

## Diagnosing the plasma formed during acoustic cavitation in [BEPip][NTf2] ionic liquid

Rachel Pflieger, Manuel Lejeune, Cédric Noel, Thierry Belmonte, Sergey I. Nikitenko, Micheline Draye

► **To cite this version:**

Rachel Pflieger, Manuel Lejeune, Cédric Noel, Thierry Belmonte, Sergey I. Nikitenko, et al.. Diagnosing the plasma formed during acoustic cavitation in [BEPip][NTf2] ionic liquid. *Physical Chemistry Chemical Physics*, Royal Society of Chemistry, 2019, 21 (3), pp.1183-1189. 10.1039/c8cp06967k . hal-02105350

**HAL Id: hal-02105350**

**<https://hal.univ-lorraine.fr/hal-02105350>**

Submitted on 21 Nov 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



# Diagnosing the plasma formed during acoustic cavitation in [BEPip][NTf<sub>2</sub>] ionic liquid

Rachel Pflieger,<sup>a,\*</sup> Manuel Lejeune,<sup>b</sup> Cédric Noel,<sup>c</sup> Thierry Belmonte,<sup>c</sup> Sergey I. Nikitenko,<sup>a</sup> Micheline Draye,<sup>b</sup>

<sup>a</sup> Institut de Chimie Séparative de Marcoule, ICSM UMR 5257 – CEA, CNRS, Univ Montpellier, ENSCM, Bagnols-sur-Cèze Cedex, France.

<sup>b</sup> Univ Savoie Mont Blanc – LCME, Chambéry, France

<sup>c</sup> Université de Lorraine, Institut Jean Lamour, UMR CNRS 7198, Nancy, France

\* Corresponding author. E-mail: rachel.pflieger@cea.fr

## ABSTRACT

Sonoluminescence (SL) spectra of a very dry [BEPip][NTf<sub>2</sub>] ionic liquid were measured in the first minutes of sonication under Ar. The intense sonoluminescence allowed us to monitor the time-evolution of the SL spectra. Several molecular emissions were observed. Rovibronic temperatures of C<sub>2</sub> and CN were determined giving vibrational temperatures of  $5800 \pm 500$  K and  $6000 \pm 500$  K and rotational temperatures (i.e. translational or gas temperatures) of  $4000 \pm 500$  K. These temperatures stay remarkably constant during the sonolysis, while SL spectra undergo strong changes that illustrate the very fast evolution of the plasma during the first minutes of sonication. The expected strong decrease in the plasma electron energy also reflects in the evolution of the populations of CH electronically excited states. The physical meaning of temperatures derived from molecular emissions in SL spectra is discussed.

## Introduction

Sonochemistry is the chemical activity observed under ultrasonic irradiation of a liquid. Its origin is acoustic cavitation, i.e. nucleation, growth and implosive collapse of microbubbles of gas and vapor. Though its formation mechanism is still a subject of debate, it is widely admitted that a plasma forms in acoustic cavitation bubbles at collapse.<sup>1</sup> This plasma emits light, the so-called sonoluminescence, whose emission spectra are the signature of the formed plasma.

Ionic liquids (IL) are solvents with very interesting properties (they have a very low vapor pressure, are non-flammable, nonexplosive, liquid over a wide range of temperature, possess a high thermal stability and high ionic and thermal conductivities) that explain their use in many applications in organic synthesis, separation technology, energy, materials, analytical applications, biotechnology etc.<sup>2-5</sup> These properties and in particular their essentially zero vapor pressure make them ideal solvents for sonochemistry<sup>6</sup> since they a priori do not interfere in chemical reactions inside bubbles. Indeed, a significant increase in the rate of several sonochemical reactions was reported,<sup>7,8</sup> as well as some selectivity in the reaction products.<sup>9,10</sup> The same properties also make ionic liquids potentially an ideal medium as far as reaching extreme conditions is concerned since the bubble content would consist purely of the dissolved gas, which optimizes the concentration of energy at collapse, limits any loss of energy by vibrational excitation and chemical reactions, and hence allows more extreme conditions (e.g. higher temperatures) in the collapsing bubbles.<sup>11</sup>

Despite the growing interest in the combined use of IL and ultrasound, acoustic cavitation in these media has been poorly characterized. Oxley et al.<sup>12</sup> studied sonochemistry and sonoluminescence of *N,N'*-dialkylimidazolium IL at 20 kHz under Ar. They observed some degradation of the IL resulting in its coloration, in the presence of several decomposition products in the head gas and in molecular emissions in the SL spectra. The degradation mechanism by pyrolysis, either at the bubble– liquid interface or more probably inside the intra-bubble plasma (after droplet injection or maybe vaporization of the IL in the overheated zone surrounding the bubble, where the temperature would be high enough to increase the IL volatility<sup>13</sup>), was later confirmed on methyloctylpyrrolidinium bis(trifluoromethylsulfonyl)- imide sonicated at 20 kHz under Ar.<sup>14</sup> It is to be underlined that though the effects (coloration of the IL, absorption of light in SL spectra) were obvious, degradation remained at the trace level. The formation of degradation products however opened a way for an experimental determination of the reached temperatures in sonicated IL. To the best of our knowledge, only one single experimental temperature<sup>15</sup> was reported in the literature, in a study on the sonication of 1-ethyl-3-methylimidazolium-ethyl sulfate at 213 kHz under Ar. This temperature was determined by the methyl radical recombination method, which relies upon the kinetics of recombination reactions of methyl radicals. As acknowledged by the authors, the obtained temperature (3500 K) was surprisingly low and similar to that obtained in water, though it was expected to be much higher.<sup>11</sup> This apparent discrepancy can be ascribed to the biases of the method: thermal equilibrium is assumed, parallel reaction pathways are neglected and a “mean chemical temperature” is obtained, whose spatial and temporal resolutions are not well defined.<sup>16,17</sup> For these reasons, other experimental determinations of the reached temperatures in IL are needed. Thanks to the presence of several molecular emission bands,<sup>6,14</sup> SL spectra offer an insight into the sonochemical plasma and the temperatures reached during the bubble collapse. The present work reports SL spectra obtained during the sonication of *N,N*-butyl-ethyl-piperidinium bis(trifluoromethylsulfonyl) imide ([BEPip][NTf<sub>2</sub>]) at 20 kHz under Ar and the rovibronic temperatures obtained from spectroscopic fitting of the observed molecular emissions. Their physical meaning and link to the plasma electron temperature are questioned. Furthermore, SL spectra were monitored over time of sonication to follow the impact on the plasma of the degradation of the IL. The latter was made possible by an optimization of experimental conditions, and in particular by the use of a very dry IL – indeed, previous works<sup>14,15</sup> showed that a decrease in the water concentration in the IL strongly increased the SL intensity but also the degradation of the IL.

