

# CLUSTERS WITH POLAR MOLECULES: ULTRAFAST DYNAMICS, TIME RESOLVED PHOTOELECTRON SPECTROSCOPY AND FEMTOSECOND CONTROL

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For  $\text{Na}(\text{NH}_3)_n$  and  $\text{Na}(\text{H}_2\text{O})_n$  with  $n$  up to 20 we survey and discuss binding and excitation energies (including recent results from depletion spectroscopy) and report a systematic fs pump-probe study of the excited state as a function of cluster size. For  $(\text{NH}_3)_2$  the excited state dynamics is explored using fs time resolved photoelectron spectroscopy and pump-control-probe experiments.

## 1 Introduction

The progress of femtosecond laser technology and ultrafast spectroscopy during the last years has opened new avenues for studying and even controlling the dynamics in excited states of molecular clusters. This is highlighted by the pioneering work of A. Zewail et al. [1] and the Nobel prize for chemistry in 1999. Further progress warrants a high level of sophistication in accompanying experimental tools, such as time resolved photoelectron spectroscopy (TRPES) and preparation of well defined ensembles of clusters – in addition to ever improving short pulse light sources and nonlinear methods for pulse length reduction, wavelength conversion and tuning. Access to a broad spectral range from VUV to MIR is now a prerequisite to address key issues of femtochemistry. Furthermore, sufficient knowledge of structure and energetics of the systems (e.g. obtained by standard laser spectroscopy and by quantum chemical calculations) is mandatory for a conclusive interpretation of dynamical studies with fs pump-probe techniques.

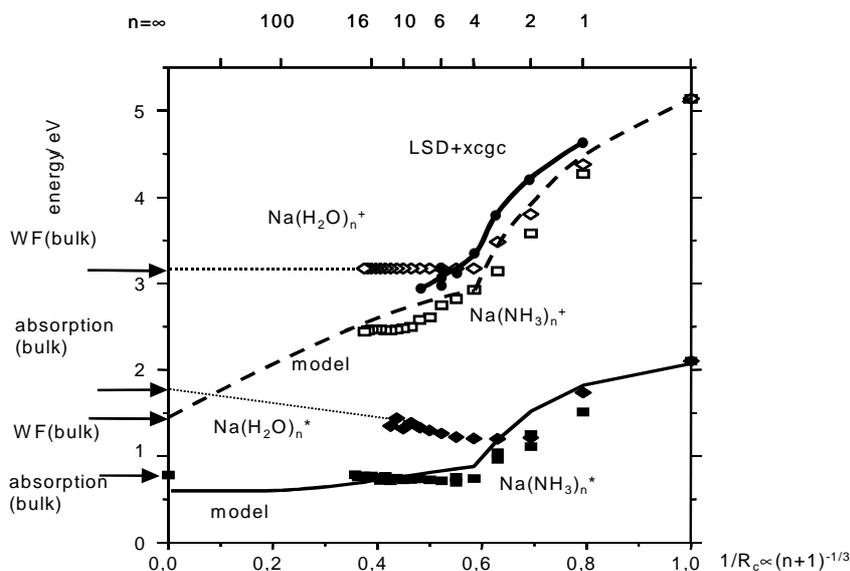
Here we present two case studies for model systems involving polar molecules:

- solvated alkali atoms,  $\text{Na}(\text{NH}_3)_n$  and  $\text{Na}(\text{H}_2\text{O})_n$  and
- ammonia clusters  $(\text{NH}_3)_n$  focusing on dimers.

A key issue in both cases is the dynamics of hydrogen and electron transfer (or delocalization) after photo-excitation. In addition to a systematic analysis of the excited state dynamics by two color fs pump-probe experiments and TRPES we also report a first successful experiment on controlling this dynamics with one additional photon. We will concentrate on the experimental results and only indicate briefly the specific merits of our experimental efforts. The results will be discussed in the light of theoretical *ab initio* calculations as far as they are available.

