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Molecular dissociative ionization and wave packet dynamics studied using two-colour XUV+IR pump-probe spectroscopy

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We present a combined theoretical and experimental study of ultrafast wavepacket dynamics in the dissociative ionization of H₂ molecules as a result of irradiation with an extreme-ultraviolet (XUV) pulse followed by an infrared (IR) pulse. In experiments where the duration of both the XUV and IR pulses are shorter than the vibrational period of H₂⁺, de-phasing and re-phasing of the vibrational wave packet that is formed in H₂⁺ upon ionization of the neutral molecule by the XUV pulse is observed. In experiments where the duration of the IR pulse exceeds the vibrational period of H₂⁺ (15 fs), a pronounced dependence of the H⁺ kinetic energy distribution on XUV-IR delay is observed that can be explained in terms of the adiabatic propagation of the H₂⁺ wave packet on field-dressed potential energy curves.

With recent advances in laser technology, real-time imaging of ultrafast molecular phenomena has become possible. Femtosecond laser pulses have led to the development of transition state spectroscopy and femtosecond chemistry [1], and have been applied in pump-probe experiments to map out time-dependent nuclear motion in molecules [2]. The advent of attosecond pulses [3] has given rise to endeavours where it is the even faster electronic motion that is probed in a time-resolved manner [4]. The high-harmonic generation (HHG) technique that is responsible for the formation of attosecond laser pulses has been exploited as a probe of molecular structure and dynamics, both with regards to the position or motion of the constituent atoms [5–7] and that of the electrons [6, 8]. An important concern in these experiments is the question to which extent the structure and dynamics of the molecule(s) under investigation are influenced by the presence of the intense infrared (IR) laser field that drives the high-harmonic generation process [9].

In this work we present a combined theoretical and experimental study of ultrafast wavepacket dynamics in the $1s\sigma_g^+$ potential of a H₂⁺ molecular ion created by an ultrashort extreme ultra-violet (XUV) pump pulse, with the initial H₂⁺ geometry reflecting that of the neutral ground state. Subsequently molecular dissociation by the process of bond-softening (BS) [10–12] is induced by an infrared pulse with different durations, ranging from 7 fs up to 35 fs. In the first case (experiment A, hereafter) the IR pulse is significantly shorter than the H₂⁺ vibrational period, implying that the vibrational wave

packet freely propagates on the H₂⁺ ($1s\sigma_g^+$) potential energy curve until it finally dissociates under the influence of the IR pulse. By contrast, in experiment B, the duration of the IR laser pulse is comparable to or longer than the H₂⁺ vibrational period. This implies that the IR field is present during the propagation of the wave packet before dissociation, which, depending on the XUV-IR delay, may or may not include the time at which the ionization by the XUV took place. In experiment A, few-cycle 750 nm laser pulses were obtained by means of hollow-core fiber compression [13] and were split into a central and an annular part. The central part (5 fs FWHM) was used to generate attosecond XUV laser pulses in a Kr gas cell. By using the polarization gating technique this resulted in isolated attosecond pulses with an estimated pulse duration of 400 as [14, 15]. The attosecond pulses, which spanned an energy range from 15 to 35 eV, were collinearly recombined with the annular part (7 fs FWHM) of the few-cycle IR pulse (with a variable time delay) and focused into the active region of a velocity map imaging spectrometer [16]. The velocity- and angular distribution of H⁺ ions resulting from two-colour excitation of H₂ molecules was measured. Experiment B made use of a similar setup (previously described in ref. [17]), except for the fact that the IR laser pulse was about 35 fs long. Consequently, the XUV pulse generated by HHG then consisted of a train of attosecond pulses. This, and differences in the XUV spectrum, do not affect our observations significantly.

