H2+ in intense laser field pulses: ionization versus dissociation within moving nucleus simulations

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Abstract. The theory of the interaction of the H_2^+ molecular ion with an intense short laser pulse is modelled by solving the time dependent Schrödinger Equation for the electronic degree of freedom while the nuclear motion is described classically. This method allows us to discuss the influence of the pulse duration on the respective weights of ionisation and dissociation.

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1. Introduction

The interaction of intense laser pulses with either atoms, molecules or clusters has motivated a large number of studies describing interesting non-pertubative effects such as high-order harmonic or X-rays generation [1], above threshold ionisation -dissociation- [2, 3, 4] or very energetic ions emerging from Coulomb explosion [5] . The major difficulty with molecules is to deal with both the electronic and the nuclear degrees of freedom. Regarding the latter, one has often neglected it, through the use of the Born-Oppenheimer approximation, keeping the nuclei fixed, [6, 7], or considered only the lowest, or essential, electronic states, [4], ignoring the role of ionisation. More refined approaches are based on a full quantum description of the system in 1-D, [8, 9] or 3-D, [10, 11]. Here we propose to use a semi-classical approach, somewhat similar to the one used routinely in collision theory, [12] i.e. we describe the electron quantum mechanically while the motion of the two nuclei is described classically. In this letter, we restrict ourself to a 1-D configuration, using soft-core potentials, since such a model describes reasonably well both the atomic electron, [13], and the molecular dynamics, [14], in linearly polarized laser fields. We note that this approach can be straightforwardly extended to 3-D. This method gives an insight on what parameters are essential in the evolution of the molecular ion in the presence of a laser pulse and it sheds light on the competition between the different processes like ionisation, dissociation or excitation of the vibrational levels. We first present the model, then we compare the results

obtained with either frozen or moving nuclei, exhibiting, in both cases, charge-resonance-enhanced-ionisation (CREI) already seen in previous works, [6, 7, 8, 9, 10]. We will use atomic units throughout this letter.

2. Model

The electronic state of the H_2^+ ion is described by its wavefunction, the time evolution of which is derived by solving the following 1-D time dependent Schrödinger Equation (TDSE), in the velocity gauge:

$$\begin{aligned} i\frac{\partial\psi(x,t)}{\partial t} &= [-\frac{1}{2}\frac{\partial^2}{\partial x^2} + V(x,t) + \frac{i}{c}A(t).\frac{\partial}{\partial x}]\psi(x,t) \qquad (1)\\ V(x,t) &= -\frac{1}{\sqrt{a^2+(x-X_1(t))^2}} - \frac{1}{\sqrt{a^2+(x-X_2(t))^2}}, \end{aligned}$$

where $X_1(t)$, $X_2(t)$ are the positions of the two nuclei. The electric field $E(t)$ was chosen as $E_0 f(t) sin(\omega t)$, with $f(t)$ representing the field envelope. It is related to the vector potential $A(t)$ through the relation $E(t) = -\frac{1}{c}.\frac{\partial A(t)}{\partial t}$. The smoothing parameter a was set equal to $\sqrt{2}$ in order to get $-0.5\, a.u.$ as an asymptotic energy for the isolated atom. The motion of the protons is treated classically via the equations:

$$M\frac{d^2X_i}{dt^2} = F_{j\to i}(t) + F_{e^-\to i}(t) + F_{laser}(t), \qquad (2)$$

with $F_{j\to i}(t), F_{e^-\to i}(t), F_{laser}(t)$ represent the repulsive internuclear, attractive electronic and laser forces, respectively. Their expressions are given by:

$$F_{j\to i}(t) = \frac{X_i(t) - X_j(t)}{(q + R^2(t))^{3/2}} \qquad (3)$$

$$F_{e^-\to i}(t) = -\int_{-L}^{+L} \frac{(X_i(t) - x) \mid \psi(x,t) \mid^2}{(a^2 + (X_i(t) - x)^2)^{3/2}} dx \qquad (4)$$

$$F_{laser}(t) = E(t), \qquad (5)$$

where $R(t) = \mid X_1(t) - X_2(t) \mid$ is the internuclear distance, and $M \approx 1836\ a.u.$ the mass of the proton. The smoothing parameter q in the internuclear term was chosen equal to 0.03, in accordance with previous works, [8, 9]. The time evolution of the different particles was obtained by the Crank-Nicholson method for Eq.(1), [15] and the Verlet method for Eq.(2), [16]. In order to avoid reflexions of the electronic density from the boundaries of the box we have used an absorber, [17]. Therefore, the norm of the wavefunction can decrease in time, providing a measure of the ionisation. We can also compute the positions of the two nuclei as well as the electronic probability density P_i around each proton (in a box of $5\ a.u.$). The variations in time of the latter quantity can indicate dissociation or vibrational excitation of the molecular ion.