## 2 Solvated alkali atoms

Solvation is a very fundamental concept of liquid phase chemistry and has attracted the attention of physicists and chemists alike for more than a century. When metal ions or atoms are solvated in polar molecules substantial solvation energy is released when forming complexes of the atom and the solvent molecules and the electronic properties of the system are changed dramatically. E.g. if an alkali atom is solvated in liquid water or ammonia, its binding and excitation energy decreases rather drastically. First observations of this effect go back into the last century and a basic quantitative explanation has been given early in this century by Max Born [2]. In a polar liquid the alkali valence electron is separated from its donor atom and forms a cage of surrounding polar molecules. This celebrated *solvated electron* has also been subject to many experimental and theoretical studies (e.g. the work of Jortner et al. [3]). A challenging question in the context of cluster physics which we have followed over the past ten years is how and at what size of the solvent shell the transition occurs from the well localized atomic valence electron to the delocalized solvated species. How is this process affected by electronic excitation and what are the relevant time scales?



**Figure 1.** Ionization potentials (IP) and excitation energies for the first electronically excited state in  $\text{Na}(\text{NH}_3)_n$  (open and filled squares) and  $\text{Na}(\text{H}_2\text{O})_n$  clusters (open and filled diamonds) as a function of inverse cluster radius  $1/R_c$ . The measured values converge (extrapolation  $\cdots$ ) to the bulk value of work function and absorption maximum, respectively. Also shown is a simple dielectric model for the IP ( $\cdots$ ) and the excited state ( $\text{---}$ ) as well as the IP's from the LSD xcgc calculation ( $\text{---}\bullet\text{---}$ ) [8].

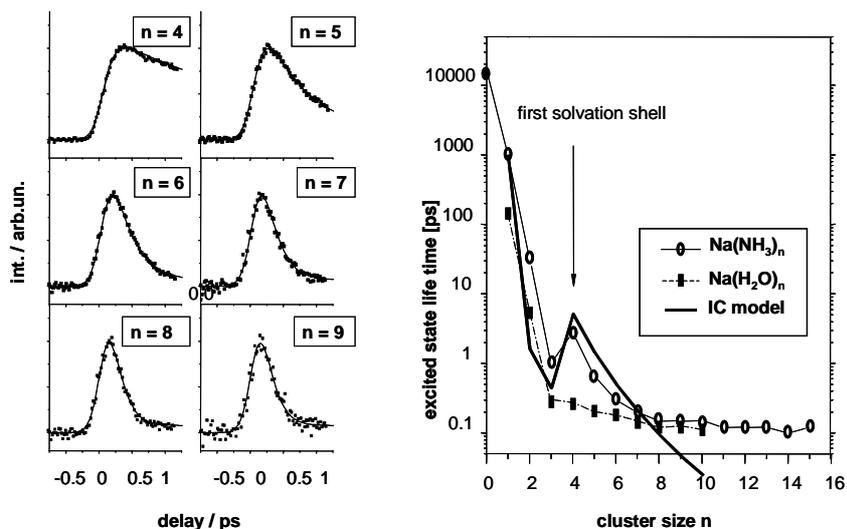
The binding (ionization) energies of electrons in solvated Na, Li and other alkali atoms in a finite water and ammonia environment, e.g. for  $\text{Na}(\text{NH}_3)_n$  and  $\text{Na}(\text{H}_2\text{O})_n$  clusters as a function of cluster size, have been determined using one photon ionization by us and others some years ago [4-6]. Somewhat more difficult to determine are excited state energies: except for  $\text{NaNH}_3$  the electronic excited states have only a very short lifetime so that classic two photon REMPI spectroscopy cannot be used. However, by using depletion spectroscopy [7] this problem can be overcome. The thus determined absorption spectra are rather broad and unstructured, reflecting the short lifetime of the excited state and the complexity of the cluster. Nevertheless, we can extract meaningful maxima as a measure of the excitation energy.

