Quantum-Phase Resolved Mapping of Ground-State Vibrational D_2 Wave Packets via Selective Depletion in Intense Laser Pulses

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Applying 7 fs pump-probe pulses (780 nm, 4×10^{14} W/cm^2) we observe electronic ground-state vibrational wave packets in neutral D_2 with a period of $T = 11.101(70)$ fs by following the internuclear separation (R-)dependent ionization with a sensitivity of $\Delta\langle R\rangle \leq 0.02$ Å. The absolute phase of the wave packet's motion provides evidence for R-dependent depletion of the ground state by nonlinear ionization, to be the dominant preparation mechanism. A phase shift of about π found between pure ionization (${D_2}^+$) and dissociation ($D^+ + D$) channels opens a pathway of quantum control.

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Ultrafast molecular dynamics in strong laser fields continues to attract increasing attention (see, e.g., [1–3]), fueled experimentally by the tremendous progress in femtosecond laser as well as multiparticle detection technologies [4], driven intellectually by the desire to understand and by the vision to control ultrafast molecular quantum dynamics in different physical, chemical, or biological processes [5]. Starting with the pioneering work in 1990 [6], the so-called pump-probe techniques have proven to be an extraordinarily rich source of information. With the pump pulse, the molecular dynamics is initiated in a controlled way, i.e., rotational, vibrational, or dissociative wave packets are launched, while their evolution in time is followed by probing with a second pulse at variable delay times. Recently, this scheme has been pushed towards ultrashort times investigating the fastest molecular processes, namely, dissociation and vibration in H_2^+ or D_2^+ [7–9].

So far, the experimental investigation of vibrational wave packets was nearly exclusively restricted to electronically excited and/or ionic states, easily accessible by (multi)-photon absorption from the pump pulse. Three experimental methods known to the authors, often restricted to special situations, have been demonstrated so far to excite vibrational motion of neutral molecules in their electronic ground state (EGS): Stimulated emission within the pump or probe-pulse for "high" intensities ($\sim 10^{12}$ W/cm^2) [10], a "pump-dump" scheme involving resonant two-color Raman scattering [11], and "NeNePo" (negative-neutral-positive) where a negative ion is photodetached creating a wave packet of the neutral which is then probed by multiphoton ionization [12]. Theoretically, adiabatic climbing of vibrational ladders using chirped infrared pulses has been suggested as well as Raman chirped adiabatic passage far-off-resonance (see [13] and references therein) without any experimental realization for homonuclear diatomics, to the best of our knowledge.

Very recently, a novel, nonresonant route for the creation of EGS vibrational wave packets in neutral molecules by ultrashort laser pulses, named "Lochfrass" has been predicted [14]. The calculation was based on a strong dependence of the tunnel ionization rate on the internuclear separation R for certain diatomic molecules [15]. As schematically depicted in Fig. 1(a) for D_2 and calculated for H_2 exposed to an 8 fs laser pulse of 6×10^{14} W/cm^2 [14], tunnel ionization of the molecule is predominantly induced at large R since the effective ionization potential $I_P = E_{D_2^+}(R) - E_{D_2}(R)$, where $E_{D_2^+}(R)$ and $E_{D_2}(R)$ are the Born-Oppenheimer potential curves, respectively, is decreasing with increasing R. Thus, the ground-state vibrational wave function prepared in $v = 0$ is depleted with higher probability at larger R such that the remaining wave packet moves inwards with progressive ionization during the presence of the laser pulse illustrated in Fig. 1(a). Being no longer an eigenstate of D_2 after the 8 fs pulse is over, the wave packet bounces back to larger R inducing vibrational motion in the EGS. Calculations predict that mainly the

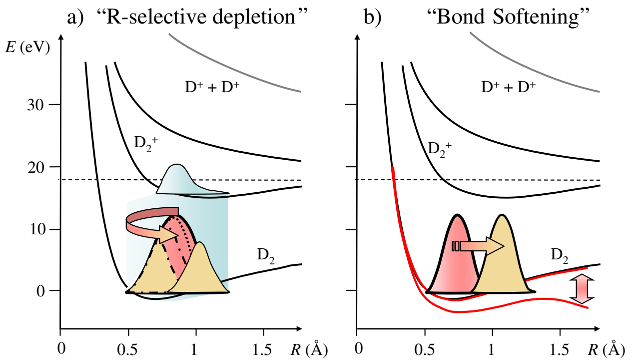

FIG. 1 (color online). (a) Illustration of the mechanism as well as the absolute phase imprinted for preparation of a ground-state vibrational wave packet by R-selective depletion. (b) The same for bond softening.

