Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Spectroscopic evidence of cholinium 'jumping and pecking' and H-bond enhanced cation-cation interaction in ionic liquids*

*Anne Knorr, Koichi Fumino, Anne-Marie Bonsa, and Ralf Ludwig**

[*] Dipl.-Chem. Anne Knorr, Dr. Koichi Fumino, Dipl.-Chem. Anne-Marie Bonsa, Prof. Dr. R. Ludwig
Universität Rostock, Institut für Chemie, Abteilung für Physikalische Chemie
Dr.-Lorenz-Weg 1, 18059, Rostock (Germany)
Tel: (+49) 381-498-6517
E-mail: ralf.ludwig@uni-rostock.de

Prof. Dr. R. Ludwig
Leibniz-Institut für Katalyse
an der Universität Rostock e.V.
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)

Supporting Information

Contents

SI0 Sample preparation

The sample of [Ch][NTf_2] was purchased from Iolitec (>99% mass fraction). [TMPA][NTf_2] was received from Solvionic (99,9% mass fraction). Both ionic liquids were dried under vacuum for around 48 hours in order to reduce the water content under 100 ppm and remove other volatile impurities as well. The water content was checked using a Karl Fischer titrator (Titroline KF Trace, Schott Instruments GmbH) resulting in 64 ppm for [Ch][NTf_2] and 63 ppm for [TMPA][NTf_2].

SI1 Experimental

Far infrared (FIR) measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with an extension for measurements in the FIR region that consists of a multilayer mylar beam splitter and a room temperature DLATGS detector with preamplifier. Polyethylene (PE) windows with an internal optical path of 0.1 mm were used. Further improvement could be achieved by using a high-pressure mercury lamp and a silica beam splitter. The accessible spectral region for this configuration now lies between 10 and 680 cm^{-1} (0.3 and 20.3 THz).

