PRL **99,** 183902 (2007) PHYSICAL REVIEW LETTERS week ending 2 NOVEMBER 2007

Laser Steered Ultrafast Quantum Dynamics of Electrons in LiH

F. Remacle,[1,2,*] M. Nest,[3] and R. D. Levine[2,4]

[1]*Département de Chimie, B6c, Université de Liège, B4000 Liège, Belgium*
[2]*The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*
[3]*Institut für Chemie, Universität Potsdam, 14476 Potsdam, Germany*
[4]*Department of Chemistry and Biochemistry, The University of California–Los Angeles, Los Angeles, California 90095-1569, USA*

(Received 30 June 2007; published 1 November 2007)

The response of the electronic system of LiH to a few-cycle strong field is computed by a time-dependent multiconfiguration method using a large, adaptive, basis set. The intensity, pulse duration, polarization, and phase of carrier frequency can all be tuned to steer the motion of the electrons. It is shown possible to, e.g., direct the electrons to move along the Li-H bond or normal to it. By shifting the phase, the electrons can be driven toward the Li nucleus or away from it. When the pulse is polarized not along the bond the result is a rotation of the charge density.

DOI: 10.1103/PhysRevLett.99.183902 PACS numbers: 42.65.Re, 31.10.+z, 33.80.−b, 82.53.Kp

Few-cycle ultrashort pulses in the soft x-ray region have been used to ionize atoms and simple molecules [1–3]. The shorter wavelength of such pulses means that few cycles of light can be contained in an envelope whose width is sub fs (femtosecond), thereby giving rise to the new attosecond physics [4,5]. The chemical properties of molecules are governed by the valence electrons. To excite bound motions of the valence electrons requires light of lower frequencies, typically in the UV. The envelope of the pulse must then necessarily be longer [6]. We here explore the interaction of a molecule with such a pulse at a realistic quantitative level of computation. It is shown that even at the high powers required to pump a sizable fraction of molecules it is possible to coherently excite only a few states and thereby maintain tight control over the dynamics of the electrons. Developing few-cycle sources in the near UV region will allow access to a hitherto unexplored post Born-Oppenheimer regime where real time electron dynamics is pumped in an interval shorter than and comparable to the onset of the motion of the heavier nuclei.

The time scale of chemistry is the duration of the chemical change that for direct processes is the time scale of nuclear motions. It will be of particular interest to modify the dynamics of the nuclei and thereby control reactivity through pumping different electron dynamics.

This Letter deals with the quantitative assessment of the pumping of electrons in molecules on a time scale comparable to the electronic period. (The period is defined by the frequency difference between adjacent states.) To describe the electronic dynamics the wave function is expanded in a large adaptive basis using time-dependent coefficients [7,8]. The initial state is the ground state, so the early time dependence arises because of switching the laser on. A key observation is that despite the almost sudden onset of large amplitude motion induced by the few-cycle pulse [9], only a few states are excited with the result that the response of the electrons is not multiply periodic. When in our computation the pulse intensity is increased enough to significantly populate higher lying states and as these are nearer in energy, their interference does result in more complex motions. Another characteristic is that the system preferentially responds to the highest field amplitude in the pulse so there are no transients that occur while the field strength changes rapidly. Once the electrons respond to the field, the orbital of an electron, determined in a mean field self-consistent procedure, changes with time also because of the oscillation in time of the mean field due to the other electrons.

The temporal evolution of the electrons is described by a multiconfiguration time-dependent self-consistent field approach [7,8]; see also [10,11], where the N electrons wave function $\Psi(\mathbf{x}_1, \ldots, \mathbf{x}_N; t)$ is expressed as a linear combination of Slater determinants with time-dependent coefficients $A_J(t)$, $|\Psi(t)\rangle = \sum_J A_J(t)|J(t)\rangle$. Each determinant, $|J(t)\rangle$, is itself time dependent, being an antisymmetrized product of N time-dependent (spin) orbitals. The index J lists the N spin orbitals. The N orbitals are expressed as linear combinations of M atomic basis functions, and they are continuously adapted as the time evolution unfolds. For LiH the atomic basis is a triple zeta Gaussian basis set with polarization and diffuse functions, 6-311 ++ $G(2df, 2p)$, which comprises 49 Cartesian atomic orbitals. These are used to construct 10 time-dependent spin orbitals for 4 active electrons giving rise by a combinatorial counting of all states to 210 determinants.