Figure 1 shows a comparison of the time-dependent

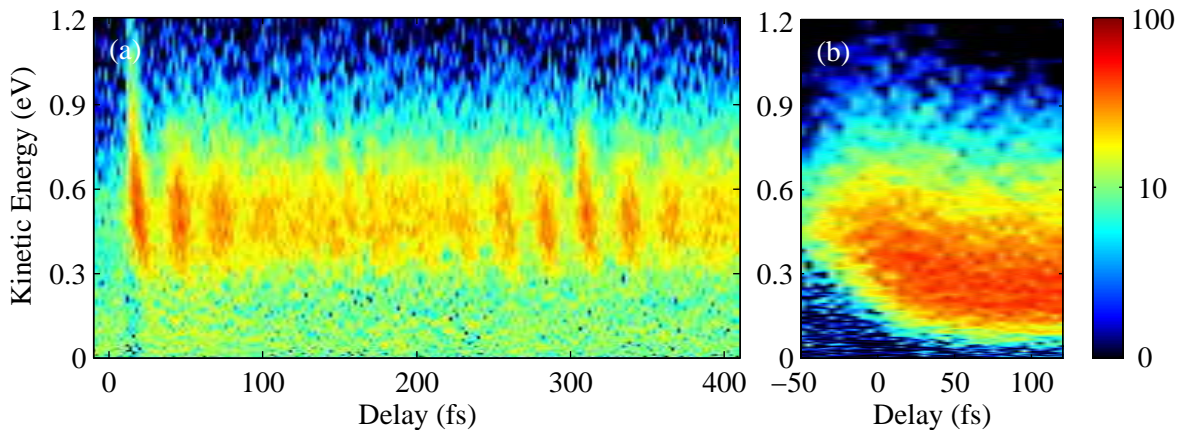


Figure 1: Measured time-dependent H^+ kinetic energy distributions for two-colour XUV+IR dissociative ionization of H_2 , with 7 fs IR laser pulses (A) and 35 fs IR laser pulses (B). In the latter case the XUV pulse consisted of a train of attosecond laser pulses.

H^+ kinetic energy (KE) distributions measured in experiments A and B. For delays $\tau > 0$ fs, the XUV pulse precedes the IR pulse. In experiment A, the yield of fragments with energies below 1.2 eV oscillates in time with a period of about 27 fs. The results for experiment B, where the IR pulse duration is somewhat longer than the vibrational period of the H_2^+ molecule, are radically different. The time dependence of the H^+ KE distribution evolves smoothly as a function of time. The most striking feature in measurement B is that the KE release shows a pronounced decrease when the peak of the IR pulse comes after the XUV pulse.

In order to simulate the experimental results, a one-dimensional model was used. The molecular system H_2 , originally in its ground vibrational and electronic state, is considered to be ionized by an XUV pulse or a pulse train at time $t = 0$. The ionization occurs by a single XUV pulse in the presence of a 7 fs FWHM IR laser pulse (experiment A), or by an XUV pulse train consisting of 15 attosecond pulses in the presence of a 35 fs FWHM IR laser pulse (experiment B). The centre of the laser pulse is positioned at a delay $t = \tau$ with respect to the XUV pulse(s). Based on the favorable Franck-Condon (FC) overlap between the neutral ground state and the ionic $|1s\sigma_g^+\rangle$ state and based on the fact that our energy-resolved detection allows us to selectively investigate the BS channel, we will consider that the attosecond pulse promotes the $v = 0$ vibrational state of the parent molecule vertically onto the $|1s\sigma_g^+\rangle$ state of the molecular ion. We consider the nuclear motion to occur on two electronic manifolds of the molecular ion H_2^+ : the ground state $|1s\sigma_g^+\rangle$ and the first excited electronic state $|2p\sigma_u^+\rangle$. In the simulations, the molecule is assumed to be aligned along the laser polarization. Experimentally, the angle-resolved H^+ detection allows us to selectively observe fragments along the polarization axis. As it turns out, none of the observations reported here depend very strongly on the ejection angle of the H^+ fragment with

respect to the polarization axis. The nuclear dynamics is obtained by solving the one dimensional time-dependent Schrödinger equation using a wave packet propagation procedure largely described in previous work (see [10] for complete details). The resulting kinetic energy spectra are compared with the experimental spectra.

Fig. 2 displays the theoretical proton KE distributions as a function of the time delay between the XUV pump and the IR probe for experiments A and B at intensities of $1 \cdot 10^{13}$ W/cm² and $3 \cdot 10^{12}$ W/cm² respectively, which corresponds to the peak intensity in the experiments. Clearly, the calculations contain very detailed structures which are partially washed out by the volume averaging in the experiment. However the main observations of Fig. 1 are qualitatively reproduced.

In experiment A, the XUV laser pulse prepares a coherent superposition of vibrational states of H_2^+ , which evolves under essentially field-free conditions, oscillating back and forth and spreading out on the $1s\sigma_g^+$ potential before encountering the IR pulse. The short durations of the IR pulse evokes a situation, in which the laser-molecule interaction opens a "gate" to dissociation at some internuclear distance. The dissociation yield, hence, depends on a synchronization between the wave packet and the opening of this gate at the maximum of the IR field. Stated differently, the oscillations in the dissociation yield are a result of the coherence between the various vibrational components of the initial wave packet [2]. This coherence is further explored in Figure 3, which shows the Fourier transforms of the H^+ fragment yield integrated over the KE distribution in the range of 0-1.2 eV for the experimental (Figure 3a) and the theoretical (Figure 3b) results. This reveals that the oscillatory signal is composed of a series of two-level beats at frequencies that are given by the energy difference between adjacent vibrational levels centered around the level $v^+ = 9$ [18, 19]. A correlation between frequency and kinetic energy is observed when the Fourier transform is shown as a function