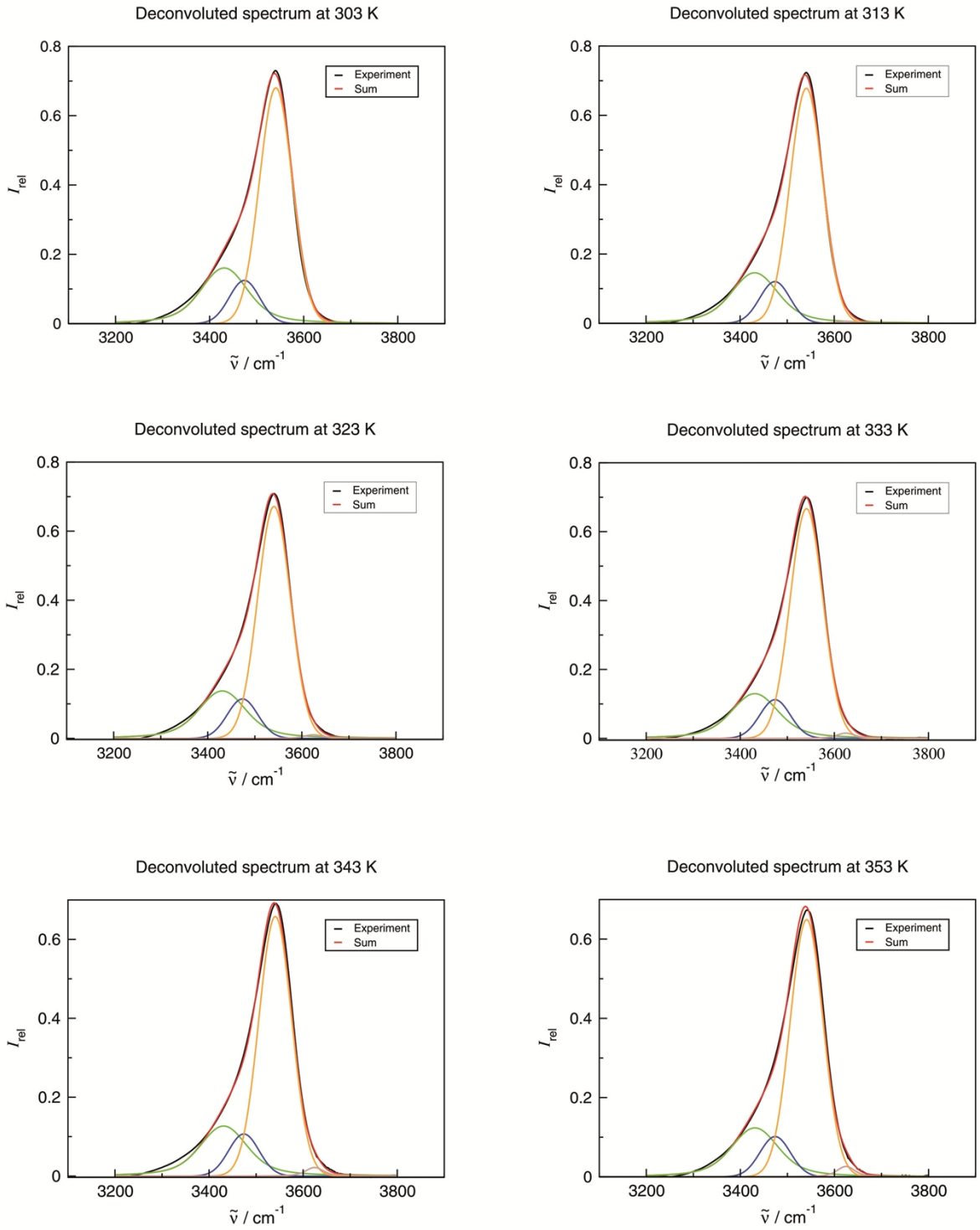
Mid infrared (MIR) measurements were performed with a Bruker Vector 22 FTIR spectrometer. An L.O.T.-Oriel variable-temperature cell equipped with CaF2 windows having a path length of 0.05 mm was used for the variable-temperature experiments. Temperatures were maintained with an external Haake C25P cryostat and were monitored with a thermocouple attached directly to the cell. For each spectrum 128 scans were recorded at a spectral resolution of 1 cm^{-1}. The sample chamber was purged with dry air during data collection.

The spectra were deconvoluted simultaneously as well as separately into a number of Voigt-profiles (convolution of Lorentzian and Gaussian functions) following the Levenberg-Marquardt procedure. The Voigt-profile has four parameters: the intensity, the frequency, the half-width of the Lorentzian, and the half-width of the Gaussian.

The conductivity measurements were carried out in a specifically designed glass cell to minimize evaporation of the solvent during measurements. The sensor used was a SE 204 Conductivity Sensor from Knick coupled with a Knick Portamess Cond 911 conductivity meter. The sensor was equipped with a temperature probe for direct temperature control.