## Materials and methods

*N*-Ethylpiperidine and 1-bromobutane were purchased from Aldrich and distilled immediately prior to use. Lithium bis-(trifluoromethyl)imide salt was purchased by abcr GmbH and used as received. Acetonitrile was dried from conventional method and stored under argon over molecular sieves 3 Å.<sup>18</sup>

The Room Temperature Ionic Liquid (RTIL) was prepared in two steps (Scheme 1) according to a previously published procedure:<sup>19</sup> (i) piperidinium bromide salt was synthesized by Mentschukin's reaction between *n*-ethylpiperidine (1 eq.) and 1-bromobutane (1 eq.) in acetonitrile at 80°C for 16 h under argon; (ii) BEPipBr salt was then dissolved in deionized water and reacted with LiNTf<sub>2</sub> (1 eq.) overnight at room temperature, to give [BEPip][NTf<sub>2</sub>] as a viscous colorless liquid. [BEPip][NTf<sub>2</sub>] was dried at 80°C for 24 h under vacuum and stored under dry argon (yield: 80%, two steps). The water content was determined by Karl Fischer titration and was found less than 10 ppm. Synthesized ionic liquids were then characterized by nuclear magnetic resonance <sup>1</sup>H NMR. <sup>1</sup>H NMR (400.13 MHz, CDCl<sub>3</sub>, 298 K): δ 0.99 (t, 3H, <sup>3</sup>J = 7.2 Hz), 1.40 (sex, 2H, <sup>3</sup>J = 7.2 Hz), 1.57–1.65 (m, 2H), 1.72 (quin, 2H, <sup>3</sup>J = 6.0 Hz), 1.86 (bs, 4H), 3.16–3.20 (m, 2H), 3.31 (t, 4H, <sup>3</sup>J = 6.0 Hz), 3.36 (q, 2H, <sup>3</sup>J = 7.2 Hz) ppm. Note that no brominated impurities were detected by Headspace Gas Chromatography Mass Spectrometry (Perkin Elmer) by thermal desorption experiment, performed by PerkinElmer.

Sonication was performed in a stainless steel reactor specifically designed for the SL measurements of small volumes of ionic liquids, and described in detail elsewhere.<sup>14</sup> The 20 kHz horn (1 cm<sup>2</sup>, 750 W Sonics generator) was set to work at 35% of its maximum amplitude. The specific heat capacity of [BEPip][NTf<sub>2</sub>] is not known, but the absorbed acoustic power can be estimated to be around 15 W by analogy with similar ionic liquids.<sup>14</sup> For all experiments, 30 mL of [BEPip][NTf<sub>2</sub>] were submitted to continuous Ar (99.999% purity, Air Liquide) gas flow about 30 minutes before sonication and during the ultrasonic treatment, at a controlled rate of 14 mL min<sup>-1</sup>. The reactor was continuously cooled using a Huber Unistat Tango thermo-cryostat set at 1°C. The temperature of the IL was thus initially 1°C and reached 33°C after 12 min of sonolysis.

Light emission spectra were collected through a flat quartz window using parabolic Al-coated mirrors and recorded with a SP 2356i Roper Scientific spectrometer coupled with a CCD camera with UV coating (SPEC10-100BR Roper Scientific) cooled by liquid-nitrogen. A low-resolution grating (150blz500; spectral resolution 1.6 nm) was used to enable the measurement of the whole spectrum (from 230 nm up to 750 nm) at once. Spectral calibration was performed using a Hg(Ar) pen-ray lamp (model LSP035, LOT-Oriel) and correction for background noise and for the quantum efficiencies of grating and CCD was performed. Each spectrum corresponds to 60 s of acquisition time.

Emissions from the C<sub>2</sub> Swan system (*A*<sup>3</sup>Π<sub>g</sub>–*X*<sup>3</sup>Π<sub>u</sub>) and CN violet system (*B*<sup>2</sup>Σ–*X*<sup>2</sup>Σ) were simulated by the spectroscopy code Specair,<sup>20</sup> after subtraction of a baseline and normalization. The simulation input parameters vibrational temperature *T<sub>v</sub>*, rotational temperature *T<sub>r</sub>* and “effective pressure” *p* (combining pressure and Stark effects<sup>21</sup>) were manually varied and optimized to fit experimental spectra as well as possible.

Quadrupole mass spectrometry (PROLAB 300, Thermo Fischer) was used to monitor the composition of the gas phase during sonication.

## Results and discussion

### Time-evolution of the SL spectra

Fig. 1 presents the SL spectra measured during the first 10 minutes of sonolysis of [BEPip][NTf<sub>2</sub>]. Light emission is observed from the first minute of sonication (Fig. 1a) and the corresponding SL spectrum presents emission bands that can be assigned<sup>22</sup> to C<sub>2</sub>, CN, CH, and possibly to SO<sub>2</sub>, species that may arise from the degradation of [BEPip][NTf<sub>2</sub>]. The strongest transitions of SO<sub>2</sub> (at 300.1 and 296.1 nm) cannot be observed due to light absorption by the IL.<sup>14</sup> This sign of degradation is quite surprising since it is expected that the initial bubble content will be pure Ar, due to the essentially zero vapor pressure of IL. This presence of emission bands in the SL spectrum thus clearly points out that some degradation

of [BEPip][NTf<sub>2</sub>] occurs from the very beginning of the sonolysis, possibly by a mechanism of droplet injection of the IL into the bubble core.

During the first two minutes of sonication (Fig. 1a), the intensities of the SL continuum and of the molecular emission bands strongly increase, which can be traced back to the evolution of the IL's temperature: it shows a very fast increase in the first minute of sonication and temperature reaches its steady-state value after 2 minutes. As an IL, [BEPip][NTf<sub>2</sub>] is very viscous at room temperature and below, but in general the viscosity of RTIL decreases exponentially with temperature.<sup>23</sup> A high viscosity hinders nucleation and therefore limits the number of cavitation bubbles.<sup>24</sup> As the bulk temperature increases, the rates of nucleation and coalescence increase, leading to the formation of more (light emitting) cavitation bubbles, hence the higher SL intensity. After 2 minutes of sonication, the steady-state bulk temperature being reached, the number of cavitation bubbles is expected to be constant, reflecting in a much slower evolution of the SL continuum intensity. Fig. 1b also shows that absorption of the SL light by the formed degradation products becomes intense. However, emission bands can still be observed.

Fig. 2 provides a closer look at the time evolution of the intensities of the SL continuum, taken at 600 nm, and of the main molecular emissions (whose intensities were corrected for absorption). During the first two minutes, all intensities strongly increase due to the increase in number of cavitation bubbles induced by the lowering of viscosity. Up to  $t = 5$  min, the SL continuum intensity then stays constant while molecular emissions decrease. The following decrease in the continuum intensity ( $t \geq 5$  min) indicates progressive poisoning of the plasma by gaseous by-products. Interestingly, the intensities of the various emission bands follow different trends: CN shows a strong decrease after 2 min sonolysis, while the intensities of C<sub>2</sub> and CH continue to increase or slowly decrease. This observation can be explained by considering that the various excited species can be formed from different sources: directly from the ionic liquid, but also from secondary (volatile) degradation products of [BEPip][NTf<sub>2</sub>], e.g. methane or acetylene, the presence of which was confirmed by MS analysis. The study of the degradation mechanism of this IL and the formed degradation products will be the object of a separate paper.

