Multiple electron trapping in the fragmentation of strongly driven molecules

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Abstract. We present a theoretical quasi-classical study of the formation, during Coulomb explosion, of two highly excited neutral H atoms (double H*) of strongly driven H$_2$. In this process, after the laser field is turned off each electron occupies a Rydberg state of an H atom. We identify the route for forming two H* atoms and show that two-electron effects are important. We also find that both ionization steps are ‘frustrated’ in double H* formation, whereas only one ionization step is ‘frustrated’ for both the routes leading to single H* formation, as was shown by Emmanouilidou et al (2012 Phys. Rev. A 85 011402). Moreover, we compute the screened nuclear charge that drives the explosion of the nuclei during double H* formation.

Many interesting physical phenomena arise during the fragmentation of molecules driven by intense infrared laser fields. Examples of such phenomena are bond-softening and above-threshold ionization [1, 2], molecular non-sequential double ionization [3–6] and enhanced ionization [3, 7–10]. Another interesting phenomenon, the formation of single highly excited neutral fragments, has recently been observed in strongly driven H$_2$ [11] and other molecules [12–15]. The formation of excited fragments has been attributed to ‘frustrated’ tunnel ionization [16]. In a very recent theoretical study of strongly driven H$_2$ [17], two main routes

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leading to single H* formation were identified. These two routes differ regarding whether the first (pathway B) or second (pathway A) ionization step is ‘frustrated’.

In this work, using the theoretical model developed in [17], we study the formation of two highly excited H* atoms during the breakup of H2 by intense infrared laser fields. Multiple electron capture in Rydberg states was recently observed in strongly driven Ar2 dimers [18]; no breakup channel with two neutrals as end fragments was reported in the latter study. We identify the route leading to double H* formation and find that both ionization steps are ‘frustrated’, with each electron remaining bound to a highly excited state of an H atom. On the other hand, as was shown in [17] during both routes leading to single H* formation, only one ionization step is ‘frustrated’, with one electron escaping to the continuum and the other remaining bound in a highly excited state of an H atom. We also show that two electron effects are important in double H* formation, as is the case for pathway B of single H* formation [17]. Moreover, we quantify how the two highly excited electrons in double H* formation screen the nuclear charge and compute the effective charge that drives the Coulomb explosion of the nuclei.

Our quasi-classical model was discussed in detail in [17]. It fully accounts for both the electronic and nuclear motion in order to accurately describe, among other processes, the formation of one and two H* atoms. Treating both electronic and nuclear motion in theoretical studies of strongly driven molecules is a challenging task. This is the reason why, with a few exceptions [19, 20], in most studies either the nuclei are fixed [6, 21] and only electronic motion is considered or the electronic continuum is ignored and only nuclear motion is studied [22].

For completeness, we briefly describe our quasi-classical model. Firstly, we set up the initial electronic phase-space distribution. We consider parallel alignment between the molecular axis and the laser electric field (along the z-axis) to complement our studies of single H* formation in [17]. The field is taken to be \( E(t) = E_0(t)\cos(\omega t) \) at 800 nm corresponding to \( \omega = 0.057 \text{ au} \) (atomic units). In our simulation, the pulse envelope \( E_0(t) \) is defined as \( E_0(t) = E_0 \) for \( 0 < t < 10T \) and \( E_0(t) = E_0 \cos^2(\omega(t - 10T)/8) \) for \( 10T < t < 12T \), with \( T \) the period of the field. We start the time propagation at \( \omega \theta_0 = \phi_0 \), where the phase of the laser field \( \phi_0 \) is chosen randomly; see [23–25]. If the instantaneous field strength at phase \( \phi_0 \) is smaller than the threshold field strength for over-the-barrier ionization, we assume one electron (electron 1) tunnel-ionizes, i.e. tunnels through the field-lowered Coulomb potential to the continuum, whereas the initially bound electron (electron 2) is described by a one-electron microcanonical distribution. If the instantaneous field strength at phase \( \phi_0 \) allows for over-the-barrier ionization, we use a double-electron microcanonical distribution (see [25]). For both intensity regimes, we use the tunneling rate provided by the semiclassical formula in [26] with field strength equal to the instantaneous one at \( \phi_0 \). We use 0.57 au (1.28 au) as the first (second) ionization potentials. Secondly, for the initial phase-space distribution of the nuclei we use the Wigner function of the ground state (energy 0.01 au) of the Morse potential [27]; the parameters in the latter potential best describe the ground vibrational state of H2; for details see [17].

