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The dynamics of multiphoton processes in H_2^+ ions interacting with strong femtosecond fields is investigated by solving the time-dependent Schrödinger equation in the Born-Oppenheimer approximation. We use a spectral method with prolate spheroidal coordinates to represent the electronic wave functions. The theoretical approach is of spectral type in which the electronic and vibrational wave functions are represented with L^2 basis functions. In order to check the accuracy of these wave functions we have investigated the cases of the multiphoton ionization and dissociation of H_2^+ at long wavelengths. First, we calculate the ionization probabilities and the electron spectra at 228 nm and 400 nm, and we compare our results with other calculations when available. The effect of the initial dispersion of the internuclear distance R in the equilibrium region is discussed in the context of short pulses. Then, we study the dissociation of H_2^+ at 350 nm and we compare our results with other recent calculations. Finally, the case of two-photon ionization of H_2^+ at short wavelength is investigated, and we examine the electronic and vibrational spectra that have been obtained.

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I. INTRODUCTION

In recent years, with the appearance of high-power lasers, interest has been revived for the ionization and dissociation of H_2^+ as prototype processes for the study of molecular dynamics under extreme conditions where the perturbation theory is not applicable. Most of the techniques applied until now in the nonperturbative regime used the Floquet method [1] or a direct numerical integration of the time-dependent Schrödinger equation (TDSE) [2,3]. Baik *et al.* [4] resummed the Rayleigh-Schrödinger perturbation series and they showed that, by using prolate spheroidal coordinate, the number of computational operations and the storage requirement are significantly reduced. More recently, we showed that, by confining the molecular ion in an elliptical box and expanding the wave functions on B -spline functions, a very accurate discretized representation of the whole molecular electronic spectrum (bound and continuum states) is obtained and multiphoton ionization amplitudes can be calculated with a high degree of accuracy [5]. The latter work concerned the perturbative regime; the amplitudes were calculated in the lowest order perturbation theory (LOPT). The limit of the perturbation theory has been already discussed by Barmaki *et al.* [6] (denoted as paper I in the following) who treated the TDSE with a B -spline basis set and a spectral method. This method, extensively used in the atomic case (see [7,8] for reviews), has received much less attention from the molecular side, except the close-coupling study of the dissociation dynamics of H_2^+ proposed by Geltman [9]. The basis set consists of bound vibrational states and a group of dissociating states that represent the “essential” continuum

states (see [9]). It is straightforward to extend this approach to the case of the multiphoton ionization of molecules but, in general, it is not possible to identify the “essential” states and a “quasicomplete” basis set of wave functions is needed to achieve full numerical convergence of the electron spectra. The present work follows paper I where the TDSE was treated with the L^2 approach in the approximation of the fixed internuclear distance. Our objective is to include both the electronic and vibrational motions in our treatment.

In the first part of the work we present the theory, the calculation of the electronic part is briefly reviewed, and details can be found in paper I. Then, we study the multiphoton ionization of H_2^+ at R fixed and long wavelengths in order to compare our results with other works. These calculations, which involve a large number of photons, necessitate a highly accurate description of the electronic spectrum of the molecular ion and provide an excellent test of the B -spline expansion of the electronic wavefunctions. We put emphasis on the ionization in the region of the equilibrium distance ($R \approx 2$ a.u.) to illustrate the crucial effect of the initial dispersion of R on the electron spectrum in the context of femtosecond pulses. Then, we study the dissociation of H_2^+ at long wavelengths, solving the TDSE in the Born-Oppenheimer (BO) approximation, and we compare the density of probability for dissociation with the Geltman's results. These calculations are a good test of the accuracy of the representation of the vibrational spectrum since they involve two electronic states [$(1s\sigma_g)$ and $(2p\sigma_u)$] and a large number of vibrational levels. Finally we investigate the ionization of H_2^+ through the absorption of two photons of energy 0.6 a.u. solving the TDSE in the BO approximation. Both the vibrational and electronic spectra are obtained and discussed. We neglect rotational effects.

Unless otherwise stated, atomic units are used throughout.

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II. THEORETICAL APPROACH

First, we briefly describe the numerical approach used for R fixed. Then, we present the calculation of the vibrational states and the way to solve the TDSE in the BO approximation.

