Ionization and dissociation of molecular ion beams
caused by ultrashort intense laser pulses

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Abstract. Studies of the simplest one-electron molecule, \(\text{H}_2^+\), are the first step towards understanding the interaction of ultrashort intense laser pulses with molecules. We conduct coincidence 3D imaging measurements of \(\text{H}_2^+\) beams following their exposure to intense ultrashort laser pulses. These measurements are compared with our time-dependent calculations as well as a simple model we recently proposed. Our findings include above threshold Coulomb explosion – a surprising structure in the energy spectrum near the ionization appearance intensity; above threshold dissociation (ATD) of the excited electronic states of \(\text{H}_2^+\); and enhanced high-order ATD – involving the net absorption of at least 3 photons – brought about by closing the 2-photon channel.

1. Introduction

Intense laser fields that are comparable to the typical binding electric fields in a molecule lead to new molecular dissociation mechanisms due to the non-perturbative nature of the interaction in the strong field limit (see, for example, \([1, 2, 3, 4, 5, 6, 7]\)). These multi-photon processes are commonly interpreted using the dressed potential energy curves (PEC) of the molecule (i.e. the Floquet formalism) either in their diabatic or adiabatic form, the former of which is shown in figure 1 for \(\text{H}_2^+\). Examples of such processes are the bond-softening, vibrational-trapping, and above threshold dissociation mechanisms. In the bond-softening (BS) mechanism, the molecule dissociates through the gap formed between the ground state and the first excited state dressed by one photon, thus resulting in a higher dissociation probability with increasing laser intensity \([1, 2, 3, 6, 7]\). Vibrational trapping (VT), also known as bond hardening (BH), in contrast refers to the reduction in dissociation probability of highly excited vibrational states due to their trapping in the laser-induced well in the upper dressed PEC \([3, 6, 7, 8, 9, 10]\). Above threshold dissociation (ATD) is the dissociation of the molecule with higher kinetic energy release resulting from the absorption of more photons than the minimum number needed for dissociation \([1, 2, 6, 7, 11, 12, 13]\). In figure 1 we show two kinetic energy release (KER) values resulting from ATD of the vibrational state located near the 3-photon crossing. The higher KER is associated with 3-photon ATD while the lower KER results from an additional crossing to the \(1\sigma_u - 2\sigma_u\) curve on the next curve crossing and is referred to as "2-photon ATD". Several

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studies have also been done on enhanced ionization of “stretched” $H_2^+$ (e.g., [14, 15, 16, 17]) and the propagation of nuclear wave functions (e.g., [18, 19, 20]), the latter becoming feasible experimentally with the development of laser pulses shorter than the typical vibration time scale.

Figure 1. (Colour online) Diabatic Floquet potential energy diagram for $H_2^+$ in a 790 nm laser field ($R$ is the internuclear distance). The dissociation mechanisms of bond softening (BS), vibrational trapping (VT, also referred to as bond hardening), and above threshold dissociation (ATD) are marked with arrows. Note that ATD of the vibrational level near the 3-photon crossing can lead to two different KER values depending on the path the dissociating wave packet follows (see text). (Adapted from Ref. [21].)

In this paper we present our studies of ionization and dissociation of an $H_2^+$ beam by intense ultrashort laser pulses. This one-electron system has been the subject of many studies due to its importance as a benchmark, and one hopes to be able to extend our understanding to more complex systems where complete calculations are beyond present capabilities. The experimental method is described in the next section. That is followed by a discussion of a couple of intriguing recent results: (i) a surprising structure in the KER spectra near the ionization threshold and (ii) the enhancement of high KER dissociation due to high-order ATD (i.e. 3 photons and higher) as a result of reducing the pulse duration. These results are interpreted using the dressed-state Floquet picture (diabatic curves are used for simplicity). Furthermore, to understand ionization we use a unified Floquet picture suggested by Esry et al. [21].