Thirdly, we transform to a new system of ‘regularized’ coordinates [28, 29]. This transformation explicitly eliminates the Coulomb singularity [25]. We then propagate the full four-body Hamiltonian using the classical trajectory Monte Carlo method [30]. During the time propagation, we allow the initially bound electron to tunnel at the classical turning points along the molecular axis using the Wentzel–Kramers–Brillouin (WKB) approximation [31, 32]. Finally, we select only those trajectories that during the breakup of H2 result in the H* + H* channel (where * denotes an electron in an \( n > 1 \) quantum state). To identify the electrons captured in a Rydberg \( n \) quantum state of H*, we follow the method described in [33].
In order to study the intensity dependence of double H* formation, we have considered an intensity of $1.5 \times 10^{14} \text{W cm}^{-2}$ in the tunneling regime and an intensity of $2.5 \times 10^{14} \text{W cm}^{-2}$ in the over-the-barrier regime; however, for the latter intensity, most of the trajectories are initiated with the tunneling model. We compute the final $n$ quantum number (see figures 1(a) and (b)) for either H* fragment for both intensities; at least 20 000 double H* events are considered.

The final $n$ quantum number distribution peaks at $n = 8$ for both intensities resembling the $n$ distribution for singly excited neutrals formed either in strongly driven H$_2$ [17] or in strongly driven atoms [16]. Moreover, the final energy distribution of either H* fragment in the H* + H* channel (see figures 1(c) and (d)) resembles that for the H* or H+ fragments in the H* + H* + e$^-$ channel [17]. For the lower intensity (figure 1(c)), the energy distribution peaks at approximately 3.5 eV. For the higher intensity (figure 1(d)), the peak shifts to higher energies since the nuclei Coulomb explode at smaller internuclear distances.

In figure 2(a), we show the pathway leading to double H* formation where electron 1 tunnel-ionizes very quickly, quivering in the laser field, whereas electron 2 tunnel-ionizes after a few periods of the laser field. However, when the field is turned off, both electrons 1 and 2 do not have enough drift energy to escape, and occupy instead a Rydberg state of an H atom. Similarly, in pathway B for single H* formation [17] (see figure 2(b)), electron 1 tunnel-ionizes very quickly, quivering in the field, whereas electron 2 tunnel-ionizes and escapes after a few periods of the laser field; however, when the field is turned off, electron 1 does not have enough drift energy to escape and occupies a Rydberg state of an H atom. Hence, while in the pathway leading to double H* formation both ionization steps are ‘frustrated’, in pathway B only the first one is.
Figure 2. Schematic illustration of the route leading to double H* formation (a) and that of pathway B of single H* formation (b). Shown is the time-dependent position along the laser field for electrons (black lines) and ions (gray broken lines).

Figure 3. The distribution of the field phase $\phi_0$ at the time when electron 1 tunnel-ionizes in the initial state for the double H* formation channel (•) and for pathway B of the single H* formation channel (>). Panel (a) is for an intensity of $1.5 \times 10^{14}$ W cm$^{-2}$ and panel (b) is for $2.5 \times 10^{14}$ W cm$^{-2}$.

We explore the route to double H* formation by first plotting in figure 3 the distribution of the field phase, $\phi_0$, when electron 1 tunnel-ionizes in the initial state. Two H* atoms form when $\phi_0$ is around 0° for the lower intensity (figure 3(a)) and around $-30^\circ$ for the higher intensity (figure 3(b)). The reason why double H* formation shifts from small values (extrema of the field) to larger values with increasing intensity is because of the onset of saturated ionization of the neutral molecule [25]. Comparing the distributions of the field phase $\phi_0$ for pathway B of single H* formation and for double H* formation in figure 3(a) (low intensity) and (b) (high intensity), we find that the two distributions are almost identical.