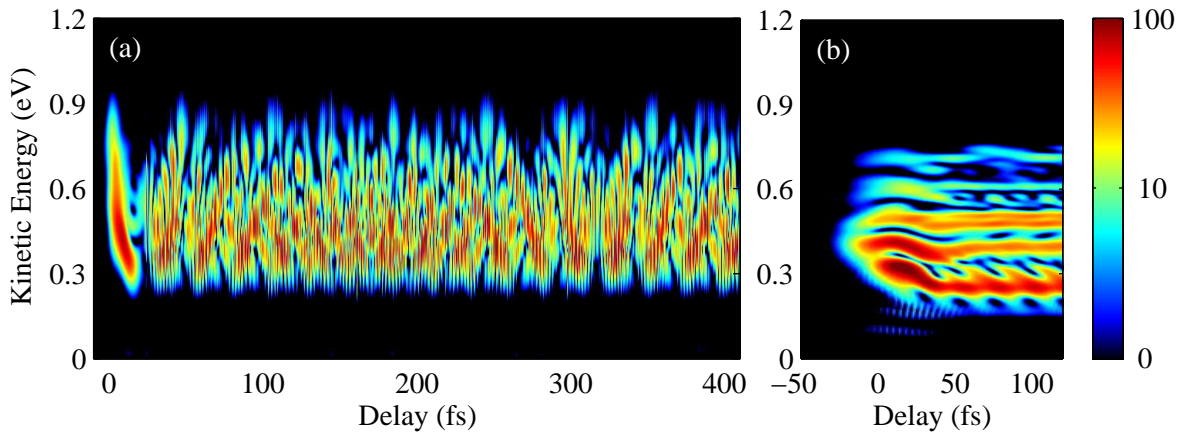


Figure 2: Comparison of the time-dependent kinetic energy distributions resulting from model calculations for two-colour XUV+IR dissociative ionization of H_2 , making use of a 7 fs FWHM IR pulse (A) and a 35 fs FWHM IR pulse (B). In the latter case the XUV pulse consisted of a train of attosecond laser pulses

of the fragment KE (see insets in Figure 3). This can be understood from the fact that higher vibrational levels, which lead to larger observed kinetic energies, have a smaller energy separation.

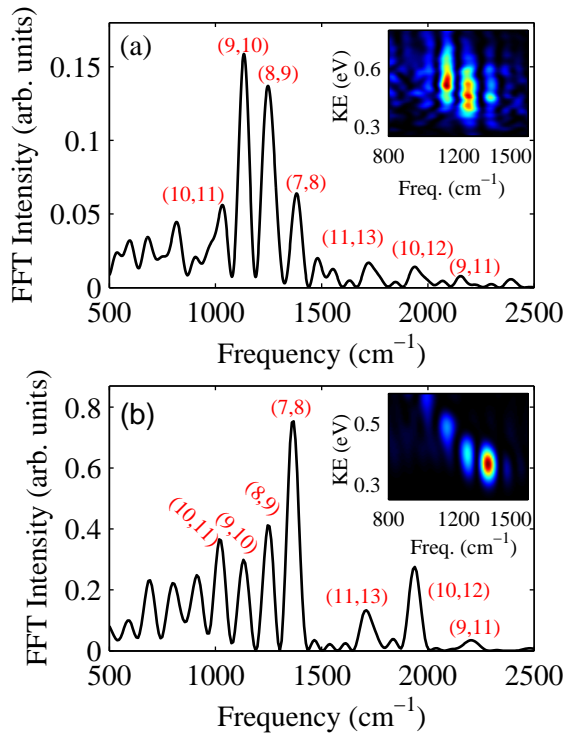


Figure 3: Fourier transform of the H^+ fragment yield integrated over the energy range between 0 and 1.2 eV for the experimental (a) and theoretical (b) results, in the case a 7 fs FWHM IR laser pulse. The spectra reveal the two-level beats that are responsible for the observed time-dependence. The insets show an energy-resolved Fourier transformation and reveal a correlation between the fragment KE release and the vibrational level occupied prior to dissociation, observed both in the experiment and the simulations.

When the H_2^+ vibrational wave packet interacts with the longer IR pulse, as in experiment B, little or no dependence of the KE spectrum on the time delay τ is expected when the XUV pulse precedes the IR without overlapping. This is indeed what is observed for time delays $\tau > 20$ fs. In contrast, for $\tau < 20$ fs the fragment KE is strongly delay-dependent, where at near zero delay it reaches energy values similar to those encountered in experiment A.

The dependence of the H^+ kinetic energy on XUV-IR delay in experiment B can be understood in terms of the adiabaticity of the dissociation process, and the way the IR intensity affects both the preparation and the propagation of the wave packet. To understand this, it is useful to discuss the dissociation dynamics in terms of Floquet states. The probe pulse projects the various vibrational components of the wave packet onto Floquet resonances, whose widths and energies vary with the intensity of the IR pulse.