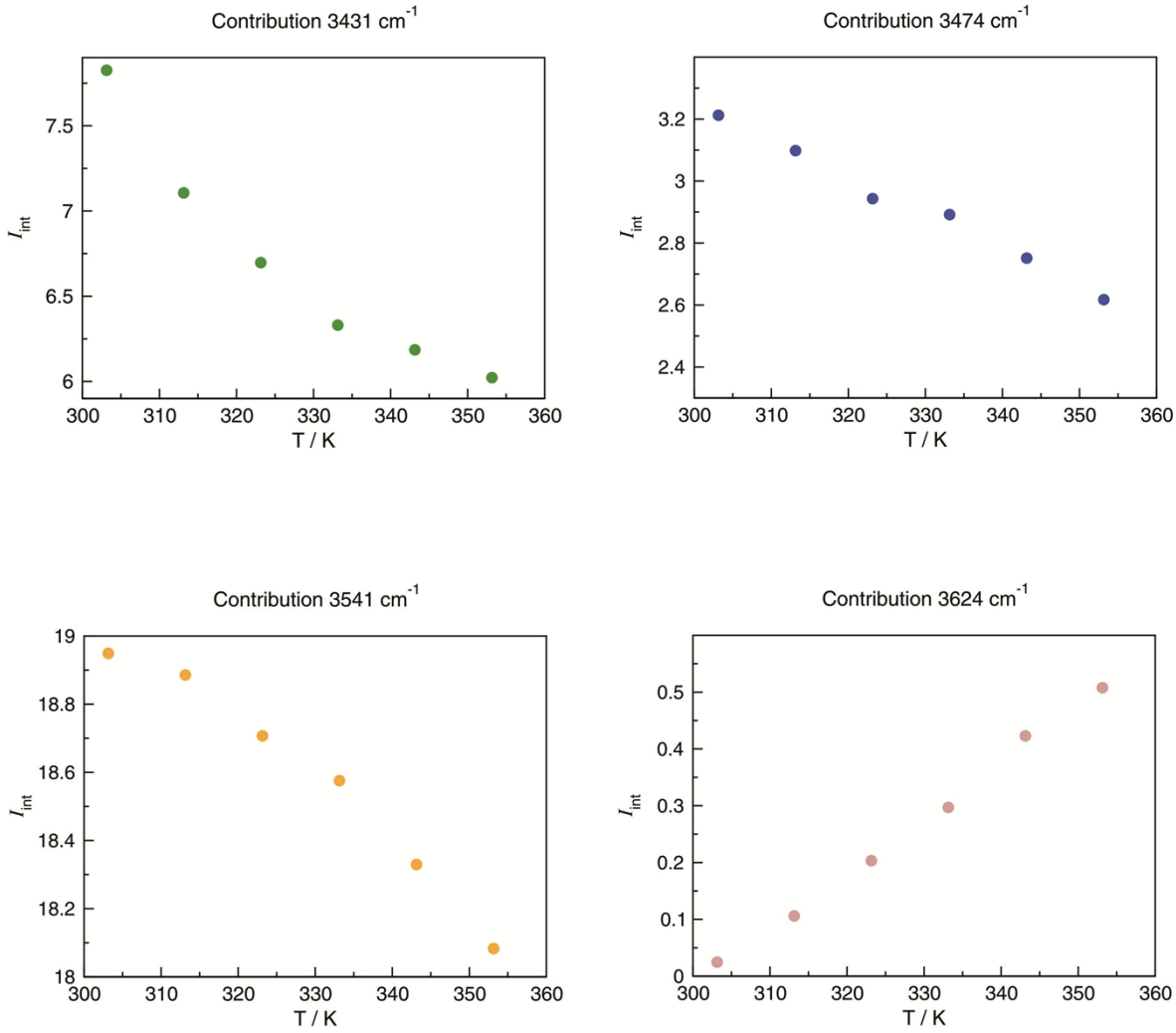
The viscosities of the pure ionic liquids were determined using a microviscosimeter (Lovis 2000 ME / Anton Paar Austria) based on the rolling ball principle. The estimated accuracy of the viscosity measurements was ± 0.5 percent.

SI2 Deconvoluted mid infrared (MIR) spectra of [Ch][NTf_2] between 303 K and 353 K



SI-FIG1 Deconvoluted MIR spectra of [Ch][NTf_2] as a function of temperature. The spectra are shown for the frequency range between 3200 and 3600 cm^{-1}.

SI3 Intensities of the vibrational bands deconvoluted from the mid infrared (MIR) spectra of [Ch][NTf_2] between 303 K and 353 K



SI-FIG2 Intensities of the vibrational bands deconvoluted from the MIR spectra of [Ch][NTf_2] as a function of temperature. The intensities of the cation-cation vibrational modes at 3431 cm^{-1} and 3474 cm^{-1} decrease stronger than the cation-anion vibrational band at 3541 cm^{-1}. Instead, the intensity of the 'quasi free' OH band at 3624 cm^{-1} increases with temperature.

