

Quantum Control by Ultrafast Polarization Shaping

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We demonstrate that the use of time-dependent light polarization opens a new level of control over quantum systems. With potassium dimer molecules from a supersonic molecular beam, we show that a polarization-shaped laser pulse increases the ionization yield beyond that obtained with an optimally shaped linearly polarized laser pulse. This is due to the different multiphoton ionization pathways in K_2 involving dipole transitions which favor different polarization directions of the exciting laser field. This experiment is a qualitative extension of quantum control mechanisms which opens up new directions giving access to the three-dimensional temporal response of molecular systems.

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Coherent control is a powerful method which allows one 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, among others the control of chemical reactions [3–5], molecular population transfer [6–9], atomic multiphoton absorption [10], Rydberg wave packets [11], high-harmonic generation [12], crystal lattice vibrations [13], or single-pulse Raman spectroscopy [14]. In all of these experiments, the spectral-temporal intensity and phase characteristics of laser fields are manipulated and exploited in a sophisticated manner, in many cases employing automated learning loops based on experimental feedback [15–17]. “Conventional” pulse shaping [2], however, accesses only the scalar properties of ultrashort laser pulses, while the electric field is a vectorial quantity. Since quantum systems and their wave functions are three-dimensional objects, the use of polarization as an active agent could tremendously increase the degree of attainable control. The same is true for any type of nonlinear optical spectroscopy, where to date the polarization states of the employed light fields (continuous wave or pulsed) have always been constant in time.

We have developed femtosecond polarization pulse shaping techniques [18–20] by which the polarization state of light (i.e., degree of polarization ellipticity and orientation of elliptical principal axes) as well as the temporal intensity and the momentary oscillation frequency can be varied as functions of time within a single femtosecond laser pulse. Time-dependent polarization states have been suggested, for example, for the generation [21,22] and characterization [23] of attosecond light pulses, optical control of lattice vibrations [24], and the selective production of enantiomers [25,26]. Simple time-dependent polarization profiles (without using pulse shapers) had already been exploited in several experi-

ments on optical [27,28], atomic [29], and molecular systems [30]. In an optical demonstration experiment, we have recently implemented adaptive shaping of complex polarization profiles within a learning loop [20], and Oron *et al.* have used spectral modulation of phase and polarization direction in coherent anti-Stokes Raman spectroscopy [31].

However, the prospect for manipulating light-matter interactions in three dimensions using complex polarization-modulated laser pulses goes beyond these initial suggestions or demonstrations. While this interaction is governed by the scalar product $\vec{\mu} \cdot \vec{E}(t)$, in most experimental and theoretical studies on quantum control or nonlinear spectroscopy the vectorial character of $\vec{E}(t)$ is ignored completely and only $\mu E(t)$ is considered. However, if the momentary polarization 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. This opens many experimental perspectives, e.g., controlling which dipole transitions are allowed at any particular time during a wave packet evolution. Thus, one can address and exploit the spatiotemporal properties of quantum wave functions.

In the work reported here, we carry out molecular quantum control making explicit use of polarization variation on an ultrashort time scale, i.e., the duration of the bandwidth-limited laser pulse [32]. 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 [33] populates the $2^1\Pi_g$ state as an intermediate before the final ionization step [Fig. 1(a)]. The $2^1\Pi_g$ state can be reached from the $X^1\Sigma_g^+$ ground state by a two-photon process with intermediate wave packet propagation in the $A^1\Sigma_u^+$ state. This pathway is strongly polarization dependent because according to selection rules the two involved electronic transitions,