The Schrödinger equation describing the motion of the electron in the field of the nuclei is

$$(H - E)\Psi = \left(-\frac{1}{2}\Delta - 2\frac{(Z_1 + Z_2)\xi - (Z_1 - Z_2)\eta}{R(\xi^2 - \eta^2)} - E \right)\Psi = 0. \quad (1)$$

We have introduced the prolate spheroidal coordinates

$$\xi = (r_1 + r_2)/R, \quad \eta = (r_1 - r_2)/R, \quad \phi, \quad (2)$$

with $1 \leq \xi < \infty$, $-1 \leq \eta \leq 1$, and $0 \leq \phi \leq 2\pi$. We call E the purely electronic energy that, as usual, is positive for continuum states and negative for bound states. We assume that the internuclear distance is oriented along the z axis (no rotation), R varies from 0 to ∞ . We recall that, in the molecular ion H_2^+ , only the lower bound state (i.e., the fundamental state) is stable with a large binding energy, whereas the excited electronic bound states correspond to dissociative channels in the region of $R=2$ a.u. The solution of the above equation takes the form

$$\Psi(\xi, \eta, \phi; R) = \mathcal{N} Z(\xi, \eta; R) \frac{e^{im\phi}}{\sqrt{2\pi}}, \quad (3)$$

where m is the magnetic quantum number ($\pm m=0, 1, 2, \dots$) and \mathcal{N} is a normalization constant.

In order to solve Eq. (1), $Z(\xi, \eta; R)$ is expanded on a basis of B -spline products

$$Z(\xi, \eta; R) = (\xi^2 - 1)^{|m|/2} (1 - \eta^2)^{|m|/2} \sum_{i=1}^{N_\xi} \sum_{j=1}^{N_\eta} c_{ij} B_i^k(\xi) B_j^k(\eta). \quad (4)$$

B_i^k denotes the i th B -spline of order k (see de Boor [11]). The Schrödinger equation being separable in prolate spheroidal coordinates, $Z(\xi, \eta; R)$ can be written as a product of radial (ξ) and angular (η) spheroidal functions

$$Z(\xi, \eta; R) = X(\xi; R) Y(\eta; R). \quad (5)$$

In this problem, the good quantum numbers are m and q , q being the number of zeros of the angular function $Y(\eta; R)$ in the interval $[-1, 1]$. In what follows, the value of the quantum number m is zero. Therefore it will be omitted in the wave function arguments. For the sake of consistency the solutions of Eq. (1) are written Ψ_n^q [instead of $\Psi_n^q(\xi, \eta, \phi; R)$] and the associated eigenvalues $E_n^q(R)$.

Once the electronic energies are obtained, for various values of the internuclear distance R , the vibrational states can be determined. Within the BO approximation and in the model of no rotation, the total stationary wave function may be written as

$$\Xi_{nv}^q(\mathbf{r}, R) = \frac{\chi_{nv}^q(R)}{R} \Psi_n^q, \quad (6)$$

where \mathbf{r} represents the electronic coordinates. The nuclear wave function $\chi_{nv}^q(R)$ corresponds to either a bound or free vibrational states. For given n and q values, the integer number v enumerates the state in the series, $v=0$ being the lower one. $\chi_{nv}^q(R)$ is a solution of the equation

$$[T(R) + \mathcal{E}_n^q(R) - W_{nv}^q] \chi_{nv}^q(R) = 0, \quad (7)$$

where W_{nv}^q is the total energy of the molecule, $T(R)$ represents the kinetic energy related to the nuclear motion and $\mathcal{E}_n^q(R)$ is the BO potential energy curve of the n th electronic state of the molecule [$\mathcal{E}_n^q(R) = E_n^q(R) + 1/R + 0.5$]. Hereafter, this potential energy curve is labeled (n, q) . The above equation is solved by expanding the functions $\chi_{nv}^q(R)$ on a basis of B -splines (in a box of length R_{max}). Since the numerical procedure to calculate the nuclear wave functions and the associated density of states is similar to the one employed for the determination of the electronic functions, we do not repeat it here (see [10] for details). Due to the mass difference between electrons and protons, it is necessary to define two sets of B -splines to calculate the electronic and vibrational states. In particular the vibrational states are defined in a much smaller box than the electronic ones. Ψ_n^q and $\chi_{nv}^q(R)$ are normalized to one.

