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Abstract. We studied the dependence of dissociative ionization in H_2 on carrier-envelope phase (CEP) of few-cycle (6 fs) near-infrared laser pulses. For low-energy channels, we present the first experimental observation of the CEP dependence of combined dissociation yield (with protons emitted in both directions), as well as the highest degree of asymmetry reported to date (40%). The observed modulations in both asymmetry and combined yield could be understood in terms of interference between different n-photon dissociation pathways—n and $(n+1)$ photon channels for asymmetry, n and $(n+2)$ photon channels for yield—as suggested by the general theory of CEP effects (Roudnev and Esry 2007 *Phys. Rev. Lett.* **99** 220406). The yield modulation is found to be π-periodic in CEP, with its phase strongly dependent on fragment kinetic energy (and reversing its sign within the studied energy range), indicating that the dissociation yield does not simply follow the CEP dependence of maximum electric field, as a naïve intuition might suggest. We also find that a positively chirped pulse can lead to a higher dissociation probability than a transform-limited pulse.

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The control of electron localization during the laser dissociation of molecules is currently an active area of research due to its potential application in controlling the chemical reaction processes. In homonuclear diatomic molecules, such control requires the breaking of inversion symmetry. Several schemes for doing this have been suggested and implemented recently for hydrogen and deuterium molecules: combining near-infrared (NIR) pulses with extreme ultraviolet (XUV) isolated attosecond pulses [2] or attosecond pulse trains [3]; controlling the asymmetric waveform of NIR–visible pulses by combining a fundamental frequency with its second harmonic [4]; using few-cycle NIR [5] or mid-IR [6] pulses with stable (or measured for each pulse) carrier-envelope phase (CEP).

The CEP control with few-cycle pulses was the scheme first demonstrated experimentally by Kling *et al* [5] and continues to be the most extensively studied. In the original study of Kling *et al*, the authors demonstrated significant (∼20%) CEP-controlled asymmetry of deuteron emission for only the higher energy (kinetic energy release (KER) >6 eV or >3 eV for individual fragments) dissociation channels, which was attributed to recollision excitation of the dissociative $2p\sigma_u$ state of D_2^+. However, no noticeable asymmetry was reported for the dominant low-energy channels, i.e. bond softening (BS) and above-threshold dissociation (ATD). More recently, Kremer *et al* [7] observed a significant (∼15%) asymmetry for these low-energy (0.5 eV $<$ KER < 2.5 eV) channels in H_2. Neither of these studies reported on the CEP dependence of the combined dissociation yields including fragments emitted in all directions. We report such measurements of the CEP-dependent total dissociation yield. We also report the highest degree of asymmetry ever measured for dissociation fragments with KER between 1.8 and 3 eV for this control scheme of 40%.

As to the theoretical modelling of these processes, extensive efforts have been made to understand the underlying physics of the control of electron motion on the sub-femtosecond time scale [3–7]. For each reported experimental scheme, numerical models solving the time-dependent Schrödinger equations for nuclear motion on two field-coupled electronic potentials (two electronic states of opposite parity are needed for localization), supplemented by an ad hoc wavepacket initiation procedure, qualitatively accounted for the observations. More generally, all CEP-dependent effects could be viewed as resulting from the interference between two (or more) quantum pathways corresponding to different numbers of absorbed photons. This general view follows directly from the periodic dependence of the time-dependent Schrödinger equation on CEP, which allows Floquet representation of the wavefunction, as was first demonstrated by Roudnev and Esry [1]. In this interpretation, CEP control (and also the two-colour control [4]) is a form of more general coherent control [8].

