Determination of the conduction band edge of liquid ammonia by femtosecond spectroscopy

Tim Vogler[1], Jörg Lindner[1], and Peter Vöhringer[1]

[1]*Institut für Physikalische und Theoretische Chemie, Universität Bonn, D-53115 Bonn, Germany*

E-mail: p.voehringer@uni-bonn.de

Until today the electronic structure of liquid ammonia is mostly unknown. While absorption and photoelectron spectra of solid and gaseous ammonia are reported in the literature, those of the liquid and supercritical phases remain unresolved.[1][2]

In our recent experiments we used the solvated electron in liquid ammonia as a probe to investigate fundamental electronic properties of the solvent, such as the conduction band edge and the energetic location of the conduction band relative to the valence band. The conceptual idea and the experimental results ought to be presented.

The optical band gap determines the excess kinetic energy with which the electrons are dressed upon the primary matter-field interaction with a fixed excitation energy E_g. This in turn affects the mean distance the electrons travel before they get trapped and subsequently solvated in the liquid, also referred to as the average thermalization length r_0 (cf. Figure 1).
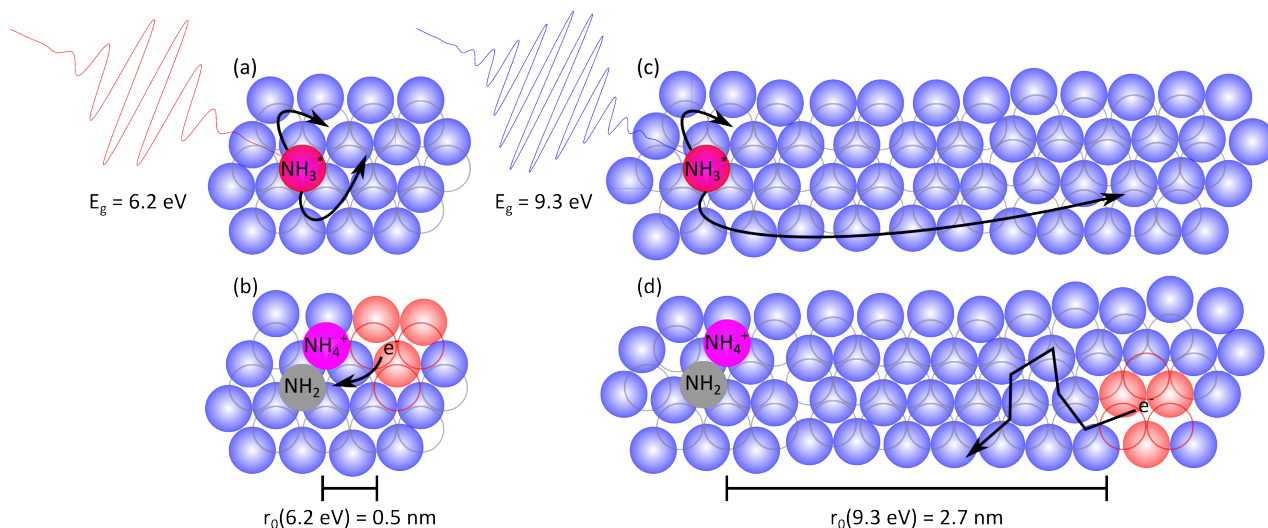

Figure 1: Sketch of the solvated electron generation after a primary matter-field interaction with 6.2 eV and 9.3 eV[3][4] excitation energy E_g in liquid ammonia. Part (a) and (b) correspond to the below-band-gap ionization and ensuing geminate recombination in the neat liquid. The vertical photoionization (c,d) incorporates the creation of a (highly mobile) conduction band electron that travels a mean distance of $r_0(9.3\ eV) = 2.7\ nm$[4] before it becomes trapped and eventually solvated.

