Free electrons and ionic liquids: Electron-Energy Loss Spectroscopy and DFT/MRCI study of the excited states.

Supplementary information

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This Supplementary Information contains primarily material interesting from the electron scattering point of view but too specialized for readership interested primarily in ionic liquids (IL). It also contains more technical details of the calculations.
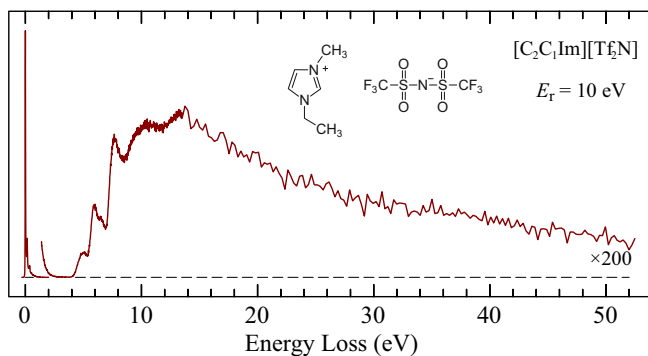

Fig. S1 Electron energy loss spectrum of $[C_2C_1Im][Tf_2N]$ extending to a larger energy loss.

S.1 Electron Energy Loss Spectra

Fig. S1 shows an energy loss spectrum extending to a higher energy loss than those presented in the main paper. The spectrum in the energy loss range above $12\,eV$ is continuous and does not reveal any narrow bands which could be assigned to definite electronic states. It is informative for a discussion of radiation chemistry, for example, because the energy losses above $12\,eV$ will also contribute to the stopping power for electrons, and they will lead to chemical damage of the IL by radiation.

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Fig. S2 compares spectra recorded at residual energies of $E_r = 10$ and $20\,eV$. The spin forbidden band at $5\,eV$ is weaker relatively to the spin and dipole allowed bands in the spectrum recorded at $E_r = 20\,eV$ as expected.
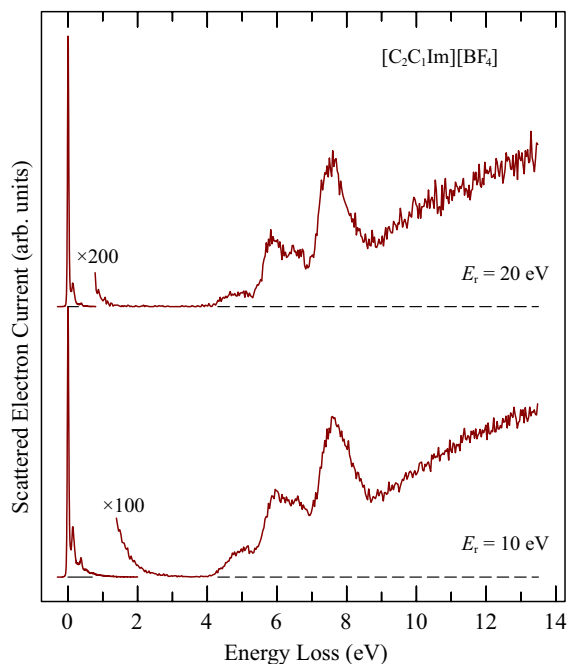

Fig. S2 Electron energy loss spectra of $[C_2C_1Im][BF_4]$ recorded at residual energies of 10 and 20 eV.

S.2 Excitation Functions

An interesting issue in electron collisions are transient anions, also called resonances, formed in the collisions at specific energies.[1] Resonances greatly enhance the majority of the interesting processes like vibrational and electronic excitation, as well as electron-driven chemistry, specifically dissociative electron attachment.[1] Resonances are therefore manifested as
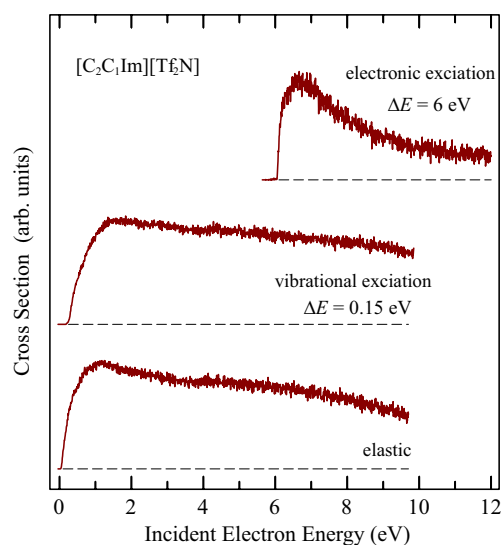
Fig. S3 Cross sections plotted as a function of incident electron energy. Bottom curve: Elastic cross section. Center curve: Cross section for vibrational excitation with an energy loss of 0.15 eV. Top curve: Cross section for electronic excitation with an energy loss of 6 eV.

