# Adaptive polarization control of molecular dynamics

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**Abstract.** We demonstrate that the use of time-dependent light polarization opens a new level of control over quantum systems. With $K_2$ molecules we show that polarization-shaped laser pulses increase the multiphoton-ionization yield compared to linearly-polarized laser pulses.

Coherent control is a powerful method which allows to "steer" quantum-mechanical processes toward a desired outcome by applying optimal light fields [1]. The main experimental tool for achieving this goal has been spectral phase shaping of femtosecond laser pulses [2]. Numerous implementations were reported in recent years, but in all these experiments only the scalar properties of ultrashort laser pulses were optimized. The light–matter interaction is governed by the scalar product $\vec{\mu} \cdot \vec{E}(t)$ with $\vec{E}(t)$ a vectorial quantity. If the momentary polarization state of the applied electromagnetic field is varied, $\vec{\mu} \cdot \vec{E}(t)$ can be optimized throughout the complete temporal evolution of a quantum system.

In the work reported here, we carry out molecular quantum control making explicit use of polarization variation [3] on an ultrashort time scale. In order to illustrate the novel features of such experiments, we maximize photoionization in a small prototype system, the potassium dimer $K_2$. Within the bandwidth of our laser system, the dominant transition pathway that contributes to the $K_2^+$ yield [4] populates the $2^1\Pi_g$ state as an intermediate before the final ionization step (Fig.1a). The $2^1\Pi_g$ state can be reached from the $X^1\Sigma_g^+$ ground state by a two-photon process with intermediate wavepacket propagation in the $A^1\Sigma_u^+$ state. This pathway is strongly polarization dependent because according to selection rules the two involved electronic transitions require electromagnetic fields with polarizations parallel and perpendicular to the molecular axis, respectively.

In order to illustrate these issues further, we performed a “conventional” pump–probe experiment in partially aligned $K_2$ molecules where the alignment is due to suitable molecular beam conditions. First, we used equally intense pump and probe laser pulses both polarized parallel to the mass-spectrometer axis. The amount of $K_2^+$ as a function of pump–probe delay (Fig.1b, solid line) is symmetric and shows a minimum with respect to time zero. On the other hand, if the probe-pulse polarization is perpendicular to that of the pump pulse, the signal is asymmetric (Fig.1b, dashed line), and for negative time delays the $K_2^+$ production is significantly enhanced. This result proves the polarization dependence of the $K_2^+$ ionization pathways.

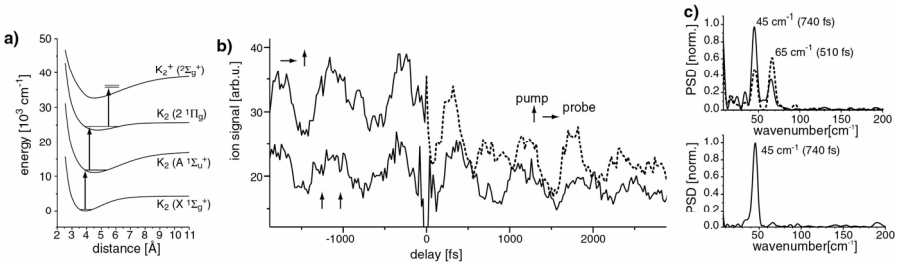


**Fig. 1.** a) Calculated potential energy curves of the potassium dimer system. b) Section of pump–probe transients with mutually parallel (solid line) and crossed (dashed line) linear polarizations around delay time zero. c) FFT-analysis of pump–probe transients with parallel (lower graph) and crossed (upper graph) mutual polarizations.

Fourier analysis of the pump–probe transients reveals that for mutually parallel pump and probe polarizations (Fig.1c, bottom graph) only the dynamics in the $2^1\Pi_g$ state with a vibrational period of 740fs [4] is visible. For mutually perpendicular pump and probe polarizations (Fig.1c, upper graph) an additional Fourier peak is found at $65cm^{-1}$ (corresponding to 510fs) which can be attributed to vibrational dynamics in the $A^1\Sigma_u^+$ state. This result proves that a time-dependent polarization of the controlling laser field gives access to the observation of additional dynamics on different electronic states. Note that all other experimental parameters in the two cases of Fig.1 were identical (pulse intensities etc.), so that the differences in the observed transients are entirely due to light polarization properties. This type of polarization sensitivity can then be exploited even in much more generality in connection with femtosecond laser pulse shaping.