Within the dipole approximation the TDSE is given by

$$i \frac{\partial}{\partial t} \Phi(t) = [\mathcal{H} + D(t)] \Phi(t). \quad (8)$$

\mathcal{H} is the Hamiltonian of the diatomic molecule [see expression (3) in [10]], including the relative kinetic energy of the nuclei, the usual electronic Hamiltonian which depends parametrically on R and the nucleus-nucleus repulsion. $D(t)$ is the laser-molecule interaction, expressed in the velocity gauge or in the length gauge. In velocity gauge, we use the vector potential, polarized along the vector \mathbf{e}_z , i.e., in the direction of the internuclear axis. It is defined in the interval $[-T/2, +T/2]$ as

$$\mathbf{A}(t) = A_0 \left(\cos \frac{\pi}{T} t \right)^2 \cos(\omega t) \mathbf{e}_z, \quad (9)$$

where T is the total pulse duration and ω the photon energy. In length gauge, the electric field is

$$\mathbf{E}(t) = - \frac{\partial}{\partial t} \mathbf{A}(t). \quad (10)$$

The molecular wave function $\Phi(t)$ is expanded on the basis set of functions $\Xi_{nv}^q(\mathbf{r}, R)$,

$$\Phi(t) = \sum_q^{q_{max}} \sum_n^{n_q} \sum_v^{v_{max}} c_{n,v}^q(t) \Xi_{nv}^q(\mathbf{r}, R). \quad (11)$$

Equation (8) is integrated over the whole pulse duration T , in the interaction representation. Note that the eigenstates $\Xi_{nv}^q(\mathbf{r}, R)$ are normalized to unity in the above expansion.

This gives a set of first-order coupled equations where the coupling matrix, in length gauge, is

$$D_{ij} = \int_0^\infty dR \chi_{nv}^q(R) \chi_{n'v'}^{q'}(R) \int d\tau \Psi_{nz}^q \Psi_{n'}^{q'}. \quad (12)$$

The second integral is the electronic dipole element, which depends parametrically on R . The expressions of the volume element $d\tau$ and of the dipole operator z (or $\partial/\partial z$ in velocity gauge) in elliptic coordinates can be found in [4].

Once the TDSE is integrated, the vibrational or electronic differential energy spectra are easy to determine. The normalization on the proper energy scales is obtained through the density of states, which is straightforward to calculate in the context of the discretization [5]. In an experiment, either the energy of the nuclei or the energy of the electrons (in the ionization case) is measured, it is therefore important to calculate the associated differential energy spectra. At the vibrational energy $E_v^{n,q} = W_{nv}^q - E_n^q(R=\infty)$, the vibrational density of probability is given by (we assume that the vibrational states belong to the continuum)

$$\frac{dP(E_v^{n,q})}{dE_v^{n,q}} = 2 \frac{|c_{n,v}^q(T/2)|^2}{|W_{n(v-1)}^q - W_{n(v+1)}^q|} \quad (13)$$

where the factor $2/|W_{n(v-1)}^q - W_{n(v+1)}^q|$ represents the density of vibrational states. In the ionization channel, the vibrational energy $E_v^{n,q}$ is the total kinetic energy of the outgoing protons, the differential energy spectrum is obtained by adding the contributions associated to the potential energy curves (n, q) . In the dissociation channel the energy $E_v^{n,q}$ is the total kinetic energy of the dissociating ion-atom pair.

Similarly, at the electronic energy $E_n^q(R=\infty)$, the ionization density of probability in the channel q is given by

$$\frac{dP(E_n^q(R=\infty))}{dE_n^q(R=\infty)} = 2 \frac{\sum_v^{v_{\max}} |c_{n,v}^q(T/2)|^2}{|E_{n-1}^q(R=\infty) - E_{n+1}^q(R=\infty)|}. \quad (14)$$

The total ionization density of probability is obtained by summing the contributions of the q channels.

III. RESULTS AND DISCUSSION

A. Ionization and dissociation of H_2^+ at long wavelengths

1. Multiphoton ionization of H_2^+ at 228 nm and 400 nm

We focus here on the ionization of H_2^+ at $\lambda=228$ nm ($\omega=0.2$ a.u.), with a total pulse duration of 10 cycles (7.6 fs). We will consider that the initial vibrational state is the lower one ($v=0$) in the $(1s\sigma_g)$ potential for H_2^+ . In what follows, the associated wave function is labeled $\chi_0(R)$. The probability density $|\chi_0(R)|^2$ extends approximately from $R=1.3$ a.u. to $R=3$ a.u. and it has a maximum at $R=2$ a.u.; at this distance, the multiphoton ionization of H_2^+ requires a six photon absorption. We calculate the electron spectrum in the sudden approximation [6] which consists in solving the TDSE for different fixed values of R and in integrating the spectra over R with a weight coefficient $|\chi_0(R)|^2$. This approximation is acceptable since the total pulse duration