3. Results

We have first computed the energies of the two first molecular states, $1\sigma_g$ and $1\sigma_u$, of the ion as determined by diagonalizing the laser-free hamiltonian for fixed internuclear distance, R. With the help of this simple model we have obtained the two first molecular states i.e. a pure dissociative state $1\sigma_u$, while $1\sigma_g$ has a minimum located at $R = 3.5$ $a.u.$ with a dissociation energy of 0.07 $a.u.$. These values, which are typical of 1-D simulation, are in reasonable agreement with results for full 3-D simulation ($R_e \approx 2$ $a.u.$).

3.1. Fixed nuclei ionisation rates

We have first determined the ionisation rates for a Nd:YAG laser ($\omega = 0.043\, a.u.$, with a cycle duration of $T_L \approx 3.5$ fs). To this end we have used a trapezoidal laser pulse with two cycles linear turn-on and turn-off and 6 cycles flat part. The ionisation rates were deduced from the decrease of the norm of the wavefunction absorbed at the boundaries.

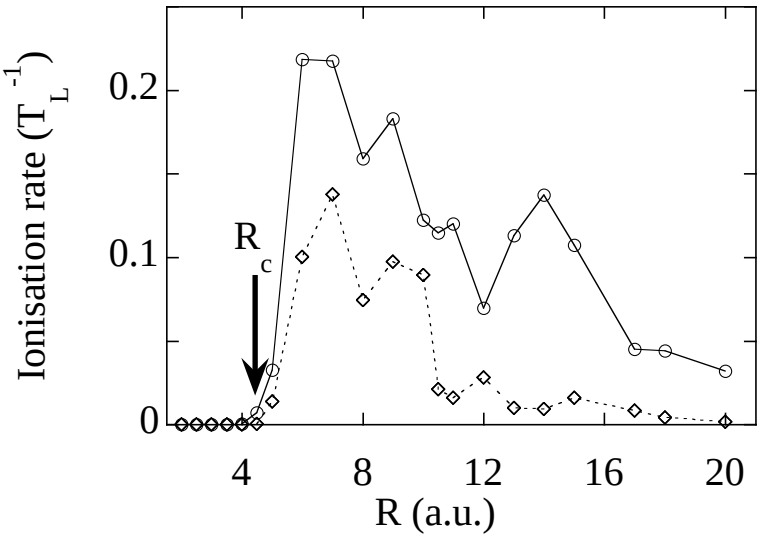

Figure 1. Ionisation rate as a function of the interatomic distance R for a YAG:Nd laser ($\omega = 0.043\, a.u.$). Solid line: $I = 10^{14}$ W/cm^2; Dashed line: $I = 5 \times 10^{13}$ W/cm^2. The critical internuclear distance R_c (see text) is indicated by an arrow.

The variations of the ionisation rate with the internuclear distance R for two intensities, $I = 5 \times 10^{13}$ and 10^{14} W/cm^2 are shown in Fig. 1. There exists an intensity dependent critical value for R_c around 5 $a.u.$ where ionisation starts to be enhanced. The value of R_c increases when the intensity decreases. For larger values of R one observes local minima. For distances longer than 20 $a.u.$, we recover the ionisation rate for an isolated 1-D hydrogen atom. This phenomenon can be explained in terms of Charge-Resonance states, using the quasi-static approximation and the associated tunelling rates, [18, 19]. Briefly, in the presence of the low frequency electric field the HOMO $1\sigma_g$ and the LUMO $1\sigma_u$ states are transformed in localised atomic states with an energy separation of the order of $E_0 R$. Each state has its own ionisation rate, that

is strongly dependent on its energy in the "laser-modified" potential barrier. Therefore, for particuliar values of R the electron can be localised in one of these states and can ionise more rapidly.