For this purpose, the experimental setup is complemented by a polarization pulse shaper [5] and a computer with the optimization algorithm. We performed two types of adaptive control experiments to maximize the $K_2^+$ yield: spectral polarization-and-phase laser pulse shaping as well as phase-only shaping. In both cases the same number of free parameters is optimized and the two strategies are run in a parallel implementation. This ensures identical experimental conditions in terms of the molecular beam parameters and laser performance, allowing us to compare the results directly. The evolution of the $K_2^+$ signal as a function of generation number within the evolutionary algorithm is shown in Fig.2. The increase for phase-only pulse shaping (solid circles) is due to the adaptation of the laser pulse structure to the vibrational dynamics of the potassium dimer, providing high laser intensities when the wavepacket is in a suitable Franck–Condon region. This general type of mechanism is what had been exploited and discussed in the theoretical and experimental literature on quantum control to date.

However, when the additional mechanism of light-polarization control is used (open circles), one can go beyond the limitations set by linearly polarized fields, and achieve significantly higher product yields. This demonstrates not just a quantitative improvement but rather a qualitative extension of quantum control mechanisms, because it goes beyond one-dimensional addressing of transition dipoles and rather makes use of their directional properties by shaping the polarization state of the controlling laser pulse.

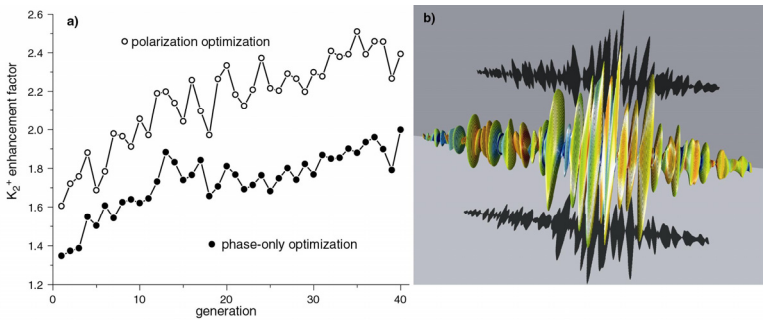


**Fig. 2.** a) Evolution curves show the $K_2^+$ ion yield relative to that obtained with an unshaped laser pulse. b) Quasi-three-dimensional representation of the optimal polarization-shaped laser pulse. Time evolves from −1.5ps (left) to +1.5ps (right), and electric field amplitudes are indicated by the sizes of the corresponding ellipses. The momentary frequencies are indicated by colors and the shadows represent the amplitude envelopes of the two orthogonal components.

Fig.2b) shows a representation of the best laser pulse shape reached in the final generation of the polarization optimization. The momentary frequency and the polarization state of the optimized pulse changes substantially in a complex fashion as a function of time. Some reasons for this complexity are briefly discussed now. First, the detection step in this experiment (i.e., the ionization) needs to be considered in more detail. Observation of $2^1\Pi_g$ state dynamics in our pump–probe measurement (Fig.1) proves that ionization from the $2^1\Pi_g$ is dependent on the internuclear distance and occurs predominantly at the outer turning point [4]. Another reason for the complicated pulse structure is the broad spectrum of the ultrashort laser pulse. The vibrational dynamics of the potassium dimer are known to depend strongly on the center frequency of the excitation laser pulse [4]. In our case this means that the optimized polarization needs to be provided for a wide distribution of frequencies and timings. While all these factors complicate the analysis and interpretation efforts of the optimal pulse shape, the important point is that despite of the complexity an optimized electric field time-varying polarization indeed has been exploited by the evolutionary learning algorithm as a novel control agent.

In conclusion we have demonstrated that time-dependent shaping of femtosecond light polarization can give access to a further level of control of quantum systems. Comparative optimizations of $K_2^+$ yield show that polarization laser pulse shaping is superior to phase-only shaping, because the vectorial electric field can adapt to the time evolution of the polarization-dependent transition dipole moments. We have hence exploited the vectorial properties of light–matter interaction to achieve quantum control in a molecular model system.

## References

1 T. Brixner and G. Gerber, ChemPhysChem 4, 418, 2003.
2 A. M. Weiner, Rev. Sci. Instrum. 71, 1929, 2000.
3 T. Brixner and G. Gerber, Opt. Lett. 26, 557, 2001.
4 C. Nicole et al., J. Chem. Phys. 111, 7857, 1999.
5 T. Brixner, G. Krampert, P. Niklaus, and G. Gerber, Appl. Phys. B 74, S133, 2002.