Formation of Ground-State Vibrational Wave Packets in Intense Ultrashort Laser Pulses

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The formation of coherent vibrational wave packets in the electronic ground state of neutral molecules in intense ultrashort laser pulses and their subsequent detection by means of recently developed pump-probe experiments are discussed. The wave packet formation is due to the pronounced dependence of the strong-field ionization rate on the internuclear distance. This leads to a deformation of the initial wave function due to an internuclear-distance dependent depletion. The phenomenon is demonstrated with a time-dependent wave packet study for molecular hydrogen.

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The rapid development of laser technology and elaborate detectors allows nowadays a very detailed study of the behavior of atoms and molecules exposed to intense ultrashort laser pulses. There is an increasing interest in effects that are specific to molecules, like bond softening, light-induced states, and enhanced ionization (see, e.g., [1] for a recent overview) or suppressed ionization (see, e.g., [2] and references therein). Furthermore, the interplay of the recurrence time of the electrons ejected in one cycle of a laser pulse and the periodic motion of the nuclear wave packet created in the ionization process leads to the concept of molecular clocks [3]. Also the influence of the additional nuclear degrees of freedom in molecules on the strong-field ionization process itself has attracted recent attention. For example, a strong dependence of the ionization rate on the internuclear separation R was claimed to be responsible for a pronounced deviation from the Franck-Condon distribution found for H_2^+ produced from strong low-frequency field ionization of H_2 [4]. Another consequence of this R dependence, the creation of a coherent vibrational wave packet in the electronic ground state of H_2, is the subject of this Letter.

While the preparation of vibrational wave packets in excited electronic states is nowadays a very well-developed field, there are only a few approaches that deliver wave packets in the electronic ground state of a molecule. For homonuclear diatomic molecules with forbidden dipole transitions between vibrational levels of the same electronic state, excited electronic states are involved either directly (pump-dump experiments) or indirectly (stimulated Raman scattering) in the wave packet formation [5]. While these states are easily accessible with optical photons for alkali dimers, such schemes require coherent photons of very large frequency for a molecule like H_2. Theoretically proposed schemes like Raman chirped adiabatic passage [6] are quite demanding as they require chirped pulses (with correct energy difference) and work only for sufficiently strong Raman transitions, since otherwise the required very long pulse duration at high-intensity favors ionization [7]. Another approach to produce ground-state wave packets is NeNePo (negative-neutral-positive), where first an anion is created whose vibrational wave function is then mapped onto the potential curve of the ground state of the neutral by a fast ionization step [8]. The creation mechanism of a ground-state wave packet that does not require a resonant coupling to an excited state or the intermediate formation of an anion and is thus very robust is discussed here for the specific example H_2. Its occurrence is due to a purely quantum-mechanical effect, the nonuniform depletion of the wave packet which we name *Lochfraß* (the German word for eating a hole or pitting corrosion). In fact, this effect occurs in currently available ultrashort laser pulses and thus has to be accounted for in a proper theoretical analysis. A direct verification of the predicted effect via a pump-probe experiment is proposed for available laser parameters. This allows the so far fastest molecular motion to be observed in real time [9].

The time-dependent Hamiltonian describing the vibrational motion of H_2 in the presence of the laser field is given within the Born-Oppenheimer approximation by $\hat{H} = \hat{H}_0 + \hat{V}$. Here, $\hat{H}_0$ is the time-independent Hamiltonian describing the motion of the nuclei (in the relative internuclear-distance coordinate R) on the field-free electronic ground-state potential curve of H_2, and the time-dependent operator $\hat{V}$ describes the interaction with the laser pulse. Instead of solving the full problem (requiring the solution of the interaction of the electrons with the laser pulse), the ionization process can be incorporated as a loss channel by means of an imaginary potential $W(R, t)$ that is equal to the ionization rate. This leads to the time-dependent Schrödinger equation (in a.u.)

$$\left(\hat{H}_0 - i\frac{W(R,t)}{2}\right)\Psi(R,t) = i\frac{\partial}{\partial t}\Psi(R,t) \qquad (1)$$

with the time-dependent nuclear wave function $\Psi(R, t)$.

