Femtosecond spectroscopy of the primary relaxation dynamics of solvated electrons in liquid ammonia

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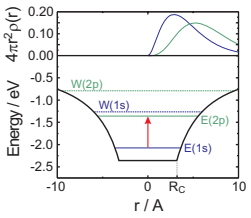
Introduction

An excess electron, which localizes in a dielectric medium by polarizing its surroundings is often termed a "solvated" electron. Such self-trapped charges have fascinated researchers ever since their existence was acknowledged more than half a century ago [1]. However, the detailed molecular mechanisms and timescales associated with their binding dynamics (i.e. their solvation and localization) remain until today heavily debated subjects.

Here, we present the first ever femtosecond pump-probe study aimed at unraveling the time scales and detailed mechanisms involved in the relaxation dynamics of solvated electrons in liquid ammonia following their ultrafast resonant excitation in the near-infrared spectral region [3].

The polaron localizes in a Coulomb-type potential by polarizing the surrounding medium (i.e. self-trapping)

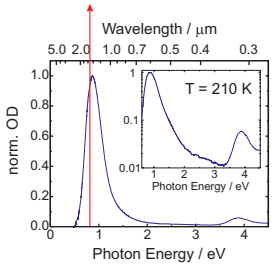


Solve the Schrödinger equation by variation method

⇨

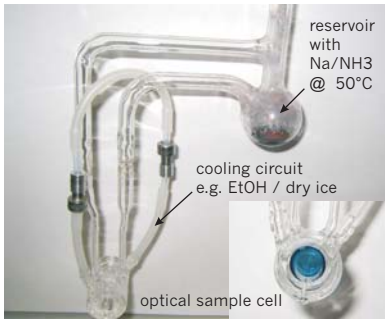
vary cavity radius dielectric constant

Primitive Cavity Model prediction with R = 3.2 Å



What are the mechanisms and time scales that give rise to the enormous spectral width of the electron resonance?

Experiment



Sample preparation

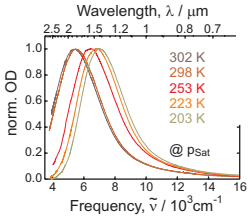
requires highly purified sodium, ammonia & rigorously cleaned fused silica equipment.

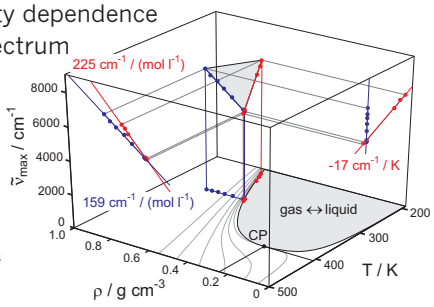
sample consists of a paramagnetic solution w/ mole fractions of electrons $<10^{-4}$

Stability > 1 day

Results

Temperature & density dependence of the absorption spectrum





absorption shifts to lower frequencies w/
* increasing T
* increasing p

(data Farhataziz, et.al, JCP, 60 (1974) 4383)

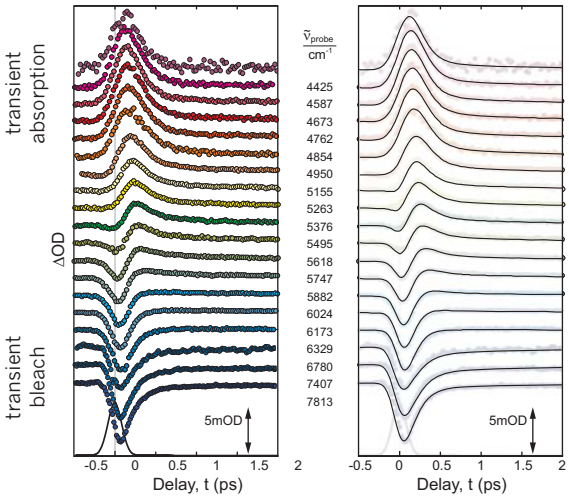
$\left(\frac{\partial \tilde{\nu}_{max}}{\partial T}\right)_{Sat} = -17\,\frac{cm^{-1}}{K}$	$\left(\frac{\partial \tilde{\nu}_{max}}{\partial \rho}\right)_{Sat} = 225\,\frac{cm^{-1}}{mol\,dm^{-3}}$
$\left(\frac{\partial \tilde{\nu}_{max}}{\partial \rho}\right)_{T} = 159\,\frac{cm^{-1}}{mol\,dm^{-3}}$	$\left(\frac{\partial \rho}{\partial T}\right)_{Sat} = -0.0771\,\frac{mol}{dm^3\,K}$