### Determination of rovibronic temperatures

Rovibronic temperatures were determined on two spectroscopic probes (C<sub>2</sub> Swan bands and CN violet) using Specair<sup>20</sup> software. Fig. 3 presents the measured Swan band emission for the second minute of sonication, together with its simulation. Derived vibrational and rotational temperatures are  $T_v = 5800 \pm 500$  K and  $T_r = 4000 \pm 500$  K. The inequality  $T_v > T_r$  is the usual case in a non-equilibrium plasma. Interestingly, simulated vibrational and rotational temperatures remain constant during the sonolysis, at least in the first 6 minutes, before absorption prevents computational fitting of the emission.

Fig. 4 presents the measured CN violet emission for the second minute of sonication, together with its Specair simulation. Due to absorption, only the first two minutes of sonolysis are usable. Both can be fitted by the same vibrational temperature:  $T_v = 6000 \pm 500$  K, in good agreement with C<sub>2</sub> vibrational temperature. In the particular case of CN and with the present spectral resolution,  $T_r$  cannot be derived accurately because its influence on the spectral shape (at the used spectral resolution) cannot be easily separated from that of the effective pressure.

It is remarkable that CN and C<sub>2</sub> vibrational temperatures stay constant in the first minutes of sonolysis, while the plasma characteristics obviously change: the viscosity of the IL decreases (impacting the bubbles' dynamics and thus the violence of their collapse), and the intensities of molecular emissions vary with time, indicating changes in the bubble content. Due to the almost zero vapor pressure of the IL, the initial bubble content is pure Ar, a monoatomic gas very favorable for cavitation.<sup>24</sup> The IL then starts to be degraded after being introduced into the plasma by droplet injection. Among its degradation products many are volatile, such as sulfur dioxide, carbon dioxide, acetylene, ethylene, methane etc. (that were detected by MS of the produced gases). They diffuse into the bubbles where

they consume part of the collapse energy by chemical reactions and electronic, vibrational and rotational excitations. The electron temperature is expected to strongly decrease concurrently with the poisoning of the plasma. The fact that CN and C<sub>2</sub> vibrational temperatures stay constant indicates that here they cannot be used to estimate the electron temperature. In other words, these excited states were not formed directly from the ground state by electron impact but by chemical reactions induced by impacts with energy transfer, like those involving metastable Ar for instance, and therefore they cannot be used as probes of the characteristics of the electrons.

### Use of CH electronic transitions

Two different electronic systems of CH are clearly visible on the SL spectra: CH (A–X) and CH (C–X). The third one, CH (B–X), is hidden by the very strong CN emission. The formation of excited states of CH is often reported in the literature in hydrocarbon combustion<sup>25</sup> and attributed to oxidation of a fuel derived radical by O, O<sub>2</sub>, OH or even SO<sub>2</sub><sup>26</sup> – the formation of SO<sub>2</sub> in the sonolysis of [BEPip][NTf<sub>2</sub>] was confirmed by mass spectrometry analysis of the produced gases. Determination of the exact processes leading to the formation of the observed excited species is beyond the scope of this paper, considering the complexity of the present system. However, several known precursors of CH excited states were observed by mass spectrometry of the produced gases: e.g. acetylene,<sup>25</sup> methane<sup>27</sup> and ethylene.<sup>28</sup> Thus it is highly probable that several concomitant reaction pathways do produce CH, each pathway populating in a different manner CH electronically excited states.<sup>29</sup> Therefore, no equilibrium is expected between these excited states and care should be taken in using the relative intensities of their emissions for a temperature determination. To illustrate this remark, let us consider on the contrary equilibrium, and that electronic excitation of CH occurs by electron impact. In this case, one can consider that the populations of the electronic levels follow Boltzmann law, and derive CH electronic temperature  $T_e$  from the populations ( $n_A$ ,  $n_C$ ) of the emitting levels:

$$\frac{n_C}{n_A} = \frac{g_C}{g_A} \exp\left(-\frac{E_C - E_A}{k_B T_e}\right)$$

where  $g_i$  is the degeneracy of the electronic level  $i$  and  $E_i$  is its energy. These relative populations of the emitting levels (Fig. 4) can be derived from the measured emission intensities ( $I_{A-X}$ ,  $I_{C-X}$ ):

$$I_{A-X} = n_A A_{A-X} h \nu_{A-X} \frac{\Omega}{4\pi} V$$

and

$$I_{C-X} = n_C A_{C-X} h \nu_{C-X} \frac{\Omega}{4\pi} V$$

with  $A_{A-X}$  the radiative transition probability from level A to level X,  $h \nu_{A-X}$  the photon energy,  $\Omega$  the solid angle of observation and  $V$  the observed plasma volume.

It follows from the previous equations, with  $K$  a constant:

$$\ln\left(\frac{I_{i-X} \lambda_{i-X}}{g_i A_{i-X}}\right) = K - \frac{E_i}{k_B T_e}$$

The electronic temperature of CH can thus be derived from the slope of Boltzmann plot  $\ln\left(\frac{I_{i-X} \lambda_{i-X}}{g_i A_{i-X}}\right)$  vs.  $E_i$  (insert in Fig. 4). Obtained CH electronic temperatures are of 3.9 eV  $\approx$  46 000 K ( $\pm$  27 000 K) for the first minute of sonication, 0.75 eV  $\approx$  8700 K ( $\pm$  2000 K) for the second minute and 0.72 eV  $\approx$  8400 K ( $\pm$  3600 K) for the third minute of sonication.

Although the observed trend is in agreement with the expected decrease in electron temperature in the first minute(s) of sonication and as long as degradation products accumulate in the bubbles, the very high value calculated for the first minute of sonication clearly casts doubt on the made hypothesis. Indeed, such a high experimentally determined temperature has never been reported for acoustic cavitation. Moreover, it strongly disagrees with the electronic temperature previously estimated in a similar SL-favorable medium (another liquid with very low vapor pressure): Eddingsaas et al.<sup>30</sup> derived an electronic temperature of 8000 K from the Ar (4p–4s) emission in concentrated sulfuric acid sonicated at 20 kHz under Ar. The discrepancy is to be attributed to the made assumptions: CH excited states are not produced by electron impact but by different chemical reactions, and their relative populations cannot be used to estimate an electronic temperature.

That being said, it is remarkable that a very high relative population of CH ( $C^2\Sigma^+$ ) state, 0.38 31% (Fig. 5), is reached at the very beginning of sonication, when the bubble content is almost only Ar, indicating that enough energy is present to produce it. As soon as degradation products are formed and poison the bubble interior, i.e. from the second minute of sonication, CH ( $C^2\Sigma^+$ ) population relatively to CH ( $A^1\Pi$ ) one strongly decreases to 0.12. This huge change that happens in the first two minutes of sonication underlines the strong and fast change in bubble content and in sonochemical plasma characteristics during sonication, due to the degradation of the solvent.

### Discussion on the temperatures

All spectroscopically determined temperatures here are, as expected, higher than the “chemical” one (3500 K<sup>15</sup>). They also illustrate the non-equilibrium state of the plasma, with  $T_e > T_v > T_r$ . Even if comparison of spectroscopic temperatures is not straightforward, valued information can be derived from them. First of all, it is usually considered that rotational temperatures are equal to the gas (or translational) temperature since only a few collisions are needed for equilibration (the high pressure of the sonochemical plasma makes this condition easily fulfilled). Thus an estimate of the gas temperature at the time of C<sub>2</sub> emission is given by C<sub>2</sub> rotational temperature  $T_{gas} = T_r = 4000 \pm 500$  K.