In the present work, laser pulses with relatively low frequency (800 nm) and comparatively high intensity are considered. This corresponds to the quasistatic regime, and thus W can be approximated by the ionization rate of H_2 exposed to a strong static field. Such static R-dependent rates have been calculated for H_2 in a nonperturbative, fully correlated way [10], but only for a limited number of field strengths. Therefore, the simple tunneling model extended empirically to the high-intensity regime proposed in [11] was used to interpolate the *ab initio* data for arbitrary field strengths. As was shown in [12] the R dependence of the ionization rate of H_2 is well reproduced by atomic models using an R dependence of the vertical ionization potential, as was proposed in [13]. In the fit formula given in [11] the ionization potential I_p is thus substituted with the R-dependent quantity $E^{H_2^+}(R) - E^{H_2}(R)$, where $E^{H_2}(R)$ and $E^{H_2^+}(R)$ are the Born-Oppenheimer potential curves of the H_2 and H_2^+ electronic ground states, respectively. As a result, the rates and thus W increase exponentially with R. This R dependence of W leads to a correct prediction of the experimentally found vibrational distribution of H_2^+ produced in the ionization process of H_2 in strong laser fields and its pronounced deviation from the Franck-Condon predictions [4]. As is evident from Eq. (1), an R-independent W yields wave functions Ψ that have a norm that decays exponentially due to ionization, but remain eigenfunctions of $\hat{H}_0$. However, due to the R dependence of the ionization rate, Ψ will not remain an eigenstate of $\hat{H}_0$. Instead, a wave packet is created in the electronic ground state of neutral H_2.

A more accurate treatment would necessitate including also the real part of $\hat{V}$. This real part describes the field-induced shift and distortion of the potential curves. They have been calculated for H_2 [10] and are estimated to have only minor effects on the results for the field intensities considered in this work, if randomly oriented molecules are considered. The creation of a ground-state vibrational wave packet due to the time-dependent variation of the real part of $\hat{V}$ is a signature of bond softening in H_2 (not H_2^+). This effect was predicted only theoretically [10] and is an interesting topic by itself that will be discussed elsewhere. Its relative importance can be increased by lowering the intensity or using parallel aligned molecules and can be reduced by using perpendicular alignment. However, bond softening itself is now a well-established strong-field effect and can be classically understood by means of nuclei moving on distorted potential curves. The effect of *Lochfraß* discussed here is quite different, since it is intrinsically quantum mechanical and even conflicts with a statistical interpretation of quantum mechanics where a specific molecule would be either ionized or remain neutral, but in the latter case would not change its vibrational state. Thus already the occurrence of any excitation (even an incoherent one) by *Lochfraß* can be understood only from quantum mechanics, while quantum mechanics is necessary only for explaining the coherence of the wave packet created in the final state of an electronic excitation (or ionization).

In order to solve Eq. (1) numerically, the time-dependent nuclear wave function $\Psi(R, t)$ is expanded in terms of a linear combination of the field-free eigenstates $\phi_n(R)$ of $\hat{H}_0$. Inserting this ansatz into Eq. (1) yields a set of coupled first-order differential equations for the time-dependent coefficients of $\phi_n(R)$. Those equations are solved by an adaptive Runge-Kutta procedure. The $\phi_n(R)$ are expanded in a B-spline basis, using 502 B splines of order 8 distributed on a linear knot sequence covering the interval $[0, R_{\max}]$ with $R_{\max} = 10a_0$. A discretized description of the dissociative continuum is achieved by the finiteness of $R_{\max}$ and the imposed boundary condition $\phi_n(R_{\max}) = 0$.

In Fig. 1 the time evolution of wave function Ψ is shown for a 800 nm laser pulse with a $\cos^2$-shaped time envelope of 8 fs (full width) and peak intensity $I = 6.0 \times 10^{14}$ W/cm^2. In such a laser pulse the ionization rate peaks at the intensity maxima that are located around 3.5 and 4.5 fs. Most ionization occurs around these two intensity maxima as is reflected in a pronounced drop of the wave function norm between 3 and 4 fs and between 4 and 5 fs, respectively. A more detailed look reveals a deformation of the wave function due to the predominant depletion at large R values, which at 5 fs is, e.g., visible from a shift of the maximum of the wave function towards a smaller R value. Already at 6 fs this maximum has, however, moved back to larger R values. This is a consequence of Ψ being no longer an eigenstate of the electronic ground-state potential: the wave packet starts to move. In fact, as a result of the depletion at larger R the wave packet is initially accelerated towards the outer potential barrier as is more evident from Fig. 2 where the time-dependent expectation value of the internuclear distance R (mean value $\langle R \rangle = \langle \Psi(R, t)|R|\Psi(R, t)\rangle$) is shown for pulses with 8 and 12 fs pulse duration.