We determine the dynamics for such short times that the Hamiltonian of the system has frozen nuclear positions. It then is the familiar N electron Hamiltonian, including the nuclear Coulomb repulsion terms plus any time-dependent external field that can perturb the electrons. In the dipole approximation the coupling to the electrical field is a sum of one electron operators, $V = (\sum_{i=1}^{N} \mathbf{r}_i)\mathbf{E}(t)$.

$$\mathbf{E}(t) = \mathbf{E}[\exp(-(t - t_0)^2/2\sigma^2)]\cos(\omega_0 t + \phi). \quad (1)$$

The field envelope is Gaussian, centered at t_0 with a width σ, the carrier frequency is ω_0, and φ is the phase of the carrier wave. The components of the vector **E** define the field strength in the different directions. A one cycle pulse means that $\omega_0\sigma \geq \pi$ but not much more.

The wave function is propagated in time using equations of motion derived from a variational principle [7,8]. The time evolution of the amplitudes $A_J(t)$ of the different determinants that are used to express the wave function is generated by the full Hamiltonian

$$dA_J(t)/dt = -(i/\hbar)\sum_K \langle J(t)|H|K(t)\rangle A_K(t). \qquad (2)$$

The equations of motion are solved by representing operators as matrices in the M dimensional atomic basis set. The time dependence of the orbitals and of the expansion coefficients does not cease after the pulse is off. This is because we excite a coherent superposition of eigenstates and so the charge density will continue to move with time as is discussed below. The orbitals dynamically adjust to this changing density.

A useful diagnostic of electronic absorption spectroscopy advocated by Heller is the autocorrelation function of the initial state, $C(t) = \langle\Psi(0)|\Psi(t)\rangle$. At the intensity that is used to compute the results shown in Fig. 1 about 90% of the ground state is depleted and the mean electronic energy has increased by about 0.2 au. The ionization energy of LiH is 0.29 au. Note how the depletion of the ground state is most rapid when the laser field is at maximal amplitude and that the phase shift φ of the carrier wave modulates the envelope as shown in Fig. 1 for $\varphi = 0$.

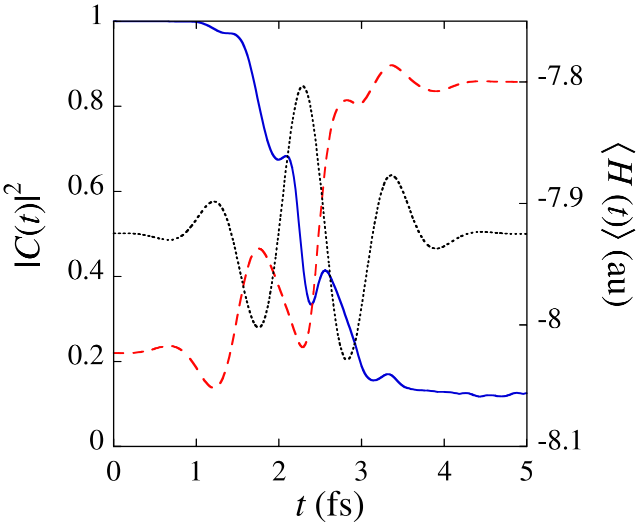

FIG. 1 (color online). The temporal evolution of the electronic excitation of LiH computed for a high power (field $|E| = 0.05$ au or 8.75×10^{13} W/cm^2) short ($\sigma = 28$ au or 0.68 fs) pulse at a carrier frequency $\omega_0 = 0.133$ au, and polarized in the xz direction A definite polarization requires aligning the molecule in a beam. $\langle H(t)\rangle = \langle\Psi(t)|H|\Psi(t)\rangle$. The time profile of the laser pulse is shown in the dotted line and the electronic energy uptake (dashed line) tracks the peaks in the field. The depletion of the ground state is shown as $|C(t)|^2$ (full lines) vs time.

At the intensity shown in Fig. 1, but if the laser is polarized along the bond axis, the z direction, about 70% of the ground state is depleted. In first order, dipole selection rules determine which states can be excited. For polarization along the z direction the Σ ground state can be one photon pumped to the lowest excited Σ and then higher Σ states can be reached by multiphoton transitions. The allowed transitions for x polarization are that the ground state can be pumped to the lowest Π state. Multiphoton transitions can reach higher states, of both Σ and Π symmetry, but the lowest excited states act as a bottleneck that takes a longer time to clear. For polarization along the xz direction it is also possible to connect the ground state coherently to the first excited Σ state and to the higher lying first excited Π state, which is not possible for a pure z polarization. When the z-polarized field is reduced by a factor of 5 the depletion is only about 10% and the perturbative limit of low depletion is reached when the field is further reduced.

