

Ultrafast Electron Solvation in Room Temperature Ionic Liquid/Metal Interfaces

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Abstract: The room temperature ionic liquid $[Bm\text{pyr}]^+[NTf_2]^-$ is studied on Ag(111). Monolayer and bilayer films both show a single state solvating, the timescale of solvation and magnitude of energy relaxation is significantly greater for the bilayer.

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1. Introduction

Due to their unique physical properties, room temperature ionic liquids (RTIL) are a novel class of compounds that have found widespread use as a substitute for traditional organic solvents. Though these materials have received an immense amount of attention and study in recent years, there remain areas where little is known about how RTILs behave. For example, it has been shown that electron solvation proceeds on multiple timescales in bulk RTILs [1], but ultrafast studies of these compounds on surfaces are limited in number.

In a recent study by our group [2], the $[Bm\text{pyr}]^+[NTf_2]^-/\text{Ag}(111)$ system was investigated using ultrafast time- and angle-resolved two-photon photoemission (TPPE). These results show that an electron injected into a thin film solvates on a fs timescale. Furthermore, the relaxation time and energy shift are strongly dependent on sample temperature. We build on those results by using temperature programmed desorption (TPD), as well as coverage-dependent TPPE, to assign accurate film thicknesses for the present study.

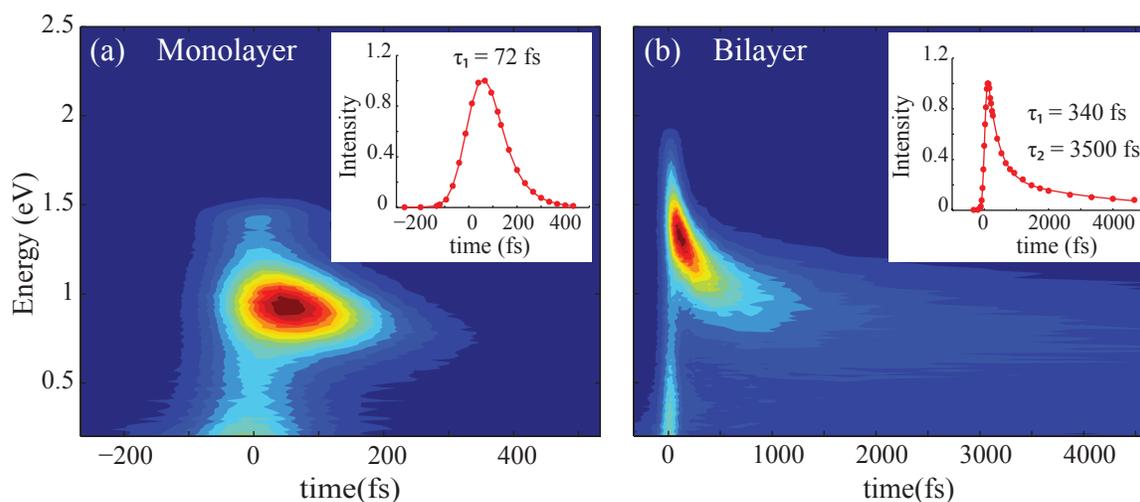


Fig. 1. Dynamics of (a) Monolayer and (b) Bilayer $[Bm\text{pyr}]^+[NTf_2]^-$ on Ag(111). Insets show amplitude of peak fits as a function of time delay and include time constants.

2. Results and Discussion

Until recently, it was difficult to assign meaningful coverages in terms of number of monolayers because it was unclear as to how the $[Bm\text{pyr}]^+$ and $[NTf_2]^-$ ions were oriented when adsorbed. A recent study was able to overcome this

difficulty with a thorough characterization of the adsorbate structure of this system. It was shown that the cation and anion adsorb side by side to form a monolayer [3].

In the monolayer, a single state is seen with TPPE. This feature shows weak solvation with an energy relaxation of 250 meV and decay back to the metal on the relatively short timescale of 72 fs. A similar state is observed for the bilayer, but relaxation for this thicker coverage increases to 700 meV and decay is best fit by a biexponential decay with time constants 340 fs and 3500 fs. In both the monolayer and bilayer case the dispersion is initially positive, the monolayer state has an effective mass of $m^* = 2 m_e$ while the bilayer state's effective mass is $m^* = 5 m_e$. These results suggest that a multi-step process is taking place upon electronic excitation in these films. It is likely that the electron is initially excited into a free-electron-like image potential state (IPS), then undergoes solvation on a timescale faster than our pulse cross correlation of 120 fs, leading to our measuring a heavy but positively dispersing state at the point of pulse overlap. The solvation then proceeds on a hundreds of femtoseconds timescale in the case of the monolayer, and a few picosecond timescale in the case of the bilayer, similar to the behavior of electrons photoinjected into H₂O films on Cu(111) [4]. The long lifetimes of the states indicate that the $[Bmpyr]^+[NTf_2]^-$ screens the injected electron from the metal effectively, as the thickness increases so does the screening effect, leading to an increase in the timescale of relaxation.

3. Conclusions

We have characterized the electron solvation and decay dynamics in two different coverages of the RTIL $[Bmpyr]^+[NTf_2]^-$. The energetic relaxation during solvation was shown to be a factor of three greater for the bilayer film, and solvation proceeded on the several picosecond timescale in the bilayer as opposed to the hundreds of femtosecond timescale for the monolayer. Furthermore, extended lifetimes of these states show that the RTIL is effectively screening the injected charge from the metal surface. These results are the first demonstration of coverage dependent ultrafast behavior at an RTIL/metal interface.

References

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