecular modes though their intensities are not that strong. It may be realized from Figure 12 that the low-frequency Kerr spectrum of [C₂MIm]-[FAP] shows the strong intensity at ca. 10 cm^{-1} despite the absence of a strong Raman active intramolecular mode in the anion. As discussed above, the ILs with bis(fluorosulfonyl)amide and bis(perfluoroalkylsulfonyl)amide anions display similar bimodal spectral shapes. Like the case of the ILs with bis(fluorosulfonyl)amide and bis(perfluoroalkylsulfonyl)amide anions, the strong intensity at ca. 10 cm⁻¹ for [C₂MIm][FAP] is attributable to the intermolecular vibration, such as libration, of the anion.

4.2.3 Imidazolium Cations vs. Pyridinium Cations: So far, most aromatic ILs studied by fs-RIKES are imidazolium-based ILs. Indeed, only four pyridinium-based ILs, 1-meth-oxyethylpyridinium dicyanamide,⁹⁰ 1-butylpyridinium bis(tri-fluoromethylsulfonyl)amide,⁸⁶ 1-cyclohexylmethylpyridinium bis(trifluoromethylsulfonyl)amide,⁸⁹ and 1-benzylpyridinium bis(trifluoromethylsulfonyl)amide⁸⁹ were studied for their low-frequency vibrational dynamics by fs-RIKES, as far as we know. In this section, we compare the low-frequency spectra between imidazolium- and pyridinium-based ILs to clarify the difference of the two major types of aromatic cations.

Figure 13 displays the low-frequency Kerr spectra of [C₄MIm][BF₄], [C₄Py][BF₄], [C₁₀MIm][NTf₂], and [C₁₀Py]-[NTf₂]. As seen in the figure, the line shapes of the low-frequency Kerr spectra of the imidazolium and pyridinium cationbased ILs with the same anions and the same alkyl groups are quite different. Namely, the strong spectral densities at ca. 80-100 cm⁻¹ are found in the pyridinium-based ILs compared to the imidazolium-based ILs. This characteristic difference in the low-frequency Kerr spectra between pyridinium- and imidazolium-based ILs is also found in the other comparisons, e.g., $[C_6Py][BF_4]$ vs. $[C_6MIm][BF_4]$, $[C_8Py][NTf_2]$ vs. $[C_8MIm]$ -[NTf₂], etc. (see Supporting Information). A similar feature was also reported in [NTf2]⁻ salts of 1-benzyl-3-methylimidazolium, 1-benzylpyridinium, 1-cyclohexylmethyl-3-methylimidazolium, and 1-cvclohexvlmethvlpvridinium cations.⁸⁹ Because the large spectral density in the high-frequency region (>ca. 50 cm⁻¹) for the broad low-frequency Kerr spectra of imidazolium- and pyridinium-based ILs arises mainly from the aromatic ring libration, it is plausible that the difference in the spectra between the pyridinium- and imidazolium-based ILs is attributed to the difference in the librational motions of the pyridinium and imidazolium rings. For example, the polarizability anisotropy of [C₄Py]⁺ estimated from the quantum chemistry calculations based on the B3LYP/6-31+G(d,p) level of theory is about 10% larger than that of $[C_4MIm]^+$ (Supporting Information). The larger spectral intensity in the Kerr spectra for the pyridinium-based ILs than the imidazoliumbased ILs having same anions and alkyl groups can be attrib-



Figure 13. Low-frequency Kerr spectra of (a) [C₄Py][BF₄], (b) [C₄MIm][BF₄], (c) [C₁₀Py][NTf₂], and (d) [C₁₀MIm]-[NTf₂]. Pyridinium and imidazolium cations are compared.

uted to the larger polarizability anisotropy of the pyridinium cations than the respective methylimidazolium cations. In addition, the methyl group likely influences the imidazolium ring libration with the asymmetry and bulkiness in the case of 1-alkyl-3-methylimidazolium based ILs. We will discuss this in the later section (*effects of methylation in aromatic cations*).