3.2. Moving nuclei simulation

As shown above, ionisation yields are very small for femtosecond laser pulses if the internuclear distance is smaller than $R_c \approx 5\, a.u.$. However, as ionisation takes place, as the electronic density starts to expand, the bond is softened and, therefore, R increases. Then, if R_c is reached while the laser is on, enhanced ionisation can take place, thus leading to the Coulomb explosion of the molecule. This is the case when, starting from the equilibrium internuclear distance $R = 3.5\, a.u.$, we take the same pulse shape as above with an intensity of $I = 10^{14}\, W/cm^2$. One can see, in Fig. 2, that the critical distance is reached for $t \approx 20\, fs$. Ionisation is the predominant phenomenon in this case with a final ionisation yield $\geq 99.5\%$. It should be noted that, for fixed nuclei, ionisation would only amount to less than 0.1%

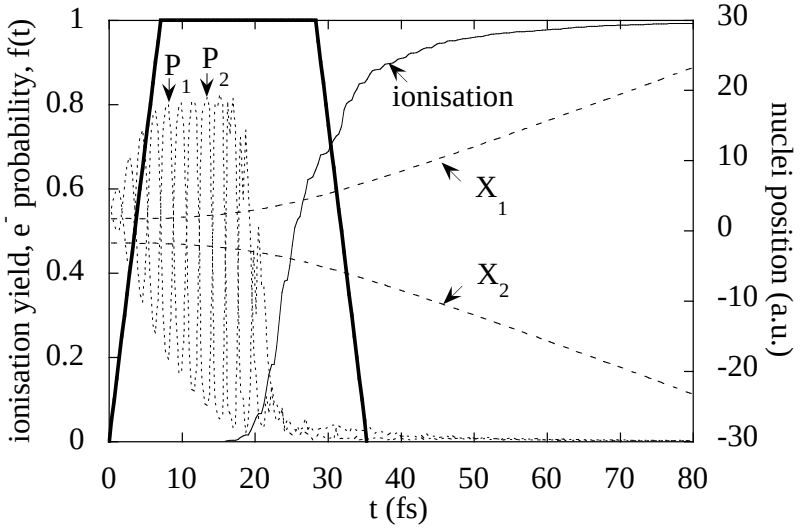

Figure 2. Ionisation yield (solid line), nuclei positions X_i (dashed lines) and electronic probabilities P_i around the two nuclei (dotted lines) for trapezoidal laser pulse (thick line) with $I = 10^{14} W/cm^2$ and $\omega = 0.043 a.u.$

If we now consider more realistic gaussian pulse shapes, $f(t) = e^{-\frac{t^2}{\tau^2}}$, we can easily identify three regimes – excitation of the molecular ion, dissociation and ionisation – corresponding to – very short, short and long – pulse durations as measured by the Full Width Half Maximum (FWHM $= 2\tau\sqrt{ln2}$) illustrated in Figs. 3.

As said before, the value of R_c increases when the intensity decreases. Therefore, the final state reached by the system will mainly depend on what time, in the pulse, this critical distance is reached. If we are in the long pulse regime, Fig. 3a, e.g. if R_c is reached for $t \leq \tau$, we are in a situation close to the one of Fig. 2 and ionisation,