$\upsilon = 1$ vibrational state is excited with an oscillation period of $T \sim 8$ fs ($\sim$11 fs) for H_2 (D_2), widely independent of the pulse length (varied between 8 and 12 fs) as well as on the intensity (0.4–0.6 PW/cm^2).

In the present Letter we report on the experimental observation of a ground-state vibrational wave packet in D_2 oscillating with $T = 11.101(70)$ fs, the fasted motion in a molecule that has ever been traced in the time domain. By measuring the absolute phase of the oscillation with respect to the laser pulse maximum (7 fs FWHM), i.e., by inspecting whether the wave packet first moves towards smaller or larger R, respectively, we provide experimental evidence that R-selective depletion (RSD) is the dominating mechanism to create the wave packet at a pump intensity of (0.4 ± 0.1) PW/cm^2 as was theoretically predicted [14]. The wave packet is probed by measuring the D_2^+ rate as a function of the delay between the pump and probe pulses, exploiting again the pronounced R dependence of the ionization probability. Indirectly, we are sensitive on changes of the mean internuclear separation as small as $\Delta\langle R\rangle \leq 0.02$ Å, the most accurate distance determination which we are aware of.

The experimental pump-probe arrangement [7] as well as the reaction microscope [4] have been described in detail before and are only briefly summarized here. We used linearly polarized light from a Kerr-lens mode locked Ti:sapphire laser at 795 nm central wavelength with 25 fs pulse width (FWHM) and 3 kHz repetition rate. Few-cycle pulses are generated by spectral broadening in a gas-filled hollow fiber and subsequent compression to 7 fs (FWHM). The laser beam was fed through a Mach-Zehnder–type interferometer with one arm variable in length, providing two pulses separated by a time delay which can be scanned from 0 to 3 ps with a resolution of better than 0.3 fs. By measuring the autocorrelation directly at the reaction volume using the ion rate as nonlinear signal we verify *in situ* the length of the pulse and the absolute time zero of the delay. Both laser beams were focused to a spot size of $\sim$5 μm onto a supersonic molecular gas jet in the center of an ultrahigh vacuum chamber (2×10^{-11} mbar). Charged reaction fragments were guided onto two position-sensitive channel plate detectors by weak electric (2 V/cm) and magnetic (7 G) fields applied along the laser polarization axis. From the time of flight and position on the detectors the full momentum vectors of the coincident recoil ions $\vec{P}_R$ and electrons $\vec{P}_e$ were calculated. By inspecting the thermal spread of the recoil ion momenta the internal temperature of the jet was determined to be about 3 K such that D_2 molecules are well prepared in their vibrational ground state.

In Fig. 2 the observed D_2^+ ion yield is displayed as a function of the pump-probe delay between the pulses [both (0.4 ± 0.1) PW/cm^2], exhibiting a clear oscillation on a constant background that is produced by D_2 ionization by either the pump or the probe pulse alone. The oscillation period is deduced from a linear fit of the observed number of oscillations vs delay time from 100 to 1200 fs. The result, $T = 11.101(70)$ fs, is in good agreement with the prediction from [14] and with existing spectroscopic data for the frequency difference between $\nu = 0$ and $\nu = 1$ corresponding to 11.1425(15) fs [16]. The absolute time scale was calibrated with an error of 0.6% through the spacing of the interference fringes in the region of overlapping pulses and the measured central frequency of the pulse. With a statistical error of the linear fit of only 1 asec this points to the feasibility of future high-resolution measurements with a frequency accuracy of 10^{-4}. Only small irregular modulations of the amplitude and none in the frequency are visible over 100 oscillations. Their contrast of about 10%, slightly depending on the pulse duration, is in reasonable agreement with the predictions for a similar intensity of 0.6 PW/cm^2, 8 fs pulses [14].