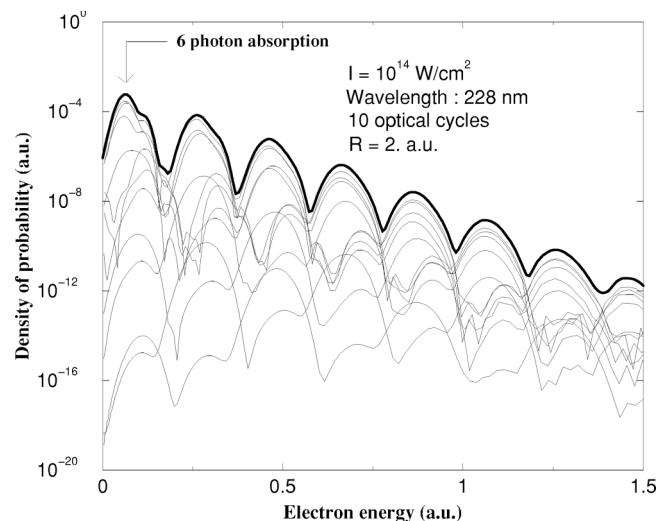


FIG. 1. The ATI spectrum for fixed H_2^+ at $R=2$ a.u. (thick line). The laser parameters are given in the figure. Contributions associated with the channels $q=0-10$ (thin lines).

(7.6 fs) is shorter than the vibrational period of the lower vibrational state $\chi_0(R)$, which is about 14 fs. A more refined calculation would require to solve the TDSE in the BO approximation, as in the case of two-photon ionization studied below. The sudden approximation is in fact much less computationally involved and sufficient to show the effect of the initial vibrational state on the electron spectra. In our calculations we use $k=7$ for the B -spline order, $N_\eta=15-25$ and $N_\xi=400-600$ in the expansion (4). The box size is defined by $\xi_{\max}R=600-1000$ a.u. Thus, in terms of spherical coordinates the box has a radial length of $r_{\max} \approx 300-500$ a.u. If we consider that the effective duration for the electron emission is the FWHM pulse duration of 3.8 fs, the outgoing wave packet should not reach the limit of the box for electron energies smaller than 1.5 a.u. We use a maximum of 10000 terms in the expansion (4); it is worth noting that the resolution of Eq. (1) leads to band-structure matrices with a matrix bandwidth of $(2k-1) \times N_\eta$. It shows the advantage of using B -splines; a considerable amount of CPU time and memory is saved. The diagonalization of Eq. (1) directly gives the full spectrum of the molecular ion with a high accuracy, both for continuum and bound states [5,6]. As usual, we check the convergence of the results by changing the basis parameters N_η , N_ξ and/or the box length. In practice, higher values of k ($k>7$) do not improve significantly the calculations. In general, we use the velocity gauge which converges must faster than the length one. We have checked that the results are gauge invariant for selected cases. Figure 1 shows electron spectra resulting from the resolution of the TDSE at a fixed internuclear distance, an intensity of $I=10^{14}$ W/cm² and a photon of energy $\omega=0.2$ a.u. ($\lambda=228$ nm). The calculation is performed at the equilibrium distance $R=2$ a.u. The contribution of the different channels “ q ” ($m=0$) are shown in the figure as well as the total electron spectrum. We recognize a characteristic above threshold ionization (ATI) spectrum associated with the multiple photon absorptions in the continuum. The lower peak in energy corresponds to a six-photon absorption, the (field-free) elec-

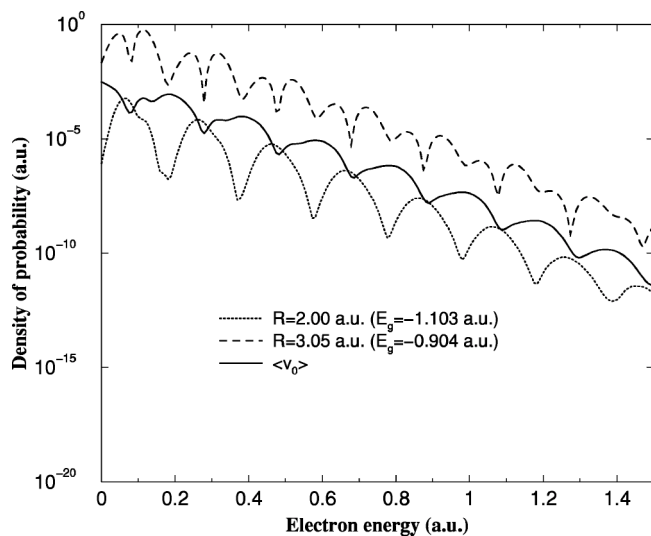


FIG. 2. The ATI spectrum for fixed H_2^+ at $R=2$ a.u., $R=3.05$ a.u., and averaged over the distribution of internuclear distances $|\chi_{nv}^{q=0}(R)|^2$ in the lower vibrational state $v=0$ (see full line $\langle v_0 \rangle$). The energies indicated on the figure are the electronic energies of the fundamental states. The laser parameters are given in Fig. 1.

