

Femtosecond solvation dynamics of indium dimers inside superfluid helium nanodroplets

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Abstract. Indium dimers (In_2) solvated inside helium nanodroplets are studied with femtosecond photoelectron and photoion spectroscopy. The solvation dynamics triggered by photoexcitation of the In_2 include expansion of the solvation shell and dopant ejection from the droplet, which both proceed more slowly than for In atoms. Oscillation of the solvation shell, in contrast, is similar to the case of In atoms. These processes are observed in combination with intrinsic dynamics of the molecule and set the time-frame for the dopant interaction with the quantum fluid environment.

1 Introduction

Superfluid helium nanodroplets (He_N) represent a special approach for the synthesis of tailor-made or fragile molecules and clusters. In view of time-resolved spectroscopy, they provide access to novel classes of systems that have eluded ultrafast dynamical studies so far. Pure He_N [1] and surface-located alkali-metals [2] have been subject to femtosecond experiments. Concerning molecules immersed inside the He_N , the only attempt to observe ultrafast dynamics used the salt molecules sodium- and lithium iodide, which, however, was not successful [3].

Recently, we demonstrated that time-resolved photoelectron (PE) spectroscopy can be used to observe photoinduced dynamics of single atoms that are fully solvated inside the droplet [4]. The PE kinetic energy turned out to be a sensitive observable to follow the temporal evolution of the solvation shell around the photoexcited dopant. Supported by time-dependent density functional theory, we developed the following mechanistic picture: Photoexcitation of a single indium (In) atom inside a He_N leads to expansion of the solvation shell within 600 fs, followed by an oscillation of the bubble with a period of about 30 ps, and, finally, ejection of the In atom from the droplet after about 60 ps.

Here, we investigate the photoexcitation dynamics of the In_2 - He_N system, for which we observe solvation dynamics similar to the monomer case, as well as intrinsic In_2 molecular dynamics. In the presented work we concentrate on the former and interpret the corresponding transient signals by comparison to the previous In- He_N results.

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2 Method

As described in detail previously [4, 5], He_N with a mean number of $\bar{N} = 8000$ He atoms are generated in a supersonic expansion and doped inside a resistively heated pickup cell with two In atoms per droplet, which form an In_2 molecule. Dynamics of the In_2 - He_N system are investigated with a femtosecond pump-probe photoionization experiment with variable time-delay, where the kinetic energy of photoelectrons (PEs) and charge-to-mass ratio of ions are measured with a time-of-flight spectrometer. Pump pulses are obtained from a commercial Ti:sapphire laser system and frequency upconverted by an optical parametric amplifier to a photon energy of 3.59 eV (345 nm) in order to excite the $B^3\Pi_g(\text{II}) \leftarrow X^3\Pi_u$ transition of In_2 inside He_N [5]. Probe pulses are frequency doubled to 3.05 eV (406 nm).

3 Results and Discussion

Figure 1a shows the time evolution of the PE spectrum within the first two picoseconds after photoexcitation. The signal is modulated with a period of about 400 fs, which we ascribe to a nuclear wave packet oscillation of the In_2 molecule. The periodic signal maxima correspond to ionization from the excited $B^3\Pi_g(\text{II})$ state to the cationic ground state of In_2 , at a certain nuclear distance of the two In atoms (Condon point) [6]. The In_2 wave packet dynamics will be further analysed in an upcoming publication.