Also vibrational temperatures could be derived from CN and C<sub>2</sub> emissions: fitting with Specair is possible because populations of excited vibrational levels follow Boltzmann law. Excited species undergo enough collisions to reach a vibrational equilibrium, which illustrates in the good agreement obtained between C<sub>2</sub> and CN vibrational temperatures ( $T_v(C_2) = 5800 \pm 500$  K and  $T_v(CN) = 6000 \pm 500$  K). In this view, it is interesting to compare C<sub>2</sub> and CN rovibronic temperatures during the sonication of [BEPip][NTf<sub>2</sub>] at 20 kHz under Ar with literature values derived from multibubble SL spectra (considering the same ultrasonic frequency and gas) of aqueous solutions or concentrated acids. Fitting of C<sub>2</sub> Swan bands in a 10<sup>-3</sup> M aqueous benzene solution gave  $T_v = 4300 \pm 200$  K,<sup>31</sup> and in aqueous tert-butanol solutions (0.05–0.4 M)  $T_v = 6300 \pm 1000$  K.<sup>17</sup> It was also shown, though at high ultrasonic frequency, that decreasing the tert-butanol concentration led to an increase in C<sub>2</sub> vibrational temperature,<sup>17</sup> so that higher temperatures would be expected at lower concentration. In a 0.1 M ammonia solution, vibrational temperatures of 9000 ± 1000 K for OH ( $A^2\Sigma^+ - X^2\Pi$ ) and 7000 ± 1000 K for NH ( $A^3\Pi - X^2\Sigma^-$ ) were estimated.<sup>21</sup> Concerning concentrated acids, Ar (4p–4s) emission in sulfuric acid corresponded to an electronic temperature of 8000 K, while in phosphoric acid OH ( $A^2\Sigma^+ - X^2\Pi$ ) and PO ( $B^2\Sigma^+ - X^2\Pi$ ) indicated vibrational temperatures of 9500 K and 4000 K, respectively. All these temperatures show a strong similarity, although more extreme conditions would be expected for IL (and concentrated acids, that share with IL a very low vapor pressure) than for aqueous solutions. Thus, the comparison of rovibronic temperatures leads to the same paradox (shifted to somewhat higher temperatures) as previously observed with chemical temperatures:<sup>15</sup> temperatures estimated for ionic liquids (and in concentrated acids) are of the same order of magnitude as in aqueous solutions, although more extreme conditions are expected from the quasi adiabatic heating model. This is not necessarily discordant, considering that the plasma is non-equilibrium, so that vibrational temperatures are smaller than electronic temperatures. In this view, they are only an order of magnitude estimate of the electron temperature  $T_{el}$ .

Moreover, as discussed above, CN and C<sub>2</sub> vibrational temperatures staying constant while the electron temperature is expected to strongly decrease concurrently with the poisoning of the plasma indicates that they are disconnected from the electron temperature. These excited states and their emissions are probes of the chemical reactions that formed them, which explains why different temperatures were obtained in the literature from OH, C<sub>2</sub>, PO or NH emissions.

In a similar way, the emissions from two electronic systems of CH observed in the SL spectra of [BEPip][NTf<sub>2</sub>] unfortunately cannot be directly used to determine the plasma electron energy, although they reflect its evolution and that of the bubble content. The ratio of populations of CH (C<sup>2</sup>Σ<sup>+</sup>) and CH (A<sup>1</sup>Π) states measured in the first minute of sonication is 0.38 (31%), i.e. very high (under the assumption that CH electronically excited states would be populated by electron impact and that their populations would follow Boltzmann law it would correspond to an electronic temperature of 3.9 eV). It shows a very fast and strong decrease and equals 0.12 in the second minute of sonication. Present SL spectra measurements are integrated over one minute, and it is expected that the relative population of CH (C<sup>2</sup>Σ<sup>+</sup>) vs. CH (A<sup>1</sup>Π) be even higher in the first seconds of sonication, betraying a very energetic initial plasma.

## Conclusion

Sonication of a very dry [BEPip][NTf<sub>2</sub>] ionic liquid under Ar produces an intense sonoluminescence, which allowed us to monitor the time-evolution of the SL spectra. Several molecular emissions were observed, the origin of which is the direct degradation of the ionic liquid and that of its degradation products. Rovibronic temperatures of C<sub>2</sub> and CN were determined, giving vibrational temperatures of the order of 5800 K and rotational temperatures (i.e. gas temperatures) of 4000 ± 500 K. These temperatures stay constant during the first minutes of sonolysis, as long as absorption of SL light by the sonolysis degradation products does not prevent from simulating the emissions. This stability of rovibronic temperatures is contradictory to the observed changes in SL continuum intensity and in excited states emission intensities that reflect the changes in the plasma state induced by the changing bubbles' contents. This apparent discrepancy indicates that these rovibronic temperatures cannot be used as estimates of the plasma electron properties.

Two electronic systems of CH are observed in the SL spectra of [BEPip][NTf<sub>2</sub>]. Their relative intensities strongly decrease in the first two minutes of sonication, reflecting the uptake of volatile degradation products inside the bubbles. The ratio of populations of CH (C<sup>2</sup>Σ<sup>+</sup>) and CH (A<sup>1</sup>Π) states measured in the first minute of sonication is very high, but strongly decreases in the second minute of sonication due to the change in the bubble content, from pure Ar to a mixture of Ar and volatile degradation products, that leads to poisoning of the plasma and to a much lower ability to produce highly excited states (e.g. CH (C<sup>2</sup>Σ<sup>+</sup>)).

Future work will follow two directions. First it will focus on measuring SL spectra in the very early stages of sonication (i.e. in the first seconds), to characterize the formed plasma when the degradation of [BEPip][NTf<sub>2</sub>] is still negligible. This aim requires further technical developments of the experimental set-up and in particular an amplification of the SL light that is very dim, even in the optimized conditions of a very dry IL. These experimental data will help reconsidering the model of formation of the sonochemical plasma, and its comparison with "more conventional" plasmas. Second, it should study and compare more molecular emissions in SL, to try and shed some more light on the mechanisms of formation of the excited species and determine which useful information can be derived from them.

## Acknowledgements

The Réseau Plasmas Froids from French CNRS is acknowledged for providing some of us with an IPMC. The Agence Nationale de la Recherche is acknowledged for financial support through the SILEXE project (ANR-13-CDII-0010). C. Meillat and PerkinElmer are acknowledged for GC-MS experiments.