In the case of the 8 fs pulse the first electric field maximum within the ionization window leads to a decrease of $\langle R \rangle$ due to the preferential ionization at large R. After

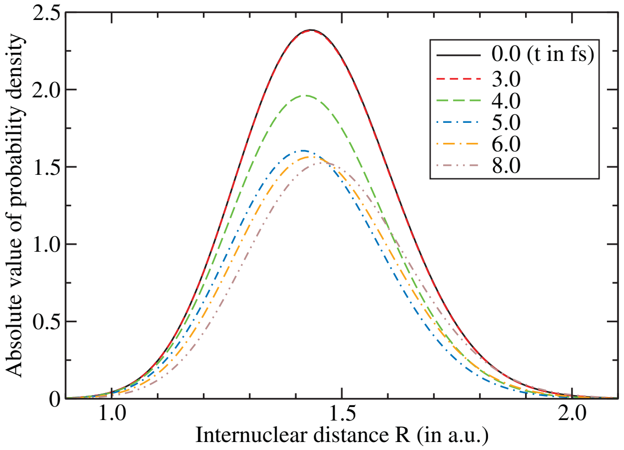

FIG. 1 (color). Time evolution of the H_2 ground-state wave function in a laser pulse of 8 fs duration (peak intensity, $I = 6 \times 10^{14}$ W/cm^2; wavelength, 800 nm; $t = 0$, onset of pulse).

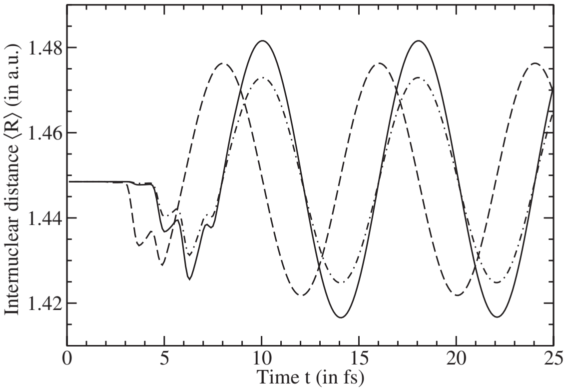

FIG. 2. Expectation value of $\langle R\rangle$ as a function of time during and after 800 nm laser pulses of 8 fs (dashed line) and 12 fs (solid line) duration and a peak intensity $I = 6.0 \times 10^{14}$ W/cm^2 ($t = 0$, onset of pulse). Also shown is the result for a 12 fs pulse but reduced peak intensity $I = 5.264 \times 10^{14}$ W/cm^2 (chain).

the field has passed this maximum at 3.5 fs, the decreasing field strength does not allow for further ionization while at the same time the wave packet starts to move to larger R values. This leads to a small increase of $\langle R\rangle$. However, the next cycle of the laser pulse leads again to a pronounced ionization around 4.5 fs. The preferred ionization of the large R component of the wave packet is reflected by the second decrease of $\langle R\rangle$. After this ionization step the now even more deformed wave packet is moving towards larger R values. The remaining field maxima are insufficient for further noticeable ionization. The wave packet moves towards the outer potential barrier where it is reflected at 8 fs. Afterwards, the wave packet motion is periodic, following its inherent time scale (about 8 fs) that is defined by the dominant wave packet components (and their energy difference). The resulting wave packet consists mainly of the vibrational ground state and the first excited one, the components (squared wave function coefficients) being 0.653 393 ($v = 0$), 0.004 412 ($v = 1$), and 0.000 005 ($v = 2$). For a pulse with the same peak intensity and wavelength, but a duration of 12 fs, a larger oscillation amplitude of $\langle R\rangle$ (0.065 instead of $0.054a_0$) is obtained, as is also shown in Fig. 2. This is reflected by larger components of the excited vibrational states in the wave packet: 0.533 269 ($v = 0$), 0.005 069 ($v = 1$), and 0.000 036 ($v = 2$).

