Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Probing the band gap of liquid ammonia with femtosecond multiphoton ionization spectroscopy

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Absorption spectrum of the ammoniated electron

An experimentally determined stationary absorption spectrum of a sodium-ammonia solution at room temperature and saturation pressure is displayed in Figure S1.[1] The resonance peaking at 6830 cm^{-1} (i.e. at a wavelength of 1464 nm or at a photon energy of 0.847 eV) is usually attributed to the "1s-to-2p"-transition of the ammoniated electron. It has a full spectral width at half maximum of 3226 cm^{-1} or equivalently, 0.40 eV. The absorption band is highly asymmetric with a rather steep low-energy edge and a very long high-energy tail. Thus, the "1s-to-2p" electronic resonance spreads between the mid-to-near infrared spectral region (wavelength ~ 4 µm) and the visible-to-near ultraviolet region (wavelengthy 500 nm and shorter). The origin of this peculiar line shape has been the subject of a controversial debate for many years.[2-3]

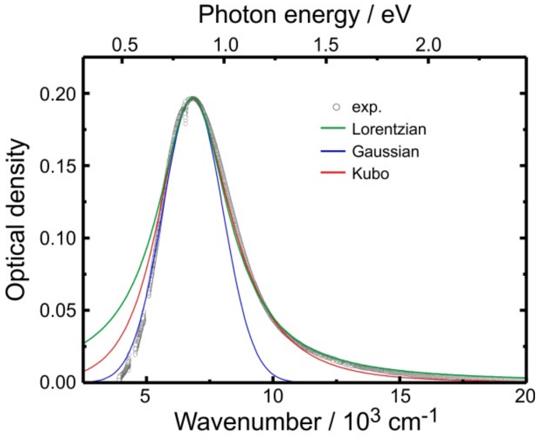

Fig. S1. Experimental absorption spectrum of the ammoniated electron (gray symbols) together with fits to difference line-shape functions (curves).

Phenomenologically, the normalized line shape, $S(\tilde{\nu})$, can be fitted section-wise using either a Gaussian of a Lorentzian line shape

$$S(\tilde{\nu}) = \begin{cases} exp\left[-4ln2\left(\frac{\tilde{\nu}-\tilde{\nu}_0}{\Delta_G}\right)^2\right] & \text{for } \tilde{\nu}\le\tilde{\nu}_0 \\ \frac{\left(\frac{\Delta_L}{2}\right)^2}{\left(\frac{\Delta_L}{2}\right)^2+(\tilde{\nu}-\tilde{\nu}_0)^2} & \text{else} \end{cases}$$

where $\tilde{\nu}_0$ is the peak wavenumber of the band (6830 cm^{-1}) and Δ_G and Δ_L are the full spectral widths at half maximum (FWHM = 2800 cm^{-1} and 3450 cm^{-1}) of the Gaussian and Lorentzian components, respectively. The individual components are also shown in Figure S1, which demonstrates that the above composite function would provide indeed a very good fit.

In contrast, Kubo's stochastic theory[4] of the line shape provides a non-arbitrary, physically motivated ansatz to the fit the solvated electron's absorption band. Here, $S(\tilde{\nu})$ is given by the Fourier transform of the relaxation function

$$\psi(t) = \left[\frac{\Delta^2}{\gamma}(1 - e^{-\gamma t})cos(\omega_0 t) + \omega_0 sin(\omega_0 t)\right] exp\left[-\frac{\Delta^2}{\gamma^2}(e^{-\gamma t} + \gamma t - 1)\right]$$

where $\omega_0 = 2\pi c\tilde{\nu}_0$ and c is the speed of light. Within the model, the "1s-to-2p" energy gap experiences stochastic frequency excursions, $\delta\tilde{\nu}_0(t)$, whose correlation function decays exponentially with a time constant $1/\gamma$ and has an amplitude of Δ^2, corresponding to the mean-squared magnitude of the fluctuations. Using $\Delta/2\pi c$ =2600 cm^{-1} and $1/\gamma = 1.5$ fs, a fit is obtained that presents a very good compromise between the Gaussian and Lorentzian component fits from above. The ratio $2\pi\gamma/\Delta$ is equal to 8.6 indicating that the resonance is in the fast modulation limit. A correlation time of 1.5 fs is therefore in good agreement with the homogeneous lifetime estimate of 1.6 fs that can be derived simply from the FWHM of the absorption band.

