Ultrafast laser-induced photodissociation dynamics of H_2^+: measuring adiabatic avoided crossings

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Introduction

The photodissociation (PD) and Coulomb explosion of molecules in intense (>10 TW/cm^2) ultrafast (<100fs) laser fields continues to attract considerable experimental and theoretical attention$^{1)}$. The hydrogen molecular ion is of special interest as it is amenable to rigorous quantum theory (for recent examples see reference $^{2)}$. However, experimentalists generally rely on ionizing H_2 early in the same laser pulse used to study the nascent H_2^+, which readily photodissociates, and it is assumed that the consequent PD dynamics is governed solely by the lowest bound ($1s\sigma_g$) and dissociative ($2p\sigma_u$) states.

Dissociation dynamics in H_2^+

Current studies of H_2 reveal that ionization to H_2^+ by an ultrafast laser pulse is not a simple case of electron removal by the tunnelling or multiphoton mechanism$^{3)}$. These studies are of particular interest, as it had been assumed that the Franck-Condon (FC) distribution of vibrational levels would be populated in the H_2^+ ion (for examples, see$^{4)}$). This assumption leads to a somewhat unsatisfactory explanation of the observed dissociation spectra. Rather, in the ultrafast regime, it is found that the distribution of vibrational states is heavily skewed towards the lowest levels, and the distribution of population depends on intensity, wavelength and pulse duration$^{3,5)}$. The efficient control of the distribution of population requires tailoring a combination of the absorption of N photons and the pondermotive energy gained from the field to couple vibrational levels in H_2 to H_2^+.

In the present work, we concern ourselves purely with PD: a well-documented$^{6)}$ procedure for understanding this process is through the creation of a light-induced molecular state, where the bound $1s\sigma_g$ and dissociative $2p\sigma_u$ states are "dressed" by multiples of the photon energy. Due to the parity of the states, the multiphoton dressing of the molecular potential creates curve crossings. At very low intensities (typically <100 MW/cm^2) the dressing is diabatic, and the system is essentially unperturbed by the laser field. However, at intensities > 100 MW/cm^2, the molecule can only respond adiabatically to the intense laser field, and the curve crossings become repulsive: "avoided crossings" result. The degree of repulsion of these avoided crossings due to the intense laser field is of interest in the current work.

Only two research groups internationally are involved in experimental investigations on the unbound H_2^+ molecule. The Newell (UCL) – Williams (QUB) Collaboration working at the Rutherford Appleton Laboratory (UK)$^{7)}$ and the Hänsch & Figger Group (MPQ Garching)$^{8)}$ specialise in generating beams of H_2^+ using DC plasma discharge ion sources. Unlike experiments on H_2, such experiments preserve the FC distribution of vibrational population as the unbound ion is generated remotely from the laser interaction. This experimental was carried out at the Astra Laser Facility, TA1, with typical operating parameters: 790 nm, 40fs pulses delivering 30mJ at a repetition rate of 10Hz, and f/11 focused. Despite the shallow focus, a peak intensity $I_0 \approx 100$ PW/cm^2 is produced, and as the unbound molecular ion photodissociates at intensities many orders of magnitude lower, the experiment is truly macroscopic: the usable range of the focused Astra beam extends over centimetres. Hydrogen gas is introduced into magnetically confined DC plasma; following extraction, momentum selection, collimation and modulation, a 1keV beam of H_2^+ ions was crossed with the focused Astra laser pulse.

Because the PD laser pulse does not generate the H_2^+ ions, the laser-H_2^+ interaction is dramatically different to the situation with H_2. The well-defined and far broader distribution of vibrational levels populated in the discharge source means that the laser-H_2^+ interaction probes a wider range of energies in the laser-dressed potential. As the molecule photodissociates $H_2^+ + N\hbar\omega \rightarrow H + H^+$, the energy gained through photon absorption will manifest as kinetic energy shared between the fragments. Recorded over four orders of magnitude of intensity (from 3 TW/cm^2 to 30PW/cm^2), we report novel measurement of the distortion of the adiabatic curve crossings generated during a 40 femtosecond laser pulse by measuring the kinetic energy of the neutral H fragment.

Figure 1 is a comparison of the kinetic energy shared during PD under identical optical conditions. In both cases, the kinetic energy released is measured as the focusing optic is translated (Intensity Selective Scanning$^{9)}$). In H_2^+ (Figure 1a) the limited width (0.6 mm) of the ion beam acts as a slot through which the focus is systematically scanned. A 0.25 mm aperture in our TOF mass spectrometer performs the analogous role in the H_2 experiment (Figure 1b). This figure illustrates two important points. Firstly, the narrow distribution in Figure 1b is due to the necessity to create H_2^+ from H_2 before PD can occur (Figure 1b).

