

Mapping of Vibrational Wave Packet Motion and Coherent Control of Molecular Ionization by a Chirped fs Laser Pulse

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Abstract. Energy resolved photoelectron spectroscopy in combination with femtosecond pump-probe and molecular beam techniques is used to map vibrational wave packet motion along the internuclear coordinate. The kinetic energy of photoelectrons released provides information about the internuclear distance where ionization takes place. In addition coherent control of molecular multiphoton ionization by a single chirped femtosecond laser pulse is reported.

Energy resolved photoelectron spectroscopy is an ideal tool to monitor the evolution of molecular vibrational wave packets along the internuclear distance in real time. According to the Franck-Condon principle the photoelectron energy distribution resulting from direct ionization sensitively depends on the nuclear configuration. Mapping a vibrational wave packet with the help of femtosecond pump-probe techniques and energy resolved photoelectron spectroscopy was suggested by C. Meier and V. Engel in a theoretical publication [1]. We show for the first time experimentally, that the dynamics of an intermediate molecular state can be followed along *all* energetically allowed internuclear distances simultaneously. The femtosecond time resolved experiments were performed in a Na_2 molecular beam with electron Time-of-Flight (TOF) detection using bandwidth limited 40fs pump and probe pulses at 618nm.

Femtosecond time resolved experiments on multiphoton ionization of the Na_2 molecule at 2 eV photon energy with ion detection reveal vibrational wave packet motion in the intermediate electronically excited states [2]. As depicted in Fig. 1 the wave packet in the first excited state ($A^1\Sigma_u^+$) is transferred at the inner turning point into the ionization continuum resonantly enhanced by the $2^1\Pi_g$ state. Direct photoionization of the wave-

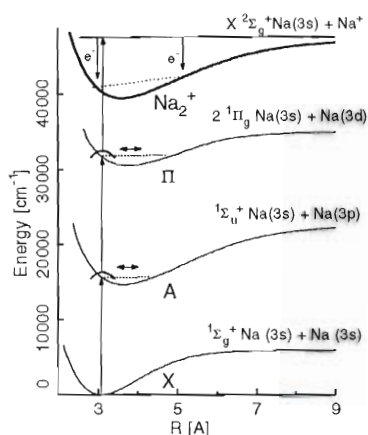


Fig. 1: Excitation scheme

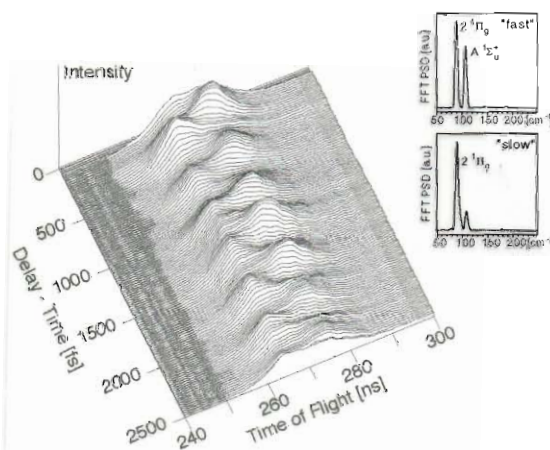


Fig. 2: Mapping of vibrational wave packet motion

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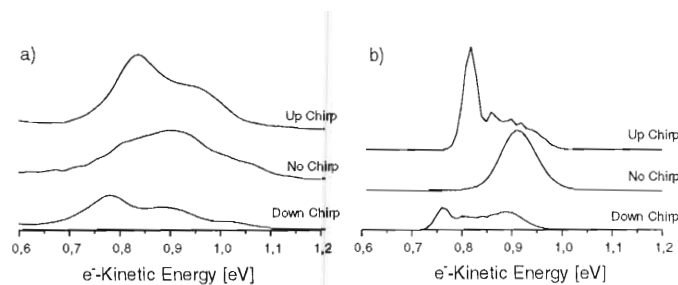


Fig. 3: a) measured photoelectron spectra for up-chirped ($+3500 \text{ fs}^2$), down-chirped (-3500 fs^2) and transform limited 40 fs pulses at 618 nm b) calculated spectra

packet out of the $2 \ ^1\Pi_g$ state leads to a time independent ion signal [1]. However, the difference potential $\text{Na}_2^+ - 2 \ ^1\Pi_g + 2\omega$ (dashed line; ω is the excitation energy) indicates that upon direct ionization out of the $2 \ ^1\Pi_g$ into the ionic $2 \ ^2\Sigma_g^+$ state the kinetic energy of the photoelectrons depends on the internuclear distance. In Fig. 2 the measured TOF photoelectron distribution as a function of pump-probe delay is shown. This femtosecond time resolved photoelectron signal shows the vibrational wave packet motion on the neutral electronic states. Cuts at a constant TOF, i.e. at a specific electron energy, reveal the wave packet dynamics at a specific internuclear distance. The inserts of Fig. 2 display the Fourier transform of transient photoelectron signals obtained at two different cuts. At an earlier TOF photoelectrons with higher kinetic energy are released ("fast" photoelectrons) and therefore the inner turning point is probed, whereas at a later TOF "slow" photoelectrons are released and the outer turning point is probed. Consequently the Fourier transform of the "fast" photoelectron transient reflects wave packet motion in the $A \ ^1\Sigma_u^+$ and $2 \ ^1\Pi_g$ state, whereas the Fourier transform of the "slow" photoelectron transient reflects mainly the wave packet motion in the $2 \ ^1\Pi_g$ state.

In a single pulse experiment using chirped femtosecond laser pulses coherent control of a molecular multiphoton ionization process is reported. Both the pulse duration and the chirp (introduced by a prism sequence) of the ultrashort laser pulse are active control parameters. The experimental results together with calculated photoelectron spectra are displayed in Fig. 3. The "no chirp" laser pulses are short compared to vibrational periods and restrict the ionization process to small internuclear distances where photoelectrons of higher energies are formed. For up-chirped laser pulses the ionization yield is about twice as high as for down-chirped pulses. The quantum mechanical calculations agree qualitatively with the experimental data. Analysis of these calculations show that a higher ionization yield in the multiphoton ionization process is observed when simultaneously the population in the intermediate molecular states is minimal [3]. This kind of optimization is desired in coherent control schemes.

References

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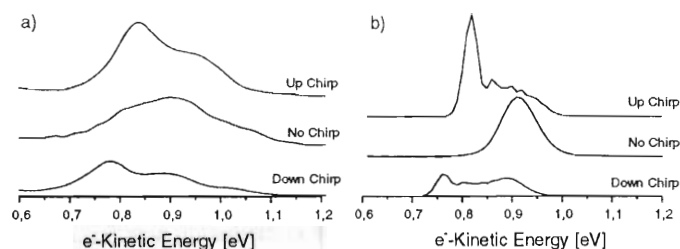


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