4.2.4 Alkyl Group Dependence: There are several reports on the alkyl group dependence (or comparisons of different alkyl groups) of cations in ILs on the low-frequency Kerr spectra less than ca. 200 cm^{-1} .^{76,82,88} However, only the series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-amides [C_nMIm][NTf₂] were investigated for the alkyl group dependence of the low-frequency spectra so far. In this study, we compare three different series: [C_nMIm][NTf₂], [C_nMIm]-[BF₄], and [C_nPy][NTf₂]. We focus on the [C_nMIm][BF₄] and [C_nPy][NTf₂] series in this section, because they are reported here for the first time.

Figure 14 shows the low-frequency spectra with the frequency range of $0-300 \text{ cm}^{-1}$ for the [C_nMIm][BF₄] and [C_nPy]-



Figure 14. Low-frequency Kerr spectra of (a) $[C_2MIm][BF_4]$, (b) $[C_3MIm][BF_4]$, (c) $[C_4MIm][BF_4]$, (d) $[C_6MIm][BF_4]$, (e) $[C_8MIm][BF_4]$, (f) $[C_{10}MIm][BF_4]$, (g) $[C_4Py][NTf_2]$, (h) $[C_6Py][NTf_2]$, (i) $[C_8Py][NTf_2]$, (j) $[C_{10}Py][NTf_2]$, and (k) $[C_{12}Py][NTf_2]$. Alkyl group dependence is shown.

[NTf₂] series. Because of the simpler anion's structure, let us take a look at the low-frequency spectra of the [C_nMIm][BF₄] series first. As seen in Figure 14a, there is a clear intramolecular vibrational mode at 155 cm⁻¹ in [C₂MIm][BF₄]. Further, the spectral intensity at the low-frequency ca. 20 cm⁻¹ relative to that at the high-frequency ca. 70–100 cm⁻¹ is decreasing with alkyl group substitution from the ethyl group to the hexyl group, but is increasing by the substitution from the hexyl group to the decyl group.

The low-frequency spectrum of $[C_2MIm][BF_4]$ inspires us to think that the intramolecular vibrational modes of the cations influence the low-frequency spectra. Figure 15 shows the calculated Raman spectra of the optimized $[C_nMIm]^+$ and $[C_nPy]^+$ cations based on ab initio quantum chemistry calcu-



Figure 15. Calculated Raman spectra of (a) $[C_nMIm]^+$ (n = 2 (red), 3 (blue), 4 (green), 6 (light blue), 8 (brown), and 10 (black)) and (b) $[C_nPy]^+$ (n = 4 (green), 6 (light blue), 8 (brown), and 10 (black)) based on the B3LYP/6-31+G(d,p) level of theory. The bending mode between aromatic rings and alkyl groups shifts to the lower frequency with the longer alkyl group.

lations (B3LYP/6-31+G(d,p)). With the coexistence of trans and gauche conformations of the butyl group of a 1-butyl-3methylimidazolium-based IL,²⁰² it is helpful to understand a general feature of the alkyl group length dependence of the bending mode of the optimized (all trans alkyl group) cations. It is found from the quantum chemistry calculation results that the bending modes between the alkyl groups and the imidazolium ring depend on the length (or the weight) of the alkyl group: 136 cm^{-1} for the $[C_2 \text{MIm}]^+$; 104 cm^{-1} for the $[C_3MIm]^+$; 85 cm⁻¹ for the $[C_4MIm]^+$; 53 cm⁻¹ for the $[C_6MIm]^+$; 39 cm⁻¹ for the $[C_8MIm]^+$; 27 cm⁻¹ for the $[C_{10}MIm]^+$. Ab initio quantum chemistry calculation results of $[C_4MIm]^+$ and $[C_6MIm]^+$ whose conformations of the end methyl groups of the alkyl groups are gauche also show that the bending mode shifts to the lower frequency with increasing the length of alkyl group (gauche $[C_4MIm]^+$: 99 cm⁻¹ and gauche $[C_6MIm]^+$: 59 cm⁻¹). Therefore, it is plausible that the longer alkyl groups of the cations provide the lower frequencies in the bending modes, whether they are trans or gauche.