To validate the method for LiH it is verified that the energies of the excited states determined by a Fourier transform of $C(t)$ match well computations performed by the MOLPRO [12] programming suite at the MC-SCF level (with 16 active MOs including the core orbital). By this comparison we know that higher excited states are described by our basis set and can be accessed by the dynamics. The transition dipoles to the lowest excited states computed at the MC-SCF level are $\langle\Sigma_{\mathrm{GS}}^+|\mu_z|\Sigma_1^+\rangle = 1.043$ au and $\langle\Sigma_{\mathrm{GS}}^+|\mu_{x,y}|\Pi\rangle = 1.407$ au. The sign of the transition dipole is relevant to the discussion below of the control provided by changing the phase shift.

The ground state of LiH is not quite Li$^+$H$^-$, but there is a definite excess of negative charge on the H atom. Upon electronic excitation to a more covalent Σ state electronic charge will move from the H to the Li atom. Similarly, exciting from the ground to Π states will move charge off the bond axis. Both these expectations are verified by the computational results; see Fig. 2. Consider first the electronic mean position ($\equiv$ the electronic dipole moment) in the z direction. Starting at $t = 0$ in the ground state, it is seen that the value of $\langle z\rangle(t) = \langle\Psi(t)|N^{-1}\sum_{i=1}^{N} z_i|\Psi(t)\rangle$ is near to the position of the H atom along the bond direction. (Li, being heavier than H, sits nearer to the center of mass, i.e., at $z = 0.397$ au.) Within the duration of the pulse $\langle z\rangle(t)$ moves toward 0, settling at an intermediate value for lower power, as expected when there is some significant amplitude remaining on the initial state. But at a higher laser power, when the ground state is almost depleted $\langle z\rangle(t)$ moves all the way to 0 and settles at about that value. The polarization is in the xz direction, so while for the cylindrically symmetric charge distribution in the ground state, $\langle x\rangle(t = 0) = 0$ the pulse displaces charge off the z axis to a significant extent.

While the time dependence of the orbitals and coefficients in the wave function is rather involved, it is still

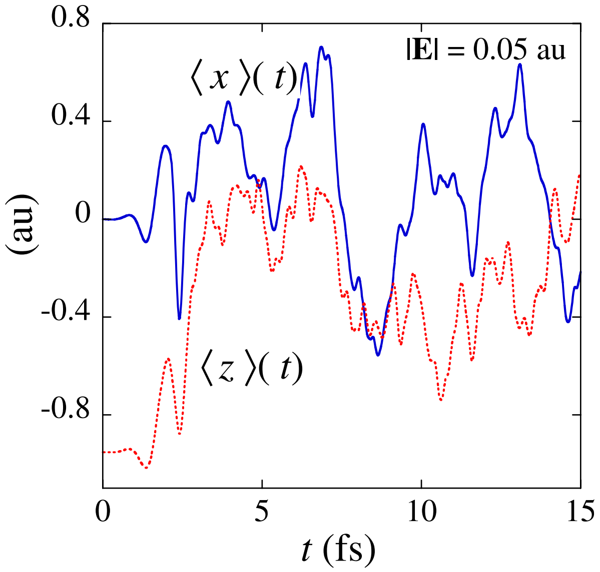

FIG. 2 (color online). The electronic dipole moment of LiH in the z and the x directions, $\langle z\rangle(t)$ and $\langle x\rangle(t)$, in au, computed vs time for a high power pulse, same as in Fig. 1. The bond length is 3.08 au. The period of the nuclear vibration is 24 fs and the electronic coherence is expected to dephase in a few vibrations.