Fig. S4 Spectra of kinetic energies of electrons ejected following the impact of a 1.25 eV electron (bottom spectrum) or 2 eV electron (top spectrum) on an ionic liquid (bottom spectrum) and the dimer of formic acid (top spectrum).

Fig. S5 Spectra of two ionic liquids with and without methylene green dissolved in them. The concentration of methylene green was about 1 mol/L in both cases.

structures, generally enhancements, of the cross sections for these processes at specific energies and a way to detect them is to record the cross sections as a function of electron energy. These spectra are called excitation functions or energy dependence spectra and three examples, for elastic scattering and representative vibrational and electronic excitations, are shown in Fig. S3.

These excitation functions may be discussed for example in comparison with our recent results for isolated furan and ethene molecules shown in Fig. 12 of Ref. 2. Whereas furan and ethene have pronounced resonant bands both in the vibrational and electronic excitation cross sections, no such bands appear the spectra of Fig. S3.

We thus have two pieces of evidence with respect to resonances. (a) Overtone vibrations are observed quite strongly in vibrational EEL as shown in the main paper–much more strongly than when excited by absorption of IR photons in IR spectrum. This indicates a resonant excitation mechanism by electron impact. (b) The absence of bands in the excitation functions. This evidence thus suggests that resonances are present, but the condensed phase makes them very broad and possibly shifted to higher energies–similarly to Rydberg states.

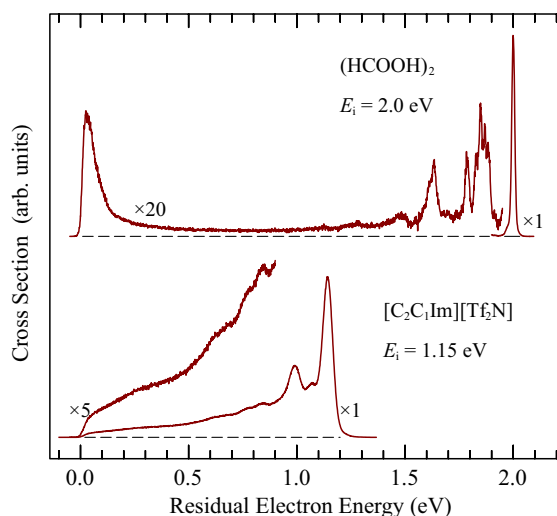Excitation functions have also been recorded for molecules in solid films.[3]

S.3 Ejected Electron Spectra

Interesting information about the fate of electrons injected into the ionic liquid may be derived from the spectra of kinetic en-

ergies of ejected electrons such as presented in Fig. S4. It may be discussed in comparison with the dimer of formic acid, which may be considered to be a first step towards a liquid, and the spectrum[4] of which is also presented in Fig. S4. Elastic peak is the most intense in both cases, that is, when the electrons leave with the same energy as that with which they arrived. In both cases a group of electrons is ejected with slightly lower energies after having excited specific vibrational modes–the spectrum shows vibrational structure. The spectrum of electrons ejected with even lower energies, down to 0 eV, does not have any structure– the electrons have excited a quasicontinuum of vibrational modes (unspecific vibrational excitation in the terminology of Ref. 5).