Next, we ask how electron 2 gains energy to transition from the ground state of the H$_2$ molecule to a high Rydberg state of an H atom. We find that electron 2 gains energy through a strong interaction with the laser field that resembles 'frustrated' enhanced ionization in H$_2^+$ ('frustrated' since electron 2 occupies a Rydberg state instead of escaping). This resemblance is corroborated by (i) the final energy distribution being similar for double H* formation (figures 1(c) and (d)) and enhanced ionization [19] and (ii) by our finding that electron 2 preferentially tunnel-ionizes when the nuclei are roughly 5 au apart, as is the case for enhanced ionization. In figure 4, we plot the double differential probability of the inter-electronic distance.
versus the inter-nuclear distance at the time when electron 2 tunnel-ionizes. Indeed, we find that electron 2 preferentially tunnel-ionizes when the nuclei are roughly 5 au apart, with the inter-nuclear distance shifting to smaller values for higher intensity. This is similar to our finding in [17] for single $\text{H}^*$ formation.

The questions that naturally arise next are whether electronic correlations are present during the formation of two $\text{H}^*$ atoms. In the case of pathway B of single $\text{H}^*$ formation, we have shown that electron–electron correlation mostly resembles the delayed pathway of non-sequential double ionization (NSDI) [34] (also referred to as re-collision-induced excitation with subsequent field ionization (RESI) [35]) where the electronic correlation is weak. For the delayed NSDI pathway, the re-colliding electron returns to the core close to a zero of the field, transfers energy to the second electron, and one electron escapes with a delay more than a quarter laser cycle after re-collision. Comparing, in figure 5, the mean inter-electronic distance as a function of time for the pathway where two $\text{H}^*$ atoms form and for pathway B of single $\text{H}^*$ formation, we find that the two mean distances are similar. Indeed, a soft re-collision is present in both cases. Moreover, the two electrons stay closer to each other during double $\text{H}^*$ formation rather than single $\text{H}^*$ formation; this is to be expected since in the former case it

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**Figure 4.** The two-dimensional distribution of the inter-electronic distance $|\vec{r}_1 - \vec{r}_2|$ versus the inter-nuclear distance $R$ at the time when the initially bound electron 2 tunnel-ionizes, for an intensity of $1.5 \times 10^{14} \text{ W cm}^{-2}$ (a) and $2.5 \times 10^{14} \text{ W cm}^{-2}$ (b).

**Figure 5.** The mean inter-electronic distance $\langle |\vec{r}_1 - \vec{r}_2| \rangle$ as a function of time for an intensity of $1.5 \times 10^{14} \text{ W cm}^{-2}$, for double $\text{H}^*$ formation (solid) and for pathway B of single $\text{H}^*$ formation (dashed line).
Figure 6. The mean total kinetic energy of the nuclei \( \langle E_{\text{kin}} \rangle \) versus the mean inverse inter-nuclear distance \( \langle 1/R \rangle \), for \( 1.5 \times 10^{14} \) W cm\(^{-2} \) (a) and \( 2.5 \times 10^{14} \) W cm\(^{-2} \) (b). The solid line is for the double H\(^+\) formation channel and the dashed black/gray line is for the H\(^+\) fragments in the double ionization channel through re-scattering/enhanced ionization. The arrows indicate the \( \langle 1/R \rangle \) corresponding to a time equal to 12\( T \) (duration of the laser pulse). The insets show the segments we fit for times larger than 12\( T \) to obtain slopes of 0.86 for the double H\(^+\) formation channel and of 1 for the double ionization channels.

is both electrons that undergo ‘frustrated’ ionization oscillation in the vicinity of the nucleus. Thus, electron–electron correlation is weak in double H\(^+\) formation and slightly stronger than for pathway B of single H\(^*\) formation.

Further, we find that the probability (out of all trajectories) for double H\(^+\) formation reduces from 0.3% for the lower intensity to 0.1% for the higher one. Thus, forming two H\(^*\) atoms is roughly 40–50 times more rare than forming one H\(^*\) atom. The reduction of the probability from 0.3 to 0.1% for double H\(^+\) formation is consistent with a decrease, for increasing intensity, of electronic correlation in the form of re-collisions. Indeed, when comparing figure 4(a) with (b) we find that at the time when electron 2 tunnel-ionizes the two electrons can be much closer to each other (smaller inter-electronic distance) for the lower intensity.