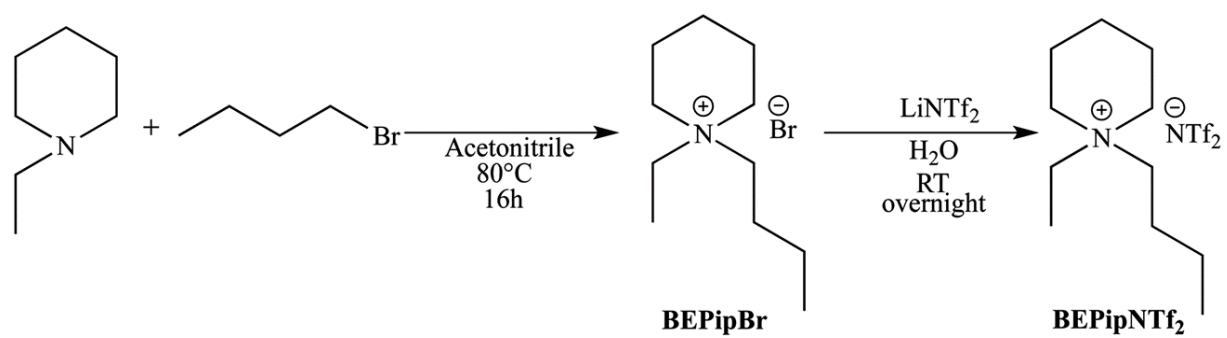


## References

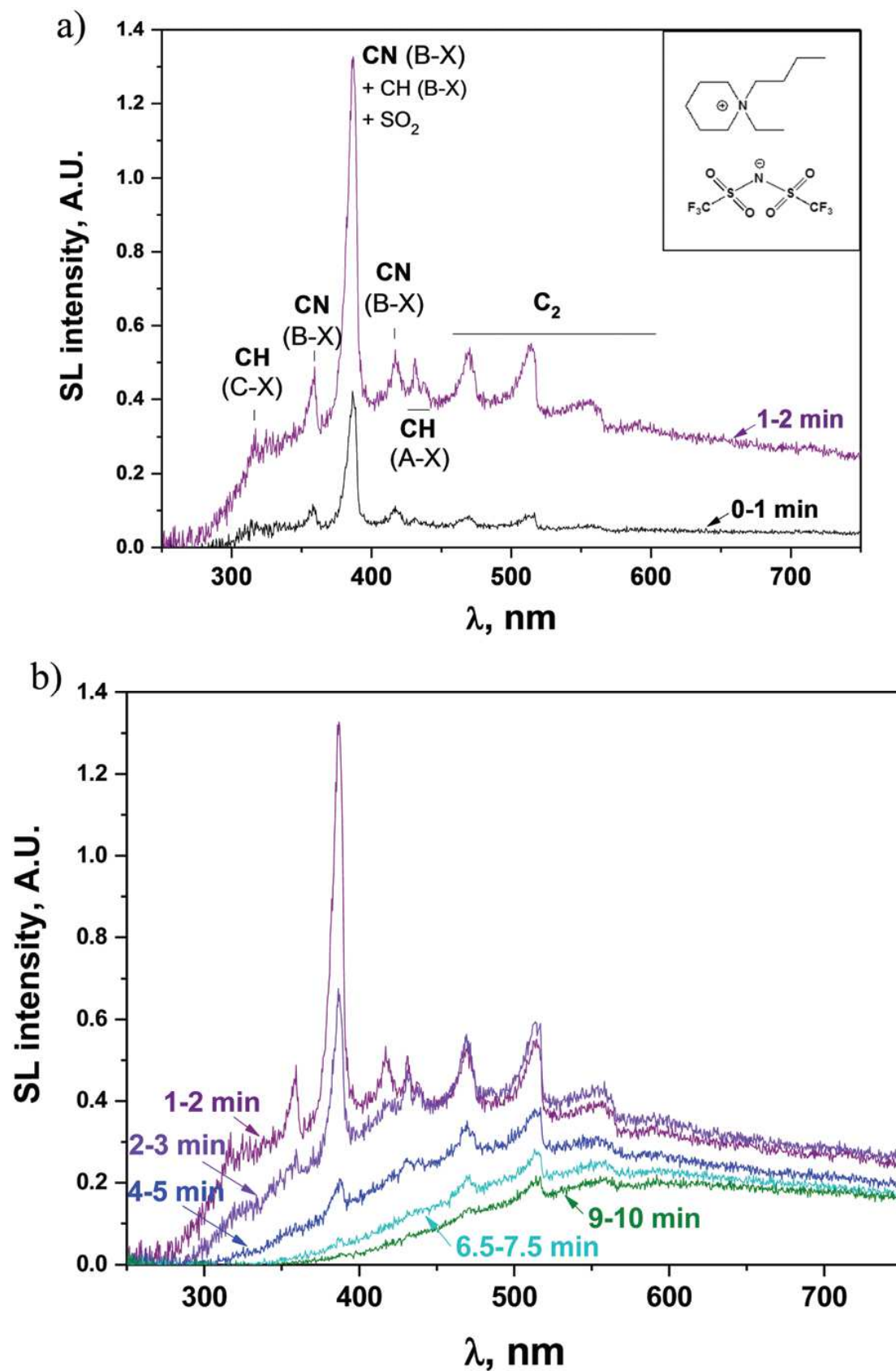
- 1 P. J. Bruggeman, M. J. Kushner, B. R. Locke, J. G. E. Gardeniers, W. G. Graham, D. B. Graves, R. Hofman-Caris, D. Maric, J. P. Reid, E. Ceriani, D. F. Rivas, J. E. Foster, S. C. Garrick, Y. Gorbanev, S. Hamaguchi, F. Iza, H. Jablonowski, E. Klimova, J. Kolb, F. Krcma, P. Lukes, Z. Machala, I. Marinov, D. Mariotti, S. M. Thagard, D. Minakata, E. C. Neyts, J. Pawlat, Z. L. Petrovic, R. Pflieger, S. Reuter, D. C. Schram, S. Schroter, M. Shiraiwa, B. Tarabova, P. A. Tsai, J. R. R. Verlet, T. vonWoedtke, K. R. Wilson, K. Yasui and G. Zvereva, Plasma-liquid interactions: a review and roadmap, *Plasma Sources Sci. Technol.*, 2016, 25, 053002.
- 2 J. Claus, F. O. Sommer and U. Kragl, Ionic liquids in biotechnology and beyond, *Solid State Ionics*, 2018, 314, 119–128.
- 3 R. Kore, P. Berton, S. P. Kelley, P. Aduri, S. S. Katti and R. D. Rogers, Group IIIA Halometallate Ionic Liquids: Speciation and Applications in Catalysis, *ACS Catal.*, 2017, 7, 7014–7028.
- 4 D. R. MacFarlane, N. Tachikawa, M. Forsyth, J. M. Pringle, P. C. Howlett, G. D. Elliott, J. H. Davis, M. Watanabe, P. Simon and C. A. Angell, Energy applications of ionic liquids, *Energy Environ. Sci.*, 2014, 7, 232–250.
- 5 R. Turgis, G. Arrachart, S. Michel, S. Legeai, M. Lejeune, M. Draye and S. Pellet-Rostaing, Ketone functionalized task specific ionic liquids for selective tantalum extraction, *Sep. Purif. Technol.*, 2018, 196, 174–182.
- 6 D. J. Flannigan, S. D. Hopkins and K. S. Suslick, Sonochemistry and sonoluminescence in ionic liquids, molten salts, and concentrated electrolyte solutions, *J. Organomet. Chem.*, 2005, 690, 3513–3517.
- 7 R. Rajagopal and K. V. Srinivasan, Ultrasound promoted para-selective nitration of phenols in ionic liquid, *Ultrason. Sonochem.*, 2003, 10, 41–43.
- 8 R. Rajagopal, D. V. Jarikote and K. V. Srinivasan, Ultrasound promoted Suzuki cross-coupling reactions in ionic liquid at ambient conditions, *Chem. Commun.*, 2002, 616–617.
- 9 G. Chatel, C. Goux-Henry, A. Mirabaud, T. Rossi, N. Kardos, B. Andrioletti and M. Draye, H<sub>2</sub>O<sub>2</sub>/NaHCO<sub>3</sub>-mediated enantioselective epoxidation of olefins in NTf<sub>2</sub>-based ionic liquids and under ultrasound, *J. Catal.*, 2012, 291, 127–132.
- 10 S. Letort, M. Lejeune, N. Kardos, E. Metay, F. Popowycz, M. Lemaire and M. Draye, New insights into the catalytic reduction of aliphatic nitro compounds with hypophosphites under ultrasonic irradiation, *Green Chem.*, 2017, 19, 4583–4590.
- 11 S. Merouani, O. Hamdaoui and B. Haddad, Acoustic cavitation in 1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide based ionic liquid, *Ultrason. Sonochem.*, 2018, 41, 143–155.
- 12 J. D. Oxley, T. Prozorov and K. S. Suslick, Sonochemistry and sonoluminescence of room-temperature ionic liquids, *J. Am. Chem. Soc.*, 2003, 125, 11138–11139.
- 13 M. J. Earle, J. Esperanca, M. A. Gilea, J. N. C. Lopes, L. P. N. Rebelo, J. W. Magee, K. R. Seddon and J. A. Widegren, The distillation and volatility of ionic liquids, *Nature*, 2006, 439, 831–834.
- 14 G. Chatel, R. Pflieger, E. Naffrechoux, S. I. Nikitenko, J. Suptil, C. Goux-Henry, N. Kardos, B. Andrioletti and M. Draye, Hydrophobic Bis(trifluoromethylsulfonyl)imide-Based Ionic Liquids Pyrolysis: Through the Window of the Ultrasonic Reactor, *ACS Sustainable Chem. Eng.*, 2013, 1, 137–143.