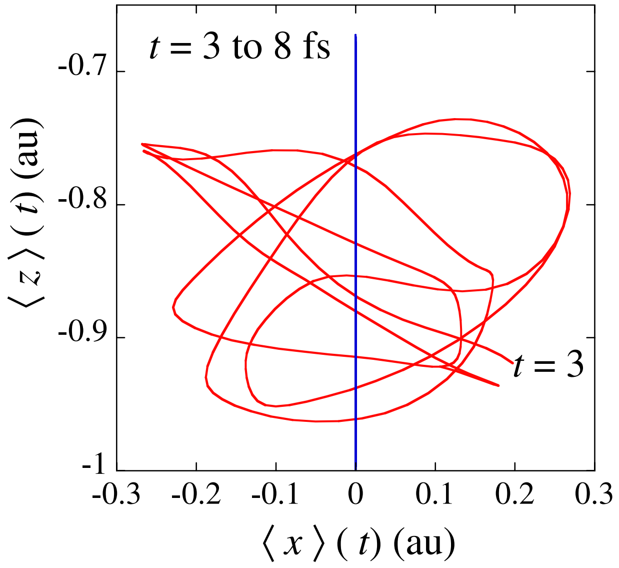

FIG. 3 (color online). The trajectory of the center of charge of the electronic density plotted in the zx plane at sequential equidistant time points, $3 < t$ (fs) < 8. The pulse, $|\mathbf{E}| = 0.025$ au, $\sigma = 0.26$ fs, is effectively over by 2 fs. Shown (curve) is the regular rotational motion after the field is off for a pulse polarized in the zx direction. A pulse polarized in the xy direction induces rotation in a perpendicular, xy, plane by pumping a coherent combination of excited Π states. A pulse polarized in the z direction pimps Σ states and the motion is oscillatory along the z axis as shown (vertical line).

possible to describe the evolution of the electronic wave packet as an interference of a few eigenstates where the beat frequency between two states will be proportional to their separation in energy. The fast oscillation corresponding to the beating between the ground state and the lower excited states can clearly be seen in Fig. 2. We emphasize that higher excited states can be accessed by the pulse and are seen to be accessed at much higher laser powers. It is a result of the computation rather than an assumption that even at quite high levels of excitation it is predominately the lower states of a given symmetry that are excited.

As seen in Fig. 2 the electronic density swings from above to below the x axis while it moves away from and then somewhat toward the Li atom along the z axis. This is the "rotational motion" of the electronic wave packet as discussed for a "sudden" excitation of a superposition of the lowest Σ and Π excited states of LiH [6]. To visualize this rotation Fig. 3 shows the motion of the electronic center of charge in the x-z plane. The trajectory shown is a series of points equidistant in time. It shows two trajectories, one for a pulse polarized in the zx direction and one for a polarization in the z direction. For the polarization in the zx direction, it is clear that initially the motion is very anharmonic, but even at the high power used at no time does the motion look turbulent. It takes an even higher power pulse to pump a coherent superposition of several excited states with very different beat frequencies so that the several interference terms makes the behavior look irregular. When the density of electronically accessible excited states is higher, e.g., in a polyatomic molecule, the high power laser could induce a stormy electronic density.

The temporal evolution of the electronic density is even more regular when the laser is polarized along the z direction. Now only states of Σ symmetry can be pumped, and the motion of the electronic charge density is confined to be along the Li-H bond. This is essentially the same kind of charge migration along the molecular backbone found upon sudden ionization [13].

The results shown in Fig. 3 demonstrate that high power few-cycle laser pulses can induce regular oscillatory motion of the electronic density. Only few characteristic frequencies contribute to the time evolution because there are only a few accessible electronic excited states. Otherwise, with many states coherently excited, the motion will be multiply periodic. The results shown in Figs. 1–3 also demonstrate that the excitation need not be strictly sudden and that even for a pulse that is about as wide in time as the period of the motion we want to set up, it is possible to induce and to characterize coherence effects. The real caveat is that in a short while the nuclei will start moving and likely dephase the electronic coherence.

The results shown in Fig. 3 further demonstrate that there is a laser power range where the ground state is significantly depleted, so that we are far from the lowest order limit, but where multiphoton pumping is not yet dominant. In this range one can not only induce clear dynamic effects, but it is also possible to offer simple

