

# FEMTOSECOND PUMP-PROBE PHOTOELECTRON-SPECTROSCOPY ON ELECTRONIC STATES OF $\text{Na}_2$ : A TOOL TO STUDY ULTRAFAST CONTROL OF CHEMICAL REACTIONS

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Various one-parameter quantum control schemes applied to  $\text{Na}_2$  serve as prototype for current multi-parameter control techniques in order to obtain physical insight into the underlying molecular dynamics.

## 1 Introduction

Microscopic control of the outcome of a chemical reaction is a long-standing dream in physical chemistry. Recently femtosecond lasers have emerged as a particularly suitable tool for quantum control of reaction dynamics. Assion et al. [1] were the first to demonstrate the use of tailored femtosecond laser pulses from a computer-controlled pulse shaper to control the branching ratios of various photodissociation channels in  $\text{CpFe}(\text{CO})_2\text{Cl}$ . Moreover, quite recently Levis et al. [2] have shown that high intensity laser pulses permit to control a dissociative rearrangement reaction in which chemical bonds are not only selectively broken, but also newly formed. Quantum control over chemical reactions may be obtained employing various so-called one parameter schemes [3-6]. Currently much attention has been focused on the utilization of adaptive feedback controlled femtosecond pulse shaping making available a most versatile instrument for multi-parameter control schemes [1, 7-10]. These techniques have proven to be universal in the sense that they enable to optimize virtually any conceivable quantity and are capable to deliver the optimal electric field without the knowledge of the underlying potential energy surfaces (PES). However, the individual control mechanisms may be inferred, if at all, only for very simple systems. In order to get a better physical insight into the multi-parameter control driving such an experiment it is essential to investigate one parameter control schemes in detail on pertinent model systems.

## 2 The sodium dimer as model system for quantum control schemes

The choice of a suitable model system is governed by several requirements: in order to support the validity of the physical pictures of the control process full quantum mechanical simulations of the experiment should be feasible. Therefore one-dimensional systems such as diatomic molecules are most workable. Moreover, a detailed knowledge of all PES involved is prerequisite. Insight in the dynamics of the control can only be accomplished if the experiment allows structural and electronic changes in the configuration to be monitored with high spatial and temporal resolution. Measurements of kinetic photoelectrons using time-of-flight spectrometry (TOF) combined with a femtosecond multiphoton ionization pump-probe technique on  $\text{Na}_2$  in a molecular beam allows to map molecular motion with sub-Angström spatial and femtosecond temporal resolution. Therefore they are ideally suited for detailed studies how quantum control can be achieved. Published and unpublished examples for such one parameter control schemes elucidating the mechanism of quantum control are presented.

## 3 The Tannor-Kosloff-Rice scheme

In the time domain the so called Tannor-Kosloff-Rice scheme [3] is a very illustrative way of how to obtain control over different products via photoexcitation of a molecule. In practice a pump laser prepares a vibrational wave packet on an electronic excited potential and a time-delayed probe laser populates the product state either by dumping the wave packet down again or by further excitation. In the case studied here we obtain a higher kinetic energy of photoelectrons at the inner turning point and a lower kinetic energy of the photoelectrons at the outer turning point from the ionization of a vibrational wave packet propagating on the electronic states (see Fig. 1a for relevant PES and Fig. 1b for measured data). By controlling the duration of the wave packet on the  $2^1\Pi_g$  state we have access to different product states (not shown here). By this means we demonstrate the control of the photoproduct ratio  $\text{Na}^+/\text{Na}_2^+$  in a pump-probe experiment [11].

## 4 Intensity of the laser pulses

In general, the wavelength range needed for the excitation of an intermediate state will differ from the wavelength range to reach the product state at a certain bond configuration. If the two wavelength regimes are not contained within the spectral width of the laser pulse a weak field approach may not be efficient. A solution can be found by utilizing intensity dependent effects in order to shift energy levels involved into the accessible spectral range. This was demonstrated on  $\text{Na}_2$  [12] and also applied in the work of Levis [2]. In a set of measurements the pump laser

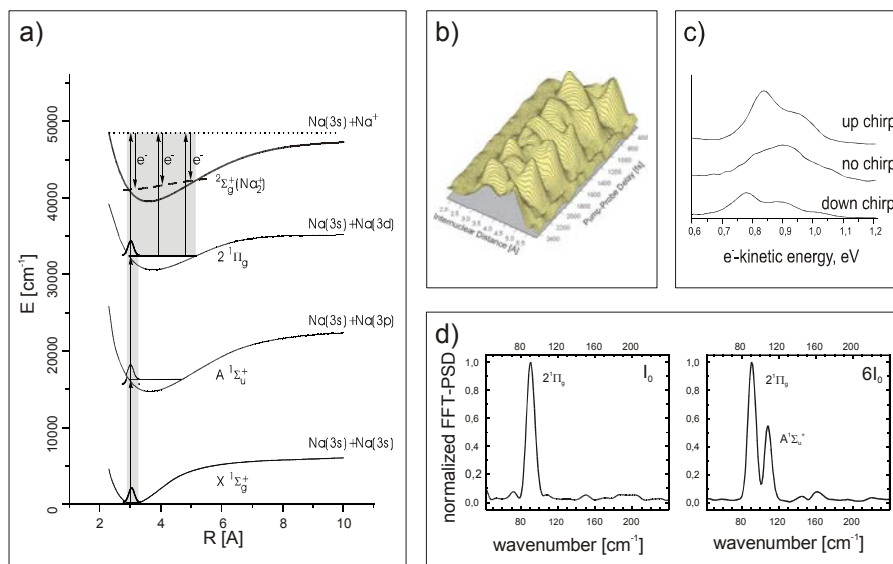


Fig. 1a: Excitation scheme of sodium dimer for 620 nm photons.