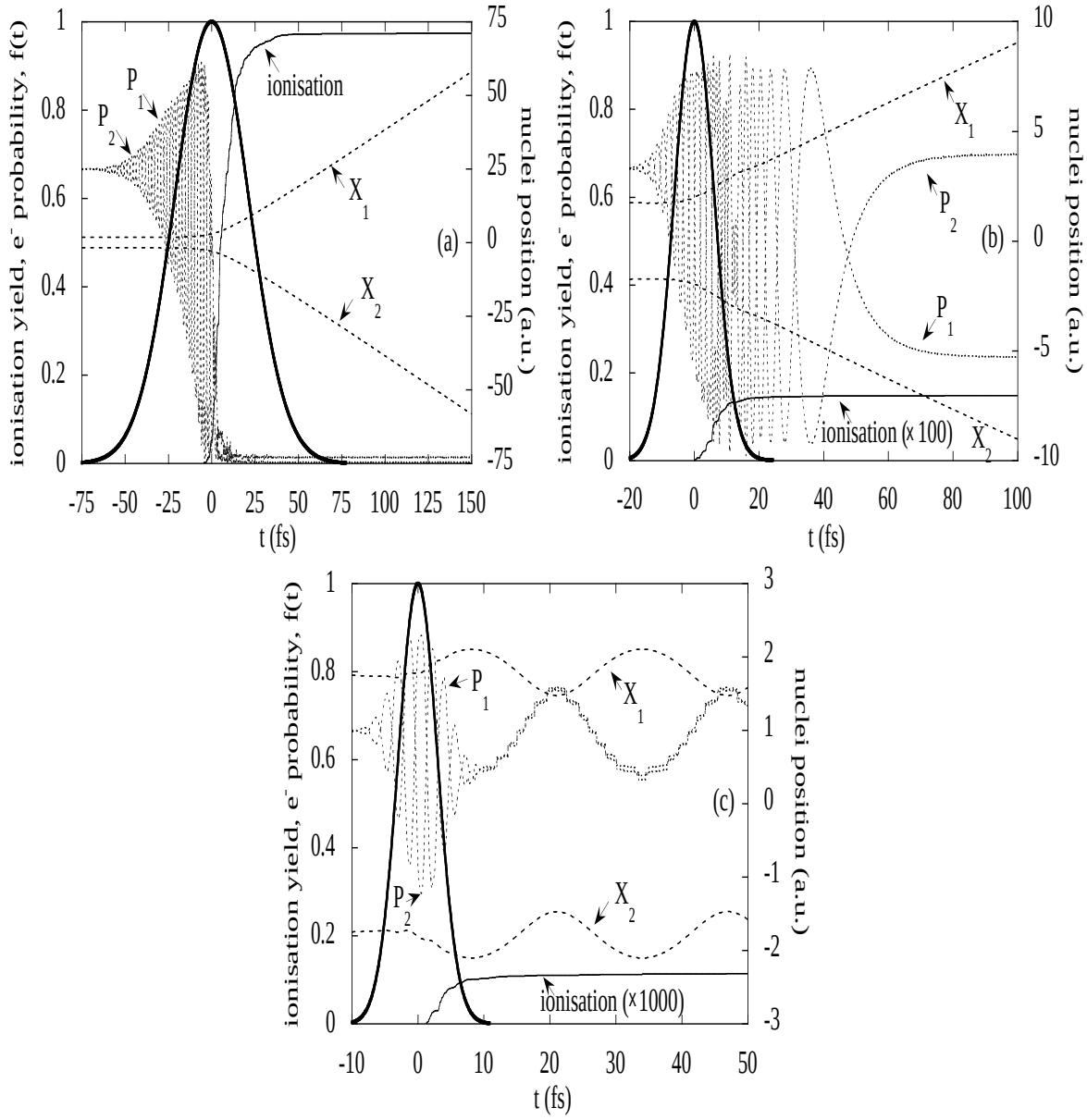

Figure 3. Ionisation yield (solid line), nuclei positions X_i (dashed lines) and electronic probabilities P_i around the two nuclei (dotted lines) for a gaussian laser pulse (thick line) different durations. Here $I = 10^{14} W/cm^2$ and $\omega = 0.043 a.u.$. (a) : $FWHM = 50\ fs$, (b): $FWHM = 14.5\ fs$, (c): $FWHM = 7\ fs$.

followed by Coulomb explosion of the two bare nuclei, is dominating the dynamics. In the very short pulse regime, the ion is not stretched enough while the laser is on and there is almost no ionisation. One can see, in Fig. 3c, the two nuclei oscillating as H_2^+ is vibrationaly excited. The period of oscillation ($\approx 25\ fs$) is in agreement with the one we would expect from the potential curve of the $1\sigma_g$ state.

More interesting is the intermediate case (short pulse regime, Fig. 3b) corresponding to the situation when R_c is reached for $t \approx \tau$, i.e. when the electric field

intensity is already decreasing. Then, the system can evolve in two different channels leading either to excitation, as previoulsy described, or to dissociation. The latter corresponds to the case when there is separation of one ion, the electron staying close to the other nucleus. It turns out that the choice between either final state depends critically on the phase of the laser field, see Paulus *et al*, [20] for a similar situation in atoms. Interestingly, our simulation indicates that, when there is dissociation, the electron is in a superposition of the two states ($1\sigma_u$ and $1\sigma_g$) and its probability of presence oscillates between the two nuclei. Then the nuclei move apart from each other, the internuclear potential barrier increases and the oscillating electron will end eventually being trapped in one of the potential holes. Again, the choice of which nuclei, right or left, depends on the laser phase.

4. Conclusions

In the present letter we have presented an analysis based on a 1-D model of the response of a simple molecular ion to an intense infrared laser pulse. Our findings show that it is necessary to include the motion of the nuclei in order to properly address the question of the competition between the different processes: excitation, ionisation (leading to Coulomb explosion) and dissociation. We have shown also that which final state is reached depends critically on the duration of the laser pulse and also on the absolute phase of the laser. It would be most interesting to extend this model to a 3-D treatement in order to analyse the effects of the alignment of the molecule on its behaviour.

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