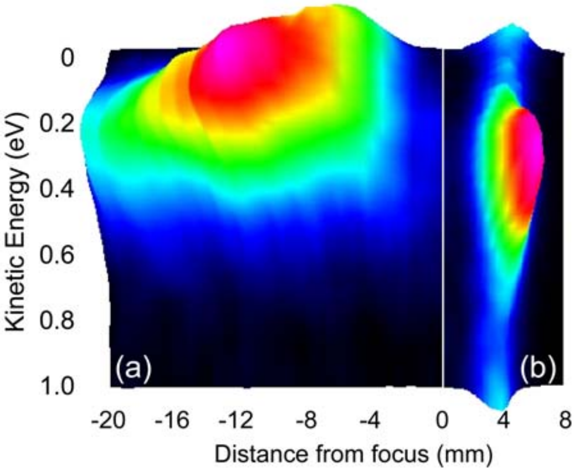

Figure 1. Comparison of kinetic energy spectrum as a function of focusing optic position (i.e. laser intensity) for identical focal conditions. (a) H from the photodissociation of H_2^+, (b) H^+ from the ionization and photodissociation of H_2. The major difference in the range of intensity is due to the need to ionize H_2 before photodissociation. The change in kinetic energy distribution is due to a change in vibrational population.

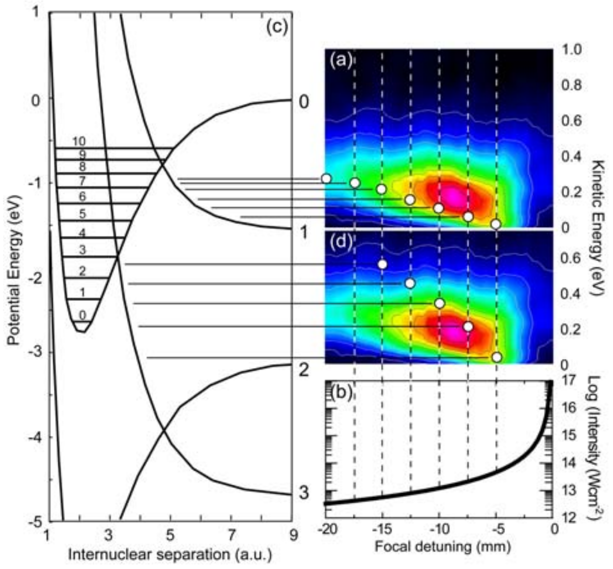

Figure 2. Measuring the adiabatic avoided crossings during photodissociation of H_2^+ with a Franck-Condon distribution of vibrational states. (a) White markers indicate evolution of the one-photon crossing with increasing laser intensity, quantified in (b), the on-axis intensity distribution. (c) The kinetic energy measured in (a) compared to the known light-dressed potential. (d) Opening of the two-photon crossing, showing intensities (b) and corresponding kinetic energies (c).

Without the barrier to dissociation that the binding electron creates, H_2^+ the hydrogen molecular ion readily fragments at very low intensities, as clear from far broader distribution in Figure 1a. Indeed, for the $v = 9$ state, the absorption of only one photon from at an intensity < 10 MW/cm^2 will suffice. Secondly, the observed differences in kinetic energy reflect the vibrational population. H_2^+ (Figure 1a) is purely FC, whereas the distribution in H_2 (Figure 1b) is biased by the laser pulse towards the lowest states through the coupling process described earlier.

To clarify the mechanism behind PD, we move now to the core argument of the present work: the data presented in Figure 1a is recast in terms of the light-dressed molecular potential. Figure 2 is a compound illustration intended for a straightforward visual summary of our results: by reversing the kinetic energy axis of Figure 1a, and setting zero kinetic energy equal to the asymptote of the light-dressed potential, the PD mechanism may be observed. In Figure 2a, a series of markers are superimposed on the observed kinetic energy distribution indicating the lowest contribution from one-photon absorption. Focal detuning in Figure 2a is converted to on-axis laser intensity in Figure 2b (vertical dashed line). The familiar diabatic light-dressed potential energy diagram is presented in Figure 2c, where the numerals to the right indicate photon number. The horizontal lines between Figures 2a and 2c indicate the expansion of the one-photon avoided crossing with increasing laser intensity, thus an increasing number of vibrational levels (between $v = 5$ and $v = 9$) are liberated via PD.

Two-photon PD is also observed as a “shoulder”, indicated by the markers in Figure 2d. As the simultaneous absorption of three photons is necessary, a sharper response to the laser intensity is observed. While the form of the $1s\sigma_g$ and $2p\sigma_u$ potentials is reasonable under field-free conditions, it should be pointed out that the intense laser pulses will also induce an electric field which will distort the molecular potential, before the adiabatic crossings come into play. We are continuing a quantitative analysis, and will remove the modification imposed by the variation in focal volume, yielding data against which theoretical predictions will be tested.

Conclusion

Ultrafast photodissociation dynamics have been studied in hydrogen. By creating a beam of H_2^+ remotely from the laser interaction, we observe a very different vibrational population to that reported in a comparable experiment on H_2. Such a difference is a consequence of the 40fs laser pulse used coupling a narrow range of vibrational levels from the H_2 molecule to H_2^+. We discuss the results of the laser-H_2^+ beam interaction in terms of light-dressed potentials, and find that the distribution of neutral H atoms observed is a direct measurement of the opening of the adiabatic avoided crossings created when the laser pulse “dresses” the molecule.

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