Before proceeding, it is worthwhile to answer the question of why one should study molecular-ion beams rather than ions produced from neutrals via ionization with the same laser pulse, as is commonly done (see, for example, the recent review [7]). The main advantage of a molecular beam as a target is the ability to conduct kinematically complete measurements of dissociation, since the neutral fragments continue their flight toward the detector at their initial beam velocity, thus enabling their detection. A few other advantages are: (i) the one-electron $H_2^+$ beams can be studied in linearly polarized fields without electron recollision, (ii) dissociation can be studied at intensities lower than the intensity needed to ionize the $H_2^+$, and (iii) highly excited vibrational states of $H_2^+$ are significantly populated in the $H_2^+$ beam produced in an ion source (an incoherent Franck-Condon distribution), thus giving access to different processes. Pioneering studies of the interaction of intense lasers with $H_2^+$ beams were conducted a few years ago by the group of Figger and Hänisch [22] and by Williams et al. [23]. These demanding experimental studies were soon followed by others (see, for example, Refs. [24, 25], and a recent review [26]).

2. Experimental

The molecular ion beam interrogated by the laser beam is produced by electron impact in an electron cyclotron resonance (ECR) ion source (resulting in an approximately Franck-Condon distribution of vibrational states), accelerated to energies of a few keV, collimated to less than $1 \times 1$ mm$^2$, and directed toward the interaction region using standard ion transport techniques. The molecular ions that do not dissociate are collected in a 2 mm diameter Faraday cup (FC) mounted on a 0.8 mm bar about 200 mm in front of the imaging detector, thus, limiting measurements to KER above $\sim0.01$ eV [30]. The fragments of dissociation are detected about 774 mm downstream from the interaction region by a time and position sensitive detector consisting
of microchannel plates (MCP) and a delay-line anode, as shown in figure 2. The time and position information of each fragment hitting the detector is recorded in coincidence with a timing signal generated by a photodiode exposed to the laser pulses. From this information recorded in event mode (typically at a rate of a few tens of Hz) the momentum vectors of both fragments of dissociation are reconstructed for each molecular ion. It is important to note that the laser-ion interactions take place in a weak longitudinal electric field which accelerates the charged fragments relative to the neutral ones, thus separating them in time of flight (TOF) and distinguishing the different dissociation channels from each other as shown in figure 2.

The laser beam is provided by a Ti:Sapphire chirped-pulse amplification laser system with a central wavelength of 790 nm, a Fourier-transform-limited pulse duration of 35 fs (FWHM in intensity), a 1 kHz repetition rate, and a pulse energy of about 1 mJ. For measurements with longer pulses it is stretched by introducing a positive chirp. The linearly polarized pulse is then focused by an \( f = 200 \) mm lens into the centre of the ion beam, and the laser polarization, laser propagation, and ion beam are normal to one another. A hollow-core fibre and chirped mirrors are used to compress the pulse below 10 fs (FWHM) when needed. In this case an off-axis parabolic mirror with a similar focal length is used in order to preserve the temporal shape of the pulse. The peak intensity is about \( 10^{14} - 10^{15} \) W/cm\(^2\) at peak laser power for the longer pulses and about an order of magnitude higher for the sub 10 fs pulses.

Finally, it is important to note that measurements conducted at a specific peak intensity, \( I_0 \), have contributions from all lower intensities due to the spatial intensity distribution of the focused laser beam. This volume effect (i.e. intensity averaging) is less important when a lower intensity limit is imposed, such as the need to first ionize an H\(_2\) target when gas targets are used. However, for molecular ions in highly excited vibrational states, dissociation can occur at much lower intensities making this problem more severe. The problem can be reduced by using a very narrow ion beam [22]. We took advantage of the fact that the ion beam is much wider than the laser beam waist, but much smaller than the Rayleigh length (i.e., \( I(z) \approx I_0 \)), and introduced a method (named the “Intensity Difference Method”) for eliminating the contributions from the low-intensity tail altogether assuming a Gaussian laser-beam profile [27, 28].