the pure temperature dependence is surprisingly weak ⇨

$$\left(\frac{\partial \tilde{\nu}_{max}}{\partial T}\right)_{\rho} = \left\{\left(\frac{\partial \tilde{\nu}_{max}}{\partial \rho}\right)_{Sat} - \left(\frac{\partial \tilde{\nu}_{max}}{\partial \rho}\right)_{T}\right\} \times \left(\frac{\partial \rho}{\partial T}\right)_{Sat} = -5.3\,\frac{cm^{-1}}{K}$$

Results & Discussion

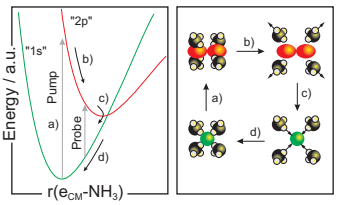
Femtosecond pump-probe spectroscopy, w/ exc. @ 1280 cm^{-1}

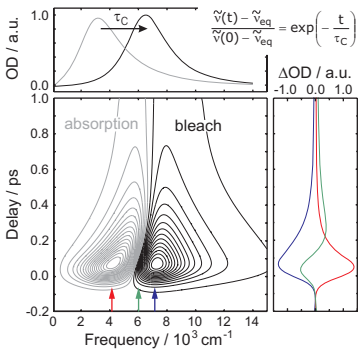


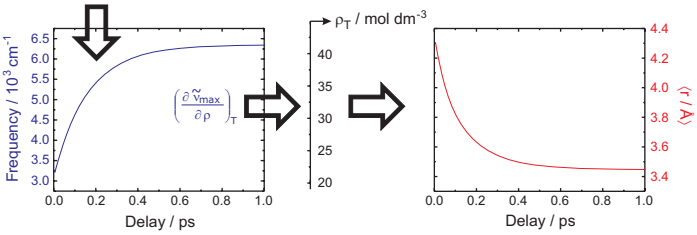
1.) no isosbestic point can be observed
2.) temporal response is highly non-exponential
3.) a simple 2-state interconversion (e.g. 2p → 1s) impossible
4.) response reminiscent of continuous spectral shift w/ time

Analysis using a laser-induced density-jump model

In a polaron notion, the 1s→2p transition prepares a spatially more demanding solvated electron charge distribution thereby causing a substantial spatial overlap w/ solvent electrons. The resultant Pauli-repulsion drives the electron towards a conical intersection allowing them to return to their original quasi-spherical ground-state within the experimental time resolution. At this instant, the 1s→2p transition is strongly red-shifted and the ensuing contraction of the solvent cavity can then be observed as a dynamic Anti-Stokes shift of the electronic absorption spectrum on a 150-fs time scale.







Literature

[1] Sir H. Davy, Laboratory Notes, 1806, Archives Royal Society London; W. Weyl. Ann. Phys. 121, 601 (1864); R.A. Ogg, Phys. Rev. 69, 668 (1946); J. Jortner, J. Chem. Phys. 30, 839 (1959);

[2] J. Lindner, A.N. Unterreiner, P. Vöhringer. Femtosecond relaxation dynamics of solvated electrons in liquid ammonia; ChemPhysChem 7, 363 (2006)