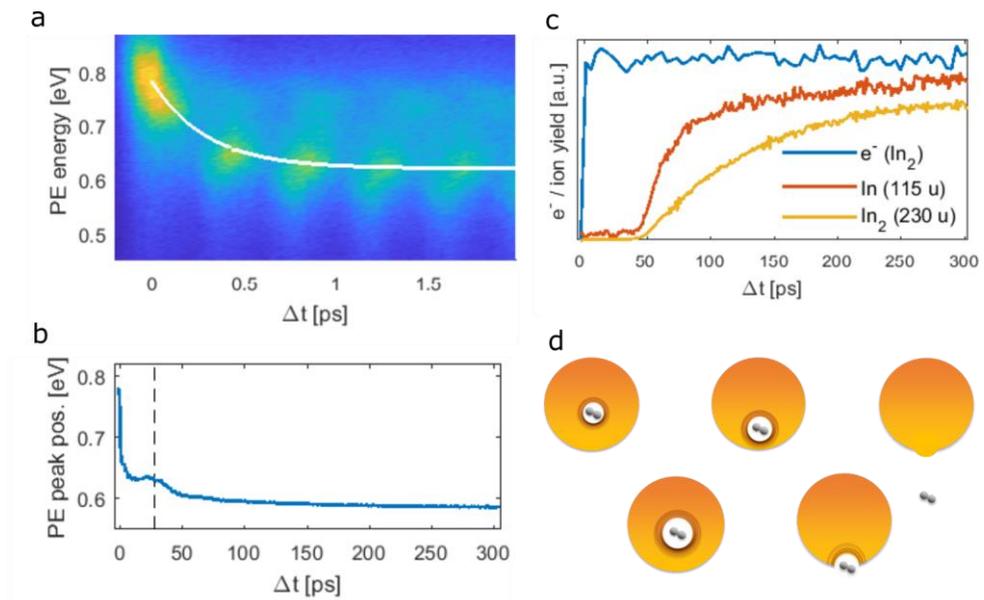


Figure 1: Time evolution of the In_2 - He_N system after photoexcitation. (a) PE spectrum within the first 2 ps. The white line connects the signal maxima. (b) PE peak position up to 300 ps, as determined by Gaussian fits to the corresponding PE spectra. The dashed line at 28 ps indicates the maximum of the temporal increase in PE energy. (c) Ion yields recorded at the In monomer/dimer masses of 115/230 u for photoexcitation at the monomer/dimer band at 376/345 nm (red/yellow line) and total PE yield integrated over all kinetic energies for excitation at 345 nm (blue line). (d) Sketch of the In_2 ejection process.

The maxima are energetically shifted by 150 meV from 780 meV to 630 meV within the first picosecond, as indicated by a white line in Figure 1a. This shift is related to the expansion of

the He bubble as consequence of the enlargement of the valence electron orbital during photoexcitation [4]. Compared to the In-He_N system, where a shift of 290 meV is observed within 1 ps and 90% peak shift are completed within 500 fs, the shift of the In₂-He_N is smaller (150 meV) and takes longer (90% within 700 fs). Both indicate that the excited state interaction with the He solvation shell is less pronounced for the In dimer compared to the monomer.

The PE peak shift up to 300 ps is shown in Figure 1b. After a steep, initial decrease, representing the bubble expansion, the peak position is shifted further towards lower energies with a temporal energetic increase around 28 ps (marked by the dashed line), before it slowly approaches a constant value of ~590 meV. The impulsive expansion of the solvation shell triggers an oscillation of the He bubble, the first contraction of which leads to the temporal increase in energy. This contraction is observed at the same time as for the monomer [4]. The decrease after 1 ps of the PE energy represents the ejection process of In₂ from the droplet, as the ionization energy inside the He_N is reduced due to polarization effects [7], compared to that of bare In₂.

Ejection from the He_N is particularly well observed by the transient ion yield. In Figure 1c the transient dimer ion yield for photoexcitation at the In₂ band (345 nm, yellow line) is compared to the monomer yield for excitation at the monomer band (376 nm, red line) [5]. Additionally, the total electron yield over time for excitation at 345 nm (blue line) is shown. While the electron signal shows an immediate rise at time-zero and remains constant afterwards, the ion signals both exhibit a delayed onset at 50 ps followed by a faster rise of the monomer within ~50 ps and a slower dimer rise within ~200 ps. This shows that In₂ is ejected from the droplet, in consequence of a repulsive, heliophobic excited state, as it is also the case for the In monomer [4]. Due to the cylindrical symmetry of In₂ the repulsive force experienced by the molecule depends on its orientation inside the He_N, which is not the case for the spherically symmetric monomer. This would be a possible explanation for the similar onset time and slower rise of the dimer compared to the monomer.

In conclusion, the photoinduced solvation dynamics of the In₂-He_N system, as sketched in Figure 1d, show all three signatures previously observed for In-He_N [4] – bubble expansion, bubble oscillation and dopant ejection. Bubble expansion and ejection proceed more slowly and are less pronounced for In₂ dopants, while the bubble oscillation is surprisingly similar to the atomic case.

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