Absorption spectrum of gaseous and liquid ammonia

Figure S2 compares the electronic absorption spectra of ammonia in the gas phase (top panel, data compiled from Refs. [5-6]) and in the amorphous film (bottom panel, data from Ref. [7]). It can be seen that the most dominant bands of the gas phase spectrum translate directly into distinct features of the condensed phase spectrum. The monomer's $\tilde{A} \leftarrow \tilde{X}$ transition around 6.4 eV is energetically up-shifted on condensation to 7.0 eV. The gas phase absorption around 9.2 eV is due to transitions into the $\tilde{D}$ and $\tilde{E}$-systems and is still discernible in the condensed-phase data as a marked shoulder around 10.2 eV. Thus, the major resonances are shifted significantly to higher energies; an effect often traced back to the diffuse Rydberg-nature of the excited states and exchange repulsion of excitations on neighboring particles in the condensed phase.

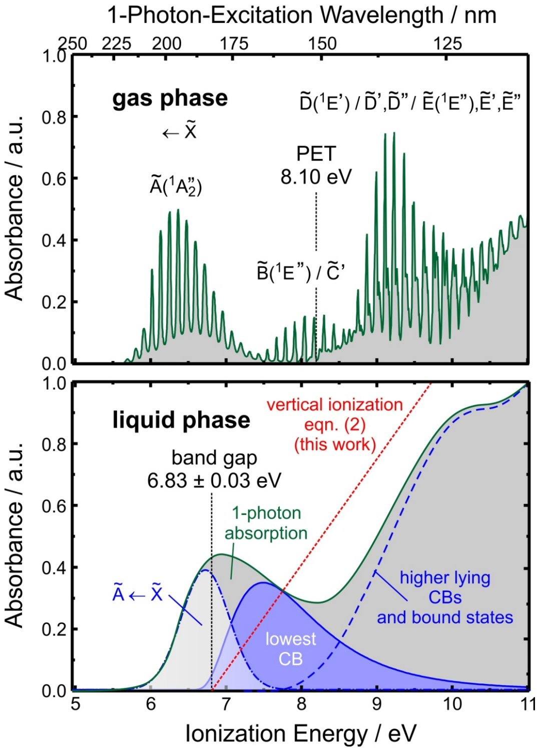

Fig. S2. Absorption spectrum of gaseous (top) and amorphous (bottom) ammonia. The spectrum of the liquid can be decomposed into various contributions, one of which is indicative of absorptions into the conduction band (shaded in blue).

Moreover, the vibrational fine structure of the absorption bands disappears upon condensation, which simply reflects the overwhelming inhomogeneous broadening introduced by the dense particle packing. However, whereas in the gas phase, the absorption essentially vanishes between 7.5 and 8.5 eV (except for the very small absorptions due to the $\tilde{B}$ and $\tilde{C}$-states), there is still a very large absorption at these energies for the condensed phase. We attribute this spectroscopic activity to transitions into the conduction bands.

More quantitatively, the broad low-energy band at 7.0 eV can be decomposed into a Gaussian contribution peaking at 6.75 eV with a fully spectral width at half maximum (FWHM) of 0.74 eV (dotted-dashed curve in Figure S2) and a asymmetric log-normal contribution peaking at 7.51 eV with an FWHM of 1.4 eV and a skewness of 1.9 (blue-shaded spectrum). The particular asymmetric line shape resembles the typical spectral profile expected for photodetachment spectra. The residual absorption (dashed curve) is then brought about by transitions into higher lying conduction bands and/or transitions to higher lying bound states that can be traced back to the $\tilde{D}$ and $\tilde{E}$-states of the monomer in the gas phase. Most importantly, the onset of the conduction band absorption spectrally coincides with our estimate of the band gap, which we derived on the basis of our 2-photon ionization experiments.

References

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