A summary of our measurements is shown in figure 1 along with the ionization potential for the clusters as a function of the inverse cluster radius  $1/R_c \propto \sqrt[3]{n+1}$ . One outstanding result is the very rapid drop of the ionization potential observed for both  $\text{Na}(\text{NH}_3)_n$  and  $\text{Na}(\text{H}_2\text{O})_n$  between  $0 \leq n \leq 4$ . For water as a solvent the bulk value is already reached at  $n=4$  – i.e. the delocalization of the electron is almost complete when the first solvation shell is closed. In contrast, for ammonia the decrease continues, though with reduced slope until the bulk value.

The excitation energies displayed in figure 1 show a similar behavior: the most dramatic decrease occurs up to  $n=4$  and again  $\text{H}_2\text{O}$  as solvent behaves significantly differently from  $\text{NH}_3$ . The energies in the former case even rise for  $n>4$ ! The traditional continuum model fails to explain this behavior. We have used such a model in the spirit of Jortner et al. (e.g. [3]) with some fit parameters reflecting essentially the screening of the ion core (for details see ref. [4]). We can, however, only fit the  $\text{Na}(\text{NH}_3)_n$  data with reasonable assumptions while  $\text{Na}(\text{H}_2\text{O})_n$  obviously requires a more realistic treatment. Also shown in figure 1 are local spin density functional calculations by Barnett and Landman [8] which give a rather satisfactory interpretation of the ionization potentials for  $\text{Na}(\text{H}_2\text{O})_n$ . This calculation indicates a rapid delocalization of the electron with cluster size and shows that the decrease of the electron binding energy to the  $\text{Na}^+$  core is roughly compensated by the increase due to its binding with the water molecules. To explain why this is so vastly different in an ammonia environment as well as the remarkable behavior of the excited state energy with cluster size remains a challenge to theory. – Similar observations have been made for other solvated alkali metals by Fuke and collaborators (see e.g. [5,6]).

Equipped with this spectroscopic information we can now turn to the dynamics of the first excited electronic state [9]. We use a typical pump-probe scheme with femtosecond (fs) laser pulses. For this we need some flexibility of wavelength in the near infrared for excitation and to ensure that the probe photon has just sufficient energy to ionize the cluster from the first electronic excited state (e.g. for  $\text{Na}(\text{NH}_3)_n$  and  $n>3$  pump wavelengths up to 1690 nm with a synchronized probe pulse at 500 nm are required). Too high photon energy would obscure the relaxation pathways of the excited state and lead to fragmentation of the ions. This requires somewhat so-

phisticated fs light sources involving various stages of frequency doubling, optical parametric generation, amplification and sum frequency generation [10]. We observe a typical exponentially decreasing excited state population as illustrated in figure 2 (left panel).



**Figure 2.** Excited state lifetime  $\tau$  of  $\text{Na}(\text{NH}_3)_n$  and  $\text{Na}(\text{H}_2\text{O})_n$  clusters. The left panel shows the raw data for  $\text{Na}(\text{NH}_3)_n$  for  $n=4$  to 9 to which exponential decay curves are fitted. The right panel gives  $\tau$  as a function of cluster size. Note that for  $\text{Na}(\text{H}_2\text{O})_n$   $\tau$  is about one order of magnitude smaller than for  $\text{Na}(\text{NH}_3)_n$ . Also shown are the results of a very simple internal conversion model for  $\text{Na}(\text{NH}_3)_n$ .

A summary of the lifetime ( $\tau$ ) measurements is given in the right part of figure 2. Again, water as a solvent has a massively different influence compared to ammonia:  $\tau$  in the former case are about one order of magnitude lower for the small cluster sizes. The drastically decreasing  $\tau$  of the (detectable) excited state population with cluster size can obviously not be explained by a unimolecular statistical decay model which would predict the opposite behavior (see e.g. [11]). In a first attempt to understand this we evoke an internal conversion (IC) process to be responsible for the decay of the ion signal: The IC conversion rate is proportional to an (unknown) transition matrix element (squared) and to the density of states in the acceptor state. The latter increases with cluster size, hence the decrease in lifetime. The results of such simulation is shown for the ammonia case in figure 3, normalized to  $n=2$ . This fits the observation rather nicely and even reproduces the (accidental) maximum for  $n=4$ . Unresolved so far is the precise nature of the transition - even for the very small cluster sizes. An intense search for a curve crossing (or rather a conical intersection) in the case of  $\text{Na}(\text{NH}_3)_2$  based on CI calculations has not lead to any result

so far. We also observe a massive isotope effect in both systems when H is replaced by D. This too is not fully understood yet.