- 15 P. M. Kanthale, A. Brotchie, F. Grieser and M. Ashokkumar, Sonoluminescence quenching and cavitation bubble temperature measurements in an ionic liquid, *Ultrason. Sonochem.*, 2013, 20, 47–51.
- 16 E. Ciawi, M. Ashokkumar and F. Grieser, Limitations of the methyl radical recombination method for acoustic cavitation bubble temperature measurements in aqueous solutions, *J. Phys. Chem. B*, 2006, 110, 9779–9781.
- 17 R. Pflieger, A. A. Ndiaye, T. Chave and S. I. Nikitenko, Influence of Ultrasonic Frequency on Swan Band Sonoluminescence and Sonochemical Activity in Aqueous tert- Butyl Alcohol Solutions, *J. Phys. Chem. B*, 2015, 119, 284–290.
- 18 D. D. Perrin and L. F. Armarego, *Purification of laboratory chemicals*, Butterworth-Heinemann, Oxford, 5th edn, 2003.
- 19 Y. Traore, S. Legeai, S. Diliberto, G. Arrachart, S. Pellet-Rostaing and M. Draye, New insight into indium electrochemistry in a Tf<sub>2</sub>N-based room-temperature ionic liquid, *Electrochim. Acta*, 2011, 58, 532–540.
- 20 C. O. Laux, T. G. Spence, C. H. Kruger and R. N. Zare, Optical diagnostics of atmospheric pressure air plasmas, *Plasma Sources Sci. Technol.*, 2003, 12, 125–138.
- 21 R. Pflieger, T. Ouerhani, T. Belmonte and S. I. Nikitenko, Use of NH (A(3)Pi-X-3 Sigma(-)) sonoluminescence for diagnostics of nonequilibrium plasma produced by multibubble cavitation, *Phys. Chem. Chem. Phys.*, 2017, 19, 26272–26279.
- 22 R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra*, Chapman and Hall, London, 4th edn, 1976.
- 23 F. G. Liu, X. W. Zhong, J. L. Xu, A. Kamali and Z. N. Shi, Temperature Dependence on Density, Viscosity, and Electrical Conductivity of Ionic Liquid 1-Ethyl-3-Methylimidazolium Fluoride, *Appl. Sci.*, 2018, 8, 356.
- 24 F. R. Young, *Sonoluminescence*, CRC Press, New York, 2005.
- 25 K. Devriendt and J. Peeters, Direct identification of the C<sub>2</sub>H(X(2)Sigma(+))+O(P-3)-4CH(A(2)Delta)+CO reaction as the source of the CH(A(2)Delta-4X(2)Pi) chemiluminescence in C<sub>2</sub>H<sub>2</sub>/O/H atomic flames, *J. Phys. Chem. A*, 1997, 101, 2546–2551.
- 26 S. Swinnen, R. M. I. Elsamra, V. S. Nguyen, J. Peeters, S. A. Carl and M. T. Nguyen, Theoretical and experimental investigation of the C<sub>2</sub>H + SO<sub>2</sub> reaction over the range T = 295–800 K, *Chem. Phys. Lett.*, 2011, 513, 201–207.
- 27 C. Alves, N. K.M. Galvao, A. Gregory, G. Henrion and T. Belmonte, OES during reforming of methane by microwave plasma at atmospheric pressure, *J. Anal. At. Spectrom.*, 2009, 24, 1459–1461.
- 28 Z. Cai, J. J. Zhu, M. B. Sun and Z. G. Wang, Spark-enhanced ignition and flame stabilization in an ethylene-fueled scramjet combustor with a rear-wall-expansion geometry, *Exp. Therm. Fluid Sci.*, 2018, 92, 306–313.
- 29 M. Gueye, T. Gries, C. Noel, S. Migot-Choux, S. Bulou, E. Lecoq, P. Choquet and T. Belmonte, Interaction of (3-Aminopropyl)- triethoxysilane With Late ArN<sub>2</sub> Afterglow: Application to Nanoparticles Synthesis, *Plasma Processes Polym.*, 2016, 13, 698–710.
- 30 N. C. Eddingsaas and K. S. Suslick, Evidence for a plasma core during multibubble sonoluminescence in sulfuric acid, *J. Am. Chem. Soc.*, 2007, 129, 3838–3839.