Fig. 1b: Mapping the wave packet with sub-Angström spatial resolution and femtosecond time resolution.

Fig. 1c: Electron spectra measured with single up-chirped (+3500 fs<sup>2</sup>), unchirped and down-chirped (-3500 fs<sup>2</sup>) laser pulse.

Fig. 1d: Cuts of FFT spectra at the outer turning point of the wave packet at  $I_0$  (left) and  $6 I_0$  (right).

intensity is kept fixed whereas the probe laser intensity is increased from  $I_0 \approx 10^{11}$  W/cm<sup>2</sup> to  $10 I_0$ . The propagation of the vibrational wave packets over all allowed internuclear distances is monitored with a probe laser of variable intensity to investigate the influence of high laser intensities on the molecular potential sensitive to the internuclear distance. In Fig. 1d the FFT of the cuts at TOFs corresponding to the outer turning point of the wave packets are shown. With increasing probe laser intensity a contribution of the  $A^1\Sigma_u^+$  is seen at the outer turning point. An explanation of this resonant behavior was given in terms of light induced potentials [13].

In order to steer a chemical reaction via wave packet motion on a particular electronic excited state it is advisable to achieve control over the population in the specific state of interest. This can be done by coherent coupling of the electronic states [18]. Fig. 2a displays results of a quantum calculation that are performed analogously to [19]. At the pump intensity  $I_3$  the population of the  $2^1\Pi_g$  state is

involved in one Rabi cycle leading to the “ $2\pi$ ” excitation of this state. In the upper part of fig. 2b the experimental results for  $I_{\text{pump}} \approx 10^{11} \text{ W/cm}^2$  and  $I_{\text{probe}} \approx 10^{12} \text{ W/cm}^2$  are displayed. Note the contributions of frequencies of the  $A \ ^1\Sigma_u^+$  and  $2 \ ^1\Pi_g$  states to the Power Spectrum Density (PSD). The data in the lower part of fig. 2b are taken with twice the pump laser intensity. The observed reduction in amplitude of the  $2 \ ^1\Pi_g$  frequencies to the PSD is attributed to the “ $2\pi$ ” excitation of the  $2 \ ^1\Pi_g$  state.

Concerning photodissociation reactions in intense fields, we have studied the transition from photodissociation on light-induced potentials to field ionization as a function of intensity on the  $\text{Na}_2^+$  system [20].

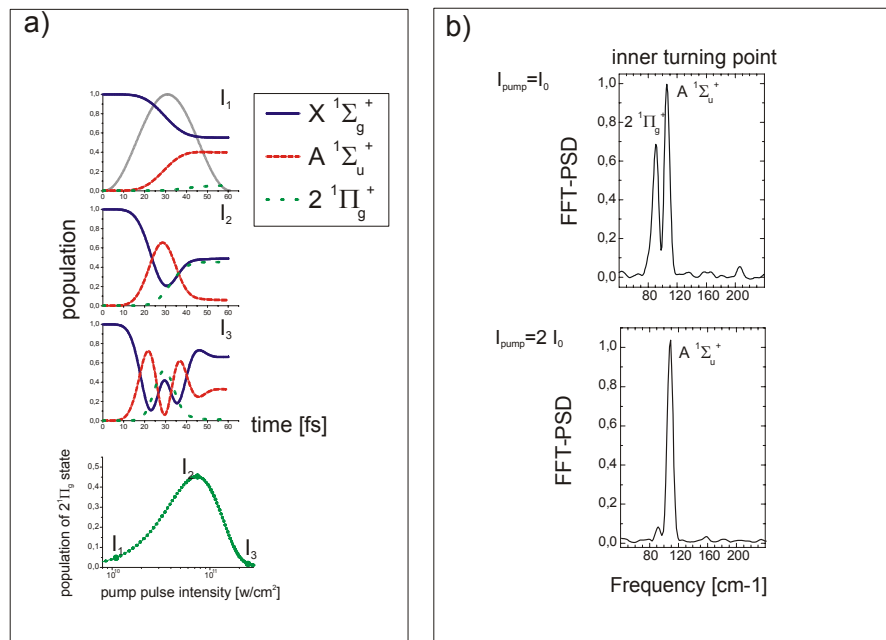


Fig.2a: Coherent coupling of electronic states (see fig. 1a) at various laser intensities.