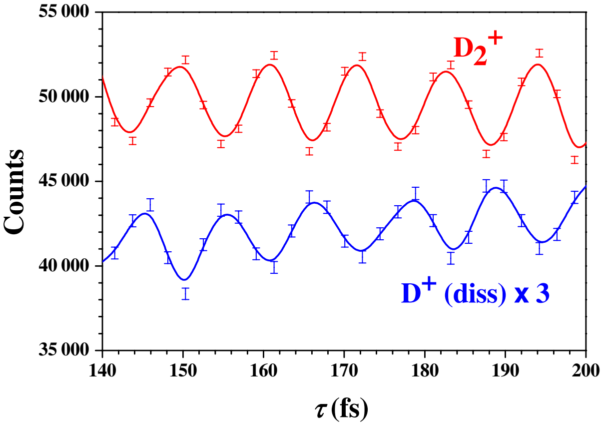

FIG. 2 (color online). Ion yield for D_2^+ (upper curve) and $D^+ + D$ channels (lower curve, scaled up by a factor of 3), respectively, as functions of the delay between two 7 fs pulses of 0.4 PW/cm^2 intensity.

As has been briefly discussed in [14] there might be another mechanism creating EGS vibrational wave packets as depicted in Fig. 1(b). Here, in a quasistatic picture the adiabatic EGS potential curve of D_2 is perturbed periodically by the laser field ranging from the maximum field strength (lower dashed curve) to zero (upper curve, i.e., the unperturbed EGS potential). In average, the bond length is released by this process, denoted “bond softening” (BS) [17]. Following the argumentation and the approximations used in Ref. [14] we have calculated the effect of the field-induced distortion of the potential curve on the ground-state wave function by solving the time-dependent Schrödinger equation for the nuclear motion in R not only for the imaginary part $W(R, t)$ of the perturbing potential $\hat{V} = iW(R, t) + V(R, t)$ describing ionization, but also for the real part $V(R, t)$, responsible for BS [17]. We find, similar to RSD, that BS as well creates an EGS vibrational wave packet with dominating contributions of $\nu = 0$ and $\nu = 1$. In the photon picture, bond-softening excitation corresponds to far-off-resonance two-photon Raman scattering where $\Delta\nu > 1$ transitions are forbidden in an ideal harmonic potential by selection rules [13].

In accordance with the intuitive picture in Fig. 1 our model calculations reveal a decisive difference between both processes, which can be exploited to separate them experimentally. For RSD the wave packet effectively moves towards smaller R until the maximum of the pulse (time zero of our delay time τ), then bounces back and starts to oscillate: $\langle R(t)\rangle = \langle R_0\rangle + \Delta\langle R\rangle \cos(\omega t - \varphi_{\mathrm{RSD}})$. BS, on the other hand, tends to release the bond within the rising pulse, launching the wave packet directly into the direction of larger R causing a different phase φ_{BS}. Quantitatively this is shown in Fig. 3 for 0.4 $\mathrm{PW/cm^2}$ and delay times in units of the oscillation period between 14 and 17. Whereas RSD (dash-dotted line) peaks at $\varphi_{\mathrm{RSD}} = \pi$, BS (dashed line) has its maximum close to $\varphi_{\mathrm{BS}} = 0.5\pi$; i.e., they are shifted by a quarter of a full period. In addition, our calculation shows that $\Delta\langle R\rangle$ induced by RSD is about a factor of 2 larger than for BS at 0.4 $\mathrm{PW/cm^2}$. Adding both oscillations in a combined calculation we arrive at the solid line, which is in excellent agreement with the experimentally determined quantum phase (solid circles and dotted line for a fitted cos function) of $\varphi_{\mathrm{exp}} = 0.946(1)\pi$ strongly supporting R-selective depletion to be the dominant mechanism to prepare the wave packet. Note: since we discuss only the phase, the experimental data, i.e., the ionization yield (right axis), is scaled in order to match the theoretical amplitude (left axis).