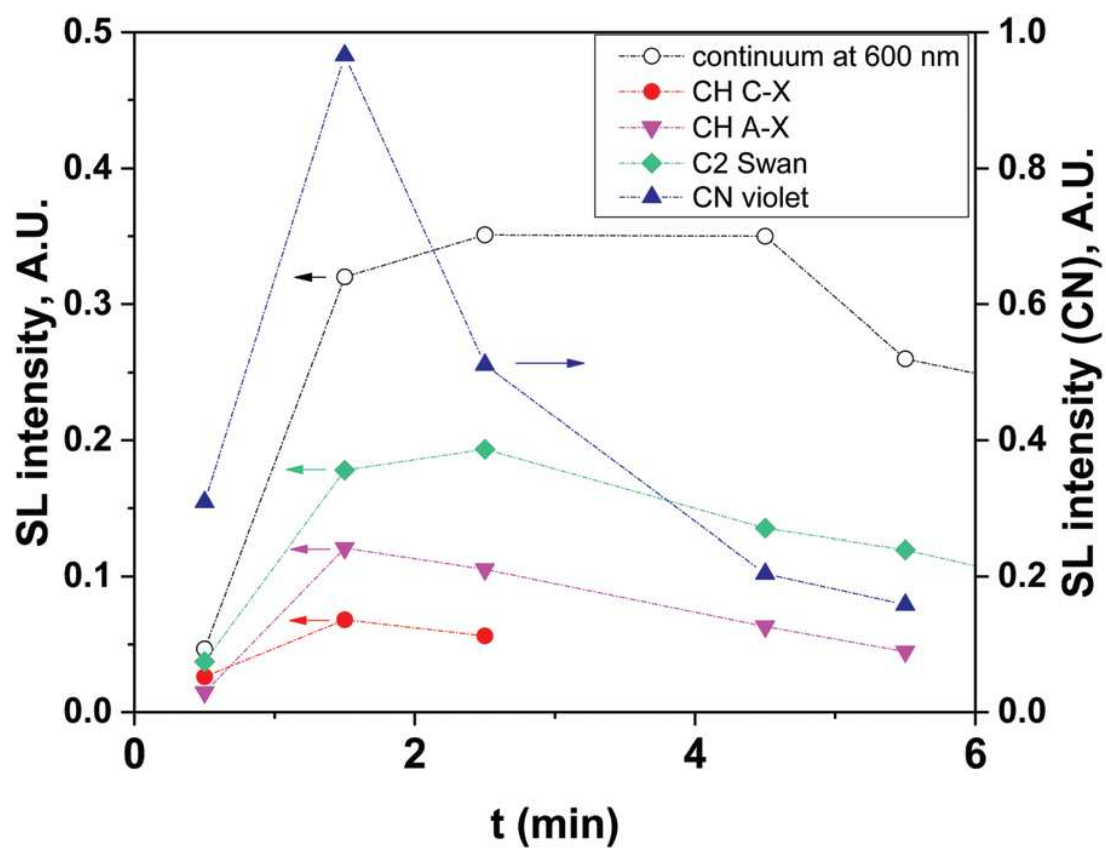
- 31 Y. T. Didenko, W. B. McNamara and K. S. Suslick, Hot spot conditions during cavitation in water, *J. Am. Chem. Soc.*, 1999, 121, 5817–5818.



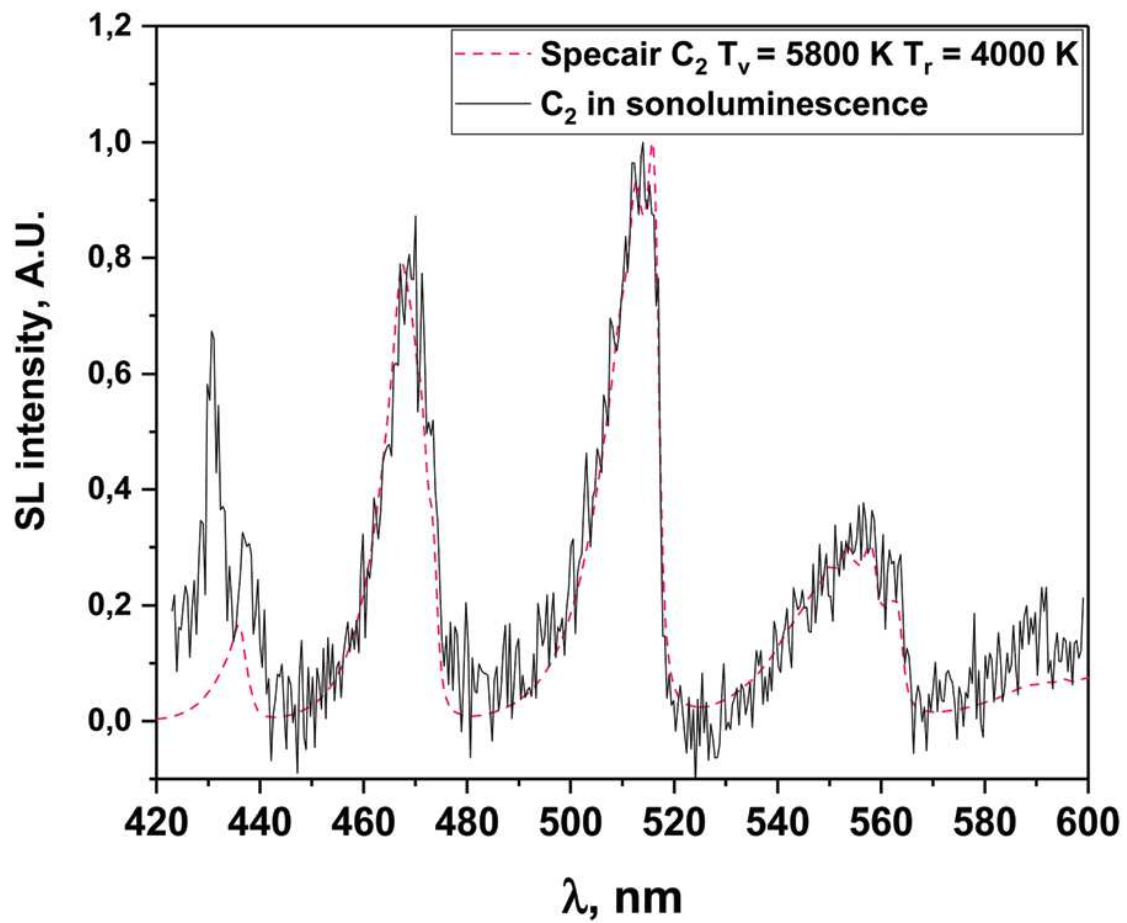
**Scheme 1:** Synthesis of [BEPip][NTf<sub>2</sub>] ionic liquid



**Fig. 1:** Time-evolution of the SL spectra of [BEPip][NTf<sub>2</sub>] (20 kHz, Ar): (a) in the first two minutes, (b) from the second to the tenth minute of sonication.



**Fig. 2:** Time-evolution of the intensities of molecular emission bands and of the SL continuum during the sonolysis of [BEPip][NTf<sub>2</sub>] at 20 kHz under Ar. The symbol size was adjusted to represent the uncertainty



**Fig. 3:** Measured Swan band emission in SL (second minute of sonication of [BEpip][NTf<sub>2</sub>] at 20 kHz under Ar) after subtraction of a baseline and normalization, and Specair simulation (T<sub>v</sub> = 5800 ± 500 K, T<sub>r</sub> = 4000 ± 500 K, “p” = 800 bar).