The major difference is that this quasicontinuum peaks at 0 eV for the formic acid dimer but declines continuously for the ionic liquid. We explain it as follows. In formic acid dimer the thermalized electrons which lost their initial energy to molecular vibrations must eventually leave, with nearly zero kinetic energy. In the ionic liquid these electrons become solvated and are eventually collected on the molybdenum wire on which the ionic liquid droplet is suspended. This reduces the number of very slow electrons ejected into vacuum.
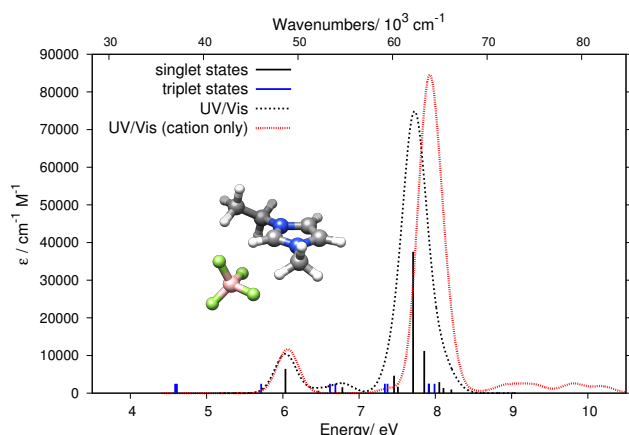

Fig. S6 Results of the DFT/MRCI calculation for the [C_2C_1Im][BF_4] ion pair. Black sticks show the singlet states with heights indicating the molar absorption coefficient ε, blue sticks show the triplet states. The red dotted line on shows the Gaussian broadened singlet states of the [C_4C_1Pipe]$^+$ cation while the black dotted line shows the broadened states of the ion pair.

S.4 Spectra of Methylene Green Dissolved in Ionic Liquids

Fig. S5 shows EEL spectra of solutions of methylene green in two ionic liquids. The EEL spectra of the neat ionic liquids and the UV/VIS spectra of methylene green are shown for
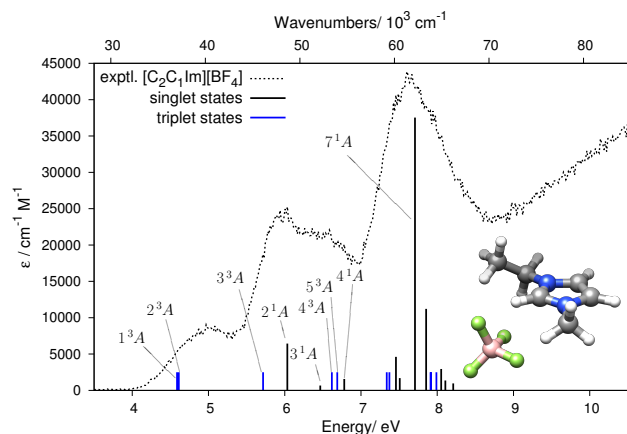

Fig. S7 Results of the DFT/MRCI calculation for the [C_2C_1Im][BF_4] ion pair with experiment.

comparison. The EEL band of methylene green is virtually absent with [C_4C_1Pipe][Tf_2N] as solvent. This is interpreted as an indication that the cation of methylene green (the chromophore) is "hidden" by a layer of ionophobic alkyl and CF_3 groups in [C_4C_1Pipe][Tf_2N], as explained in the main paper.

S.5 Effect of the counterion on the excited states of [C_2C_1Im]$^+$

We have studied the effect of the counterion ([BF_4]$^-$) on the excited state pattern in the energy range < 8 eV. We therefore computed the 10 lowest singlet and triplet states by DFT/MRCI[6] and plotted these in Fig. S6. For comparison with the single cation, the Gaussian broadened singlet states of the ion pair and the individual cation (20 singlet states) are also plotted.

The calculated energies of the excited states of the ion pair are listed in Table S1. We further compare the ion pair calculation with the experiment in Fig. S7 to point out that the inclusion of the counterion slightly improved the agreement. The improvement is two-fold. The most intense band is calculated at slightly lower energy in the ion pair, at 7.71 eV, fitting the experiment perfectly. The oscillator strengths of the 3^1A and the 4^1A bands are higher in the ion pair, also improving the agreement.

