

Femtosecond two-photon ionization of fluid NH₃ at 9.3 eV

Janus Urbanek, Annika Dahmen, Joel Torres-Alacan, and Peter Vöhringer

Institute for Physical and Theoretical Chemistry, University of Bonn, Wegelerstraße 12, 53115 Bonn, Germany, p.voehringer@uni-bonn.de

Abstract. Liquid and supercritical ammonia (NH₃) is photo-ionized at an energy of 9.3 eV with 100-fs duration pulses at a wavelength of 266 nm. The ionization involves two photons and generates fully solvated electrons via the conduction band of the solvent within the time resolution of the experiment. The dynamics of their ensuing geminate recombination is followed in real time with femtosecond near-infrared (IR) probe pulses. The recombination mechanism can be understood as an ion-pair mediated reaction. The electron survival probability is found to be in quantitative agreement with the classical Onsager theory for the initial recombination of ions.

1 Introduction

Solvated electrons are the most fundamental spin centers in condensed phase chemistry and have therefore raised considerable attention of the physical and theoretical chemistry communities. Of particular interest are their spectroscopic properties, their reactivity, and the interactions with their dense molecular environment on ultrafast timescales. Charge delocalization and trapping, solvation and thermal relaxation, or reactive and non-reactive electron-solvent scattering including charge transfer are all fundamental processes that contribute to the complex coupled electron-solvent dynamics that follow an initial injection of a single electronic spin center into the liquid. The vast majority of research on time-resolving electron-solvent phenomena focused on the solvated electron in liquid water where it can be readily prepared via pulse radiolysis or laser-induced multi-photon ionization. Historically, the solvated electron was first discovered in liquid ammonia where it can be prepared chemically by directly dissolving neat alkali metals into the solvent. With the exception of our own work on metal-ammonia solutions [1,2], nothing has been reported so far on the ultrafast relaxation and reaction dynamics of the ammoniated electron. Here, we report on the geminate recombination dynamics of the solvated electron in fluid NH₃ that was generated by two-photon ionization of the pure solvent with 266-nm light.

2 Results and Discussion

Irradiation of fluid ammonia with 266-nm, 100-fs pulses generates a transient species that is characterized by a very broad absorption spectrum in the near-IR (cf. Fig. 1a). The shape and the spectral position of this near-IR resonance are very similar to those of the well-known chemically generated solvated electron from metal-ammonia solutions. There can be no doubt that the species that is generated photolytically from the neat solvent at 266 nm and that carries the strong and broad near-IR transition is indeed the solvated electronic spin center.

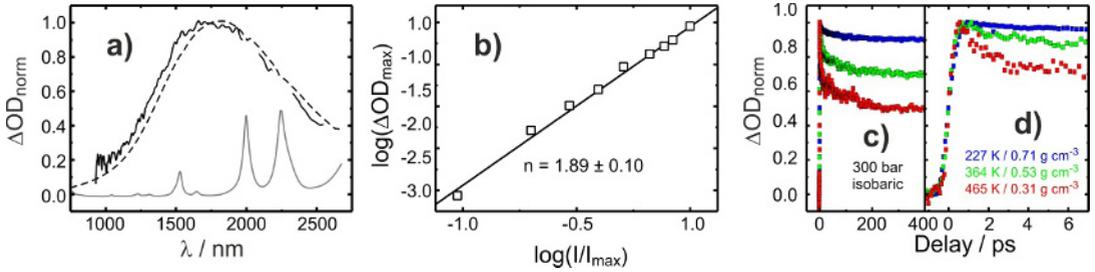
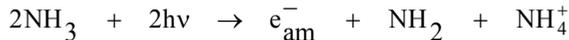


Fig. 1. a) Near-IR absorption spectrum of fluid ammonia following irradiation with 266 nm pulses (solid curve). The dashed curve is the absorption spectrum of a sodium-ammonia solution and the bottom curve is the spectrum of the neat fluid. b) Intensity dependence of the near-IR signal. c and d) Decay of the solvated electron signal emphasizing the ultrafast nature of the recombination dynamics for various thermodynamic conditions

To understand the photo-physical processes responsible for the generation and subsequent dynamics of solvated electrons following the UV irradiation of ammonia, it is important to establish the number of photons involved in the primary matter-field interaction. To this end, the dependence of the magnitude of the near-infrared absorption on the pump pulse irradiance was studied in more detail. A double-logarithmic plot of the solvated electron signal amplitude versus pump irradiance is shown in Fig. 1b. It can be seen that experimental data follow closely a straight line with a slope of roughly 2 indicating that the generation of solvated electrons involves a two-photon ionization mechanism. Since the wavelength of the femtosecond pulses was 266 nm, the solvated electron is apparently generated here by ionization of the pure ammonia fluid at a total energy of 9.3 eV. The net result of the two-photon ionization can be described in chemical terms by



from which one concludes that the fate of the solvated electron is likely to be the recombination encounter with aminyl radicals and/or ammonium cations according to



A representative selection of the pump-probe traces obtained under different thermodynamic conditions is presented in Fig. 1c and d. To facilitate their comparison, the signals were normalized to their peak values. All traces feature an instrument-limited rise around zero time delay indicating that the primary ionization and thermal relaxation dynamics are complete within the time resolution of the experiment. Furthermore, it can be seen that the subsequent decay reflect complex multi-scale dynamics ranging from of a few picoseconds to hundreds of picoseconds. A decay of the signal corresponds to a net loss of solvated electrons due to geminate recombination. The signal finally reaches to an asymptotic offset indicating that a finite fraction of solvated electrons is able to avoid this quenching mechanism.