Two conditions are necessary for achieving coherent control of electron localization: (i) the two interfering pathways must result in electronic states of opposite parity; and (ii) the two interfering pathways must result in the same kinetic energy of fragments. Additionally, to achieve maximum modulation depth, the relative probabilities of the two interfering pathways need to be close (optimally equal) to each other. The condition (ii) may only be satisfied for the regions where kinetic energies of the interfering multi-photon pathways overlap. Such an overlap would be hard to achieve with narrowband pulses, as in the monochromatic limit different dissociation processes result in distinctly different kinetic energies. However, the large bandwidth of few-cycle pulses broadens the corresponding spectra and allows such an interference to occur (figure 1(a)).
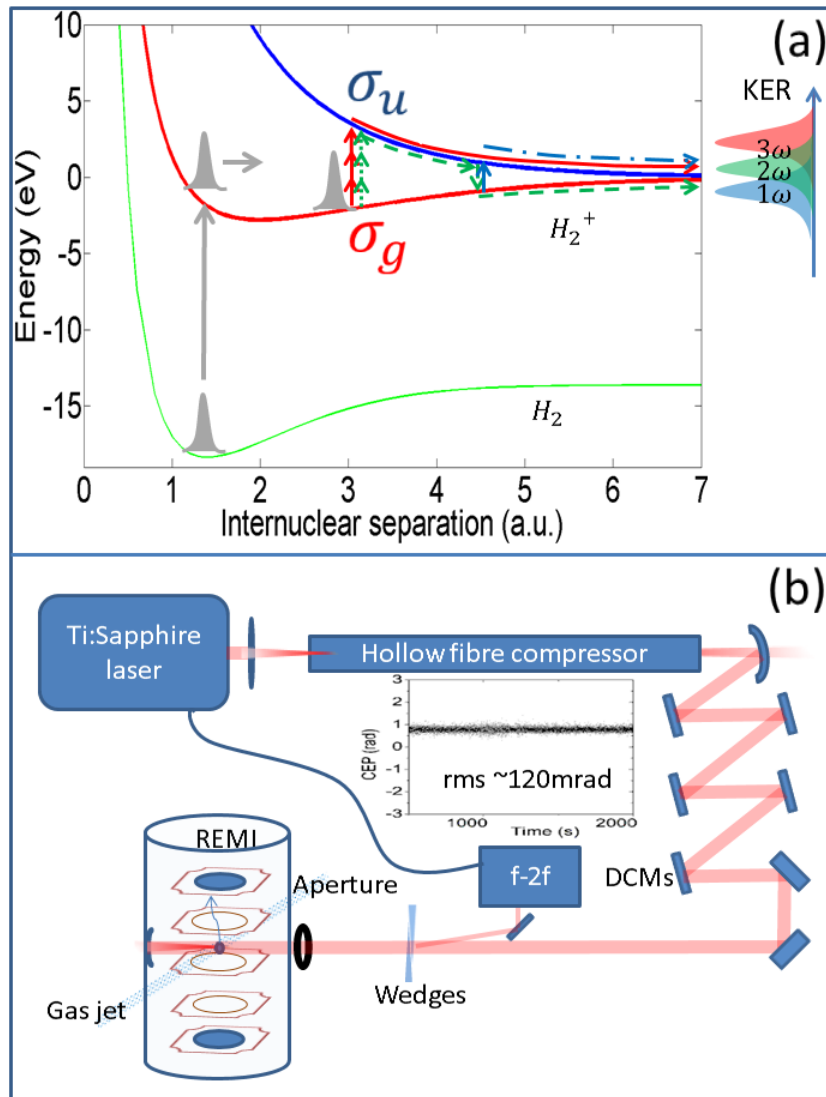
Figure 1. (a) Different pathways for dissociation of H_2^+. The arrows represent transitions corresponding to the central frequency of the few-cycle pulse—a large bandwidth leads to broad and overlapping fragment energy spectra allowing interference between the pathways. (b) Schematic diagram of the experiment (DCM, dispersion compensation mirrors; REMI, reaction microscope). CEP time trace and its rms = 120 mrad were obtained by averaging *f*–2*f* spectra over ten consecutive pulses. The estimated single-pulse rms of CEP noise was 360 mrad.