In summary, we have made significant progress in studying the energetics and dynamics of solvated metal atoms. Yet little is understood quantitatively. Such understanding remains a challenge for a more thorough theoretical treatment.

### 3 Excited state dynamics and control in the ammonia dimer

The  $(\text{NH}_3)_n$  system is a prototype for clusters of polar molecules and has been widely studied for many years, always with the most recent experimental (see e.g. [12-14]) and theoretical [15,16] methods. Our present interest focuses on the first excited  $\tilde{A}$ -state and specifically on the role and relevance of the  $\text{NH}_3 \cdots \text{NH}_3^*$  rearrangement process. A key role is attributed to what may be called a *hydrogen transfer state*  $\text{NH}_4 \cdots \text{NH}_2$  which is reached some hundreds of femtoseconds after the excitation.

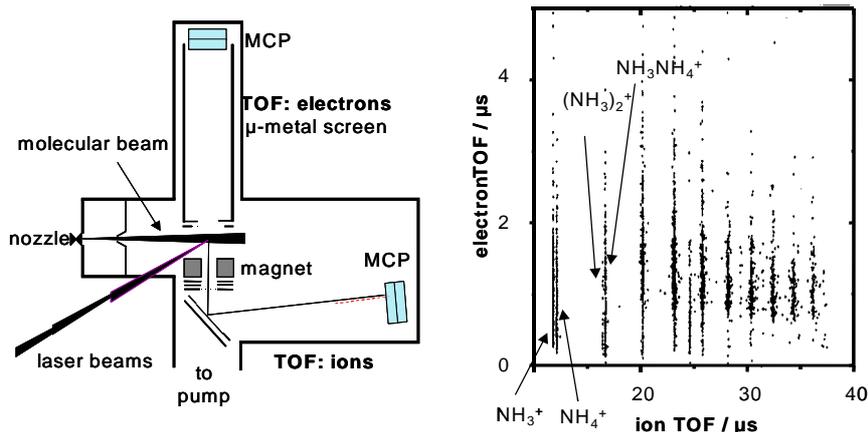
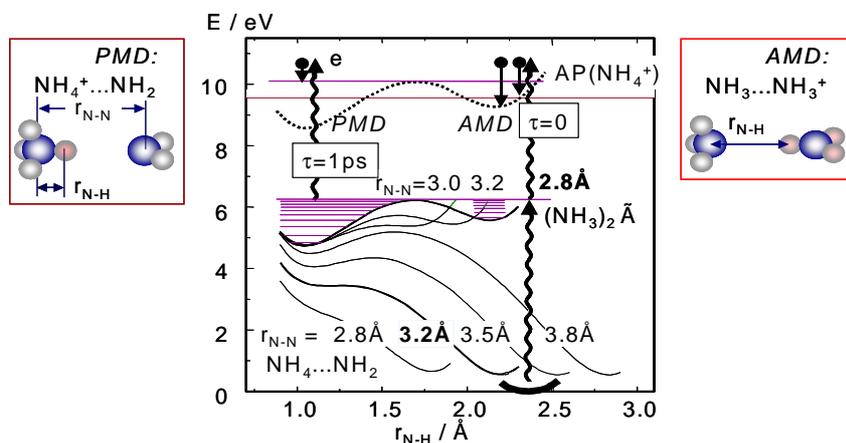


Figure 3. Experimental setup (left) and typical coincidence rates (right) for fs time resolved photoelectron spectroscopy of ammonia clusters. The photoelectrons and photoions are detected in coincidence.