We have tested the stability of the individual RSD and BS phase shifts by varying the pulse intensity between 0.3 and 0.6 $\mathrm{PW/cm^2}$ without observing any significant effects, whereas the absolute magnitude of the amplitude $\Delta\langle R\rangle$ strongly changes. Moreover, one might think that the absolute carrier envelope offset phase, which is not controlled in our present experiment, might influence the phase difference between the two processes, but only minor effects were observed in simulations using so-called sin and cos pulses, respectively. Finally, the phase shift seems to be quite stable as a function of the pulse length as our own estimates (8 and 12 fs FWHM) as well as calculations performed in [14] (8 and 12 fs total length) indicate. Bond-softening contributions to the preparation of the observed ground-state wave packet might be reflected in the slight but noticeable deviation in absolute phase between the experimental data and the prediction for pure RSD.

Therefore, we have tried to estimate the absolute magnitude of both processes and their dependence on the intensity. Both the model calculation of the BS amplitude as well as the measurement of the intensity are considerably less reliable than the absolute phase determination such that only qualitative arguments might be extracted and a more accurate theoretical treatment has to be awaited for. According to earlier calculations on two-photon Raman vibrational excitation far-off-resonance [13] one might assume the BS contribution to be small. However, one has to consider that the wave packet created by RSD contains only a fraction of about 0.5% of $\nu = 1$ such that BS might well compete in the present situation. Surprisingly, as shown in Fig. 4, our simple model predicts that both mechanisms exhibit similar amplitudes for the intensity regime (shaded area) covered in the present study (including the uncertainty of the intensity determination). In this estimate we take into account that only the projection of the molecular axis along the polarization direction contributes to BS, whereas RSD is almost independent of the relative orientation [15,18]. Interestingly, BS scales with the intensity $\sim I^2$, which is consistent with a two-photon Raman process, while RSD exhibits a much steeper growth as expected for field ionization.

While the dominance of RSD extracted from the phase determination might be considered consistent with the

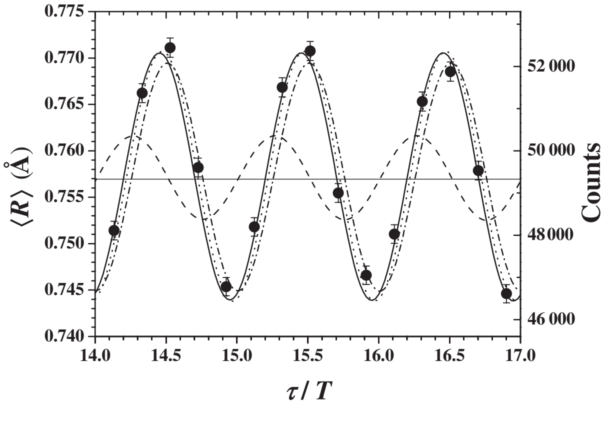

FIG. 3. Change of the mean internuclear separation $\langle R\rangle$ (left scale) as a function of the delay between pump and probe pulse calculated for 0.4 $\mathrm{PW/cm^2}$ for pure R-selective depletion (dash-dotted curve), for pure bond softening (dashed curve) and for the combination of both (solid line) in comparison with the experimental data (solid circles and dotted curve for a best fit with respect to the right scale). The delay is given in units of the measured oscillation period. Normalization: see text.

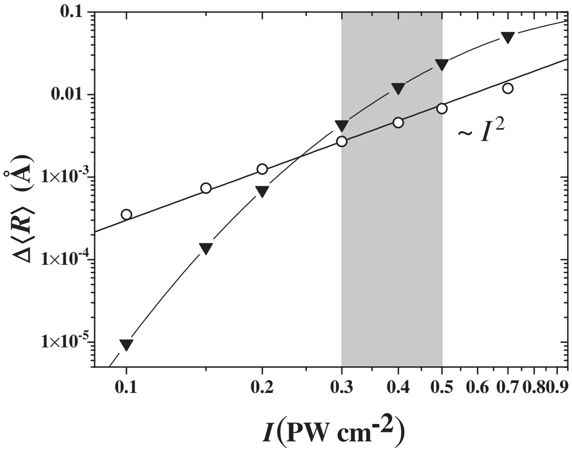

FIG. 4. Absolute amplitudes as a function of the laser intensity for R-selective depletion (solid down-pointing triangles) and bond softening (open circles) contributions as estimated from a simple model calculation (see text). Shaded area: intensity regime investigated experimentally of 0.4 ± 0.1 $\mathrm{PW/cm^2}$.