To date, both experiment and numerical modelling focused almost exclusively on the asymmetry parameter defined as

$$A = (N_{up} - N_{down})/(N_{up} + N_{down}),$$

where N_{up} (N_{down}) is the total number of protons (or deuterons) ejected into each of the two opposite directions along the laser polarization axis. Thus defined, asymmetry exhibits

periodic dependence on the CEP with 2π periodicity, which is intuitively obvious from simple symmetry considerations. The general theory of CEP effects predicts a CEP dependence of the asymmetry resulting from the interference of two dissociation pathways which differ by 1 in the number of absorbed photons [9]. The same theory also predicts that the combined dissociation yield ($N_{com} = N_{up} + N_{down}$) is CEP-dependent, but with π periodicity, which results from interference of quantum pathways differing by 2 in the number of absorbed photons. In this case numerical modelling predicts only a small (1.4% for total yield integrated over kinetic energy) modulation in total probability with CEP for H_2^+ interacting with 5.9 fs pulses [9]. Detecting such small modulations requires laser pulses which are simultaneously stable in the total energy, pulse duration and CEP. Until now, no experimental results on CEP dependence of combined dissociation probability for laser-induced dissociation of hydrogen molecules have been reported.

We present an experimental study of the CEP dependence of dissociative ionization of H_2 with a focus on the low-energy (KER < 4 eV) channels. Unlike the high-energy fragments observed by Kling *et al* [5], here the dissociative σ_u state of H_2^+ is populated not via rescattering but via radiative excitation pathways corresponding to absorption of odd numbers of photons ($n = 1, 3$). BS ($n = 1$) [10] and three-photon dissociation (3PD) ($n = 3$) [11] both populate the σ_u state. ATD is a net-two-photon ($n = 2$) process, where absorption of three photons is followed by emission of one photon resulting in the dissociation on the ground σ_g state (figure 1) [12]. We interpret our observations in terms of interference between these three channels.

It should be noted that while BS and ATD are well-established and widely accepted channels confirmed by multiple experimental and theoretical studies, 3PD was suggested only recently to explain the wavelength dependence of kinetic energy spectra observed in laser Coulomb explosion of hydrogen [11]. This role of 3PD was later confirmed by several theoretical calculations [13–16]. As 3PD becomes active at much higher intensities than BS and ATD, long pulses used in [11] invariably resulted in consequent double ionization (Coulomb explosion). It is much more likely for a hydrogen molecule undergoing 3PD to avoid the second ionization when few-cycle pulses are used. Based on that, we attribute the three-photon process needed to explain the high asymmetry at KER near 3 eV to 3PD, although this role of 3PD remains tentative awaiting proper theoretical confirmation.