### 3. Results and Discussion

Our studies of molecular ions focused mainly on the simplest molecular ion, H\(_2^+\) [21, 25, 26, 29, 30], with some initial attempts to explore more complex systems [26, 31] in this non-perturbative regime of laser-matter interactions. Below we will focus on two intriguing examples, the first...
involving ionization near the appearance intensity in 45 fs pulses, and the second demonstrating enhancement of ATD involving a large number of photons using 7 fs laser pulses.

3.1. Above threshold Coulomb explosion
The ionization of H$_{2}^{+}$ usually yields a broad featureless KER distribution centred around a value which is much lower than what one would expect from direct ionization, i.e. much less than about 1/R$_{0}$ $\approx$ 13.6 eV (somewhat higher if one starts from H$_{2}$), where R$_{0}$ is the equilibrium internuclear distance of H$_{2}^{+}$. This observation is due to enhanced ionization probabilities for H$_{2}^{+}$ when stretched to about 7-10 a.u. (e.g., [15, 16, 17, 18, 23]).

Surprisingly, a multi-peak structure appears in the KER spectrum near the appearance intensity of ionization, as recently reported by Esry et al. [21] and soon after by Staudte et al. [32], using H$_{2}^{+}$ and H$_{2}$ targets, respectively. The peak positions seem insensitive to the laser intensity, but their widths increase rapidly with intensity washing out the structure. In order to understand the origin of this structure, Esry et al. suggested a “unified Floquet” PEC diagram which treats ionization and dissociation on an equal footing instead of superimposing multi-photon ionization transitions on the Floquet diagram commonly used to interpret the dissociation mechanisms (see figure 3). In the commonly used approach, shown in figure 3(a), the dissociating wave packet can be ionized by absorbing 16 photons once it reaches the internuclear separation, R, where this is the energy difference to the 1/R curve representing the doubly ionized hydrogen molecule. Similarly, 15-photon ionization can be initiated at some larger R, and so on. Instead of using such a mixed picture in which the PECs involved in dissociation are shifted down by the energy of the photons absorbed while ionization is not part of the PEC diagram, it is better to treat them equally and shift the 1/R potential energy curve down by 16 photons, 15 photons, and so on. This yields the unified Floquet diagram shown in figure 3(b).

Now, imagine the dissociating wave packet initiated by the BS mechanism. As it travels to larger R it encounters crossings with the 1/R $- 13\omega$, 1/R $- 12\omega$, 1/R $- 11\omega$, and 1/R $- 10\omega$ curves, one after the other. Ionization can occur around each of these crossings if the laser intensity is large enough to couple them, thus producing peaks in the ionization KER at the values indicated on the figure. Note that these values include the kinetic energy gains both on the dissociative curve.

**Figure 3.** (Colour online) Left: Diabatic Floquet potential energy diagram for H$_{2}^{+}$ in a 790 nm laser field (as shown in figure 1 with 16-photon ionization superimposed indicating the R value where this multi-photon ionization channel opens). Right: A unified diabatic Floquet diagram treating dissociation and ionization on an equal footing (see text). (Adapted from Ref. [21].)
prior to ionization and on the $1/R$ curve after ionization. These peaks in the KER spectrum are separated by one photon energy, and therefore we named the process “above threshold Coulomb explosion” (ATCE) using the same convention as ATD and above threshold ionization (ATI).

The range around each crossing in which ionization occurs increases with increasing intensity, and as a result the KER peaks broaden, eventually washing out the structure completely. In a similar way, lower vibrational states of $\text{H}_2^+$ that dissociate via the 3-photon crossing pass through the $1/R = 15\omega$, $1/R = 14\omega$, $1/R = 13\omega$, and $1/R = 12\omega$, as shown in figure 3(b). This again yields a sequence of peaks separated by one photon. To summarize, this simple model is consistent with our observations, and it has predictive power as demonstrated below.