Although it is difficult to exactly distinguish the intramolecular vibrational modes from the broad and strong intermolecular vibrational bands, except for $[C_2MIm][BF_4]$, it is weakly recognizable from the low-frequency spectra of the $[C_nMIm][BF_4]$ (Figures 14a–14f) that the intramolecular vibrational band shifts to lower frequency with increasing alkyl group length of the imidazolium ring. The crude frequencies estimated from the gentle peaks or the shoulder (in $[C_3MIm]$ - $[BF_4]$) of the spectra are approximately 155, 102, 83, 69, 55, and 39 cm⁻¹ for $[C_2MIm][BF_4]$, $[C_3MIm][BF_4]$, $[C_4MIm]$ - $[BF_4]$, $[C_6MIm][BF_4]$, $[C_8MIm][BF_4]$, and $[C_{10}MIm][BF_4]$,

respectively. The tendency in the frequency shifts observed in the present experiments is almost consistent with that of the ab initio quantum chemistry calculations. We also note that the spectral area of the bending mode in [C₂MIm][BF₄] that shows the clearest bending band is about 15% of the entire broad spectrum from 0 to 200 cm^{-1} based on the line shape analysis. Accordingly, the variation of the spectral line shape for the $[C_nMIm][BF_4]$ with different alkyl groups of the cations is partially attributed to the intramolecular bending modes between alkyl groups and imidazolium ring. However, the contribution of the intramolecular vibrational mode to the broad low-frequency spectrum is more ambiguous in both the imidazolium- and pyridinium-based ILs whose cation has a longer alkyl group, as shown in Figure 14. This is probably because a longer alkyl group possibly forms a wider variety of conformers that gives a broadened band due to the different conformers.

As displayed in Figure 15, the bending mode between the alkyl group and pyridinium ring in the $[C_nPy]^+$ also depends on the alkyl group: 78 cm^{-1} for $[C_4Py]^+$; 53 cm^{-1} for $[C_6Py]^+$; 40 cm^{-1} for $[C_8Py]^+$; 30 cm^{-1} for $[C_1Py]^+$. Unlike the $[C_nMIm]$ -[BF4] series, it is hard to find the difference among the low-frequency spectra for the $[C_nPy][NTf_2]$ series (Figures 14g–14k) because of the strong intensity of the intermolecular vibrational band relative to the intramolecular vibrational modes. However, the quantum chemistry calculation results shown in Figure 15b suggest that the intramolecular vibrational modes of the pyridinium cations exist in the low-frequency region from 0 to 150 cm^{-1} though they are buried in the broad intermolecular vibrational bands.

Therefore, as shown in Figure 14, the small difference in the low-frequency spectral shapes of the ILs is likely attributed to the intramolecular vibrational motions in large part. It should also be noted that the intensities of the low-frequency bands mainly coming from intermolecular contributions (ring librations) of pyridinium-based ILs are larger than those of the comparable imidazolium-based ILs, as discussed in *"imidazo-lium cations vs. pyridinium cations"*.⁸⁹ This makes ambiguous the effect of alkyl group bending mode on the low-frequency spectrum.

4.2.5 Effect of Methylation in Aromatic Cations: In this section, we look at the effect of methylation of the cations on the low-frequency spectra. Because the aromatic ring libration contributes to the low-frequency Kerr spectra substantially, it is not surprising that the low-frequency Kerr spectra of the aromatic cation based ILs are varied by a methylation in the aromatic cations. In addition, it is known that the proton at 2 position of 1-alkyl-3-methylimidazolium cation is acidic and the substitution of the proton by methyl group (1-alkyl-2,3dimethylimidazolium) affects physical properties, especially η and thus σ (see Table 2), of the ILs.^{166,186} We thus believe that it is important to study the methylation effect in the aromatic rings of the aromatic cation based ILs on the low-frequency Kerr spectra. Actually, Wynne and coworkers compared the low-frequency Kerr spectra between [C4MIm][NTf2] and [C₄DMIm][NTf₂] in 2003.⁸² We further explore the methylation effect on the low-frequency Kerr spectra of aromatic cation based ILs, that is, the comparisons of [1C₄2MPy][NTf₂], $[1C_43MPy][NTf_2]$, $[1C_44MPy][NTf_2]$, and $[C_4Py][NTf_2]$ in



Figure 16. Low-frequency Kerr spectra of (a) $[C_4DMIm]$ - $[NTf_2]$ and (b) $[C_4MIm][NTf_2]$. Methylation effect in the imidazolium cation on the low-frequency spectrum is shown.

addition to the comparison between $[C_4DMIm][NTf_2]$ and $[C_4MIm][NTf_2]$ in this study.

