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Time-resolved dynamics of two-channel molecular systems in cw laser fields: Wave-packet construction in the Floquet formalism

T. T. Nguyen-Dang and F. Châteauneuf
Département de Chimie, Université Laval, Québec, Canada G1K 7P4

O. Atabek and X. He
Laboratoire de Photophysique Moléculaire, CNRS, Bâtiment 213, Campus d'Orsay, 91405 Orsay Cedex, France

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The description of the wave-packet time-resolved dynamics in a two-channel molecular system driven by a cw laser field is considered within the time-independent Floquet representation. It is shown that, at high field intensity, the wave-packet motions are governed solely by the pair of adiabatic dressed potential-energy surfaces (PES's) associated with a single Brillouin zone. The same expressions of the wave-packet motions in terms of the adiabatic PES's are obtained within a short-time approximation, thereby furnishing a new numerical algorithm for the wave-packet propagation in a laser-driven two-channel system at any intensity. Numerical tests of this algorithm are presented. The numerical results establish unambiguously the adiabaticity of nuclear motions at high field intensities.

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I. INTRODUCTION

Recent experiments [1,2] on the intense-field photodissociation of the dihydrogen molecular ion have spurred renewed interest in the dressed-molecule picture, or Floquet representation of the dynamics of molecules driven by intense laser fields. Emanating from atomic physics [3] the dressed-molecule picture basically views the field as a part of a supermolecular system, and, by identifying the quantized field as a set of new harmonic degrees of freedom whose fluctuations drive electronic excitations in the molecule, it places the field on the same footing conceptually as the intrinsic nuclear motions. The diabatic electronic-field representation [4] gives rise to dressed potential-energy surfaces (PES's) obtained from the field-free or intrinsic PES's by the addition of integral numbers of photons, corresponding to the definite field-mode Fock states. In this way, field-induced electronic transitions are viewed as curve-crossing processes occurring at the intersection of these dressed PES's. This picture was already evoked in the early work of Kroll and Watson [5], and those of Lau and Rhodes [6]. The analogy between intense-field photodissociation and natural predissociation was noted and exploited extensively by Bandrauk and co-workers [7]. The idea that the field modes can be regarded as additional degrees of freedom, to be treated on the same footing conceptually as the nuclear coordinates, has further been explored in the Bloch-Nordsieck representation [8] where it is given a most elegant expression.

A picture similar to that furnished by the dressed-molecule approach is also obtained when the radiation field is treated classically as a periodic function of time, the so-called cw-excitation regime. In this case, the periodicity of the time-dependent Hamiltonian permits the use of the Floquet theorem [9], and the time-dependent Schrödinger equation can be replaced by a set of coupled time-independent Schrödinger equations for the Fourier components of solutions to the dynamical problem called Floquet states [10–12]. The similarity between the coupled equations obtained in both theories justifies associating the dressed-picture concepts with Floquet concepts. Thus the integer indices, identifying the Fourier component either of the state vector or of the channel wave functions, are often referred to as "photon numbers." Many calculations of the cross sections for the photodissociation of $H_2{}^+$ in an intense cw laser field use this Floquet picture, and they determine the dynamics of the system through the properties of laser-induced resonances [13–15]. Trends of calculated branching ratios between different dressed or Floquet channels associated with these Floquet states appear to confirm qualitatively the experimental findings on the above-threshold dissociation of this system [13]. The success that the dressed-molecule picture has met in interpreting these experimental findings is such that there is a general tendency to consider the Floquet states as the actual time-dependent states describing the dynamics of the molecular system. The conceptual difficulties met in defining the proper initial state denoting the molecular system prior to laser excitation have largely been ignored, often by implicitly evoking an adiabatic transport of the initial state, considered to be an eigenstate of the field-free molecule, into the closest-lying resonance. Even in the case of excitation by a short-pulsed laser, a situation for which there is no *a priori* justification for the application of Floquet theorem, remnants of the Floquet or dressed picture can still be found in attempts to interpret the results of experimental investigations and/or theoretical wave-packet calculations [16–18]. Dressed PES properties, in particular properties of the adiabatic potential curves resulting from the diagonalization of these dressed PES's, were

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evoked to explain such effects as laser-induced bond softening [16,17] and vibrational stabilization [18,19]. In these interpretations, which generally consider the wave packets to be moving on the adiabatic potential surfaces, a precise description of the manner in which an initial wave packet is transported onto these dressed surfaces is still lacking.