All spectra were deconvoluted simultaneously as well as separately into a number of Voigt profiles (convolution of Lorentzian and Gassian functions) following the Levenberg-Marquardt procedure. The Voigt profile has four parameters: the intensity, the frequency, the half-width of the Lorentzian, and the half-width of the Gaussian. The frequency and the half-widths of each Voigt function for all vibrational modes were kept fixed in the simultaneous fitting procedure.

SI4 Optimized geometries of DFT-D3 calculated clusters of ILs I

The IL clusters have been calculated at the DFT level B3LYP, using the internal stored 6-31+G* basis set of the Gaussian 09 program.[15] Grimme's DFT-D3 method was applied for calculating dispersion forces.[16,17]

Literature

[15] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[16] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, 132, 154104.

[17] S. Ehrlich, J. Moellmann, W. Reckien, T. Bredow, S. Grimme**,** ChemPhysChem. **2011**, 12, 3414-3420.

[Ch][NTf_2] ion-pair monomer

*** Cholin_NTf2_b3lyp_6-31+Gp_monomer_D3.g09, E(RB3LYP) = -2156.14990545

6	0	-1.478271	2.465930	-0.648204
9	0	-0.267492	2.804307	-1.149692
16	0	-1.250305	1.225736	0.757337
8	0	-0.248134	1.876910	1.622829
9	0	-2.069500	3.575306	-0.187271
9	0	-2.214904	1.947208	-1.632585
7	0	-0.460140	0.013370	0.011022
16	0	-1.186181	-1.265610	-0.679474
6	0	-1.188239	-2.518211	0.733844
9	0	0.081550	-2.730008	1.155306
8	0	-2.586402	0.940435	1.269673
8	0	-2.578836	-1.105995	-1.083026
8	0	-0.211279	-1.844252	-1.623337
9	0	-1.694978	-3.683120	0.316188
9	0	-1.903803	-2.068538	1.768620
7	0	3.138114	0.628498	0.556335
6	0	4.625144	0.474143	0.689604
1	0	4.894005	-0.578237	0.601473
6	0	2.781067	2.088395	0.704902
1	0	3.220976	2.639009	-0.128601
6	0	2.443718	-0.154623	1.646494
1	0	2.677587	0.311556	2.605323
6	0	2.665397	0.168241	-0.824797
1	0	4.931148	0.849160	1.668419
1	0	5.112946	1.049684	-0.099663
1	0	1.371223	-0.124674	1.459408
1	0	2.806395	-1.182332	1.630128
1	0	3.185573	2.450635	1.652590
1	0	1.695557	2.185176	0.711983
6	0	2.836131	-1.326038	-1.138342
1	0	1.605462	0.422106	-0.878143
1	0	3.224150	0.757015	-1.557168
8	0	2.429840	-1.519382	-2.475229
1	0	3.884494	-1.637517	-1.072126
1	0	2.241420	-1.940196	-0.452169
1	0	1.457970	-1.631608	-2.462145

[Ch][NTf_2] ion-pair dimer

*** Cholin_NTf2_b3lyp_6-31+Gp_dimer_D3.g09, E(RB3LYP) = -4312.33525215

6	0	-4.643435	1.675722	-2.151582
9	0	-4.976021	0.671700	-2.970064
9	0	-3.322216	1.911451	-2.273489
16	0	-5.050433	1.235328	-0.361875
8	0	-6.496552	1.043118	-0.307820
9	0	-5.310263	2.779890	-2.513694
8	0	-4.421404	2.321648	0.413479
7	0	-4.115224	-0.072597	-0.123112
16	0	-4.582248	-1.602048	-0.356627
8	0	-3.348921	-2.387895	-0.588356
6	0	-5.077910	-2.114376	1.391172
9	0	-6.081691	-1.351784	1.838716
8	0	-5.752264	-1.843893	-1.193884