A few words about the experimental setup are in order at this point since we use several novel techniques: The femtosecond pump-probe experiments typically involve the 4<sup>th</sup> harmonics of a Ti:Saph laser to excite the  $\tilde{A}$ -state in a one photon process and the 2<sup>nd</sup> or 3<sup>rd</sup> harmonics to probe it by ionization. Very detailed information on energetics and structure of clusters can be obtained by using photoelectron spectroscopy (PES). For mass selected negative cluster ions this powerful technique has recently been extended by Neumark and collaborators into the femtosecond time domain [17]. We have applied fs time resolved PES for the first time to photoionization of neutral clusters with pulsed lasers [18,19]. Since an additional selection tech-

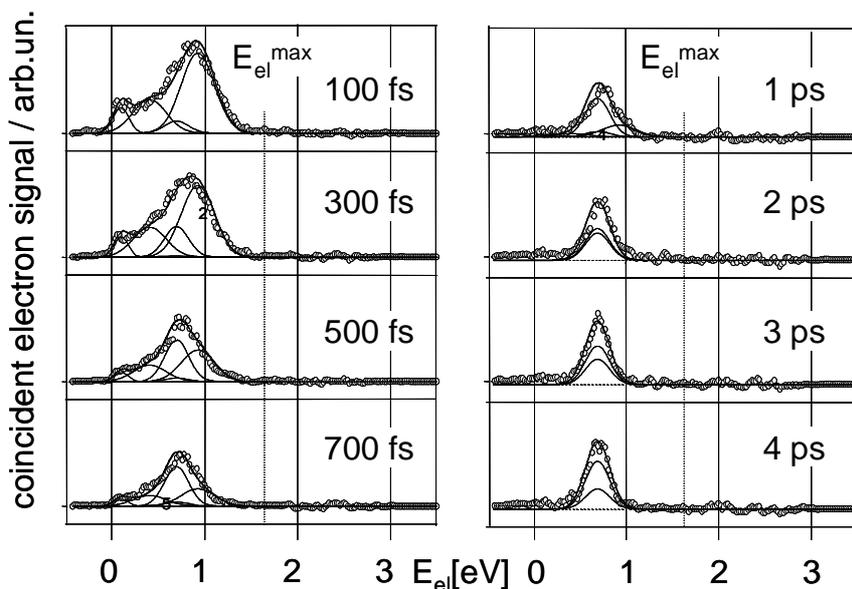
nique is required here to correlate each electron to the particular cluster ion or fragment from which it was ejected, we use photoelectron-photoion-coincidence detection (PEPICO). However, in contrast to standard PIPECO with quasi continuous sources, when using pulsed lasers normally many molecules are ionized at each laser shot so that the electrons ejected cannot be related to their parent ions, even in a coincidence experiment. To overcome this problem the rate of events per individual laser pulse has to be reduced dramatically. We have demonstrated that one can indeed obtain meaningful fs time resolved PES by using kHz repetition rate lasers and long data collection times, optimal results being obtained with an average number of events of 0.05 per pulse.

Figure 3 shows a schematic of the experiment (left). The two dimensional plot (right) of electron vs. ion time of flight (TOF) illustrates typical raw data, the density of points indicating the probability of events registered at each detector for a given pair of TOF's. Cuts parallel to the x-axis give mass spectra at a given electron kinetic energy while a trace parallel to the y-axis represents a photoelectron spectrum for a given ion mass originating from the cluster beam. In figure 3 a non-typical, high seed ratio was used for preparation of the ammonia clusters in order to show a range of masses. For the present study of the ammonia dimer, however, a very low  $\text{NH}_3$  seed pressure is used to form the molecular beam, avoiding significant amounts of clusters with  $n > 2$ . Thus, we obtain clearly discernable  $(\text{NH}_3)_2^+$  signals. Nevertheless, the mass spectra are still dominated by  $\text{NH}_4^+$  (exceeding the dimer ion typically by a factor of  $\sim 14$ ) due to fragmentation of the dimer, either in the excited state or in the ion. The underlying dynamics has been thoroughly studied and discussed e.g. by us [12,13,20] and by Castleman et al. [14,21,22].



**Figure 4.** *Ab initio* based schematic of the potential energy surface of the ammonia dimer showing the characteristic adiabatic monomer in dimer (AMD) and protonated monomer in dimer (PMD) configurations.