From the ratio of signal amplitude at infinite time to that at time zero, the so-called survival probability, Ω_∞ can be calculated. The survival probability corresponds to the fraction of solvated electrons that are able to escape from the recombination reactions with the aminyl radical and the ammonium cation. This quantity is plotted in Fig. 2a as a function of the product of dielectric constant and temperature, ϵT , reduced to the corresponding product at the critical point, $(\epsilon T)_{\text{crit}}$. It can be seen that the electrons recombine with increasing efficiency as the temperature is raised, the density is lowered and the solvent permittivity is decreased. Qualitatively, this can be understood in terms of a solvent screening of the solvated electron's interactions with the recombination partners that is gradually lifted as ϵT is lowered.

Thermodynamic data demonstrate that the recombination of the solvated electron with the ammonium cation is highly endergonic [3] such that the predominant recombination channel is the reaction with the dipole under formation of amide anions. However, in the three-body

system, the interactions are still dominated by the Coulomb attraction between the electron and NH_4^+ . Hence, the formation of an ammonium-electron ion-pair is inevitable.

Although it does not react with the electron fast enough, the cation still acts as a mediator for the electron-dipole recombination as sketched in Fig. 2c through f. The solvated electron survival probability can be calculated from the classical Onsager theory for the initial recombination of ions [4,5]. However, the theory needs to be modified to take into account that the electron is actually annihilated upon encounter of the ion-pair with the amidogen radical [6]. Model simulations of this modified Onsager theory are displayed in Fig. 2 a and b as solid curves.

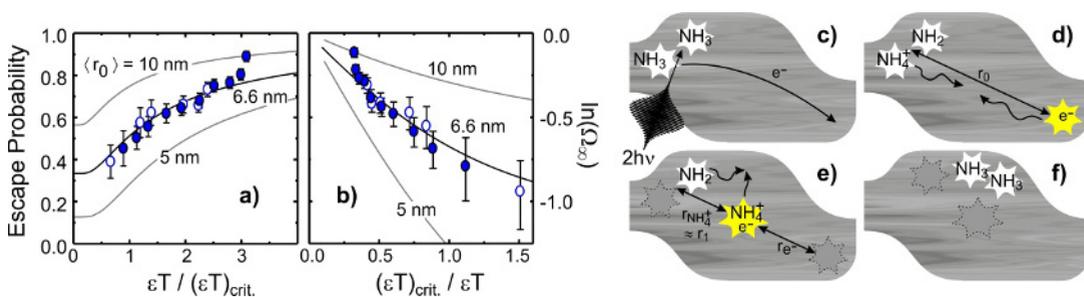


Fig. 2. a) Survival probability as a function of the reduced product ϵT . b) Onsager plot of the survival probability. The solid curves in panels a and b correspond to predictions of the classical Onsager theory for various thermalization distances. c through f: sequence of events involved in the ion-par mediated geminate recombination

The only adjustable fitting parameter that enters the model is the so-called thermalization distance, i.e. the distance from the initial ionization site at which the electron is injected and fully equilibrated with its surroundings. The model simulations can be brought into agreement with the experimental data when a thermalization distance of 6.6 nm is used. This rather large value compared to that obtained for photolytically generated hydrated electrons at the same ionization energy of 9.3 eV [7,8] gives fairly convincing evidence that the ammoniated electrons are initially created as highly mobile charge carriers in the conduction band of the solvent. More detailed experiments targeted at studying the ionization and recombination dynamics as a function of excitation energy are currently in progress in our laboratories.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft through the Collaborative Research Center SFB 813 “Chemistry at Spin Centers” is gratefully acknowledged

References

1. J. Lindner, A.N. Unterreiner, P. Vöhringer, Chem. Phys. Chem. **7**, 363 (2006)
2. J. Lindner, A.N. Unterreiner, P. Vöhringer, J. Chem. Phys. **7**, 064514 (2008)
3. U. Schindewolf, Ber. Bunsenges. Phys. Chem. **86**, 887 (1982)
4. L. Onsager, Phys. Rev. **54**, 554 (1938)
5. M. Wojcik, M. Tachiya, **130**, 104107 (2009)
6. J. Urbanek, A. Dahmen, J. Torres-Alacan, P. Königshoven, J. Lindner, P. Vöhringer, J. Phys. Chem. B **116**, 2223 (2012)
7. S. Kratz, J. Torres-Alacan, J. Urbanek, J. Lindner, P. Vöhringer, Phys. Chem. Chem. Phys. **12**, 12169 (2010)
8. J. Torres-Alacan, S. Kratz, P. Vöhringer, Phys. Chem. Chem. Phys. **13**, 20806 (2011)