Figure 1 sketches the initial spatial distribution of the three geminate products NH_2, NH_4^+, and the solvated electron following the primary matter-field interaction for two different values of excitation energy E_g. It is then intuitive to understand that the mean thermalization distance r_0 determines the fraction of solvated electrons that are able to escape from geminate recombination (see Figure 1(d)). In earlier studies, we already introduced this quantity as the escape probability Ω_∞.[3][4] The value of Ω_∞ can be directly obtained from the normalized kinetic time traces shown in Figure 2(a). To do so, one reads out the plateau value at a delay time of e.g. 550 ps, thus defining $\Omega_\infty \equiv \Delta OD_{norm}(550\,ps)$.
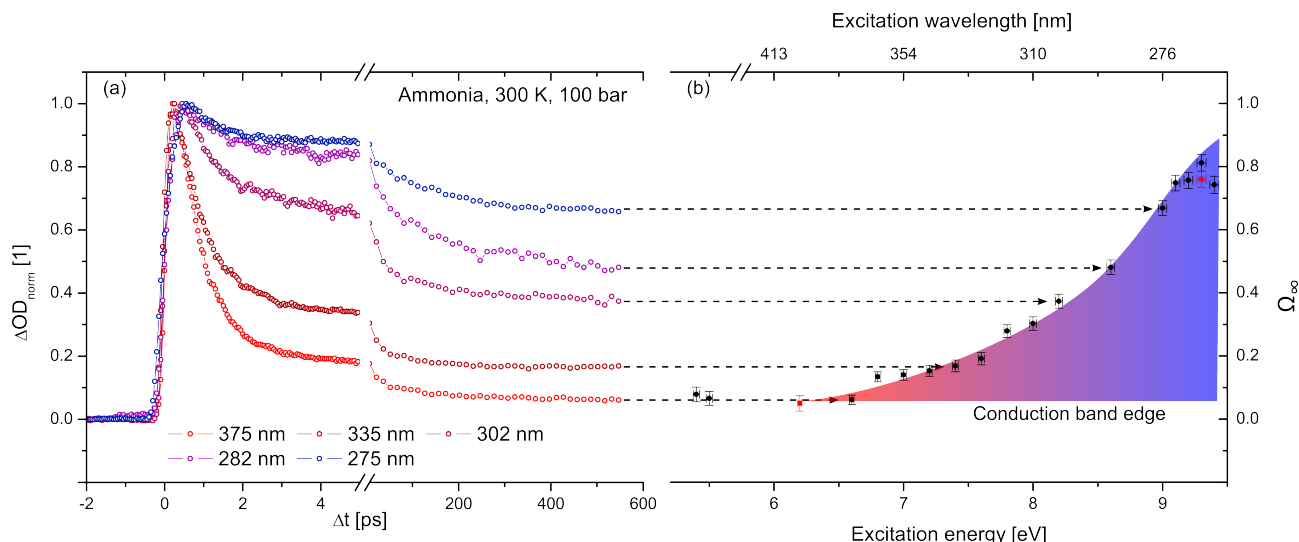

Figure 2: (a) Kinetic time traces of the solvated electron's transient absorption in liquid ammonia at 300 K and 100 bar for different excitation wavelengths. (b) Escape probability Ω_∞ as a function of the excitation energy and wavelength, respectively. Thus a first map of the conduction band edge of liquid ammonia is shown.

One key point to gain excitation-energy-resolution is to unravel the number of photons that are consumed in the generation of one solvated electron. For the transient absorption data presented here, a two-photon excitation has been determined from recording the power dependence of ΔOD_{max}. This allows to unambigiously assign each excitation wavelength with a distinct excitation energy and finally obtain a map of the conduction band edge (see Figure 2(b)).

In the recent study we were thus able to use the solvated electron as a probe to investigate the electronic structure of liquid ammonia for a fixed thermodynamic condition. By this means, we determined the energetic location of the conduction band edge of the neat liquid for the first time.

References:

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