Figure 16 compares the low-frequency spectra between [C₄DMIm][NTf₂] and [C₄MIm][NTf₂]. The difference in the spectra is not large, but the amplitude of the spectral density in the high-frequency region (ca. 90 cm^{-1}) relative to the lowfrequency region (ca. 10-20 cm⁻¹) becomes large by methylation. This feature was already reported by Wynne and coworkers.⁸² Figure 17 shows further comparisons of the lowfrequency Kerr spectra of [1C₄2MPy][NTf₂], [1C₄3MPy]- $[NTf_2]$, and $[1C_44MPy][NTf_2]$ together with $[C_4Py][NTf_2]$. In Figures 16 and 17, we clearly see several noticeable points: (i) the spectral line shape of $[1C_43MPy][NTf_2]$ is apparently different from those of [1C₄2MPy][NTf₂], [1C₄4MPy][NTf₂], and [C₄Py][NTf₂]; (ii) the spectral shape for [1C₄3MPy][NTf₂] is closer to that of [C₄MIm][NTf₂] instead of the other pyridinium-based ILs; (iii) the spectra of [1C₄2MPy][NTf₂], [1C₄4MPy][NTf₂], and [C₄Py][NTf₂] are similar but not exactly the same (e.g., the peaks in the high-frequency region above 50 cm^{-1} are ca. 95.4, 81.6, and 89.6 cm⁻¹, respectively).

As discussed above, the low-frequency Kerr spectra, especially in the high-frequency region above 50 cm^{-1} , of aromatic cation based ILs arise mainly from the aromatic ring librations. The peaks in this high-frequency region for [C₄DMIm]-[NTf₂], [C₄MIm][NTf₂], [1C₄2MPy][NTf₂], [1C₄3MPy][NTf₂], [1C₄4MPy][NTf₂], and [C₄Py][NTf₂] are ca. 89.2, 79.8, 95.4, 78.6, 81.6, and 89.6 cm^{-1} , respectively. Because the long butyl group bonded with the cation rings, the librations of the rings responsible for the low-frequency spectra likely occur about the axis along near the butyl group direction. Therefore, it is expected that the libration of an aromatic ring slows down with the methylation in the aromatic rings. When we compare the spectra of $[1C_43MPv][NTf_2]$, $[1C_44MPv][NTf_2]$, and [C₄Py][NTf₂], the trend of the peak frequencies can be reasonably explained by this consideration. Of course, the methyl group at the 4 position of the pyridinium ring most likely slows



Figure 17. Low-frequency Kerr spectra of (a) [1C₄2MPy]-[NTf₂], (b) [1C₄3MPy][NTf₂], (c) [1C₄4MPy][NTf₂], and (d) [C₄Py][NTf₂]. Methylation effects of positions in the pyridinium cations are shown.

down the ring libration less than that at 3 position because of the steric effect for the libration along near the butyl group. This is also well supported by the trend of the fastest rotational constants (3.69 GHz for $[C_4Py]^+$, 3.35 GHz for $[1C_44MPy]^+$, 2.35 GHz for $[1C_43MPy]^+$, see Supporting Information). On the other hand, [1C₄2MPy][NTf₂] shows the highest frequency of the peak in the high-frequency region among these pyridinium-based ILs, despite that the fastest rotational constant for $[1C_42MPy]^+$ is 2.18 GHz (Supporting Information), being smaller than those for the other three cations. This feature is also similar to the case of [C₄DMIm][NTf₂] compared to $[C_4MIm][NTf_2]$. It is speculated that the pyridinium ring of $[1C_42MPy]^+$ and the imidazolium ring of $[C_4DMIm]^+$ cannot fully librate about the axis near the butyl group direction because of the steric hindrance of the methyl group to the butyl group that provides a steeper potential and this causes the highfrequency librations. The bulk parameters, η and γ , for these ILs should be also noted. As shown in Table 2, both η and γ for $[1C_42MPy][NTf_2]$ are larger than those for $[C_4Py][NTf_2]$,



Figure 18. Calculated Raman spectra of (a) $[C_4DMIm]^+$, (b) $[C_4MIm]^+$, (c) $[1C_42MPy]^+$, (d) $[1C_43MPy]^+$, (e) $[1C_44MPy]^+$, and (f) $[C_4Py]^+$ based on the B3LYP/6-31+G(d,p) level of theory.