The present paper brings a contribution to fill this gap, and aims at establishing the precise connection between the time-resolved wave-packet dynamics as obtained by directly solving the time-dependent Schrödinger equation (without making use of the Floquet ansatz), and the time-independent amplitudes associated with the Floquet representation. We show that for a two-channel system driven by an intense cw field, the nuclear wave-packet dynamics is basically governed by only two adiabatic dressed potential-energy surfaces associated with a single Brillouin zone, the first one for instance. The time-dependent wave function supported by each Born-Oppenheimer (undressed) channel is at all times a superposition of two wave packets, one propagating on the lower adiabatic potential, the other one associated with the upper adiabatic potential. The dependence of these wave packets on the initial state is explicit, and the Floquet description gives the same wave-packet dynamics as obtained in the direct time-resolved approach. The demonstration of this equivalence proceeds by first evoking an adiabatic time-dependent electronic representation recently introduced by Nguyen-Dang and co-workers [20–22], and which is constructed essentially as a generalization of the Born-Oppenheimer adiabatic basis to account for the strong-field couplings in the electronic Hamiltonian. By expressing these time-dependent electronic states in terms of the local two-state Floquet representation [23], the resulting nuclear dynamics can be related to the eigenvectors and eigenvalues of the infinite diabatic dressed potential matrix. The result is the wave-packet picture alluded to above. On the other hand, starting from the construction of nuclear Floquet states which are solutions to the time-independent coupled Schrödinger equations for the nuclear amplitudes in the diabatic dressed representation, we show that at high intensities, the closure of these nuclear Floquet states also leads to the same final wave-packet description. This equivalence is shown in Sec. II. After presenting relevant computational details, in particular those on the computational technique used in obtaining the adiabatic dressed PES (without actually diagonalizing the infinite local Floquet matrix) and in propagating the wave packets, we present, in Sec. III, results of wave-packet calculations on H_2^+ using the present Floquet decomposition of the wave packets, and compare these to results of direct wave-packet propagations.

II. WAVE-PACKET AND FLOQUET DESCRIPTIONS OF A LASER-DRIVEN TWO-CHANNEL MOLECULE

For a two-channel molecular system driven by a laser field described in a semiclassical treatment, the time-dependent Schrödinger equation is

$$i\hbar\partial_t \begin{bmatrix} \chi_1(R,t) \\ \chi_2(R,t) \end{bmatrix} = \begin{bmatrix} \hat{T}_N+\varepsilon_1 & V_{12}(R,t) \\ V_{12}(R,t) & \hat{T}_N+\varepsilon_2 \end{bmatrix} \begin{bmatrix} \chi_1(R,t) \\ \chi_2(R,t) \end{bmatrix} , \tag{1}$$

where R is the internuclear distance, $\varepsilon_k(R)$, $k=1,2$ denote the Born-Oppenheimer potential-energy surfaces associated with the field-free molecular channels, and $\hat{T}_N$ denotes the nuclear kinetic-energy operator. The field-induced channel coupling

$$V_{12}(R,t)=\boldsymbol{\mu}_{12}(R)\cdot\mathbf{E}(t) \tag{2}$$

involves the transition dipole moment $\boldsymbol{\mu}_{12}(R)$ linking the Born-Oppenheimer electronic states and is periodic in a cw monochromatic laser field, since then

$$\mathbf{E}(t)=\boldsymbol{\varepsilon}E_0\cos\omega t \ , \tag{3}$$

where ω is the field frequency and $\boldsymbol{\varepsilon}$ its polarization which will be considered to be linear. The electric field amplitude E_0 is related to the field intensity via

$$V_{12}(\text{cm}^{-1})=1.17\times10^{-3}\sqrt{I(\text{W/cm}^2)}\,|\mu_{12}| \ \ (\text{a.u.}) \ . \tag{4}$$