S.6 Effect of the butyl conformation on the excited states of [C_4C_1Pyri]$^+$

We have studied the effect of the butyl conformation on the excited state pattern of [C_4C_1Pyri]$^+$ in the energy range < 8 eV. We computed the 20 lowest singlet and triplet states by
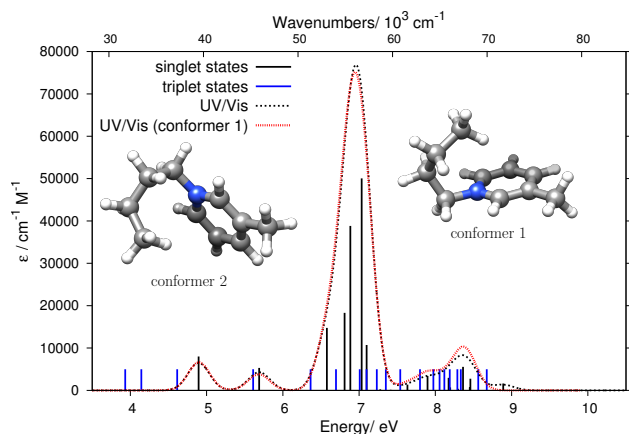
Fig. S8 Results of the DFT/MRCI calculation for the conformer 2 of $[C_4C_1Pyri]^+$. Black sticks show the singlet states with heights indicating the molar absorption coefficient ε, blue sticks show the triplet states. The black dotted line on the right shows the Gaussian broadened singlet states of the conformer 2, while the red dotted line refers to the broadened spectrum of conformer 1.

DFT/MRCI[6] and plotted these in Fig. S8. For comparison with conformer 1 (which has been used in the manuscript), the Gaussian broadened singlet states of both conformers (20 singlet states each) are also plotted.

Table S1 Excited states of the $[C_2C_1Im][BF_4]$ ion pair computed by DFT/MRCI. The vertical excitation energy (VEE) is given for the singlet and triplet states. For the singlet states, the oscillator strengths obtained from the dipole length formalism (f^L) is given as well.

	singlet states			triplet states
state	VEE (eV)	f^L	state	VEE (eV)
2^1A	6.03	0.1288	1^3A	4.59
3^1A	6.47	0.0134	2^3A	4.61
4^1A	6.78	0.0314	3^3A	5.72
5^1A	7.46	0.0924	4^3A	6.62
6^1A	7.51	0.0338	5^3A	6.69
7^1A	7.71	0.7508	6^3A	7.34
8^1A	7.85	0.2244	7^3A	7.37
9^1A	8.05	0.0590	8^3A	7.91
10^1A	8.11	0.0272	9^3A	7.92
11^1A	8.21	0.0193	10^3A	7.99

S.7 Geometries of systems investigated

$[C_2C_1Im]^+$

18

N	-0.7409027	-0.0862289	0.1066064
C	-0.8235580	-0.6877862	1.3374034
C	0.4437865	-0.8493213	1.7899662
N	1.2795401	-0.3434001	0.8272677
C	0.5406165	0.1117230	-0.1798977
H	0.9249392	0.5651312	-1.0773023
C	2.7320559	-0.3110040	0.8971327
H	0.8157110	-1.2769900	2.7057489
H	-1.7683159	-0.9482147	1.7840908
H	3.1165411	-1.3266859	0.9799628
H	3.1209120	0.1488503	-0.0084477
H	3.0431406	0.2743205	1.7613633
C	-1.8961625	0.2666924	-0.7296058
H	-2.4514418	-0.6565053	-0.9055987
H	-2.5261849	0.9290161	-0.1329409
C	-1.5087581	0.9200811	-2.0327377
H	-2.4188899	1.1478563	-2.5874796
H	-0.9789939	1.8620877	-1.8772850
H	-0.9040351	0.2603778	-2.6582468