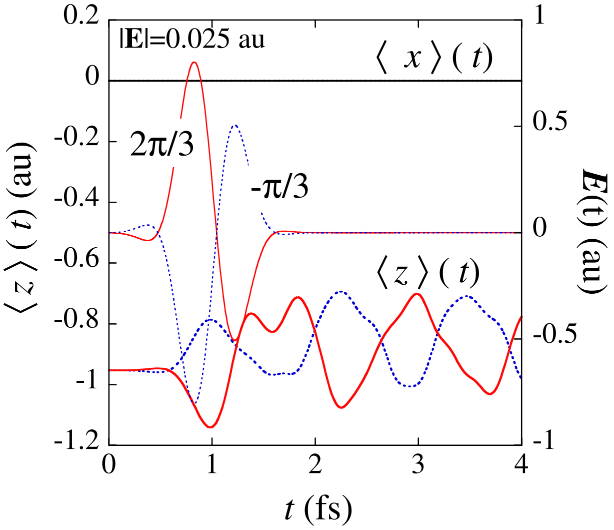

FIG. 4 (color online). Steering the charge density along the Li-H bond. Shown is the center of charge vs time and the profiles of two barely one cycle pulses, with a different phase $\varphi = 2\pi/3$ and $\varphi = -\pi/3$. The choice of phase means that the fields oscillate in opposite directions along the z axis as shown. The fields direct the charge density either toward the Li atom or away from it.

theoretical interpretation. As an example consider the rotational motion of the charge density as plotted in Fig. 3 for a laser polarized in the xz direction. For this case the exactly computed wave function can be approximated as

$$\Psi(t) \cong A_{\mathrm{GS}}(t)\Psi_{\mathrm{GS}} + A_{\Sigma}(t)\Psi_{\Sigma} + A_{\Pi_x}(t)\Psi_{\Pi_x}. \qquad (3)$$

Here each component eigenstate is a linear combination of determinants. The slowest term in $|\Psi(t)|^2$ is due to the beating between the lowest excited states of Σ and Π symmetry which have a spacing, at the equilibrium bond distance of the ground state of Li-H, of about 0.035 au. [For comparison the carrier frequency of the pump laser used for Fig. 3 is $\omega_0 = 0.133$ au (intermediate between the excitation frequency of the Σ and the Π states.)]

One can compute for pulses of several cycles. But with one or two cycle pulses a judicious choice of the phase φ of the carrier wave allows steering of the electronic density. Figure 4 shows that depending on the sign of the field at the time when its amplitude is maximal it sends the electronic density even further away from the Li nucleus, which is roughly at $z = 0.4$ au, or, and as in Fig. 2, it sends the density toward the Li.

In conclusion, computational results indicating that few-cycle pulses in the near UV region can selectively excite specific electron dynamics in the LiH molecule were presented. In the sparse electronic manifold of LiH with powers up to 10^{14} W/cm^2 the ultrafast pulse does not induce electronic turbulence. The low lying Σ and Π states that are dipole allowed from the ground state act as a bottleneck to further electronic excitation. Both rectilinear and circular motions of the charge density with respect to the axis of the molecule were demonstrated. The fastest modulation of the cloud charge is due to beating of the ground and excited electronic states. Linear motion is produced by a superposition of Σ electronic states. The direction of the motion is controlled through the phase shift of the carrier wave. A moderately slow rotational motion can be pumped as a coherent superposition of the lowest excited Σ and Π states.

This work was supported by the German-Israeli James Franck program on Laser-Matter Interaction. M. N. thanks the DFG for funding under Project No. SPP 1145. Resources for this research were also provided by the MOLDYNLOGIC STREP FET-Open EC project (www.moldynlo.ulg.ac.be) (F. R. and R. D. L.)

---

*Also at FNRS.

[1] S. Baker *et al.*, Science **312**, 424 (2006).
[2] M. F. Kling *et al.*, Science **312**, 246 (2006).
[3] H. Niikura, D. M. Villeneuve, and P. B. Corkum, Phys. Rev. A **73**, 021402 (2006).
[4] F. Krausz and M. Ivanov (to be published).
[5] A. Scrinzi *et al.*, J. Phys. B **39**, R1 (2006).
[6] F. Remacle R. Kienberger, F. Krausz, and R. D. Levine, Chem. Phys. **338**, 342 (2007).
[7] M. Nest, T. Klamroth, and P. Saalfrank, J. Chem. Phys. **122**, 124102 (2005).
[8] M. Nest, P. Padmanaban, and P. Saalfrank, J. Chem. Phys. **126**, 214106 (2007).
[9] A. D. Bandrauk, S. Chelkowski, and H. S. Nguyen, Int. J. Quantum Chem. **100**, 834 (2004).
[10] T. Kato and H. Kono, Chem. Phys. Lett. **392**, 533 (2004).
[11] J. Caillat *et al.*, Phys. Rev. A **71**, 012712 (2005).
[12] H.-J. Werner and P. J. Knowles, MOLPRO suite of programs (version 2002.6, 2002).
[13] F. Remacle and R. D. Levine, Proc. Natl. Acad. Sci. U.S.A. **103**, 6793 (2006).