[1C₄3MPy][NTf₂], and [1C₄4MPy][NTf₂], but [C₄Py][NTf₂], [1C₄3MPy][NTf₂], and [1C₄4MPy][NTf₂] show similar η and γ . η and γ for [C₄DMIm][NTf₂] are also larger than those for [C₄MIm][NTf₂]. Thus, the stronger intermolecular interactions for [1C₄2MPy][NTf₂] and [C₄DMIm][NTf₂] compared to their comparable ILs can also provide the higher frequencies of the librations of the aromatic rings.

Regarding the similarity in the spectral shapes for $[C_4MIm]$ - $[NTf_2]$ and $[1C_43MPy][NTf_2]$, it is not clear in the origin and it might be coincidence. However, the geometrical structures (positions of methyl group and butyl group at aromatic rings) of the two cations are similar. This implies that the aromatic cations having the similar geometrical structures provide the



Figure 19. Plots of the first moment M_1 of low-frequency band vs. bulk parameter $(\gamma/\rho)^{1/2}$ for aromatic cations (red circles). Linear fit is also shown by red line. For comparison, the relation for aprotic molecular liquids is also shown by black line.^{12,110,203}

similar vibrational spectral shapes. Such a behavior was observed in 1-methoxyethylpyridinium dicyanamide and a 1:1 mixture of methoxyethylbenzene and dicyanomethane.⁹⁰

In addition to the librations, we need to take the effects of the intramolecular vibrational modes on the low-frequency spectra into consideration. Figure 18 shows the calculated Raman spectra of $[C_4DMIm]^+$, $[C_4MIm]^+$, $[1C_42MPy]^+$, $[1C_43MPy]^+$, $[1C_44MPy]^+$, and $[C_4Py]^+$ cations by ab initio quantum chemistry calculations based on the B3LYP/6-31+G(d,p) level of theory. It is clear from Figure 18 that there are intramolecular vibrational modes in the frequency range of at $50-100 \,\mathrm{cm}^{-1}$. The strong modes are the bending modes between the butyl group and aromatic rings with different coordinate axes. The frequencies of the bands are not very different among the 6 cations, and they do not correlate with the line shapes of the experimental low-frequency Kerr spectra. Accordingly, the methylation effects on the low-frequency spectra for the present pyridinium- and imidazolium-based ILs are mostly due to the ring librations, but not the intramolecular vibrational modes.

4.3 Relation between Low-Frequency Spectrum and Bulk Parameters. Understanding/clarifying the relationship between the microscopic aspects such as the intermolecular vibrational band and the bulk parameters in liquids is a major issue and challenge in chemistry. Previously, we reported data for the intermolecular vibrational dynamics of 40 aprotic molecular liquids studied by fs-RIKES.¹² In that study,¹² we found correlations between the first moment (M_1) of the lowfrequency Kerr spectrum and the bulk parameters such as the square root of the surface tension (γ) divided by the liquid density (ρ) and FW: $\sqrt{\gamma/\rho}$ and $\sqrt{\gamma/FW}$. The idea of the plots was based on a simple consideration of the intermolecular vibrations in analogy with the harmonic oscillator, but we used γ and ρ instead of the force constant and reduced mass in the harmonic oscillator model because of its intermolecular nature and liquid state. Accordingly, the relation between the microscopic (low-frequency spectrum) and bulk (γ and ρ) quantities, if there is one, implies a kind of scaling relation between them. We previously suggested from the data of 20 aromatic cationbased ILs and 10 nonaromatic cation based ILs that the correlations were very different between aromatic and nonaromatic cation based ILs.⁶⁰ In this section, we see the correlation between M_1 and $\sqrt{\gamma/\rho}$ for the present aromatic cation based ILs of as many as 40 samples.