![Figure 4.](image)

In figure 4(a and b) we show the measured KER spectra for 45 fs, 790 nm pulses at two intensities, together with a fit that uses the predicted peak positions and adjustable peak amplitudes. The peak widths are also adjusted, but they are kept similar for similar processes. The fit to both spectra was conducted with the same parameters except for allowing larger widths by one scaling factor for the higher intensity spectrum in panel (b). The agreement between the model and data is very good, but one may question the usefulness of such a model with free parameters. We therefore decided to challenge the model by making predictions first and verifying them by experiment. Using the simple unified Floquet diagram one can easily see that the spacing between the KER peaks should increase with increasing photon energy. This suggests that a measurement using the second harmonic of our laser should yield fewer peaks near the appearance intensity of ionization with larger spacing between them. Our subsequent measurements indicated that our predictions were “right-on-the-money” as shown in figure 4(c).

In addition, one can observe in this figure a peak around 2 eV that does not appear in the 790 nm data. This peak is due to ionization at a crossing at a much larger $R$ (the 10- and 5-photon crossings for the 790 and 395 nm, respectively), for which the intensity dropped in the 45 fs, 790 nm pulse but was still intense enough to ionize in the 75 fs, 395 nm pulse. This model also predicts the angular distribution for ionization to be proportional to $\cos^2 m \theta$, where $m$ is the number of photons involved in the ionization. Therefore we expect the slope of the yield vs $\cos^2 \theta$ curve, on a log-log scale, to be twice as large for the 790 nm data as for the 395 nm, which proves to be the case according to figure 4(d).

Finally, our model is in good agreement with the recently published $\text{H}_2$ data of Staudte.
et al. [32]. In this case, our model has to include the effect of the moment of ionization of the neutral target. Once that is taken into account, the agreement with the data is of similar quality as the agreement with our data [33]. It is worth noting that Staudte et al. have a different theoretical interpretation for this surprising structure in the KER spectrum, based on an interference between net 2-photon and 1-photon transitions that localize electrons which subsequently ionize. Further investigation is needed to settle this “controversy”.

3.2. Enhancing high-order ATD and ATD of the $2l$ manifold

Even at higher laser intensities, dissociation of $\text{H}_2^+$ shows very little high-KER ATD. This is mainly due to the role played by the crossing following the 3-photon crossing along the dissociation path, as shown in figure 5(a). Typically, during the time the dissociating wave packet traverses this crossing the laser intensity is still high enough to induce transitions to the $1s\sigma - 2\omega$ curve. Note that this 1-photon transition requires less intensity than the intensity needed to initiate ATD through the 3-photon crossing. In other words, the adiabatic path from the 3-photon crossing leads to the $1s\sigma - 2\omega$ dissociation limit. As a result, most of the ATD ends up with KER values below 2 eV. In order to reach the next higher KER $2p\sigma - 3\omega$ curve on a purely adiabatic path, dissociation has to start on the 5-photon crossing, which requires much higher intensities and therefore indicates why the high KER component of ATD has been so difficult to observe experimentally.

We set as our goal to enhance this higher order ATD, i.e. ATD which starts from the 3-photon crossing and ends on the $2p\sigma - 3\omega$ curve, by closing the crossing between the $2p\sigma - 3\omega$ and $1s\sigma - 2\omega$ curves. This can be done by reducing the pulse duration below the time needed for the dissociating $\text{H}_2^+$ to reach this crossing. The shortest pulses we can produce, slightly below 7 fs, are not short enough to completely eliminate transitions at this crossing as the intensity is still sufficiently high to couple the states. We show, however, that it is short enough to reduce the transition probability and enhance the high-KER yield in $\text{H}_2^+$ dissociation [34]. This effect is enhanced further for a $\text{D}_2^+$ target because the travel time between the two crossings is approximately $\sqrt{2}$ longer.

