

Coherent wave packet dynamics in photo-excited NaI

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Abstract. Time and energy resolved photoelectron distributions of photo-excited NaI are presented. A splitting in the photo-excited state suggested by calculations of the intramolecular potential energy surfaces could be confirmed experimentally for the first time.

1 Introduction

In the past decades, femtochemistry has made remarkable progress and intensive research is going on the investigation of dynamic processes in molecules on the femtosecond time-scale. In 1988 the group of Zewail pioneered this progress by performing extensive studies on the temporal evolution of molecular wave packets in photo-excited NaI using femtosecond transition state spectroscopy (FTS) [1,2]. These studies have enabled the characterization of the potential energy surfaces of the excited state and the (lower) unbound states, as well as the characterization of wave packet oscillations happening in excited NaI molecule, due to an intersection of the first excited state A and the ground state X forming an effective trapping potential (see fig. 1).

For monitoring dynamics in the electronic structure, time-resolved photo electron spectroscopy (TRPES) techniques have shown to be a powerful tool [3]. In TRPES, the system is excited by a pump laser pulse λ_1 and photo-ionized by a time delayed probe pulse λ_2 . The kinetic energies of all created photoelectrons are then measured simultaneously. The experiments presented here can be seen as an extension of our former study of Br₂ dissociation [4]. A TRPES study with femtosecond pulses on NaI molecules has previously been done in 1997 by Jouvet et al. [5], but in their experiment they could only distinguish between slow and fast electrons, hence not using the advantage of resolving all electronic states simultaneously. In this contribution, we present the results from our recent experiments on the electronic structure dynamics in photo-excited NaI molecules in a photon wavelength range covering 320 nm to 370 nm. Photoelectron distributions from two-photon two-color photo-ionization were detected in a time-, energy- and angular-resolved mode.

In alkali halides, the ionic ground state Na^+I^- ($X_{Q=0}$) crosses the excited, covalent state NaI ($A_{Q=0/1/2}$), which asymptotically converges towards the dissociation limit $\text{Na}(2S_{1/2}) + \text{I}(2P_{3/2})$. Calculations of the relevant potential energy curves, including the splitting of the A state due to spin-orbit coupling are presented in fig. 1. Although, upon excitation by λ_1 the wave packet initially might be prepared only on the lowest surface due to lack of pump photon energy, all other surfaces can be

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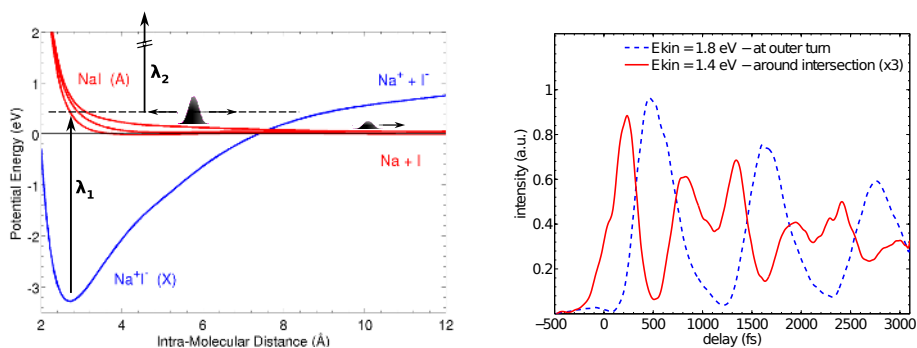


Fig. 1. Left: Calculated intra-molecular potentials of the NaI molecule. The ionic ground state X and the covalent excited state A intersect and form an effective trapping potential. A molecular wave packet created on the A state by a pump pulse λ_1 oscillates in this trap before the system is probed by photo-ionization through a delayed pulse λ_2 . In each oscillation, part of the wave packet can tunnel through the intersection, breaking the molecular bond and forming free, neutral fragments. Right: Photoelectron yield vs. delay time at $E_k=1.8$ eV, corresponding to the outer turn on the covalent X potential curve in the left picture and the yield at $E_k=1.4$ eV, around the intersection. Note, that these curves show similar behavior as those presented in [1,2,5].

populated, when the wave packet is reflected and travels through the intersection back to short intra-molecular distances. This should be visible in the corresponding time resolved photoelectron spectra as a fanning out of the corresponding peak in the photoelectron energy distribution into a whole group of peaks. Coming from short intra-molecular distances, part of the wave packet can tunnel through the intersection barrier, breaking the molecular bond and leading to free neutral fragments. Each time the wave packet goes by the intersection without tunneling through, an electron transfer takes place, switching the nature of molecular bond between covalent and ionic. Therefore a change in the geometry of the electronic structure occurs, which should be visible in the corresponding photoelectron angular distributions.