Figure 19 shows the plots of M_1 vs. $\sqrt{\gamma/\rho}$ for the data of the present 40 aromatic ILs together with the linear fit. The correlation for aprotic molecular liquids based on the data of 49 liquids^{12,110,203} is also shown as a reference. As clearly seen in Figure 19, the correlation for the aromatic ILs is obviously different from that for the aprotic molecular liquids. The M_1 values for most aromatic ILs studied here are higher than the values expected from the correlation for the aprotic molecular liquids. In addition, the slope in the correlation of the aromatic ILs is much gentler than that for the aprotic molecular liquids. Note that the data of the correlation for the aprotic molecular liquids include both aromatic and nonaromatic molecular liquids. It is found in Figure 19 that the feature of the present correlation for the aromatic ILs based on the 40 samples is quite similar to that of the previous correlation on the basis of 20 aromatic ILs.⁶⁰

The weak bulk parameter dependence of M_1 in the aromatic ILs compared to molecular liquids and nonaromatic ILs was discussed in a previous report.⁶⁰ In that report,⁶⁰ we attributed this moderate bulk parameter dependence of M_1 to the more heterogeneous structure and the stronger signal of a charged aromatic moiety. Our scenario is the following. Aromatic ILs are more segregated than nonaromatic ILs when the same anion and the same alkyl group of cations are compared.57,204 The charged aromatic moieties, such as imidazolium and pyridinium rings, have stronger signals than the charged nonaromatic parts, such as pyrrolidinium and ammonium groups. As a result, fs-RIKES probes more local information on the ionic region in aromatic ILs but more delocalized and homogeneous information in nonaromatic ILs. Of course, the neutral molecular liquids studied for the correlation that is rather simple do not show such a segregation structure. Therefore, the lowfrequency intermolecular vibrational band is weakly dependent on the bulk parameter in the case of aromatic ILs, but it is strongly dependent in the cases of aprotic molecular liquids and nonaromatic ILs. The present study supports this scenario strongly in terms of aromatic cation based ILs because of the much larger number of data than the previous report.⁶⁰ We are planning to study nonaromatic cation based ILs, such as pyrrolidinium-, ammonium-, and phosphonium-based ILs, to see the correlation between M_1 and $\sqrt{\gamma/\rho}$ for nonaromatic cation based ILs in the near future.

5. Summary

In this study, we reported data on the ultrafast dynamics of 40 aromatic cation based ILs measured by fs-RIKES, as well as some bulk properties including density, viscosity, electrical conductivity, and surface tension, of the ILs. First we showed and discussed the results of the bulk properties of the aromatic cation based ILs. From the results of the densities, viscosities, electrical conductivities, and surface tensions for the [C_nMIm]-[NTf₂], [C_nMIm][BF₄], and [C_nPy][NTf₂], we found that the alkyl group dependences of these bulk properties of the [C_nMIm][NTf₂] and [C_nPy][NTf₂] are quite similar, but that of the [C_nMIm][BF₄] is distinct. The results indicate that the

imidazolium and pyridinium cations provide the similar bulk properties of ILs, but the bulk properties of ILs vary significantly with the anion species. On the basis of the results of the bulk properties of the ILs for $[C_2MIm]^+$ and $[C_4MIm]^+$ cations, we found the following trends:

 $\begin{array}{l} \text{Density: } [FAP]^- > [NPf_2]^- > I^- > [NTf_2]^- > [PF_6]^- \approx [NF_2]^- > \\ [OTf]^- > [BF_4]^- \approx [NO_3]^- \approx [EtSO_4]^- > [SCN]^- \approx [DCA]^- > \\ [TCNB]^-. \end{array}$

 $\begin{array}{ll} \mbox{Viscosity} & ([C_4MIm]^+\mbox{-based} & ILs): \ I^- > [PF_6]^- > [NO_3]^- > \\ [NPf_2]^- > [BF_4]^- \approx [OTf]^- > [SCN]^- > [NTf_2]^- > [NF_2]^- \approx \\ [DCA]^-. \end{array}$

Viscosity ($[C_2MIm]^+$ -based ILs): $[EtSO_4]^- > [NPf_2]^- > [FAP]^- > [OTf]^- > [BF_4]^- > [NTf_2]^- > [TCNB]^-$.

