Femtosecond pump-probe spectroscopy for single trapped molecular ions

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Abstract. The vibrational dynamics of single molecular ions confined in a coulomb crystal are followed by 4 fs ultraviolet pulses. Theoretical calculations predicted the optimal laser parameters for a successful experiment under background free conditions. The ions are subject to internal heating, which has to be treated in the theory and handled in the experiment. Beyond the experiment the pump-probe scheme is extended by a coherent control scheme designed to suppress unwanted vibrational heating.

We combine for the first time the techniques of trapping and laser cooling with ultrashort intense laser pulses. Cold molecular ions are trapped in a coulomb crystal which provides an almost background and decoherence free environment [1]. The individual molecular ions are delivered at millikelvin temperatures and with micrometer positioning into few-femtosecond ultraviolet laser pulses. The first 4 fs-pump-probe experiments are carried out on MgH^+ ions [2]. They can be regarded as proof-of-principle experiments pioneering the investigations of individual molecules, such as structural determinations using few-femtosecond X-ray lasers. The complexity of the experiment needed guidance from theory. A multi-scale model was developed to describe the Pump-Probe (PP) process on the trapped single molecular ions. A coherent control scheme to prevent intermediate heating is proposed, which can improve the measurement dramatically.

Single MgH^+ ions are confined in a Mg^+ coulomb crystal which is laser cooled to ≈ 100 mK. The molecular ions are sympathetically cooled by the coulomb interactions with the atomic species, whereas the vibrational and rotational degrees of freedom of MgH^+ are decoupled from the center of mass motion [1]. The PP experiment is carried out with 4 fs ultraviolet laser pulses (285 nm). The pump laser creates a nuclear wave packet (WP) in the electronic excited A-state (Fig. 1(a)) which is detected by the probe pulse via the dissociative C-state leading to a neutral Mg and H^+. A dissociation event is detected with 100 % efficiency by the trap loss of a MgH^+ molecule. Due to the special situation of immobile molecular ions and a continuously running laser system, the same molecule can be excited by the light pulse several times without dissociating. Spontaneous decay of the A-state will lead to vibrational heating. The theoretical description of the full process thus becomes non-trivial and involves different time scales: The WP motion is tracked over a time scale of 80 fs whereas the limiting decay processes have time constants of ≈ 100 ms.

The flourescence images of the coulomb crystal are used for the detection scheme. The molecular ions appear as dark spots in the regular structure and are indicated in Fig. 1(a) by the white circle. Dissociated Mg atoms leave the crystalline structure and the dark spot disappears. The dissociation into Mg^+ + H via the B state is a spurious contribution for the pump-probe signal and is enhanced due to heating effects. The increase in temperature is directly connected to the laser repetition rate and its relation to the competing radiative cooling. To predict a well behaved parameter regime for the laser pulse we developed a multi-scale model to mirror the dynamic processes. To describe the
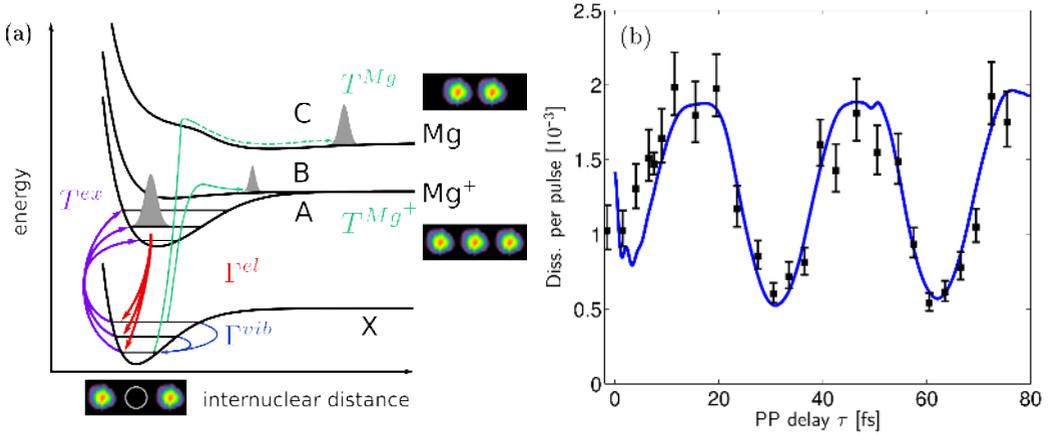
Fig. 1. (a) Schematic representation of the contributions entering the rate equation model. The excitation T^{ex} and dissociation rates T^{Mg,Mg^+} are obtained form the time depended Schrödinger equation. The PP-Signal for measuring the WP motion is the formation of Mg. The spontaneous decay $\Gamma^{el} \approx 10^9\,\text{s}^{-1}$ is responsible for heating of the vibrational degrees of freedom. The rates $\Gamma^{vib} \approx 10^1\text{-}10^2\,\text{s}^{-1}$ describe the vibrational relaxation counteracting to cool the sample. The flourescence images of the coulomb crystal are used for the detection scheme. (b) Vibrational motion of molecules derived from the dissociation of single molecules as a function of PP delay. The experimental data (squares) is compared with the theoretical predictions (solid line).