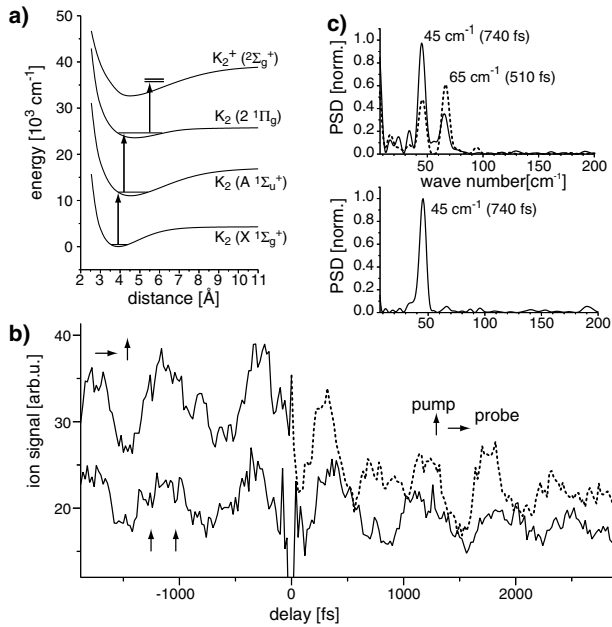


FIG. 1. (a) Calculated potential energy curves [33] of the potassium dimer system. Only those curves are shown which are relevant at the central excitation wavelength of $\lambda = 785 \text{ nm}$ used in this experiment. (b) Section of pump-probe transients with mutually parallel (solid line) and crossed (dashed line) linear polarizations around delay time zero. (c) Fast-Fourier-transform (FFT) analysis of pump-probe transients with parallel (lower graph) and crossed (upper graph) mutual polarizations. The numbers in brackets indicate the vibrational period of the associated wave packet motion. The FFTs have been performed over time periods from -4 ps to 0 ps for crossed polarizations (negative delays, solid line), 0 to $+4 \text{ ps}$ for crossed polarizations (positive delays, dotted line), and 0 to $+3 \text{ ps}$ (parallel polarizations, solid line, identical at negative delay times).

$A^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ and $2^1\Pi_g \leftarrow A^1\Sigma_u^+$, require electromagnetic fields with polarizations parallel and perpendicular to the molecular axis, respectively. This means that for maximum population of the $2^1\Pi_g$ state one needs a laser pulse sequence in which the correct direction of the electric field vector is provided at the appropriate Franck-Condon transition windows reached during vibrational wave packet motion. The enhancement factor for polarization-shaped laser pulses can be estimated in a simple model. Consider an isotropic ensemble of quantum systems in which two subsequent transitions require two electromagnetic fields with mutually perpendicular polarizations. If one employs two laser pulses with the same linear polarization, only the projections of the polarization vector onto the involved dipole moments of the randomly oriented systems contribute to the transition rates. The total transition rate is then given by averaging over the isotropic ensemble. For comparison, then, if the polarizations of the two laser pulses are perpendicular to each other the averaging procedure gives a yield that is enhanced by a factor of 2. Further advantages of polarization shaping arise if the quantum systems are aligned or

oriented with respect to the incoming light fields [34,35]. Optimal control of the multiphoton ionization process therefore requires both adjustment of the temporal intensity profile (to maximize the transition probability in the Franck-Condon regions) as well as variation of the polarization direction to fulfill the appropriate selection-rule requirements. Such a scheme cannot be achieved with shaped laser pulses of only one polarization component.

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 [36,37]. The experimental setup consists of a supersonic molecular-beam apparatus with a linear time-of-flight (TOF) mass spectrometer. Both pump and probe laser pulses have an energy of 150 nJ and are focused with a 500 mm lens onto a molecular beam of potassium dimers, thus avoiding strong field effects.

First, we used equally intense pump and probe laser pulses both polarized parallel to the TOF axis. The amount of K_2^+ as a function of pump-probe delay [Fig. 1(b), 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. 1(b), 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. It indicates that a certain final quantum state (in our case the K_2^+ ion) can be more efficiently reached by a time-dependent polarization of the controlling laser field.

Fourier analysis of the pump-probe transients reveals that for mutually parallel pump and probe polarizations [Fig. 1(c), bottom graph] only the dynamics in the $2^1\Pi_g$ state with a vibrational period of 740 fs [33] (corresponding to 45 cm^{-1}) is visible. For mutually perpendicular pump and probe polarizations [Fig. 1(c), upper graph], an additional Fourier peak is found at 65 cm^{-1} (corresponding to 510 fs), 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 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, providing a qualitatively novel mechanism for the control of quantum systems. In the following, we use flexible and automated polarization and phase shaping of femtosecond laser pulses in combination with an evolutionary algorithm to control molecular dynamics and, in this case, maximize ionization of K_2 .

For this purpose, the experimental setup is complemented by a polarization pulse shaper and a computer with the optimization algorithm (Fig. 2). For polarization