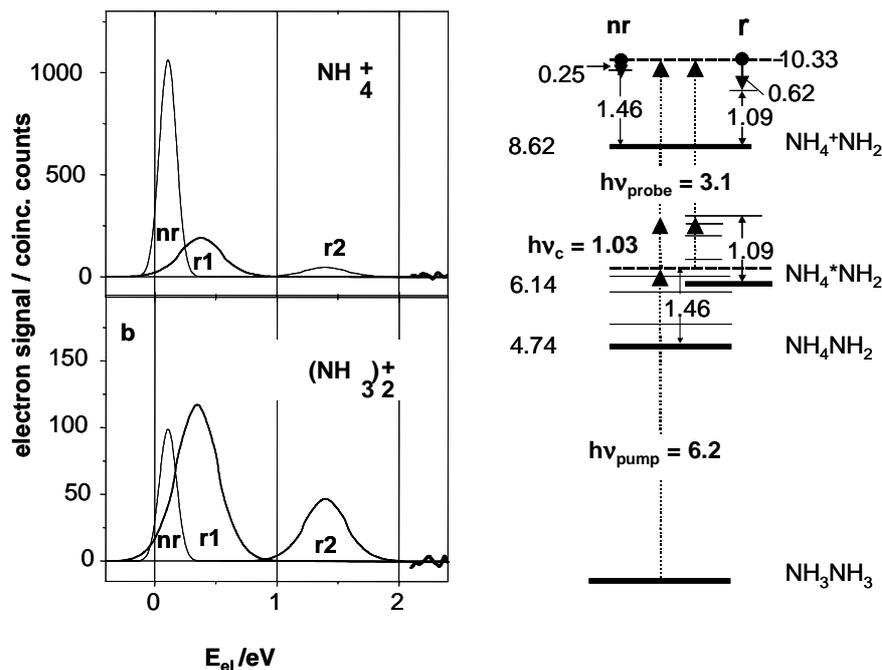
The essence of our present understanding, a certainly simplified model, is best illustrated by a schematic cut through the potential energy surface of the system depicted in figure 4. The minimum energy configuration of the ion may be described as *protonated monomer in dimer (PMD)*  $\text{NH}_2\cdots\text{NH}_4^+$  depicted in the top left panel. Due to very unfavorable Franck-Condon factors (FC) this geometry cannot be accessed directly from the neutral ground state. Rather, when  $(\text{NH}_3)_2$  is ionized by two simultaneous fs pulses (or by one single photon) the *adiabatic monomer in dimer (AMD)* geometry  $\text{NH}_3\cdots\text{NH}_3^+$  is reached, illustrated in the top right panel of figure 4. The excited  $\bar{A}$  - state has a very similar structure, its FC-accessible local minimum  $\text{NH}_3\cdots\text{NH}_3^*$  being characterized by one planar  $\text{NH}_3^*$  molecule. After excitation rapid configuration changes occur and several fragmentation channels are open, including  $\text{NH}_4$  formation. Part of the system will end in the *hydrogen transfer state*  $\text{NH}_2\cdots\text{NH}_4$  as depicted in figure 4.



**Figure 5.** PES from the ammonia dimer excited to the  $\bar{A}$ -state in a pump (200 nm) probe(267 nm) experiment at various pump-probe delay times. Dashed lines indicate the maximum possible electron energy (minimum internal vibration) as derived from the 1 photon appearance potential for  $(\text{NH}_3)_2^+$ . The fit curves indicate different pathways of the reaction (for details see ref. [12]).

Figure 5 shows the photoelectron spectra correlated with the dimer ions ( $\text{NH}_3\cdots\text{NH}_3^+$  as well as  $\text{NH}_2\cdots\text{NH}_4^+$ ) for various pump-probe delay times. A dramatic change of kinetic photoelectron electron  $E_{el}$  with pump-probe delay is seen, converging to a narrow distribution around  $\sim 0.8$  eV. We interpret this as the fingerprint of a strict selection rule  $\Delta v=0$  (FC factors) due to the nearly identical geometry of  $\text{NH}_2\cdots\text{NH}_4$  and  $\text{NH}_2\cdots\text{NH}_4^+$ . This is indicated by the photon and electron arrows on the left side

of figure 4. One surprising conclusion is that a significant part of this configuration survives on the  $\mu\text{s}$  time scale before detection - in spite of sufficient excess internal energy for further fragmentation into  $\text{NH}_2$  and  $\text{NH}_4^+$  [13].