coherent PP process and the incoherent spontaneous decay processes the time depended Schrödinger equation (TDSE) is embedded in a rate equation model. The total wave function after completion of the PP process yields the excited state populations **p** forming the WP and the dissociated fraction of the molecules (Fig. 1(a)). The explicit light matter interaction is described by solution of the TDSE. The result is averaged over the repetition interval to obtain the excitation T^{ex} and dissociation rates T^{Mg} and T^{Mg^+} . These rates are then combined with the spontaneous decay from the electronic excited state Γ^{el} and the vibrational decay Γ^{vib} in the electronic ground state potential. The rate matrix **W** for the complete process can be formed:

$$\mathbf{W} = \begin{pmatrix} \Gamma^{vib} & \Gamma^{el} & 0 & 0 \\ T^{ex} & 0 & 0 & 0 \\ T^{Mg} & 0 & 0 & 0 \\ T^{Mg^+} & 0 & 0 & 0 \end{pmatrix} \tag{1}$$

The solution of the rate equations yields the overall dissociation probabilities and the vibrational populations:

$$\frac{d}{dt}\mathbf{p} = \mathbf{W}\mathbf{p}. \tag{2}$$

The heating is a competition between the excitation due to the laser pulses T^{ex} accompanied by subsequent spontaneous emission Γ^{el} and the slow decay Γ^{vib} of the vibrational distribution in the ground state.

With this method at hand substantial predictions for the experiment has been made. The laser system should run with a repetition rate assuring that the molecules are mostly in the vibrational ground state ($< 200\,\text{s}^{-1}$). Larger repetition rates (e.g. $3000\,\text{s}^{-1}$) lead to significant heating (8000 K, Fig. 2(b) top line) and the MgH$^+$ PP signal is overlaid by an unmodulated signal originating from the Mg$^+$ channels. For the experiment a repetition rate of $140\,\text{s}^{-1}$ is selected. Here vibrational relaxation can balance the heating effects with a still reasonable data acquisition time. As a result a clean PP signal is obtained which shows excellent agreement with the theoretical prediction (Fig. 2(b)).

For further improvement of the measurement, we propose a coherent control scheme for suppression of the heating process. After a single PP pulse sequence the non-dissociated part of the vibrational WP remains in the excited electronic A state. The subsequent spontaneous decay can be avoided by
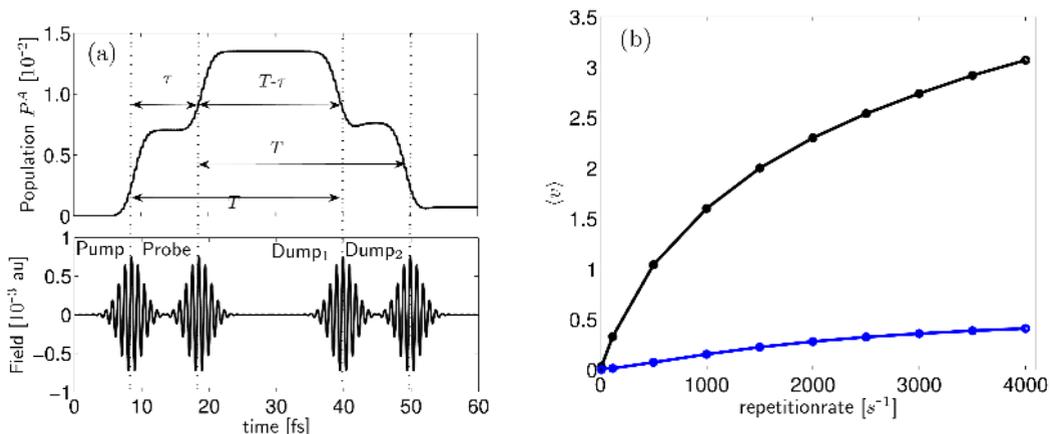
Fig. 2. PP scheme augmented with dump pulses. The pulse sequence is shown in (a) bottom. The corresponding time evolution of the population in the electronic A-state is shown in (a) top. Each dump pulse is delayed by $T \approx 31$ fs time with respect to its twin. The remaining population in A is suppressed effectively. The mean vibrational quantum number $\langle v \rangle$ vs. the repetition rate for a PP experiments with (bottom) and without (top) dump-pulses is shown in (b).

removing the remaining WP with additional dump pulses after the PP sequence is completed. The dump pulse is most efficient when the overlap of the WP with the ground state wavefunction is maximal and the electronic coherence is optimal [3]. This situation occurs at the inner turning point in the Franck-Condon region. By choosing a dump pulse with the appropriate time delay and phase the WP can be transfered back to the ground state by stimulated emission. The same strategy applies for the probe pulse which also creates a second WP in the excited state. Figure 2(a) shows the result of such an optimal four pulse sequence. The A-state is nearly completely depopulated and the heating is successfully suppressed (Fig. 2(b), bottom line). The detection of the WP motion is preserved under the influence of the dump pulses since they are chosen to create only minimal dissociation.

The demonstrated single molecule femtosecond PP scheme required (sub)micrometer positioning and careful handling of the pulse parameters. Augmenting the PP- sequence by two phase related dump pulses will improve the recording time and facilitate the measurements of larger systems.

References

1. A. Bertelsen, S. Jørgensen, and M. Drewsen, J. Phys. B: At. Mol. Opt. **39**, L83 (2006)
2. S. Kahra, G. Leschhorn, M. Kowalewski, A. Schiffrin, E. Bothschafter, W. Fuß, R. de Vivie-Riedle, R. Ernstorfer, F. Krausz, R. Kienberger, and T. Schaetz, Nature Phys. **8**, 238 (2012)
3. P. von den Hoff, R. Siemering, M. Kowalewski, and R. de Vivie-Riedle, Selected Topics in Quantum Electronics, IEEE Journal of **PP**, 1 (2011)