A schematic diagram of our experiment is shown in figure 1(b). The experimental apparatus includes a 1 kHz CEP-stable few-cycle laser system and a REMI. The few-cycle laser is a commercial femtosecond laser system (*Femtopower Compact Pro, Femtolasers*) with a hollow-core fibre compressor. The laser pulse had duration of 6 fs with a central wavelength of 800 nm. A pair of fused silica wedges installed on a translation stage was used to vary the CEP of the laser pulse. In the experiment, we scanned the CEP over a range of 3π with 14 sampling points. A small portion of the pulse energy, reflected from the front surface of the wedge pair, was diverted into an *f*–2*f* interferometer, where the spectrum was measured and used as a feedback signal for a CEP stabilization feedback loop. The estimated CEP noise (root mean square (rms)) was less than 360 mrad and was sufficiently stable for clear experimental observation of CEP-dependent effects. The laser was tightly focused by a silver-coated concave mirror ($f = 75$ mm) installed inside the REMI onto a well-collimated supersonic gas jet of hydrogen molecules. The electric field of the laser was parallel to the time-of-flight axis of the REMI spectrometer and normal to both the laser propagation direction and the molecular beam. The charged dissociation fragments (protons) were detected by a time- and position-sensitive detector (Roendtek) and their three-dimensional momentum vectors were determined.
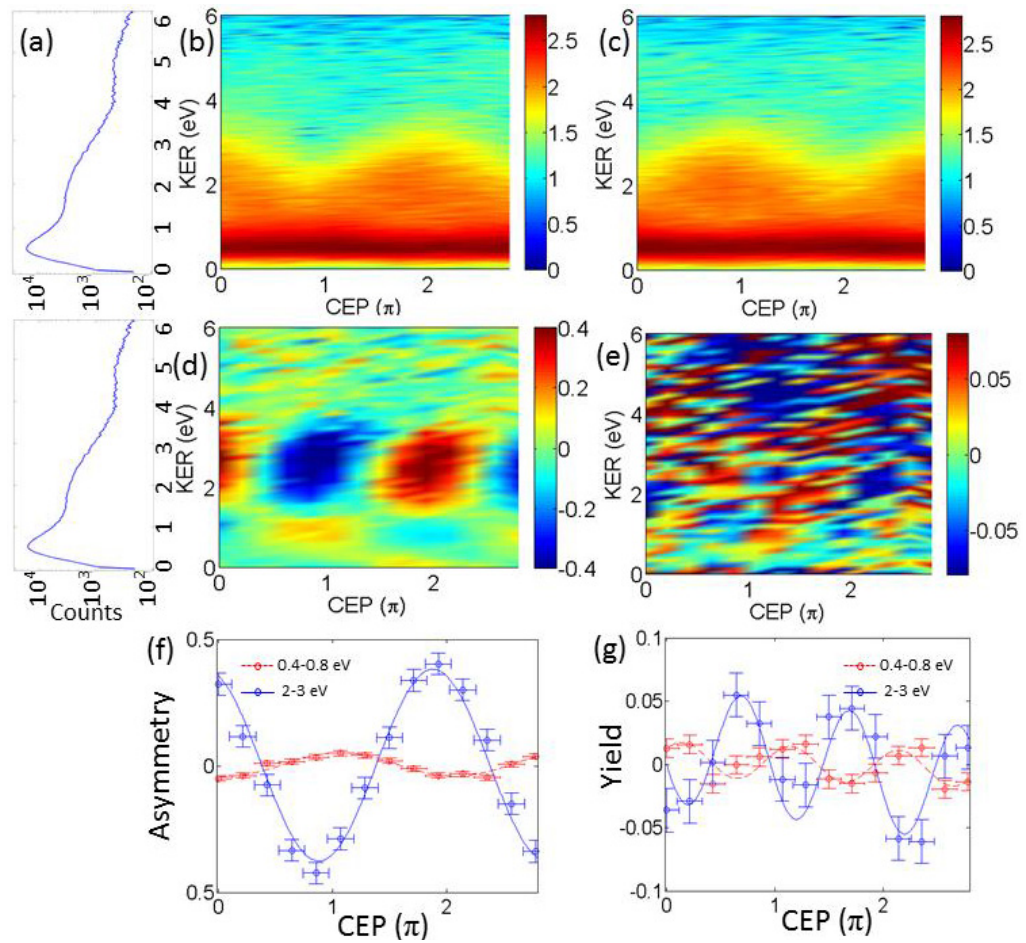
Figure 2. (a) Combined KER spectrum (both directions) integrated over all CEP values. CEP-dependent KER spectra for protons ejected towards (b) and away from (c) the detector. Colour scale represents $\log_{10}(N)$, where N is the number of counts in each two-dimensional bin. (d) Asymmetry as a function of relative CEP and KER. (e) The combined dissociation yield as a function of relative CEP and KER: colour map (linear scale) indicates the difference between the normalized total spectrum at the given CEP and the normalized CEP-averaged spectrum. CEP-dependent asymmetry (f) and relative combined yield (g) for two KER regions indicated in the insets. Horizontal error bars in (f) and (g) represent estimated CEP noise (rms)—the error for average CEP values over the measurement time was negligible in comparison.

