

Ultrafast reaction in solvated metal atom clusters: A dynamic study in the visible and near IR spectral range

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Abstract. The lifetime of the first electronically excited state of sodium-ammonia ($\text{Na}(\text{NH}_3)_n$) clusters is investigated with femtosecond laser pulses in the visible and near IR spectral range. The decay time of the pump-probe ion signal decreases drastically with increasing cluster size from 1000 ps ($n = 1$) to 0.1 ps for $n = 15$. Different decay mechanisms are discussed. A purely statistical process can be excluded to be responsible for the observed decay times.

1. Introduction

Spectroscopic and dynamical properties of solvated electrons in polar liquids have been studied for many years. The development of ultrashort laser pulses has given a new impetus to this research field. Our approach to understand the formation and dynamics of the solvated electron differs from the typical experiments with liquid samples: Free clusters containing one sodium metal atom and an arbitrary number of ammonia molecules as solvent are studied in a molecular beam.

In our previous spectroscopic investigations it was found, that the $3s \rightarrow 3p$ transition of the sodium atom is shifted from the visible to near IR spectral range with the number of solvent molecules bound to the metal atom [1,2] and that the excited state of sodium-ammonia complexes is short lived. For a detailed study of the excitation and decay dynamics we have set up a pump-probe experiment with femtosecond laser pulses tunable from the visible to the near IR spectral range.

2. Experimental Methods

Free sodium ammonia clusters $\text{Na}(\text{NH}_3)_n$ are prepared in a pickup source, where sodium atoms from an effusive beam are picked up in the expansion region of a neat ammonia jet [3]. Downstream the clusters are excited, ionized and mass separated in a time-of-flight mass spectrometer.

The femtosecond laser pulses are generated by a commercial, regenerative amplified Ti:Sapphire laser system. The output pulses with a duration of 200 fs and 440 μJ pulse energy, are tunable in a wavelength range from 770 nm to 840 nm. To extend the wavelength to the near IR spectral region an optical

parametric generator/amplifier (OPG/OPA) was build based on the design of Petrov et al. [4]. The setup provides tunable laser pulses between 1200-1500 nm (signal) and 1700-2000 nm (idler) with a pulse width of 140 fs and pulse energies of 6 μJ at the cluster beam. For the probe pulse the second harmonic of the Ti:Sapphire fundamental was used for small $\text{Na}(\text{NH}_3)_n$ clusters up to $n = 3$. Due to the low ionization potential of the larger clusters we had to use probe pulses (500-590 nm), generated by sum frequency mixing of the fundamental wavelength and either the signal or the idler output of the OPG/OPA. Pulses of 220 fs duration and 5 μJ pulse energy were obtained.

3. Results and Discussion

With this experimental setup we were able to determine to the lifetime of the first electronically excited state of $\text{Na}(\text{NH}_3)_n$ clusters up to $n = 15$. The transition corresponds asymptotically to the $3s \rightarrow 3p$ in the sodium atom, which is shifted from the yellow atomic line to the near IR spectral region when ammonia molecules are bound to the sodium atom [1,2]. To measure the lifetimes, the light pulses have to be tuned to the absorption of the corresponding clusters. For NaNH_3 and $\text{Na}(\text{NH}_3)_2$ we used 820 nm to excite and 410 nm to ionize. For $\text{Na}(\text{NH}_3)_3$ 1300nm and 410 nm were pump and probe wave length. For all $\text{Na}(\text{NH}_3)_n$ with $n \geq 4$ the pump wavelength was 1690 nm and probe was 507 nm.

Figure 1 shows the measured lifetimes for $\text{Na}(\text{NH}_3)_n$ clusters (full squares) up $n = 15$ as a function of the inverse cluster radius. The lifetime decreases drastically with increasing cluster size. While the first excited state of NaNH_3 still has a lifetime of 1 ns, the lifetime drops to 1 ps with only two additionally bound ammonia molecules ($\text{Na}(\text{NH}_3)_3$). The first solvation shell is closed when four ammonia molecules are bound to the sodium atom forming a nearly tetrahedral complex. The higher symmetry leads to slightly longer lifetime compared to $n = 3$ and 5. Towards larger clusters the lifetime decreases to less than 0.2 ps.

In order to understand the observed lifetimes different decay processes have to be considered. The simplest process would be a direct dissociation, where the cluster finds itself on a repulsive potential surface after photo excitation. This process can be excluded to play a role here since the direct dissociation leads to very short decay times with only a small dependence on the cluster size. A second mechanism one can think of is a statistical redistribution of the excitation energy with subsequent evaporation of one or more ammonia molecules. In this case the decay time can be calculated by the RRK formula [5]. In Fig. 1 the calculated lifetimes are shown (open circles) with the parameters chosen a way, that the lifetime for $n = 5$ is reproduced. It is clear from Fig. 1 that a statistical redistribution cannot describe the decay process after photo excitation of the $\text{Na}(\text{NH}_3)_n$ clusters. At present, we assume that the energy of the electronically excited state is converted into vibrations of the surrounding ammonia molecules through an internal conversion process. This vibrationally excited cluster cannot be ionized with the wavelength used in the experiment. This interpretation is also consistent with the observed lifetime for deuterated clusters. For further discussion we refer to a future publication [6].

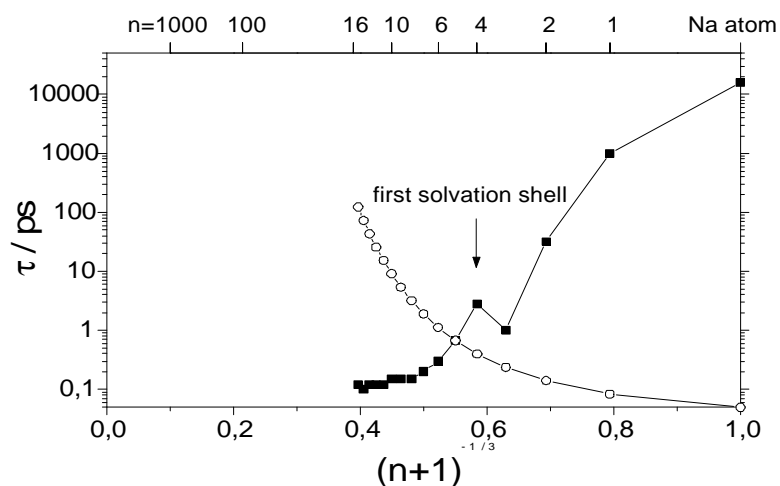


Fig. 1. Measured lifetimes of the first electronically excited state of $\text{Na}(\text{NH}_3)_n$ cluster (full squares). The observed decay cannot be described by a statistical RRK process (open circles).

4. Conclusions

The observed lifetimes for the first electronically excited state of $\text{Na}(\text{NH}_3)_n$ clusters change over 5 orders of magnitude from 1 ns for $n = 1$ to less than 0.2 ps for $n = 15$. A pure statistical process can be excluded to be responsible for the observed decay times. It is suggested that an internal conversion process can describe the observed decay times. Quantum chemical and dynamical calculations are needed for a rigorous understanding of the complex interplay between metal atoms and the polar environment.

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