tronic ground state energy being located at -1.102634 a.u. The total ionization probability is 3.16×10^{-5} ; in terms of cross section this value corresponds to $1.12 \times 10^{-182} \text{ cm}^{12} \text{ s}^5$, about 10 times larger than the cross section calculated in LOPT (see [5]). Therefore, at $I=10^{14} \text{ W/cm}^2$, the ionization regime is nonperturbative. In order to compare our results with the calculations of Mies *et al.* [3], Baik *et al.* [4] and Madsen and Plummer [14], we have performed a calculation at $I=5 \times 10^{13} \text{ W/cm}^2$. The ionization probability is 5.52×10^{-7} ; in terms of ionization rate it is $4.5 \times 10^8 \text{ s}^{-1}$. This latter value is larger than the results of [4,14] ($1.3 \times 10^8 \text{ s}^{-1}$ and $1.1 \times 10^8 \text{ s}^{-1}$, respectively) and [3] ($6 \times 10^7 \text{ s}^{-1}$, revised value given in [4]), but the order of magnitude is comparable. We do not expect a better agreement since the rates are extracted under very different conditions. In Fig. 2, we show ATI spectra corresponding to $R=2$ a.u. and $R=3.05$ a.u., for the same laser parameters as in Fig. 1. It is clear that the ionization probability is much larger at $R=3.05$ a.u. Indeed, the lower electronic state being located at the energy -0.90372 a.u., only five photons are required to ionize H_2^+ . We also note that the spectrum has complicated structures, they are due to the excitation of bound (dissociative) states through one- and multiphoton absorption. The dynamic Stark-shift plays an important role here since it induces resonant one- and multiphoton transitions between bound states. The strong dependence of the rate on the internuclear distance has been also observed by Chelkowski *et al.* [2]. The total population in the ionization channel is 4.5×10^{-2} and the population of excited bound states is 0.15. We have calculated the ATI spectra for a set of values of R and integrated the result with the weight $|\chi_0(R)|^2$. The outcome is shown in Fig. 2. We see that the initial distribution of R has a crucial influence on the electron spectra.

We have performed similar calculations up to $R=15$ a.u., convergence is achieved with the basis set presented in the

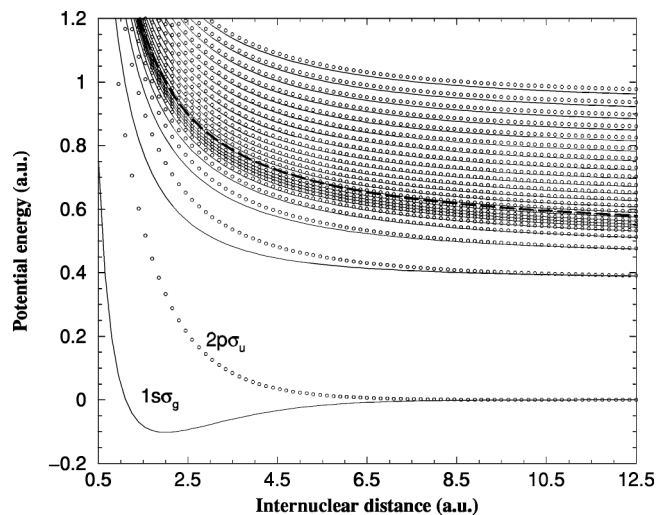


FIG. 3. The 23 lowest potential energy curves $\mathcal{E}_n^q(R)=0.5 + \mathcal{E}_n^q(R) + 1/R$ in a.u., for $q=0$ (full line) and $q=1$ (circles), as a function of the internuclear distance R . The long dashed line represents the ionization threshold (of energy $0.5 + 1/R$).