When the IR pulse follows the XUV pulse without overlapping (i.e. $\tau > 20$ fs, situation indicated in Fig. 4a) individual field-free vibrational states v^+ of the ion are, at first, transported adiabatically onto corresponding Floquet resonances. Each resonance gives rise to a characteristic contribution to the proton KE spectrum [18]. The magnitude of the kinetic energy is determined by the non-perturbative laser-induced modification of the dressed potential energy curves. On the way towards dissociation, the ion experiences an increasing IR pulse amplitude, lowering the BS barrier. The lowest barrier height is reached at the center of the pulse (maximum of intensity), resulting in most efficient dissociation when the lowest energy resonance can still tunnel before the barrier rises. Most protons contributing to the spectrum have a KE of about 0.3 eV, corresponding to the resonance issued from $v^+ = 8$. Higher energy resonances are also dissociative, but are not significantly populated by the XUV ionization step (through FC mapping of the

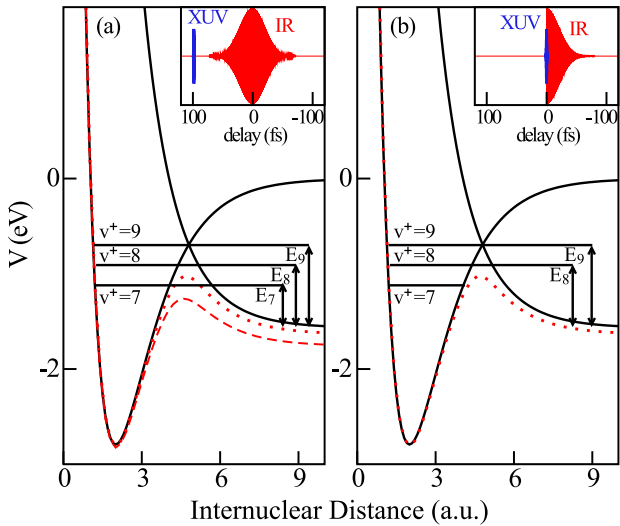


Figure 4: Potential energy curves of H_2^+ in a 750 nm laser-dressed diabatic representation (black solid lines). Also indicated are the lower adiabatic curves resulting from the diagonalisation of the radiative interaction for two intensities reached at the center of the pulse: $I = 3 \cdot 10^{12} \text{ W/cm}^2$ (dashed red line) and $I = 10^{12} \text{ W/cm}^2$ (dotted red line). E_7 , E_8 and E_9 represent the kinetic energies issued from $v^+ = 7, 8$ and 9 for XUV-IR delays of 100 fs (a) and 0 fs (b).

vibrationless ground state of H_2).

This situation is in contrast with the case where the IR and XUV pulses are overlapping ($\tau < 20$ fs). The vibrational states of the ion are then shaken up by the sudden intense IR excitation and transferred onto a superposition of resonances with weighting coefficients in the wave packet that can noticeably differ from those resulting from a FC ionization step. In particular higher energy resonances may temporarily be populated and play an important role in the dissociation step. Afterwards, as shown in Figure 4b, the ion experiences the falling edge of the IR pulse with a rising BS barrier which quenches the dissociation of low energy resonances. High energy over-the-barrier shape resonances, more populated than in the previous adiabatic case, are the ones which contribute most to the dissociation. The increasing role played by resonances issued from $v^+ = 9, 10$ explains the shift to higher energies of the proton KE distribution when the XUV pulse is close to the maximum of the IR probe.

Better quantitative experiment versus theory agree-

ment would require the relaxation of some of our model assumptions. Among these approximations are a phenomenological description of the XUV ionization step [20], the neglect of rotational degrees of freedom [21] and also of the laser focal volume averaging [21].

In conclusion, we have shown that the dynamics of two-colour dissociative ionization of H_2 under the influence of an XUV+IR pulse sequence depends considerably on the properties of the IR radiation and whether or not the IR laser is already present when the molecule is ionized by the XUV pulse. The present work represents a departure from most intense field dynamics work. Ordinarily, adiabatic laser excitation regimes result into spectral observables with finely resolved peak structures that can be interpreted in terms of isolated, non-overlapping resonances [18], and a sudden and strong laser excitation induces overlapping of large width resonances, erasing specific dynamical information (leading to structureless and less informative spectral data). However, we have described two experimental situations in this letter where the richness of the structural determination of molecules, their imaging and possible control rest on the sudden character of the strong IR excitation and the partial breakdown of the adiabatic approximation. Our experiment and numerical analysis show not only that the dynamics of a small molecule like H_2^+ is strongly dependent on the presence of a strong laser field, but moreover that the influence of the laser field is strongly dependent on its pulse duration, influencing whether any induced dynamics is adiabatic or not.

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