The right picture in fig. 1 shows exemplary delay scans extracted from our data at well-defined photoelectron energies of $E_k=1.8 \pm .1$ eV and $E_k=1.4 \pm .1$ eV, corresponding to the outer turn on the potential surface or to intra-molecular distances around the intersection, respectively. Similar response signals, characterizing the oscillating behavior were observed in [1,2,5]. However, our measurements can provide more detailed insights, as all electronic states of excited NaI, reachable with the ionizing probe pulses, were resolved at once (fig. 2).

2 Experiment and Results

The experiment was carried out in a laser lab at the Max-Born-Institute Berlin. A 40 fs, 2 mJ Ti:Sa laser served as primary light source and was split into two beams to generate pump and probe pulses via non-linear conversion schemes. For our experiment, sub 100 fs, 3-7 μ J pump pulses tunable from $\lambda_1=320$ nm to 390 nm (3.9-3.2 eV) and sub 100 fs, 2-3 μ J probe pulses at $\lambda_2=200$ nm (6.2 eV) were generated and focused in collinear geometry into the interaction volume of our experimental chamber. An oven, developed at Helmholtz-Zentrum Berlin was used at an evaporation temperature of 500-700 °C to produce an effusive jet of NaI molecules. The photoelectrons created upon ionization were detected with a velocity map imaging spectrometer (VMI). A VMI enables detecting the photoelectron angular distribution (PAD) and thus enables deriving the β_2 and β_4 anisotropy parameters of the electronic structure, see for example [6].

Fig. 2 shows the time evolution of the photoelectron kinetic energy distribution recorded from NaI molecules after excitation with a 320 nm fs laser pulse. The single peak for negative delays corresponds to photo-ionization of I^- from auto-ionization, happening when the system is excited by the 200 nm pulse and thus has enough energy to overcome the X state barrier and dissociate into ionic fragments within ~ 500 fs. For positive delays, the PES shows an oscillatory behavior with a period of ~ 1100 fs.

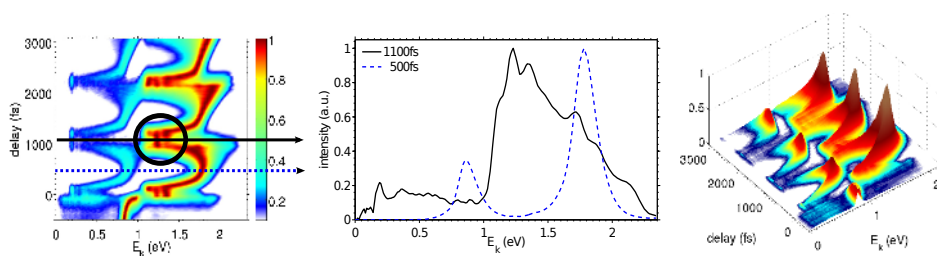


Fig. 2. Time resolved photoelectron kinetic energy distributions recorded from NaI molecules photo-excited with $\lambda_1=320$ nm. The data in the left and the center are normalized separately for each delay to maximum=1, same scaling for all delays was applied in the right surface plot. The black circle in the left picture marks the fanning out of the wave packet on the spin-orbit split family of A state potential surfaces. The fanning is still visible for the second turn, but already smeared out. The center picture presents normalized photoelectron spectra for the first outer turn around 500 fs (dashed line) and for the first inner turn around 1100 fs (solid line), showing the fanning out on several states.

The intense peaks at around 0.8 eV and 1.8 eV kinetic energy, first visible after 500 fs correspond to the lowest bound valence electrons of excited NaI at the outer turn of the wave packet oscillations. The expected fanning out of the wave packet on the whole family of potential curves belonging to the A state is clearly visible as splitting of the PES into distinguished new contributions, first occurring after ~ 1100 fs (circle in left picture of fig. 2). The splitting is still nicely visible around 2200 fs for the second oscillation, but smeared out as the wave packet underlies natural broadening and de-phasing due to different traveling speeds on the several A state potential surfaces.

Not shown here is the time dependence of the photoelectron angular distribution. Preliminary analysis shows an oscillatory behavior in the angular dependence, especially in the intersection region. This promises to give deeper insight into the mechanisms coming along with the electron transfer taking place when avoiding the crossing at the intersection, for example, electronic charge redistribution. We performed measurements for several other pump wavelengths λ_1 in the range of 320-370 nm and as well detected ion yields. A detailed analysis of the complete data set and the influence of the pump wavelength on the dynamics is currently under progress and will be presented in a future publication.

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