From the measured proton momenta, we calculated the kinetic energy spectra separately for protons emitted towards (up) and away from (down) the detector for all values of CEP (figures 2(b) and (c)). These spectra are integrated over all angles to include all fragments emitted into the upper (lower) hemisphere. From those spectra we obtained energy- and CEP-dependent asymmetry and total dissociation yield shown in figures 2(d) and (e), respectively. Note that we express the kinetic energy in terms of KER, the total kinetic energy of the two fragments. The KER is twice the single fragment energy (used in [5]), assuming equal energy

sharing between the proton and the undetected hydrogen atom. Clearly, there are two distinct energy regions (0.3–1.3 and 1.5–3.5 eV) characterized by a different, and nearly opposite, CEP-dependent directionality of proton emissions (figure 2(f)). By properly adjusting the peak laser intensity at the focus ($I = (6 \pm 2) \times 10^{14}$ W cm^{-2}), we achieved a high degree of asymmetry (40%) for fragments with KER between 2 and 3 eV. Changing this optimal intensity in either direction decreased the measured asymmetry. This intensity is significantly higher (by a factor of 6) than the one used by Kling *et al* [5]. It is also higher than the intensity used by Kremer *et al* [7]. We calibrated laser intensity by making *in situ* measurements of the momentum of Ne$^+$ ions produced by circularly polarized pulses of the same duration [20] by following the procedure described in [21]. We assign the two energy regions as corresponding to interfering one- and two-photon pathways (BS and ATD, 0.3–1.3 eV) and two- and three-photon pathways (ATD and 3PD, 1.5–3.5 eV).

The highest asymmetry modulation of 40% is achieved for the energy region corresponding to the overlap between the interfering ATD ($n = 2$) and 3PD ($n = 3$) channels, reflecting the relative populations of the three dissociation pathways at the experimental intensity of 6×10^{14} W cm^{-2}. At the relatively low intensity of 1×10^{14} W cm^{-2} in Kling *et al*'s experiment [5], it appears that only the BS channel was operational, while the ATD pathway, also required for electron localization, remained unpopulated, thus explaining the absence of asymmetry. It is also likely that our higher intensity accounts for the differences between the present results and those obtained at 4×10^{14} W cm^{-2} by Kremer *et al* [7]. Although qualitatively similar, our experimental spectra are characterized by a higher degree of asymmetry, particularly in the energy region where it reaches its maximum value—between 2 and 3 eV. It appears that the relative population of the two- and three-photon channels was less favourable for efficient CEP control of electron localization at the lower intensity used in [7].

It should also be noted, that it will be, in general, harder to achieve CEP control of electron localization in the low-energy dissociation channels for heavy (in comparison with light) hydrogen when one is starting with ionization of neutral molecules. The reason for this is the time delay between the initial ionization (typically taking place at the peak of the pulse) and radiative coupling which takes place most efficiently at much larger internuclear separations where the energy difference between the two electronic states is smaller. For very short pulses, by the time the nuclear wavepacket reaches the coupling region the instantaneous pulse intensity is substantially diminished. This is particularly true for heavier isotopes, which move slower and take more time to expand. Experimental comparison of H_2 and D_2 validates this reasoning, with light hydrogen showing twice the asymmetry modulation depth seen for D_2 under the same conditions. The detailed comparison between the two isotopes will be presented in another paper. It is also possible that in this particular case having the shortest pulse may not be the best way of maximizing the CEP effects, as a significant intensity at the tail of the pulse is required to populate two different dissociation pathways with comparable probabilities. One may need to optimize both peak intensity and pulse duration to achieve the strongest CEP effects.