In comparison to the 8 fs pulse the ionization window now comprises four active field maxima. A more detailed comparison of different pulse lengths shows that for the given peak intensity and wavelength the largest oscillation amplitudes of $\langle R\rangle$ are achieved for pulse lengths of about 12 to 14 fs. However, as will be discussed in detail elsewhere, a variation of the absolute phase of the laser pulse or its wavelength (within the validity of the quasistatic approximation) influences only the shape of the wave packet during the pulse, but has almost no influence on the final oscillating wave packet. Only very tiny changes in the amplitude are found, but the oscillation period and its absolute phase are practically unchanged. This is very important, since no pulses with stabilized absolute phase are required for forming the wave packet and also no problems due to the finite bandwidth of ultrashort lasers are expected. As is discussed in [9], the absolute phase can even be used to distinguish *Lochfraß* and bond softening induced wave packets. Short pulses are, however, required, because in long pulses the effect of the R dependence is washed out by nuclear motion. For a 50 fs pulse with $I = 4.0 \times 10^{14}$ W/cm^2 (similar ionization yield as the 12 fs pulse) the wave packet has the components 0.496 839 ($v = 0$) and 0.000 001 ($v = 1$).

In principle, higher peak intensities are advantageous for the wave packet formation. However, there is an upper limit to it, since the total number of nonionized molecules decreases with increasing intensity. For a peak intensity 6.0×10^{14} W/cm^2 the ionization yield increases, e.g., from 34% for the 8 fs pulse to 46% for the 12 fs one. In order to achieve only 34% ionization with a 12 fs pulse its peak intensity has to be reduced to 5.264×10^{14} W/cm^2. In this case the oscillation amplitude drops to $0.048a_0$ (see Fig. 2). The acceptable upper limit of the intensity depends finally on experimental parameters, especially the sensitivity to detect the created wave packet. A further and more subtle aspect with respect to the question of optimal pulse parameters is that the R dependence of the ionization rate depends itself on the intensity, as is discussed in [4]. Since the depletion of the wave function in sufficiently short pulses occurs at the internuclear distances with the highest ionization probability, further ionization can in fact be suppressed. This effect (which will be discussed in detail elsewhere) is a dynamical variant of the vibrationally suppressed ionization of molecules proposed in [13] where the time-independent version of Eq. (1) was discussed.

In the present case the motion of the created wave packet extends only to a small fraction out of the Franck-Condon window of the initial-state wave function. However, the same effect that is responsible for the creation of the wave packet, the pronounced R dependence of the strong-field ionization rate, provides also a detection tool. A pump-probe scheme with two time-delayed intense ultrashort laser pulses is thus proposed. Such a setup has very recently been achieved experimentally and applied to H_2 [14] where, however, the vibrational wave packet produced in H_2^+ was investigated.

In Fig. 3 the results for a pump-probe experiment investigating the ground-state vibrational wave packet in the neutral H_2 are simulated. The ionization yield of the probe pulse is plotted as a function of the delay time $t_{\rm del}$ between the maxima of two identical pulses (peak intensity is again 6.0×10^{14} W/cm^2). The wave packet motion reflects itself in an oscillation of the ionization yield. The oscillation depth is slightly larger (and thus the signal-to-noise ratio more favorable) for two 8 fs pulses than for two 12 fs pulses. The reason is evident. The 12 fs pump pulse is more efficient in creating a wave packet than a 8 fs pulse (of

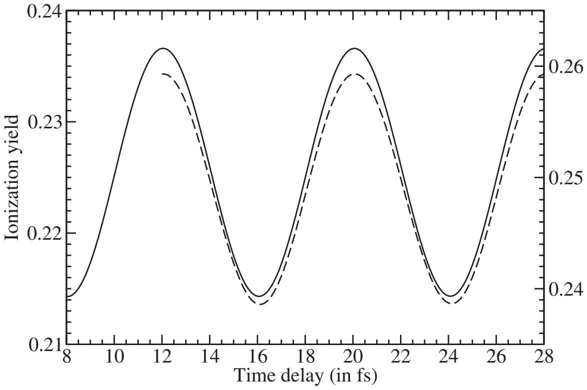

FIG. 3. Ionization yield predicted for the probe pulse of a pump-probe experiment with two identical pulses (800 nm, peak intensity $I = 6.0 \times 10^{14}\ \mathrm{W/cm^2}$) of either 8 (solid line, left scale) or 12 fs (dashed line, right scale) duration is shown as a function of the delay time between the two pulse maxima.