above section. We have compared our calculations with a recent work [12] which follows the close-coupling approach [9] with prolate spheroidal coordinates [4–6], with an expansion of the eigenfunctions in term of free wave functions. Similar laser parameters (intensity, pulse envelope, time duration) being used in both works, the comparison gives a direct test of the basis set efficiency. There is an overall agreement between the two calculations but discrepancies exist at large R . For example, for a wavelength of 400 nm ($\omega=0.1139$ a.u.), a pulse duration of 10 fs and $I=2 \times 10^{14} \text{ W/cm}^2$ our value of the ionization probability is 0.163 at $R=8$ a.u., while it is close to 0.2 in [12] (see Fig. 1). By adding explicit molecular bound states to the basis of free wave functions, it is possible to improve the results. In the case cited above, the addition of bound states in the basis set leads to an ionization probability of 0.167 [13], a value much closer to our finding. Nevertheless, discrepancies still exist at larger R . In fact the calculation of H_2^+ bound states converges slowly when a free wave expansion is used and, depending on the internuclear distance, a certain number of one-electron diatomic molecular (OEDM) orbitals must be added explicitly in the basis set [12]. This is at variance with the B -spline basis set which is well adapted to span the whole set of states and which leads to self-consistent calculations.

2. Dissociation of H_2^+ at $\lambda=350 \text{ nm}$

We treat now the problem of the dissociation of H_2^+ by solving the TDSE in the BO approximation, with the discretization approach explained in Sec. II. The dissociation density of probability is calculated with the formula (13).

Equation (1) is solved for $R=0.5-12.5$ a.u. in a box whose size is such that $\xi_{\text{max}}R=120$ a.u. Further, in the expansion (4), one has $N_\xi=200$ and $N_\eta=20$. We show in Fig. 3 the potential energy curves $\mathcal{E}_n^q(R)$ obtained for $q=0$ and $q=1$ ($n=1-23$). Similar calculations are performed for $q=2, 3, 4$.

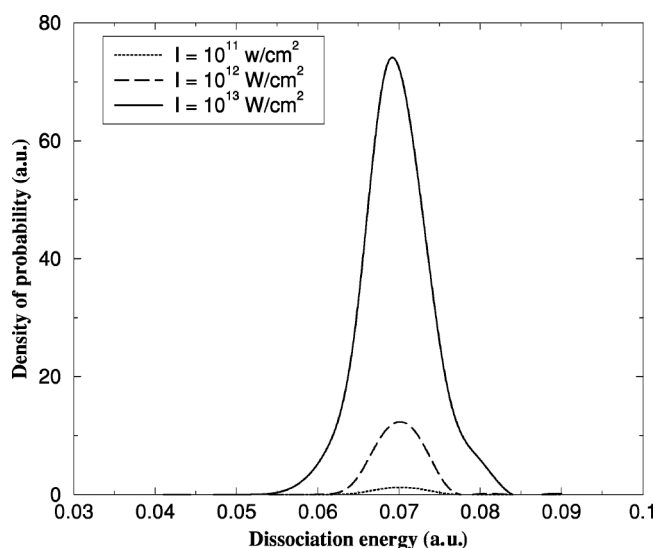


FIG. 4. Density of dissociation probability in the lowest-lying band for $v=4$, calculated with a total pulse duration of 30 fs and a laser wavelength of 350 nm. The intensities are indicated in the figure.

The advantage of prolate spheroidal coordinates is that all potential energy curves are clearly defined by the quantum number q and their position n in the series. Note that a simple extrapolation gives the value $E_n^q(R=\infty)$. Equation (7) is solved, for n and q fixed, by expanding $\chi_{nv}^q(R)$ on a set of 200 B -spline functions in the box of a length 12.5 a.u. We have checked that, owing to the nuclei energy in the dissociation channel, the nuclear wave packet has no time to reach the limit of the box (i.e., $R=12.5$ a.u.) before the end of the pulse (i.e., at $t=T/2$ a.u.). In these calculations, we retain a maximum of 18 electronic states per channels q and 150 vibrational states per potential energy curve (n, q), thus using a total of 13500 states in the expansion (11).

In order to compare our results with the close-coupling calculations of Geltman [9], we solved the TDSE for a laser wavelength of 350 nm (corresponding to a photon energy of 0.13 a.u.), a total pulse duration of 30 fs and various intensities. The initial state is the vibrational state $v=4$ in the lowest-lying band ($1s\sigma_g$). The $v=4$ vibrational state is at an energy close to -0.061 a.u., the threshold for the dissociation channel ($2p\sigma_u$) being at the energy zero, it requires only one photon absorption to leave the molecular ion in the dissociative state ($2p\sigma_u$) (see Fig. 1 in [9]). We show in Fig. 4 the differential dissociation probabilities versus the dissociation energy, the TDSE has been solved in length gauge (we have checked that the velocity gauge leads to similar results). The comparison with Fig. 4 of [9] shows that, at intensities of 10^{11} W/cm² and 10^{12} W/cm², the probabilities have similar shapes but their maxima differ. For example, at $I = 10^{12}$ W/cm², the maximum density of probability is close to 37 a.u. in [9], while our calculations give 12 a.u. At $I = 10^{13}$ W/cm², there is a better agreement on the peak amplitude but, at contrast with [9], our calculations do not show subsidiary peaks. The calculations have been performed with different numbers of electronic wave functions, we have checked that keeping only the two lowest electronic states is

