# **Supplementary Information**

Molecular-level insights into structures, dynamics, and hydrogen bonds of ethylammonium nitrate protic ionic liquid at the liquidvacuum interface

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### 1. The Lennard–Jones parameters and partial atomic charges

	atom	σ(Å)	ε (kcal/mol)	q (e)
	C (CH <sub>3</sub> )	3.500	0.066	-0.1440
	C (CH <sub>2</sub> )	3.500	0.066	0.1520
EA <sup>+</sup> Cation	H (C <sub>2</sub> H <sub>5</sub> )	2.500	0.030	0.0480
	$N (NH_{3}^{+})$	3.250	0.170	-0.2400
	$H(NH_{3}^{+})$	0.000	0.000	0.2640
NO <sub>3</sub> <sup>-</sup> Anion	Ν	3.150	0.170	0.6352
	0	2.860	0.210	-0.4784

Table S1. The Lennard-Jones parameters and partial atomic charges used in this work.

#### 2. The typical equilibrium snapshot



Fig. S1. The typical equilibrium snapshot for the system of EAN IL at the liquidvacuum interface.

### 3. The effect of the sampling time interval $\Delta t$ on the hydrogen bond dynamics

Here, it should be emphasized that the time interval  $\Delta t$  to update the trajectories has a great influence on the  $S_{HB}(t)$  since its lifetime is relatively short. To better understand such effect, we have sampled the trajectories every 1, 5, 10, 50, and 100 fs to analyze the  $S_{HB}(t)$  and  $C_{HB}(t)$  for bulk ethylammonium nitrate (EAN) IL. Fig. S2 shows the calculated  $S_{HB}(t)$  and  $C_{HB}(t)$  curves with different  $\Delta t$  values, and the corresponding average lifetime  $\tau_S^{HB}$  and structural relaxation time  $\tau_C^{HB}$  of the NH<sub>3</sub><sup>+</sup>- NO<sub>3</sub><sup>-</sup> HBs are listed in Table S2. It is clear from Fig. S2 that the  $S_{HB}(t)$  curves of  $\Delta t =$  50 and 100 fs are very distinct from those of  $\Delta t = 1$ , 5, and 10 fs. Likewise, the results in Table 1 show that the obtained the HBs lifetime  $\tau_S^{HB}$  is almost the same when  $\Delta t$  is 1 and 5 fs, whereas the corresponding of  $\Delta t = 100$  fs is about 0.90 ps, which is about 3 times greater than that of the  $\Delta t = 1$  fs. On the other hand, Fig. S1b demonstrates that the  $\Delta t$  has a negligible effect on the  $C_{HB}(t)$  profiles, which is supported by the nearly identical structural relaxation time  $\tau_C^{HB}$  in Table S1, suggesting that the  $C_{HB}(t)$  is insensitive to the  $\Delta t$  Value. Therefore, we performed an additional 100 ps NVT simulation, with a smaller time interval (5 fs), to calculate the continuous HB dynamics  $S_{HB}(t)$  and such  $\Delta t$  enables us to obtain accurate and reliable  $\tau_S^{HB}$ , while the 20 ns NVT simulation, with a time interval of 100 fs, was used to determine the intermittent HB dynamics  $C_{HB}(t)$ .



Fig. S2. Two time correlation functions (a)  $S_{HB}(t)$  and (b)  $C_{HB}(t)$  for bulk NH<sub>3</sub><sup>+</sup>-NO<sub>3</sub><sup>-</sup> HBs with different time interval  $\Delta t$ .

$\Delta t$ (fs)	$ au_S^{HB}$ (ps)	$ au_{\mathcal{C}}^{HB}$ (ps)
1	0.31	3.50
5	0.32	3.50
10	0.36	3.48
50	0.61	3.46
100	0.90	3.47

**Table S2**. The corresponding  $\tau_S^{HB}$  and  $\tau_C^{HB}$  values for bulk EAN with different  $\Delta t$ .

#### 4. Surface tension calculation

we calculated the surface tension  $\gamma$  by using the pressure tensor and the equation is defined as:<sup>1-4</sup>

$$\gamma = \frac{L_z}{2} \left[ \langle p_{zz} \rangle - \frac{\langle p_{xx} \rangle + \langle p_{yy} \rangle}{2} \right]$$

where  $p_{ii}$  is the ii component of the pressure tensor,  $L_z$  is the simulation dimension in z direction and the factor of 1/2 outside the bracket arises from the two liquid-vapor interfaces in the system.  $\langle p_{zz} \rangle$  and  $\langle p_{xx} \rangle + \langle p_{yy} \rangle$  refer to the pressure components normal and tangential to the interface plane, respectively.

## 5. Mean residence time calculation

We also calculated the residence time by employing the residence correlation function  $C_{res}(t)$ , defined as:<sup>5-7</sup>

$$C_{\rm res}(t) = \frac{\langle g(0)g(t) \rangle}{\langle g(0)g(0) \rangle}$$

where the variable g(t) is unity when the tagged ion in a given interface region remains continuously from time 0 to time t, and zero otherwise. The angular brackets represent ensemble average and  $C_{res}(t)$  is expected to decay from 1.0 to 0.0 along the time evolution. By continuous definition, the  $C_{res}(t)$  is a measure of the mean residence time  $\tau_{res}$  of the ions in specific layers of interest. The  $\tau_{res}$  values are calculated by fitting the  $C_{res}(t)$  curves through the three weighed exponentials (with a total weight of one, i.e., A+B+C=1), which can be expressed as:

$$R(t) = A \exp(-t/\tau_a) + B \exp(-t/\tau_b) + C \exp(-t/\tau_c)$$

and then

$$\tau_{\rm res} = A\tau_{\rm a} + B\tau_{\rm b} + C\tau_{\rm c}$$

where A, B, and C are the fitting parameters, while  $\tau_a$ ,  $\tau_b$  and  $\tau_c$  are the time constants. The calculated  $C_{res}(t)$  curves for Cation-1 and Cation-2 at the liquid-vacuum interface are shown in Fig. 1 and the mean residence time is listed in Table 1. The results in Fig. 1 reveal that the cations in the first interface layer (Cation-1) remain longer than those in the second interface layer (Cation-2) at all three temperatures, which is supported by the mean residence time in Table 1. Meanwhile, when the temperature increases from 300 to 400 K, the  $C_{res}(t)$  curves of both Cation-1 and Cation-2 start to show a faster decay, resulting in the mean residence time of Cation-1 (or Cation-2) decreases from 218.8 ps (or 130.5 ps) to 88.2 ps (or 23.9 ps). By comparison, it is obvious that the mean residence time of both Cation-1 and Cation-2 is much lower than the sampling time of 20.0 ns.



**Fig. S3**. The residence correlation functions of Cation-1 and Cation-2 at (a) 300, (b) 350, and (c) 400 K.

**Table S3.** The mean residence time  $\tau_{res}$  for the interfacial Cation-1 and Cation-2 at 300, 350, and 400 K.

$ au_{res}$ (ps)	300 K	350 K	400 K
Cation-1	218.8	153.4	88.2
Cation-2	130.5	37.0	23.9

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