We now gain further insight into the dynamics of the Coulomb exploding nuclei by plotting in figure 6 the mean total kinetic energy of the nuclei \( \langle E_{\text{kin}} \rangle \) versus the mean inverse inter-nuclear distance \( \langle 1/R \rangle \). Note that in figure 6, time increases as \( \langle 1/R \rangle \) decreases. From early on until the time (roughly 3.8 laser cycles) when electron 2 tunnel-ionizes at \( \langle 1/R \rangle \approx 0.15 \text{ au} \) it is mostly electron 2 that significantly screens the Coulomb repulsion of the two nuclei. This screening is corroborated by the small slope of the \( \langle E_{\text{kin}} \rangle \) versus \( \langle 1/R \rangle \) curve for distances up to \( \langle 1/R \rangle \approx 0.15 \text{ au} \). After electron 2 tunnel-ionizes the two nuclei move fast away from each other. Indeed, the slope of the \( \langle E_{\text{kin}} \rangle \) versus \( \langle 1/R \rangle \) curve increases for \( \langle 1/R \rangle > 0.15 \text{ au} \) to 0.86 for both intensities.

This slope of 0.86 quantifies how much the two electrons that remain bound to highly excited states screen the Coulomb repulsion of the exploding nuclei at large inter-nuclear distances. To show that this is the case, we plot \( \langle E_{\text{kin}} \rangle \) versus \( \langle 1/R \rangle \) for breakup channels where both electrons escape. Such channels are the double ionization through re-collision or through enhanced ionization with two H\(^+\) ions and two escaping electrons as the final fragments. To identify double ionization events through re-scattering, we use as a rough criterion the condition that electron 2 escapes without tunnel-ionizing. If, however, electron 2 tunnel-ionizes,
we register these trajectories as double ionization through enhanced ionization events. Figure 6 shows that for all times the two nuclei move more quickly away from each other in the double ionization channels than in the double H+ formation channel. This is as expected since in the former case both electrons escape quickly, not screening the Coulomb repulsion of the nuclei. Moreover, the nuclei move away from each other more quickly in the double electron escape through re-scattering than through the enhanced ionization channel. This is also as expected since in the former case electron 2 escapes at times smaller than the time it takes for electron 2 to tunnel-ionize in the latter channel. For large times (small $\langle 1/R \rangle$), after the laser pulse is off, we find that the slope of the $\langle E_{\text{kin}} \rangle$ versus $\langle 1/R \rangle$ curve for the double ionization channels is 1, consistent with two H+ nuclei Coulomb exploding unhindered by electronic motion. We finally find that the slope of the $\langle E_{\text{kin}} \rangle$ versus $\langle 1/R \rangle$ curve for pathway B of single H+ formation is 0.91 (not shown in figure 6). This finding indicates that, as expected, the nuclei in pathway B of single H+ formation Coulomb explode more quickly than in double H+ formation since in the former case there is eventually only one highly excited electron screening the Coulomb repulsion of the nuclei.

Concluding, we found that in double H+ formation both tunnel-ionization steps are ‘frustrated’, with each electron occupying a highly excited state of an H atom. As a result, the two bound electrons do not significantly screen the Coulomb repulsion of the two nuclei, allowing two H+ atoms to form through Coulomb explosion; however, the process is rare. Moreover, we found that two-electron effects are present during double H+ formation, as is the case for pathway B of single H+ formation [17]. Specifically, in double H+ formation electron 2 gains energy through a weak interaction with electron 1, resembling delayed NSDI in H2. Moreover, electron 2 gains energy mostly through a strong interaction with the laser field resembling ‘frustrated’ enhanced ionization of H2+, whereas electron 1 occupies a high Rydberg state. Two-electron effects diminish with increasing intensity, with electron 2 gaining energy mainly through an interaction with the laser field. We emphasize that our three-dimensional quasi-classical formulation for describing breakup channels during Coulomb explosion of strongly driven H2 is general and can be applied to study the breakup of driven multi-center molecules.

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