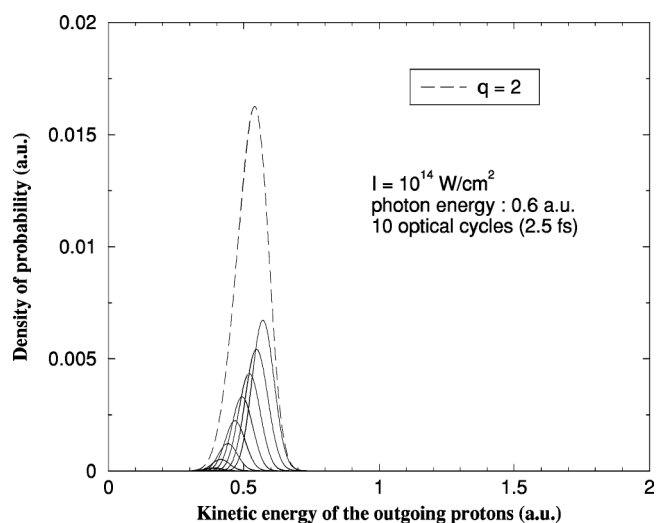


FIG. 5. Two-photon absorption from the lower vibrational level in the ($1s\sigma_g$) potential for H_2^+ . The density of probability versus the total kinetic energy of the protons in the ionization channel $q=2$, calculated with the laser parameters indicated in the figure. Each full line represents the contribution of the vibrational states associated with a potential energy curve $\mathcal{E}_n^{q=2}(R)$ of the continuum. The long-dashed line is the sum of all the contributions.

sufficient to achieve the convergence of the calculations.

B. Multiphoton ionization of H_2^+ at short wavelength

We use the basis set described in the preceding section (III A 2) to treat the ionization of H_2^+ through two-photon absorption in the BO approximation. We performed a calculation for a photon energy of 0.6 a.u. ($\lambda=75.9$ nm), a total pulse duration of 10 optical cycles (2.5 fs) and an intensity of 10^{14} W/cm². The initial state is the lowest vibrational state in the potential ($1s\sigma_g$) of H_2^+ . At the intensity under consideration, the ionization of the molecular ion is dominated by two-photon absorption to the continuum channels $q=2$ and $q=0$ (see paper I). We show in Fig. 5 and 6 the

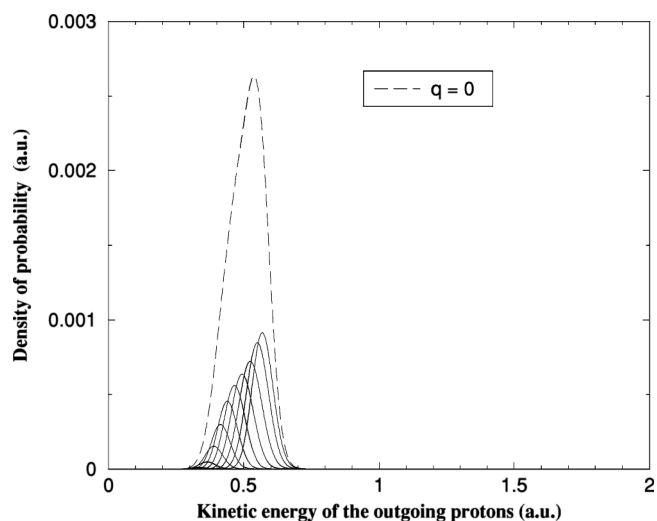


FIG. 6. Same as Fig. 5 for the channel $q=0$.