same peak intensity) as was discussed above. However, a probe pulse that is short compared to the dynamics induced by the pump pulse is, of course, favorable. The more efficient wave packet creation by the 12 fs pump pulse compared to its 8 fs counterpart is thus overcompensated by the larger convolution due to the broader probe pulse. Nevertheless, even in the nonoptimal case of two identical pulses used for pump and probe the oscillation of the ionization yield has a depth of about 10%. This ratio can be increased to 20 up to 25% when using more optimal pulse combinations like 12 fs for pumping and 4 fs for probing, but finally it will be experimental parameters like the sensitivity which decide on the optimum conditions. It is important to note that the ionization yield shown is the total yield and thus it includes a sum over all subsequent processes that are initiated by single ionization like sequential double ionization or Coulomb explosion. While this concerns the oscillation period, this is not necessarily true for the absolute phase. For example, the nondissociative (H_2^+) and the dissociative ($H + H^+$) ionization yields can oscillate out of phase as will be discussed in detail elsewhere (see also [9]).

The occurrence of an oscillating ionization yield as a function of the time delay is, of course, reflecting coherence of the wave packet. This coherence is destroyed by decoherence due to relaxation processes not incorporated in the model. The neglected radiative relaxation processes are, however, known to be unimportant on the time scales considered here, in particular, in the case of the dipole forbidden transitions in homonuclear diatomics. The experimental verification of the coherence of the wave packet is also highly exciting, since the creation process is rather unusual. Coherent vibrational wave packets are normally produced by a population transfer into the final state of a transition process, while in the present case it is formed by a depletion process. Although the terminology used, e.g., in [15] for explaining the ground-state wave packet created in resonant impulsive stimulated Raman scattering may appear to be similar to the one used here, the physical mechanisms are different. In the present scheme no coherent coupling to an excited state is involved.

The present work concentrated on the specific example of single ionization of H_2, since *ab initio* data exist for its R dependence (in the quasistatic approximation). Realistic parameters directly relevant for present experiments were adopted. In principle, the predictions of this work can easily be extended to other, possibly more favorable molecular systems, as long as at least a qualitatively correct dependence of the ionization rate on the nuclear geometry can be estimated. Following the arguments in [13], no wave packet formation is, e.g., expected for a similar molecular geometry of neutral and ion like N_2. For O_2 (antibonding highest occupied molecular orbital) a wave packet is to be expected, but the depletion will occur for small R values.

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[1] J. H. Posthumus, Rep. Prog. Phys. **67**, 623 (2004).
[2] T. K. Kjeldsen and L. B. Madsen, Phys. Rev. A **71**, 023411 (2005).
[3] H. Niikura, F. Légaré, R. Hasbani, A. D. Bandrauk, M. Y. Ivanov, D. M. Villeneuve, and P. B. Corkum, Nature (London) **417**, 917 (2002).
[4] X. Urbain, B. Fabre, E. M. Staicu-Casagrande, N. de Ruette, V. M. Andrianarijaona, J. Jureta, J. H. Posthumus, A. Saenz, E. Baldit, and C. Cornaggia, Phys. Rev. Lett. **92**, 163004 (2004).
[5] H. Schwoerer, R. Pausch, M. Heid, and W. Kiefer, Chem. Phys. Lett. **285**, 240 (1998).
[6] S. Chelkowski and G. N. Gibson, Phys. Rev. A **52**, R3417 (1995).
[7] S. Chelkowski and A. D. Bandrauk, J. Raman Spectrosc. **28**, 459 (1997).
[8] S. Wolf, G. Sommerer, S. Rutz, E. Schreiber, T. Leisner, L. Wöste, and R. S. Berry, Phys. Rev. Lett. **74**, 4177 (1995).
[9] Th. Ergler, B. Feuerstein, A. Rudenko, K. Zrost, C. D. Schröter, R. Moshammer, and J. Ullrich, Phys. Rev. Lett. **97**, 103004 (2006).
[10] A. Saenz, Phys. Rev. A **61**, 051402(R) (2000).
[11] X. Tong and C. Lin, J. Phys. B **38**, 2593 (2005).
[12] A. Saenz, Phys. Rev. A **66**, 063408 (2002).
[13] A. Saenz, J. Phys. B **33**, 4365 (2000).
[14] Th. Ergler, A. Rudenko, B. Feuerstein, K. Zrost, C. D. Schröter, R. Moshammer, and J. Ullrich, Phys. Rev. Lett. **95**, 093001 (2005).
[15] U. Banin, A. Bartana, S. Ruhman, and R. Kosloff, J. Chem. Phys. **101**, 8461 (1994).