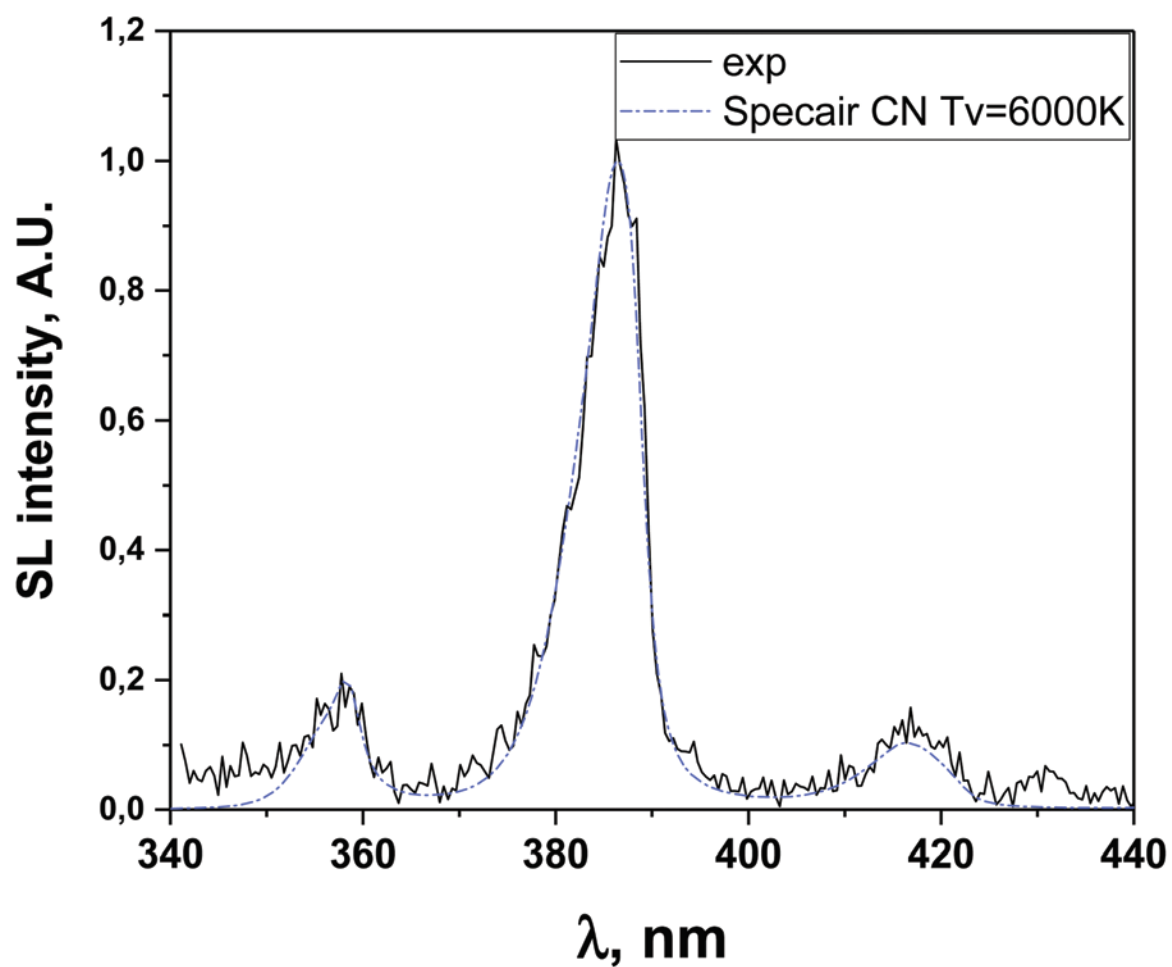
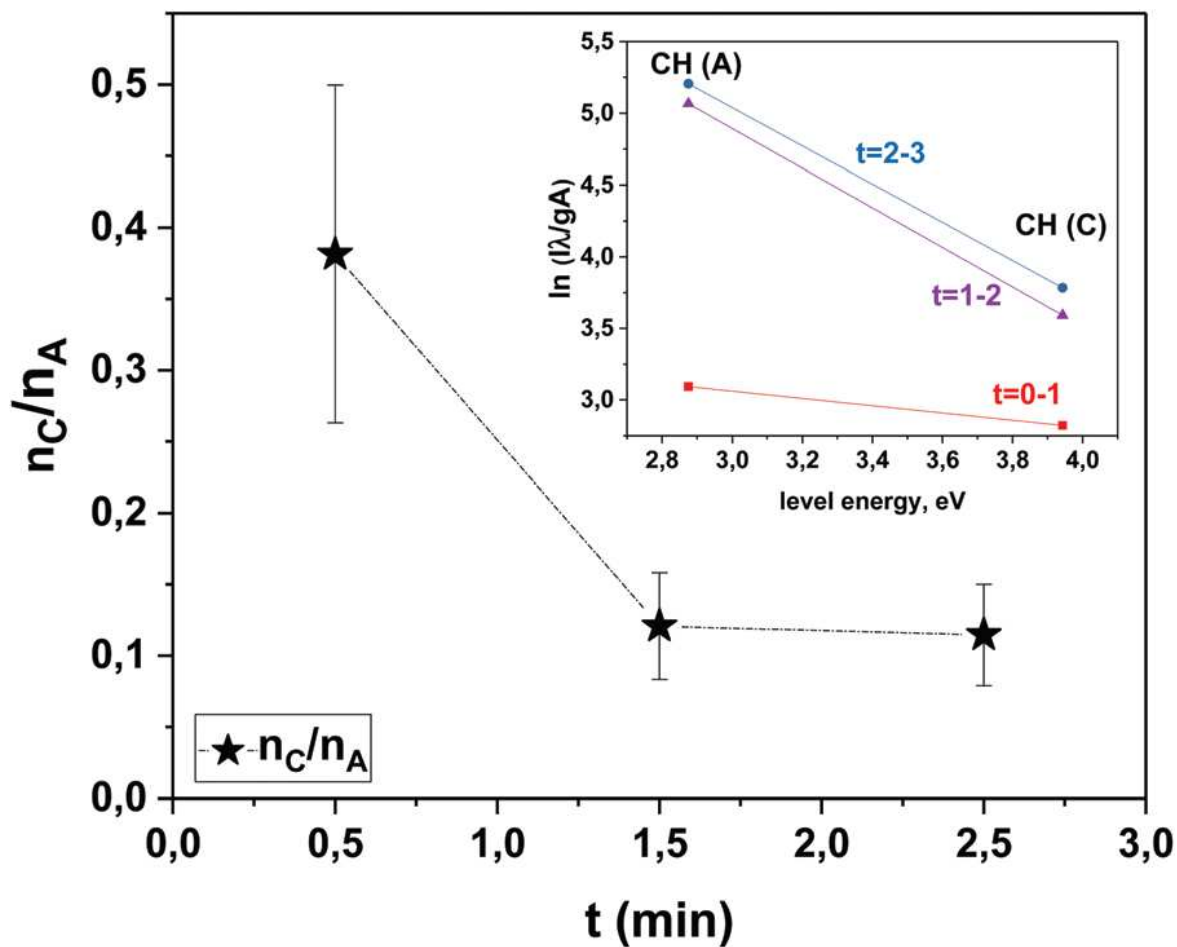


Fig. 4 Measured CN violet emission in SL (second minute of sonication of [BEPip][NTf<sub>2</sub>] at 20 kHz under Ar) after subtraction of a baseline and normalization, and Specair simulation ( $T_v = 6000 \pm 500$  K,  $T_r = 5500 \pm 2000$  K, " $\rho$ " = 4000 bar).





**Fig. 5:** Time-evolution of the relative population of C electronic level of CH, relatively to A electronic level. Insert: Boltzmann plot of CH for the first minutes of sonolysis of [BEPip][NTf<sub>2</sub>] at 20 kHz under Ar.