9	0	-4.025329	-1.963826	2.229811
9	0	-5.454103	-3.397811	1.412204
8	0	-0.803641	-1.385882	-0.553342
6	0	-0.760761	-0.789368	0.738625
6	0	-1.074000	0.699745	0.562520
7	0	-1.177775	1.504831	1.857936
6	0	-2.365468	1.059380	2.673314
6	0	0.074405	1.380107	2.682726
6	0	-1.371552	2.953560	1.472420
1	0	0.193868	0.345994	3.004902
1	0	-0.499480	3.275615	0.903625
1	0	-2.427760	1.696618	3.557924
1	0	-0.024715	2.023889	3.559216
1	0	0.929000	1.695781	2.086830
1	0	-3.262474	1.162977	2.065867
1	0	-2.229626	0.021418	2.974165
1	0	-1.468173	3.542495	2.387363
1	0	-2.284076	3.029184	0.880240
1	0	-2.037156	0.800502	0.064432
1	0	-0.293600	1.171689	-0.033318
1	0	0.248555	-0.944559	1.126362
1	0	-1.476278	-1.284030	1.404997
1	0	-1.723123	-1.703552	-0.715075
1	0	0.404949	-2.608461	-0.779206
8	0	1.185868	-3.200023	-0.898848
6	0	2.048334	-2.627166	-1.858407
6	0	3.445434	-2.752864	-1.238923
1	0	1.975102	-3.180167	-2.807109
1	0	1.801666	-1.577139	-2.045070
7	0	4.633708	-2.529988	-2.178415
1	0	3.558567	-2.031921	-0.430944
1	0	3.559232	-3.765392	-0.841831
6	0	5.898047	-2.768844	-1.389019
6	0	4.599784	-3.489657	-3.334175
6	0	4.644159	-1.112112	-2.694434
1	0	6.755517	-2.579166	-2.038457
1	0	5.911284	-2.089431	-0.537311
1	0	5.906538	-3.807516	-1.052647
1	0	5.535383	-3.399676	-3.889724
1	0	4.488863	-4.505031	-2.948750
1	0	3.762096	-3.247465	-3.986221
1	0	5.505860	-0.994053	-3.355135
1	0	3.719839	-0.926258	-3.240270
1	0	4.708698	-0.438398	-1.843794
8	0	5.088434	-0.344670	0.460695
16	0	4.571435	0.461519	1.586617
6	0	3.499346	-0.764028	2.539058
9	0	2.892843	-0.174034	3.580212
9	0	2.547048	-1.272718	1.729325
9	0	4.254501	-1.774627	2.990368
7	0	3.492103	1.604829	1.193422
8	0	5.501743	0.988167	2.577703
16	0	2.746805	1.688970	-0.233657
6	0	3.913719	2.713663	-1.306152
9	0	3.368424	2.878449	-2.521534
9	0	4.143473	3.908486	-0.760812
9	0	5.086842	2.066491	-1.451140
8	0	2.588408	0.424502	-0.971305
8	0	1.567159	2.548510	-0.063722

[Ch][NTf_2] ion-pair dimer (cation-cation interaction)