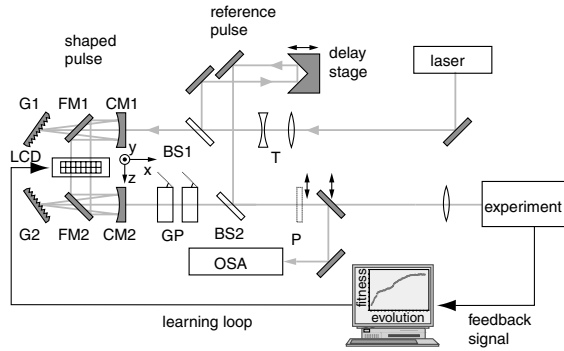


FIG. 2. Experimental setup. The pulse shaper that creates time-dependent polarization profiles consists of a telescope (T), cylindrical mirrors (CM), optical gratings (G), folding mirrors (FM), a two-layer liquid-crystal display (LCD), and a stack of glass plates at Brewster's angle (GP) to provide equal intensity and independently shaped polarization components at the output. Pulse characterization is carried out by experimentally calibrated Jones-matrix analysis [19] and dual-channel spectral interferometry with the help of a characterized and appropriately delayed reference pulse. For this purpose, shaped pulse and reference pulse are recombined collinearly along the beam path towards the experiment by a beam splitter (BS2), and the spectral interferences are recorded by an optical spectrum analyzer (OSA). A polarizer (P) selects the polarization component that is analyzed. During the actual experiment, the polarizer is removed and the reference pulse is blocked. Shaped pulses then interact with a seeded molecular beam of K_2 . Ion yields are measured in a TOF mass spectrometer and used as feedback signal in an evolutionary learning algorithm.

shaping [1,18–20], the linearly polarized input pulses (30 fs, 785 nm) are dispersed onto a two-layer liquid-crystal display (LCD) within a $4f$ -configuration zero-dispersion compressor. By applying specific voltages to the 2×128 independent LCD pixels contained in the two layers, spectral phase modulation can be imposed independently onto two orthogonal polarization directions. The interference of the resulting elliptically polarized spectral components leads to complex evolutions of the polarization state in the time domain. If the same phase function is applied to both LCD layers, the linear input polarization is maintained and conventional phase-only pulse shaping can be realized. In the actual experiment, shaped 300 nJ laser pulses are used instead of the unshaped pump and probe laser pulses.

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 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. 3. The increase for phase-only pulse shaping (solid circles) is due to the adaptation of the laser pulse structure

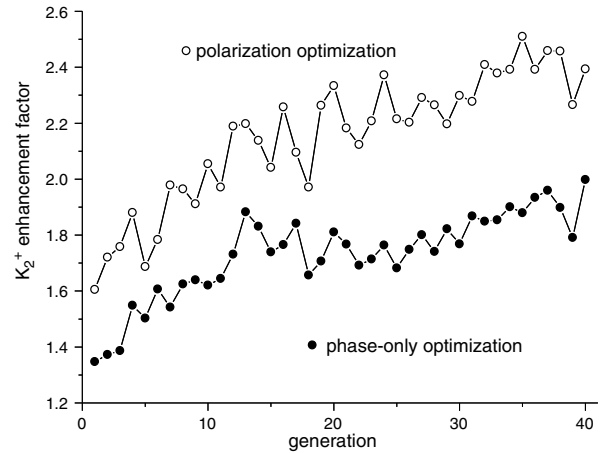


FIG. 3. Evolution curves show the K_2^+ ion yield relative to that obtained with an unshaped laser pulse. The best individual of each generation for the polarization optimization (open circles) and phase-only optimization (solid circles) is shown.

to the vibrational dynamics of the potassium dimer, providing high laser intensities when the wave packet 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.

Figure 4 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 [33]. Ionization, for example, can occur via doubly excited, autoionizing states [38]. Excitations of these doubly excited states via the outer turning point in the $2^1\Pi_g$ state as well as transitions involving the $4^1\Sigma_g^+$ state have not been considered. 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 [33]. In our case, this means that the optimized polarization needs to

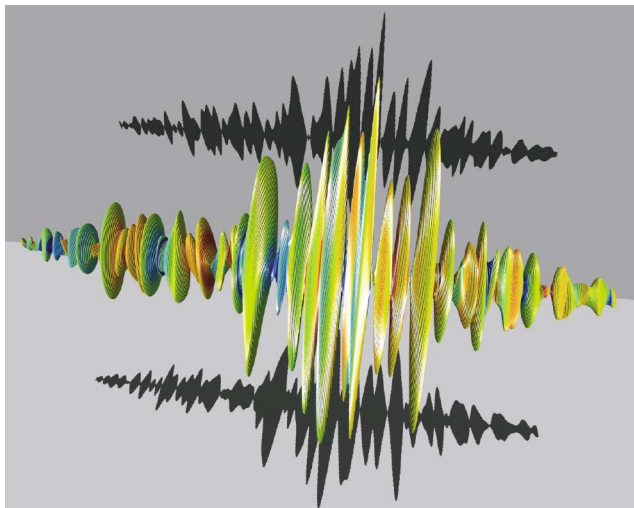


FIG. 4 (color online). Quasi-three-dimensional representation of the optimal polarization-shaped laser pulse. Time evolves from -1.5 ps (left) to $+1.5$ ps (right), and electric field amplitudes are indicated by the sizes of the corresponding ellipses. The momentary frequencies are indicated by colors or gray shading, and the shadows represent the amplitude envelopes of the two orthogonal components.