[C4C1Pyri]+

27

N	-0.5450057	0.7328237	0.5129698
C	-0.6548727	0.1291516	1.7029672
C	0.4675769	-0.1278418	2.4550783
C	1.7087569	0.2430012	1.9673076
C	1.8218937	0.8754252	0.7299701
C	0.6511158	1.1022136	0.0315066
H	-1.6545217	-0.1347860	2.0201276
H	0.3617114	-0.6132076	3.4159753
H	2.6004795	0.0443142	2.5514179
C	3.1406834	1.2931623	0.1714067
H	0.6440436	1.5838726	-0.9371659
C	-1.7632075	0.9432493	-0.2977683
H	3.0349165	1.7706395	-0.8018867
H	3.6362426	1.9955372	0.8451252
H	3.7988652	0.4288427	0.0592647
H	-2.4993031	1.4172177	0.3534905
H	-1.4984235	1.6571570	-1.0776799
C	-2.3137692	-0.3372553	-0.9026028
H	-3.2244629	-0.0318816	-1.4257023
C	-1.3859958	-1.0730578	-1.8665547
H	-2.6414411	-1.0138163	-0.1059138
H	-2.0111823	-1.6494694	-2.5522915
H	-0.8585087	-0.3475843	-2.4973706
C	-0.3968074	-2.0266241	-1.2113570
H	0.1645999	-2.5754544	-1.9687785
H	0.3352196	-1.5224843	-0.5762908
H	-0.9186035	-2.7631447	-0.5952446

[C4C1Pipe]+

33

C	-1.5621359	0.6297051	-0.7121420
N	-0.2070624	0.0083115	-0.9863501
C	0.8955678	0.9481055	-0.5864154
C	-0.0705434	-1.2953255	-0.2436315
C	-0.1559397	-0.2490188	-2.4506459
H	0.7537124	-0.7805467	-2.7078179
H	-1.0208645	-0.8498051	-2.7271251
H	-0.1843940	0.7033603	-2.9767534
H	-2.2822251	-0.1738634	-0.8833178
C	-1.8347007	1.3131427	0.6171594
H	-1.6944472	1.3658905	-1.5071569
C	2.2743872	0.3492019	-0.7608160
H	0.7572957	1.8597696	-1.1701628
H	0.7272551	1.1846151	0.4631225
C	1.3018863	-1.9214172	-0.3791118
H	-0.2832886	-1.0729420	0.7990587
H	-0.8580769	-1.9489383	-0.6215468
H	2.9921393	1.0895576	-0.4009038
C	2.4023588	-0.9502852	0.0182154
H	2.5060129	0.1949119	-1.8181579
H	1.3124902	-2.8040302	0.2644609
H	1.4637531	-2.2919374	-1.3948822
H	3.3814308	-1.4002361	-0.1508442
H	2.3356183	-0.7387955	1.0910218
H	-2.8013272	1.7909123	0.4282260
C	-1.9545844	0.4761541	1.8971534
H	-1.1459292	2.1484076	0.7698982
H	-2.8045482	0.8617508	2.4642160
H	-2.2254729	-0.5560489	1.6513618
C	-0.7410860	0.5156238	2.8143371
H	-0.9319742	-0.0428004	3.7317901
H	0.1629702	0.0923586	2.3673249
H	-0.5082777	1.5442118	3.1004352

[Tf₂N]⁻

15

N	-0.0000000	-0.0000000	0.7755498
S	0.9939827	-0.9956795	0.0701429
S	-0.9939827	0.9956795	0.0701429
O	0.7133834	-1.3306057	-1.2942234
C	2.5502233	0.0028068	-0.0175188
O	1.3263931	-2.0455748	0.9871102
O	-0.7133834	1.3306057	-1.2942234
C	-2.5502233	-0.0028068	-0.0175188
O	-1.3263931	2.0455748	0.9871102
F	-3.5230761	0.7306159	-0.5672248
F	-2.3929059	-1.0959950	-0.7565427
F	-2.9583052	-0.3772074	1.1941794
F	3.5230761	-0.7306159	-0.5672248
F	2.3929059	1.0959950	-0.7565427
F	2.9583052	0.3772074	1.1941794

[BF₄]⁻

5

B	-0.0000000	0.0000000	0.0000000
F	-0.8111345	0.8111345	0.8111345
F	0.8111345	-0.8111345	0.8111345
F	-0.8111345	-0.8111345	-0.8111345
F	0.8111345	0.8111345	-0.8111345

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