intensity prediction in Fig. 4, we have measured φ_{exp} at different intensities and found essentially the same offset phase and oscillation period between about 0.4 and 0.7 $\mathrm{PW/cm^2}$ for equal pump and probe pulses. At lower intensities the measurements become increasingly difficult and no results could have been obtained until now such that we have to leave the question open as to whether or not BS created wave packets do exist and can be identified.

Finally, we have explored another probe channel, namely, the dissociative ionization of the oscillating ground-state wave packet in Fig. 2 (lower curve), competing with pure ionization. Again, we find the oscillatory behavior at identical frequency as expected since we probe the same vibrating ground-state wave packet. Most surprisingly, however, a distinct phase shift of about π is observed. This indicates that the probability for dissociative ionization is higher at the inner turning point of the oscillating wave packet in D_2 than at the outer one. In order to give a qualitative interpretation one has to consider the population of the vibrational levels of D_2^+ as well as their dissociation probability. The former is mainly given by the overlap amplitudes of the ionized part of the wave packet with the vibrational eigenstates of D_2^+. Since the equilibrium distance in D_2 (0.74 Å) is smaller than in D_2^+ (1.06 Å) we expect at the outer turning point a preference for populating the lower v states of D_2^+ and vice versa. Considering the v-dependent dissociation probability it has been shown experimentally for H_2^+ that the states with $v > 4$ can dissociate easily via absorption of a single photon [19]. The corresponding threshold for this one-photon channel would be above $v \approx 7$ for D_2^+. Thus, the experimental observation suggests that the absolute population in the presumably highly dissociative upper-lying v states is higher for the inner turning point, whereas at the outer turning point lower v states are favored which are more stable against dissociation. It would be interesting to test this behavior quantitatively by calculations which are underway [18].

In conclusion, we have prepared and observed electronic ground-state vibrational wave packets in neutral D_2 molecules and measured their oscillation period of $T = 11.101(70)$ fs. By measuring the quantum phase of the wave-packet motion with a relative uncertainty of 10^{-3} we are able to conclude on the way how we started the oscillation, namely, by first pushing it to smaller distances, selectively depleting the wave function at larger R, in accordance with earlier theoretical predictions. According to our model calculation bond-softening contribution to the wave-packet creation might be indirectly observed by a small but noticeable phase shift compared to pure RSD. We follow the wave-packet motion by probing it via ionization or dissociation using a second pulse and find that both channels are 180° out of phase. This led us to the conclusion that dissociation probes the wave packet at its inner turning point suggesting a strongly R-dependent ν population.

Finally, we would like to emphasize that our measurement might have far-reaching consequences and applications: First, as demonstrated in the last example, on the basis of the quantum phase we can steer the reaction towards ionization or dissociation depending on the delay between the pulses. Second, this precise oscillation can be exploited to provide an absolute time scale for pump-probe experiments. For any molecular species to be investigated it is straight forward to mix D_2 into the target gas, which then serves as an inherent clock for precision frequency determination of any other time structure from few femto- to picoseconds, in future possibly even up to nanoseconds. Last but not least, this ground-state wave packet exhibits a lifetime of many, presumably hundreds, of days. Thus, our pendulum state, the smallest, fastest, and lightest analogue to a classical clock pendulum, ticks as a little quantum clock, 10 000 times faster than the Cs atomic clock, only factor 10 slower than anticipated all-optical clocks, with an unsurpassed lifetime. We have demonstrated that we can count its individual ticks, not perturbed by any sizeable external electromagnetic fields nor by collisions in the ultrahigh vacuum environment, over more than 100 cycles. Work is in progress to explore the prospects of this scheme to build a precision molecular clock by following the pendulum for a time duration as long as seconds.

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