 $\begin{array}{ll} \mbox{Electrical conductivity} & ([C_4MIm]^+\mbox{-based ILs})\mbox{:} & [DCA]^- > \\ [NF_2]^- > [SCN]^- > [BF_4]^- \approx [NTf_2]^- > [OTf]^- > [NO_3]^- > \\ [NPf_2]^- \approx [PF_6]^- > I^-. \end{array}$

We also found a good correlation between the molar electrical conductivity and the inverse of the viscosity for the present 40 ILs.

In the second part, the low-frequency Kerr spectra of the aromatic cation based ILs are discussed. Because we experimentally obtained low-frequency Kerr spectra of as many as 40 aromatic cation based ILs in this study, we focused on several topics, that is, (i) anion dependence; (ii) imidazolium cations vs. pyridinium cations, (iii) alkyl group dependence, and (iv) effect of methylation in aromatic cations. In the first subsection, anion dependence, we looked at the low-frequency spectra of several ILs with different anions. The line shapes of the low-frequency spectra of the ILs vary significantly with the different anion species. Even in the simple spherical top anions, e.g., I^- , $[BF_4]^-$, $[PF_6]^-$, the ILs show distinct low-frequency spectra. The ILs with different bis(fluorosulfonyl)amide and bis(perfluoroalkylsulfonlyl)amide anions ([NF2]-, [NTf2]-, and $[NPf_2]^-$) show a unique peak at ca. 10–30 cm⁻¹ that depends slightly on the anion species. We also picked up some other ILs that show general and unique spectral shapes. In the second subsection, imidazolium cations vs. pyridinium cations, we showed the difference in the low-frequency spectra between the imidazolium- and pyridinium-based ILs. When we compared the low-frequency Kerr spectra between the $[C_nMIm]^+$ and $[C_nPy]^+$ cation-based ILs having the same anions and alkyl groups, the pyridinium-based ILs showed the stronger intensity in the high-frequency region $(>50 \text{ cm}^{-1})$ that is attributed to the ring libration than the imidazolium-based ILs. This is an indication that the pyridinium ring libration is more active in depolarized Raman signal than the imidazolium ring libration. The alkyl group dependence of the cations on the lowfrequency spectra was discussed in the third subsection, alkyl group dependence. The line shapes of the low-frequency spectra of both the $[C_nMIm]^+$ - and $[C_nPy]^+$ -based ILs depend on the alkyl group of the cations. On the basis of the quantum chemistry calculation results, we attribute the alkyl group dependence of the low-frequency spectra to the intramolecular vibrational modes (bending modes between the alkyl groups

and imidazolium ring) of the cations. We also showed the methylation effects of the cations on the low-frequency spectra in *effect of methylation in aromatic cations*.

In the last part, we discussed the relation between the lowfrequency Kerr spectrum and bulk properties. We confirmed that the first moment M_1 of the low-frequency spectral band correlates to the bulk parameter $\sqrt{\gamma/\rho}$ for the present aromatic cation based ILs. The correlation for the aromatic cation based ILs is much gentler than that for aprotic molecular liquids. The difference in the correlation of M_1 and $\sqrt{\gamma/\rho}$ between the aromatic cation based ILs and aprotic molecular liquids is likely attributed to the differences in the microstructure and probing space scale: the Kerr spectra of aromatic cation based ILs are mostly coming from the ionic region via the strongly Kerr active aromatic moieties: on the other hand the spectra of the aprotic molecular liquids include rather homogeneous and thus delocalized information on the liquids. As a result, the low-frequency Kerr spectra of the aromatic cation based ILs are less sensitive to the bulk properties than the aprotic molecular liquids.

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Supporting Information

Data of the Kerr transients and Fourier-transform Kerr spectra and lists of the fit parameters for the Kerr transients and the Kerr spectra of the ILs are summarized in Supporting Information. Synthesis and purification procedures for some ILs synthesized in this study are also described in it. Ab initio quantum chemistry calculation results are summarized, as well. This material is available on http://dx.doi.org/10.1246/bcsj. 20160085.

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