We solved the time-dependent Schrödinger equation of $\text{H}_2^+$ numerically, including electronic, vibrational and rotational degrees of freedom [35]. These calculations agree with the simple argument given above and show enhancement of the high KER in $\text{H}_2^+$ dissociation, especially

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(Colour online) Diabatic Floquet diagram including the $n=1$ and 2 manifolds. Note that in (b) only one state of each symmetry is included from the 2$l$ manifold in order to simplify the figure.}
\end{figure}
for higher laser intensities (see figure 6). In addition, the calculation shows competition from the 2l manifold. Moreover, these contributions show an ATD-like structure (i.e., peaks spaced by the photon energy), which we refer to as ATD\textsubscript{2} to indicate that it involves ATD from the 2l manifold instead of ATD\textsubscript{1} involving only the \(n=1\). This is illustrated on the unified Floquet diagram in figure 5(b), which includes both the \(n=1\) and 2 manifolds.

The H\textsuperscript{+}\textsubscript{2} data at \(2 \times 10^{13}\) W/cm\(^2\), shown in figure 6(c), is similar to the calculations, with maybe a hint of higher KER for aligned molecular ions (i.e. \(\cos \theta=1\)). The H\textsuperscript{+}\textsubscript{2} data for \(2.5 \times 10^{15}\) W/cm\(^2\) shows a clear high KER tail in agreement with the theoretical predictions. It is important to note that the experiment is conducted at a peak intensity much higher than our calculations in order to enhance the strength of this effect, which we predict to increase with increasing intensity. However, calculations at the experimental intensity cannot be performed yet because they require that too many states be included. In spite of that, the trends in the theory and experiment are in good agreement, most likely because the intensity averaging in the experiment reduces the effective intensity of the data to lower values than the peak intensity. It is important to note that, according to our calculations, the dominant contribution to the high KER tail in this case is a near-equal mixture of ATD\textsubscript{1} and ATD\textsubscript{2} from 3- and 9-photon absorption, respectively.

Finally, the D\textsuperscript{2} data shown in figure 6(e and f) for \(2 \times 10^{13}\) W/cm\(^2\) and \(2.5 \times 10^{15}\) W/cm\(^2\), respectively, shows a much larger enhancement of the high KER tail as expected from our channel closing argument [34]. In this case our calculations indicate a larger enhancement of high-order ATD\textsubscript{1} and a decrease in ATD\textsubscript{2}. Both of these are caused by the slower propagation of the dissociating wave packet, which results in lower intensity when reaching the \(2\rho\sigma - 3\omega \rightarrow 1\sigma - 2\omega\) crossing and a lower fraction of excited 2l states whose excitation tends to occur more efficiently at larger \(R\). Note that this high KER feature is strongly aligned along the laser direction, indicating the need for high effective fields, i.e. the electric field along the molecular axis, and some possible post-pulse rotation.

4. Summary and Outlook

In summary, we have presented a few new phenomena in the interactions of intense ultrashort laser pulses with H\textsuperscript{+}\textsubscript{2}: (i) ATCE - a surprising KER structure near the ionization appearance intensity, (ii) ATD\textsubscript{2} - above threshold dissociation of H\textsuperscript{+}\textsubscript{2} (2l) excited states, and (iii) enhancement of high-order ATD yielding a high KER tail, especially for the more massive isotope. All these effects are interpreted within the unified Floquet picture, in addition to more elaborate numerical calculations. This simple model has recently been used to assign the dissociation pathways of O\textsuperscript{+}\textsubscript{2} in an intense 45 fs, 790 nm pulse [31]. This suggests that the knowledge we gain from exploring H\textsuperscript{+}\textsubscript{2} can help us interpret more complex molecular systems. Finally, advances in
laser technology, such as shorter pulses and carrier envelope phase (CEP) control, open new possibilities for controlling the pathway that an H$_2^+$ molecule follows upon dissociation (see, for example, [36, 37]). More importantly, this knowledge may lead to future control in molecular reactions having wider impact on the world around us.

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