We also measured the dependence of the combined dissociation yield (meaning yield in both directions for a particular KER range rather than energy-integrated yield) on CEP (figures 2(e) and (g)). It is clear from simple symmetry considerations that this dependence must be π-periodic with CEP. Any given pulse and its mirror image, with a CEP that differs by π, must show the same combined dissociation probability (and opposite asymmetry) in all possible channels. One may naively expect the combined yield to just follow the CEP dependence of the maximum peak electric field of the pulse, which oscillates between maximum (for cosine pulse)
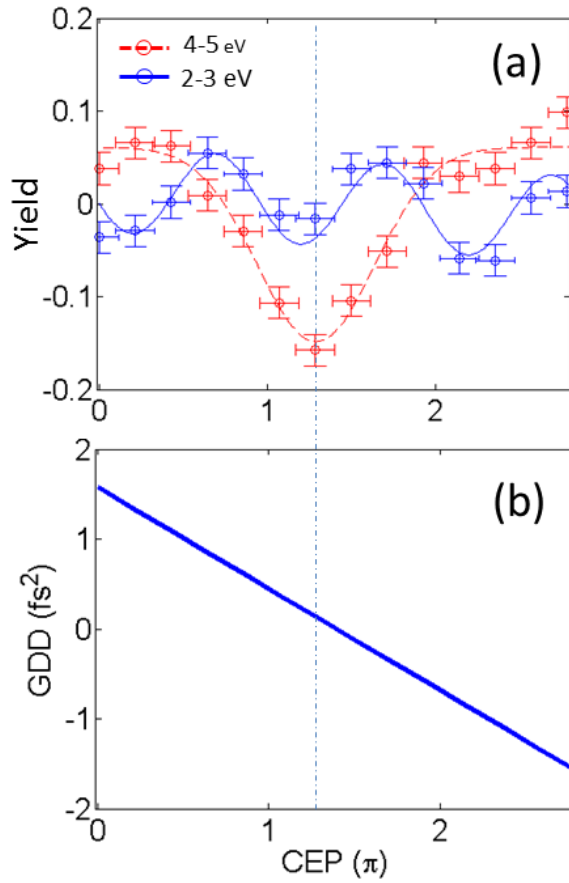
Figure 3. Combined yield in both directions for fragments with KER in the 2–3 eV range and the 4–5 eV range (a) and calculated group delay dispersion (GDD) as functions of nominal CEP (b). The point of zero GDD is indicated by the vertical dashed line.

and minimum (for sine pulse) values with a period of π. This is not what we observe in our experimental results. We do see π-periodic modulations of combined dissociation yield with modulation depth of up to 5% for fragments with KER between 2 and 3 eV. At the same time, the relative phase of those modulations is found to be strongly dependent on KER covering more than π in range. For instance, when the 2–3 eV fragments are at their maximum yield, the production of 0.4–0.8 eV fragments is minimal (figure 2(g)). We conclude that more complex interference (rather than simple intensity) effects are responsible for the CEP dependence of the combined yield. More detailed analysis based on the general theory of CEP effects reveals that the yield modulations result from interference between pathways differing by 2 in the number of absorbed photons [9]. In this case the likely interfering pathways are BS ($n = 1$) and 3PD ($n = 3$).

Finally, we would like to comment on the monotonic decrease in combined ionization yield with increasing CEP, which is seen on top of the periodic modulations in our results (figure 3). That is an artefact produced by the moving fused silica wedges to alter the CEP since this action simultaneously changes the chirp and duration of the pulse. We placed the transform-limited pulse in the middle of our CEP scanning range and confirmed this by measuring the yield of

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enhanced (double) ionization fragments [17, 18], which is very sensitive to pulse duration and is most strongly suppressed for shortest pulses [19]. It appears that it is not just the duration of the pulse, but also its chirp that affects the dissociation probability. Even a small positive chirp around the point of zero group delay dispersion seems to enhance dissociation probability in comparison with transform-limited and negatively chirped pulses.

In conclusion, we have presented an experimental study of CEP effects in the laser-induced dissociation of hydrogen molecules using 6 fs laser pulses. By optimizing the laser peak intensity we measured the strongest CEP-dependent asymmetry of proton ejection ever reported for this control scheme (40%). This control originates from interference between two distinct dissociation pathways with different numbers of absorbed photons, ATD ($n = 2$) and 3PD ($n = 3$). We also measured the CEP-dependent combined dissociation probability, which exhibited π-periodic modulations with up to 5% modulation depth. This dependence originates from the interference between BS ($n = 1$) and 3PD ($n = 3$) pathways. We also found that positive chirp favours dissociation for low-GDD few-cycle pulses.

Acknowledgments

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