**Figure 6. Left:** PES of the ammonia dimer following a *pump-control-probe* process ( $h\nu_{\text{pump}}=200$ ,  $h\nu_c=1200$  and  $h\nu_{\text{probe}}=400$  nm). Control and probe photon are delayed by 1.2 ps with respect to the pump. Shown is the pure 3 color signal. All two color components to the signal have been subtracted. **Right:** energy scheme (all numbers in eV) used to obtain the PES, indicating two different mechanisms involved: non resonant (**nr**) multiphoton ionization of the excited  $(\text{NH}_3)_2^*$  leads to very low electron energy (0.25eV) while resonant absorption (**r**) of the control photon from the  $\text{NH}_4(3s)\cdots\text{NH}_2$  to the next higher excited state  $\text{NH}_4(3p)\cdots\text{NH}_2$  results in less internal vibrational energy and larger kinetic electron energy and very little fragmentation in the ion to  $\text{NH}_4^+$ . For the labels nr, r1 and r2 see text.

Finally, in the spirit of true *femtochemistry* - aiming at control of reaction products – we address the question of how we can modify the excited states vibrational population (and hence that of the ions) so that fragmentation is reduced and the relative abundance of dimer ions increased. The idea is simply to resonantly induce a  $3s\text{-}3p$  transition in the  $\text{NH}_4$  component of  $\text{NH}_4\cdots\text{NH}_2$  to a low vibrational state by an additional *control* photon. From our own MRCI calculations (differing somewhat from published data [16]) we find a suitable control photon wavelength to be 1200 nm.

We apply this 1.2 ps after the 200 nm pump photon and finally ionize softly with a 400 nm probe pulse. First results are shown in figure 6.

Several different processes are recognized as indicated by the fitted contributions (thin lines): Nonresonant (**nr**) absorption of control and probe photon (possible at any configuration of the excited dimer molecule) yields ion ratios similar to that observed in the two-color pump-probe experiment. The electron kinetic energy detected is very small ( $\sim 0.2$  eV) in this case and the internal vibrational energy of the ion correspondingly high (1.46 eV from the total energy balance), thus nearly identical to that in the excited dimer state.

In contrast, for resonant absorption (**r**) of the control photon from the  $\text{NH}_4(3s)\cdots\text{NH}_2$  configuration to the next higher lying (3p) state we obtain for the true three-colour electron signal a significantly higher electron kinetic energy, of 0.62 eV (**1r**), corresponding to a reduced internal energy of the ion (1.02 eV). Comparing the signals for the  $(\text{NH}_3)_2^+$  ion mass (rather  $\text{NH}_4^+\text{NH}_2$ ) and that of the fragment  $\text{NH}_4^+$  a change in the ratio  $[(\text{NH}_3)_2^+]:[\text{NH}_4^+]$  for resonant and non resonant processes of nearly one order of magnitude is documented! In addition to the resonant absorption of one control photon (**1r**) we also detect resonant absorption of two (**2r**). They also are correlated dominantly with a true dimer ion signal. However, the electron spectrum shows, that the vibrational energy of the ion is not changed any further due to absorption of the second photon. The energy of the latter is simply transferred to the electron.

#### 4 Conclusions

With advanced femtosecond light sources the dynamics of a variety of clusters can now routinely be studied for  $h\nu < 8\text{eV}$  and  $\tau > 30$  fs. As exemplified for ammonia dimers, fs-time resolved photoelectron spectroscopy reveals many new details of the excited state dynamics. Finally, pump-control-probe experiments offer a new and challenging dimension of manipulating photochemical processes.

#### 5 Acknowledgement

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