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 the complexity an optimized electric field with 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. This opens the door to a number of new experimental schemes exploiting the full vectorial temporal response of systems, allowing one to address stereochemical aspects in quantum control such as chiral selectivity. The optical control of lattice vibrations [13] and the generation of attosecond light pulses [21,22] are further examples of numerous new perspectives.

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- [1] T. Brixner and G. Gerber, *Chem. Phys. Chem.* **4**, 418 (2003).
- [2] A. M. Weiner, *Rev. Sci. Instrum.* **71**, 1929 (2000).
- [3] A. Assion *et al.*, *Science* **282**, 919 (1998).
- [4] R. J. Levis, G. M. Menkir, and H. Rabitz, *Science* **292**, 709 (2001).
- [5] C. Daniel *et al.*, *Science* **299**, 536 (2003).
- [6] C. J. Bardeen *et al.*, *Chem. Phys. Lett.* **280**, 151 (1997).
- [7] T. C. Weinacht, J. L. White, and P. H. Bucksbaum, *J. Phys. Chem. A* **103**, 10166 (1999).
- [8] T. Brixner, N. H. Damrauer, P. Niklaus, and G. Gerber, *Nature (London)* **414**, 57 (2001).
- [9] J. L. Herek *et al.*, *Nature (London)* **417**, 533 (2002).
- [10] D. Meshulach and Y. Silberberg, *Nature (London)* **396**, 239 (1998).
- [11] T. C. Weinacht, J. Ahn, and P. H. Bucksbaum, *Nature (London)* **397**, 233 (1999).
- [12] R. Bartels *et al.*, *Nature (London)* **406**, 164 (2000).
- [13] T. Feurer, J. C. Vaughan, and K. A. Nelson, *Science* **299**, 374 (2003).
- [14] N. Dudovich, D. Oron, and Y. Silberberg, *Nature (London)* **418**, 512 (2002).
- [15] R. S. Judson and H. Rabitz, *Phys. Rev. Lett.* **68**, 1500 (1992).
- [16] D. Yelin, D. Meshulach, and Y. Silberberg, *Opt. Lett.* **22**, 1793 (1997).
- [17] T. Baumert *et al.*, *Appl. Phys. B* **65**, 779 (1997).
- [18] T. Brixner and G. Gerber, *Opt. Lett.* **26**, 557 (2001).
- [19] T. Brixner, G. Krampert, P. Niklaus, and G. Gerber, *Appl. Phys. B* **74**, S133 (2002).
- [20] T. Brixner *et al.*, *J. Opt. Soc. Am. B* **20**, 878 (2003).
- [21] P. B. Corkum, N. H. Burnett, and M. Y. Ivanov, *Opt. Lett.* **19**, 1870 (1994).
- [22] M. Y. Ivanov, P. B. Corkum, T. Zuo, and A. D. Bandrauk, *Phys. Rev. Lett.* **74**, 2933 (1995).
- [23] E. Constant, V. D. Taranukhin, A. Stolow, and P. B. Corkum, *Phys. Rev. A* **56**, 3870 (1997).
- [24] M. M. Wefers, H. Kawashima, and K. A. Nelson, *J. Chem. Phys.* **108**, 10248 (1998).
- [25] Y. Fujimura *et al.*, *Chem. Phys. Lett.* **306**, 1 (1999).
- [26] M. Shapiro, E. Frishman, and P. Brumer, *Phys. Rev. Lett.* **84**, 1669 (2000).
- [27] W. J. Walecki, D. N. Fittinghoff, A. L. Smirl, and R. Trebino, *Opt. Lett.* **22**, 81 (1997).
- [28] C. Altucci *et al.*, *Phys. Rev. A* **58**, 3934 (1998).
- [29] M. Kakehata *et al.*, *Appl. Phys. B* **70**, S207 (2000).
- [30] D. N. Villeneuve *et al.*, *Phys. Rev. Lett.* **85**, 542 (2000).
- [31] D. Oron, N. Dudovich, and Y. Silberberg, *Phys. Rev. Lett.* **90**, 213902 (2003).
- [32] T. Brixner, *Appl. Phys. B* **76**, 531 (2003).
- [33] C. Nicole *et al.*, *J. Chem. Phys.* **111**, 7857 (1999).
- [34] H. Stapelfeldt and T. Seideman, *Rev. Mod. Phys.* **75**, 543 (2003).
- [35] A. Ulman, *Chem. Rev.* **96**, 1533 (1996).
- [36] U. Hefter *et al.*, *J. Chem. Phys.* **85**, 286 (1986).
- [37] H. Hulsman and J. Korving, *J. Chem. Phys.* **95**, 5719 (1991).
- [38] T. Baumert, M. Grosser, R. Thalweiser, and G. Gerber, *Phys. Rev. Lett.* **67**, 3753 (1991).