Fig.2b: Experimental verification of  $2\pi$  excitation. FFT at inner turning point from mapping experiments under identical conditions: Upper:  $I_{\text{pump}} \approx 10^{11} \text{ W/cm}^2 (=I_0)$ . Lower:  $I_{\text{pump}}=2I_0$ .

## 5 Chirp and duration of laser pulses

In the last couple of years an increasing number of experiments is devoted to the use of phase shaped laser pulses in order to control atomic and molecular

properties [9]. Fig. 1c shows photoelectron spectra obtained from ionizing  $\text{Na}_2$  with up-chirped, un-chirped and down-chirped laser pulses at 620 nm. The ionization yield is seen to double when the frequency order is switched from blue first to red first in the exciting laser pulse. Calculated electron spectra qualitatively reproduce the measured results. From the analysis of this calculations the importance of synchronizing wave packet motion to chirp and intensity profile is derived for obtaining efficient population transfer and subsequent ionization.

## 6 Influence of electronic changes along the internuclear distance

Another aspect in quantum control is introduced by nonadiabatic coupling of the potential curves involved in the time evolution of a quantum system [14]. The

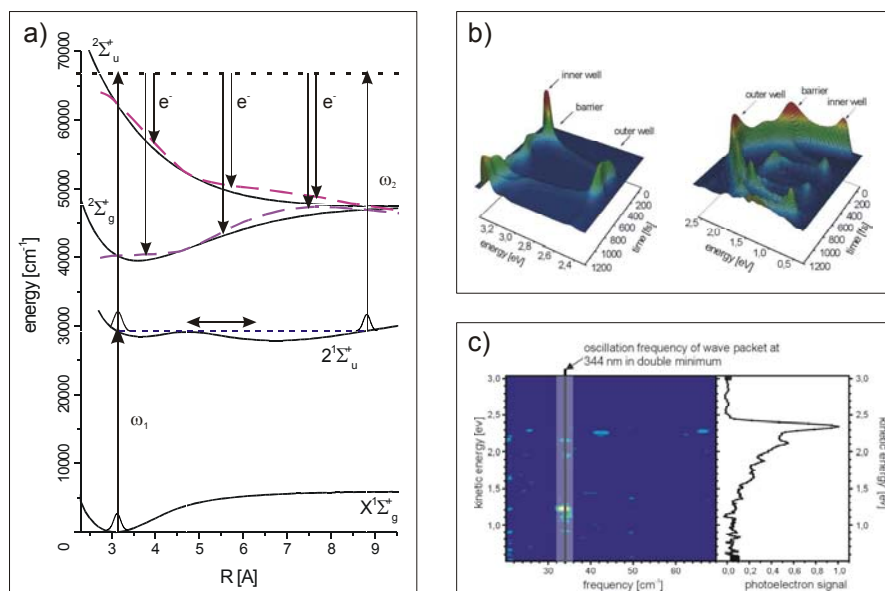


Fig.3a: Potential scheme of the double-minimum of  $\text{Na}_2$  for 344 nm photon excitation. Probe wavelength is 267 nm.

Fig.3b: Calculated photoelectron signal, left:  $e^-$ -signal from ionisation into bound ionic state, right:  $e^-$ -signal from ionisation into repulsive ionic state.

Fig.3c: Preliminary experimental results: FFT from the measured photoelectron signal at a probe wavelength of 344 nm.

coupling of the covalent and ionic potentials in NaI is a prominent example [15 and references therein]. Electronic changes along the internuclear coordinate  $R$  are also predicted for the  $^1\Sigma_u^+$  double minimum potential well in the  $\text{Na}_2$  molecule (Fig. 3a). According to [16] the change of electronic structure near the avoided crossing at 4.7 Å leads to photoionization probabilities rapidly changing with geometry. We performed quantum mechanical calculations of the temporal evolution of a wave packet in the  $^1\Sigma_u^+$  double minimum potential well and the resulting photoelectron signal assuming an  $R$ -independent ionization probability similar to [17] (Fig. 3b). More detailed calculations by Takatsuka et al. [16] taking into account the change in the electronic structure indicate no photoelectron yield from the inner well. Experiments with our newly commissioned femtosecond laser system at the University of Kassel are underway to focus on the mostly unstudied influence of  $R$ -dependent transition moment on coherent control. In this two-color experiment a wave packet is created at the inner turning point of the double minimum potential slightly above the barrier. During its temporal evolution the subsequent photoelectrons resulting from ionizing on the bound and repulsive ionic state are investigated. Preliminary results obtained at the University of Würzburg are shown in Fig. 3c.

## 7 Conclusion

Investigation of the wave packet motion of small molecules with high spatial and temporal resolution is the key feature to study a variety of one parameter control schemes in great detail. Based on this knowledge a comparison to results of feedback optimized laser pulses applied to such systems will provide valuable insights into automated multi parameter control schemes. Going to larger molecules, control schemes on isomerization, energy redistribution and molecular rearrangement can be studied using this method because of its sensitivity both to structural and electronic changes in a molecule upon excitation.

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