densities of probabilities versus the total kinetic energy of the outgoing protons for the ionization channels $q=2$ and $q=0$, respectively [see formula (13)]. Full lines represent the contribution for each potential energy curve (n, q) , while the long-dashed line is the total density of probability. In agreement with paper I, the channel $q=2$ gives the main contribution. The surface of the long-dashed line in Fig. 5 gives the probability of ionization associated to the channel $q=2$, which is 2.34×10^{-3} while for $q=0$ the ionization probability is 4.5×10^{-4} . Therefore the total ionization probability is 2.8×10^{-3} (the contribution of $q=4$ is negligible), while it is 2.4×10^{-3} in the approximation of an internuclear distance fixed at $R=2$ a.u. Finally, we show in Fig. 7 the electron spectra for the channels $q=0$ and $q=2$. We used the formula (14) to calculate the density of probability. The present ionization probability is maximum for the lowest electron energies. It differs from the prediction of the approximation where the internuclear distance is fixed at $R=2$ a.u. In the latter case, a maximum is located at 0.095 a.u. (see Fig. 2 in paper I). In fact, due to the distribution of R in the initial state, the two-photon ionization is likely to occur at internuclear distances R smaller than 2 a.u., which results in ejecting electrons at lower energies.

IV. CONCLUSION

We have presented a spectral type method, including the electronic and vibrational motions, to solve the TDSE in the case of a molecular system. We use B -spline expansions to calculate the electronic and vibrational wave functions in the Born-Oppenheimer approximation.

We have performed a full TDSE calculation for the dissociation and ionization of “rotationless” $\text{H}_2^+(1s\sigma_g)$ by short intense laser pulses. These calculations directly include the effects of the vibrational motion in the initial field-free state and during the laser-atom interaction. We take advantage that, with prolate spheroidal coordinates, each potential energy curve can be defined with a quantum number q and its position n in the series. In particular it is easy to identify and normalize the different electronic continuum states. Once the potential energy curves have been calculated, a simple diagonalization gives the vibrational states. Note that we retain all the vibrational states, up to a certain energy, in the resolution of the TDSE. As expected, these calculations are much more involved, from the computational point of view, than the resolution of the TDSE with R fixed. This is the reason why we have focused on processes which involves few photons and short interaction times. At $\lambda=350$ nm, the differential dissociation probability in the lowest-lying band for $v=4$ shows some differences with the close-coupling calculations of Geltman [9]. This illustrates well the difficulty of such calculations, and the necessity to pursue theoretical efforts. We have calculated the two photon ionization of H_2^+ from the initial state $(1s\sigma_g)$ and $v=0$, with a photon energy of

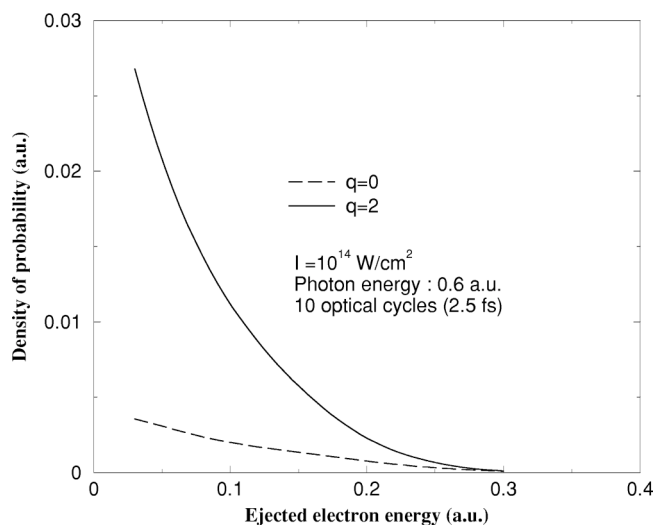


FIG. 7. Two-photon absorption. Photoelectron spectra for $q=0$ and $q=2$; the laser parameters are given in the figure.

0.6 a.u. The ionization probability is slightly larger than the one calculated in the approximation of the fixed internuclear distance while the electron spectrum is fully different.

Our results show that the ionization dynamics of H_2^+ in short and strong pulses involves complex processes like the photoexcitation of intermediate states which are very sensitive to (i) the intensity (in particular at long wavelength, due the dynamic Stark shift), (ii) the pulse duration (i.e., the bandwidth), and (iii) the internuclear distance R . Therefore it is necessary to calculate accurately the whole molecular ion spectra (both electronic and vibrational) and to solve the TDSE in a “quasicomplete” basis set of functions. Our treatment of the TDSE in the BO approximation can be applied to processes where more than two photons are involved. To this end we have to increase the number of channels in the calculations, which become more computationally involved. Another interesting application, for both the experimental and theoretical sides, is the study of the temporal evolution of a vibrational wave packet with a probe short UV field to ionize the molecular ion. We are working in these directions.

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