*** Cholin_NTf2_b3lyp_6-31+Gp_dimer_cc_D3.g09, E(RB3LYP) = -4312.33525215

6	0	-4.643435	1.675722	-2.151582
9	0	-4.976021	0.671700	-2.970064
9	0	-3.322216	1.911451	-2.273489
16	0	-5.050433	1.235328	-0.361875
8	0	-6.496552	1.043118	-0.307820
9	0	-5.310263	2.779890	-2.513694
8	0	-4.421404	2.321648	0.413479
7	0	-4.115224	-0.072597	-0.123112
16	0	-4.582248	-1.602048	-0.356627
8	0	-3.348921	-2.387895	-0.588356
6	0	-5.077910	-2.114376	1.391172
9	0	-6.081691	-1.351784	1.838716
8	0	-5.752264	-1.843893	-1.193884
9	0	-4.025329	-1.963826	2.229811
9	0	-5.454103	-3.397811	1.412204
8	0	-0.803641	-1.385882	-0.553342
6	0	-0.760761	-0.789368	0.738625
6	0	-1.074000	0.699745	0.562520
7	0	-1.177775	1.504831	1.857936
6	0	-2.365468	1.059380	2.673314
6	0	0.074405	1.380107	2.682726
6	0	-1.371552	2.953560	1.472420
1	0	0.193868	0.345994	3.004902
1	0	-0.499480	3.275615	0.903625
1	0	-2.427760	1.696618	3.557924
1	0	-0.024715	2.023889	3.559216
1	0	0.929000	1.695781	2.086830
1	0	-3.262474	1.162977	2.065867
1	0	-2.229626	0.021418	2.974165
1	0	-1.468173	3.542495	2.387363
1	0	-2.284076	3.029184	0.880240
1	0	-2.037156	0.800502	0.064432
1	0	-0.293600	1.171689	-0.033318
1	0	0.248555	-0.944559	1.126362
1	0	-1.476278	-1.284030	1.404997
1	0	-1.723123	-1.703552	-0.715075
1	0	0.404949	-2.608461	-0.779206
8	0	1.185868	-3.200023	-0.898848
6	0	2.048334	-2.627166	-1.858407
6	0	3.445434	-2.752864	-1.238923
1	0	1.975102	-3.180167	-2.807109
1	0	1.801666	-1.577139	-2.045070
7	0	4.633708	-2.529988	-2.178415
1	0	3.558567	-2.031921	-0.430944
1	0	3.559232	-3.765392	-0.841831
6	0	5.898047	-2.768844	-1.389019
6	0	4.599784	-3.489657	-3.334175
6	0	4.644159	-1.112112	-2.694434
1	0	6.755517	-2.579166	-2.038457
1	0	5.911284	-2.089431	-0.537311
1	0	5.906538	-3.807516	-1.052647
1	0	5.535383	-3.399676	-3.889724
1	0	4.488863	-4.505031	-2.948750
1	0	3.762096	-3.247465	-3.986221
1	0	5.505860	-0.994053	-3.355135
1	0	3.719839	-0.926258	-3.240270
1	0	4.708698	-0.438398	-1.843794
8	0	5.088434	-0.344670	0.460695
16	0	4.571435	0.461519	1.586617

6	0	3.499346	-0.764028	2.539058
9	0	2.892843	-0.174034	3.580212
9	0	2.547048	-1.272718	1.729325
9	0	4.254501	-1.774627	2.990368
7	0	3.492103	1.604829	1.193422
8	0	5.501743	0.988167	2.577703
16	0	2.746805	1.688970	-0.233657
6	0	3.913719	2.713663	-1.306152
9	0	3.368424	2.878449	-2.521534
9	0	4.143473	3.908486	-0.760812
9	0	5.086842	2.066491	-1.451140
8	0	2.588408	0.424502	-0.971305
8	0	1.567159	2.548510	-0.063722

Calculated 'pecking' frequencies for the IL I dimer_cc for protonated and deuerated hydroxyl groups

OH: 177.5668

OD 174.5701

The calculated difference of 3 cm^{-1} is observed in the far infrared spectra indicating that only the 2-hydroxylyethyl group and not the whole cation is involved in this intermolecular motion.

SI5 DFT-D3 calculated energies and binding energies of [Ch][NTf_2] clusters

SI Table 1. Total energies (in Hartrees) for clusters of ILs **I** and **II**.

IL	Monomer	Dimer	Dimer_cc
I	-2156.14990545	-4312.35002228	-4312.33525215
II	-2120.25074475	-4240.54735951	

SI Table 2. Interaction energies (in kJ mol^{-1}) per ion for clusters of ILs **I** and **II**.

IL	Monomer	Dimer	Dimer_cc
I	-	-436.61	-417.21
II	-	-406.17	-

For IL **I**, the **Dimer** ist favored in energy about 38,8 kJmol-1 over the **Dimer_cc**. This is reflected in the large intensity for the vibrational band at 3541 cm^{-1} and the significantly smaller intensities at 3431 cm^{-1} and 3474 cm^{-1} for the dimer including cation-cation interaction. However 'kinetic trapping' due to cooperative hydrogen bonding in **Dimer_cc** results in vibrational bands which cannot stem from other OH vibrational modes.

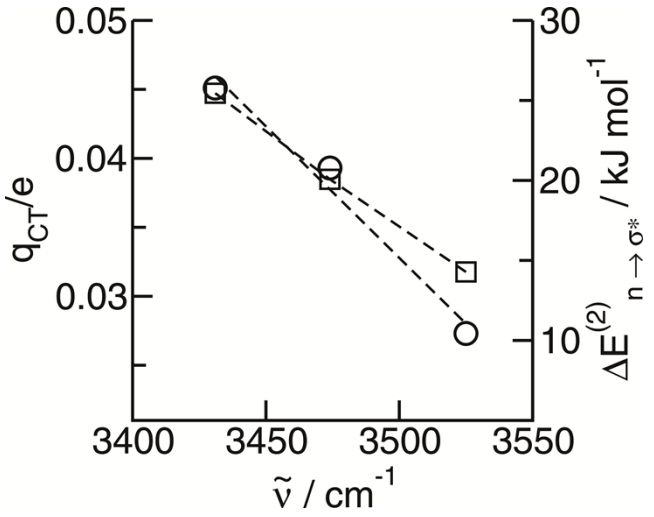
NBO Analysis

For the ion pairs the wavefunctions were analyzed by the natural bond orbital (NBO) method.[24,25] NBO analysis transforms the delocalized many-electron wavefunctions into optimized electron-pair bonding units, corresponding to the Lewis structure picture. Starting from a given input atomic orbital basis set, the program performs a transformation to form a set of high-occupancy Lewis-type (bond, lone pair) NBO's, each of which is taken to be doubly occupied. This represents the "natural Lewis structure" of the molecule. Delocalization effects, which appear as weak departures from the idealized localized picture, are reflected as nonzero occupancies of non-Lewis (antibond or Rydberg) NBO's. The total non-Lewis occupancy (1NL) constitutes a quantitative measure of electronic delocalization.The results of NBO analysis allow many of the quantitative trends in ion-pair structures, stability, and spectroscopic properties to be rationalized in terms of charge-transfer delocalization between ions or molecules.

SI Table 2. NBO-Analysis of the IL **I** dimer_cc (S=O···HO···HO) and the ethanol dimer (OH···OH).

Donor NBO (i)	Acceptor NBO (j)	kcal/mol	a.u.	a.u.
146. LP (1) O 10	/856. BD*(1) O 16 - H 36	10.04	1.26	0.101
147. LP (2) O 10	/856. BD*(1) O 16 - H 36	12.03	0.77	0.089

148.	LP	(	3)	O	10	/856.	BD*(	1)	O	16	- H	36	0.34	0.77	0.015
161.	LP	(	1)	O	16	/875.	BD*(	1)	H	37	- O	38	3.17	0.98	0.050
162.	LP	(	2)	O	16	/875.	BD*(	1)	H	37	- O	38	22.28	0.89	0.126
3.	LP	(	1)	O	3	/131.	BD*(	1)	H	10	- O	11	1.44	1.02	0.034
24.	LP	(	2)	O	3	/131.	BD*(	1)	H	10	- O	11	14.28	0.92	0.103



SI-FIG3 NBO calculated stabilization energies $E(2)_{n\leftarrow\sigma^*}$ and estimated total charge transfers q_{TC} plotted versus measured OH frequencies of IL **I**. The linear dependence indicates the strong relation between NBO stabilization energies and charge transfers with spectroscopic properties such as IR frequencies.

[24] A. E. Reed, L. A. Curtiss, F. Weinhold, Chem. Rev. **1988**, 88, 899-926.

[25] F. Weinhold, C. R. Landis, Valency and Bonding A Natural Bond Orbital Donor-Acceptor Perspective, Cambridge University Press, Cambridge, **2005**.