For the case of a periodic field, the Schrödinger equation (1) can be solved in at least two ways: In a time-resolved wave-packet description this equation is solved directly, whereas in the time-independent Floquet coupled-equation description, the time evolution is described indirectly through a superposition of vibrational quasi-energy states. It is the purpose of this paper to establish the explicit relation between these two descriptions, and thus, to assess the roles played by laser-induced resonances and their overlaps in the wave-packet dynamics on the coupled channels.

A. Direct, time-resolved wave-packet description

A direct time-resolved description of the generation and propagation of wave packets on the two coupled channels involves a Dirac transformation to the interaction picture with respect to the nuclear kinetic energy,

$$\begin{bmatrix} \chi_1(R,t) \\ \chi_2(R,t) \end{bmatrix} = \begin{bmatrix} \exp\left[-\frac{i}{\hbar}\hat{T}_N(t-t_0)\right] & 0 \\ 0 & \exp\left[-\frac{i}{\hbar}\hat{T}_N(t-t_0)\right] \end{bmatrix} \begin{bmatrix} \tilde{\chi}_1(R,t) \\ \tilde{\chi}_2(R,t) \end{bmatrix} , \tag{5}$$

followed by the solution of the local two-state problem

$$i\hbar\partial_t \begin{bmatrix} \tilde{\chi}_1(R,t) \\ \tilde{\chi}_2(R,t) \end{bmatrix} = \begin{bmatrix} \varepsilon_1(R) & V_{12}(R,t) \\ V_{12}(R,t) & \varepsilon_2(R) \end{bmatrix} \times \begin{bmatrix} \tilde{\chi}_1(R,t) \\ \tilde{\chi}_2(R,t) \end{bmatrix} + O(\delta t^2) , \tag{6}$$

which, as indicated, is equivalent to the original two-channel Schrödinger equation up to second order in $\delta t = (t - t_0)$. The δt^2 correction terms are nonadiabatic couplings originating from the R dependence of the local two-state system, i.e., from $\partial_R(\Delta\varepsilon) \neq 0$ and $\partial_R(V_{12}) \neq 0$. Thus, for the case of exactly parallel channel potentials, this nonadiabatic coupling vanishes and solving Eq. (6) amounts to solving Eq. (1) exactly, using the relation between the interaction picture amplitudes $\tilde{\chi}_k$ and the Schrödinger picture amplitudes χ_k. The transformation of the two-channel dynamics into an equivalent description in terms of local two-level dynamics can also be viewed as a change in the electronic representation. This has been noted in other work where new, time-dependent electronic basis vectors were constructed by solving the local electronic two-state Schrödinger equation with initial conditions corresponding to the field-free Born-Oppenheimer states [20–22]. In the Appendix, this construction is recalled, but with the initial conditions relaxed and replaced by the requirement that the new basis vectors are Floquet electronic states. In the presentation given here, the construction of this new electronic basis corresponds to solving Eq. (6), with or without prescribed initial conditions.

The local Schrödinger equation (6) describing a two-state system driven by a periodic field can be solved using any appropriate method; it can be integrated numerically, or by using the formally exact adiabatic representation of Ref. [23]. Alternatively, this equation can also be solved by applying the Floquet theorem [9] which is applicable due to the periodicity of the external field. In the Floquet formalism, the time-evolution operator for the local two-level problem defined by Eq. (6) is [24]

$$\underline{U}^{\mathrm{Fl}}(R,t) = \begin{bmatrix} \eta_1^{(1,0)}(R,t) & \eta_1^{(2,0)}(R,t) \\ \eta_2^{(1,0)}(R,t) & \eta_2^{(2,0)}(R,t) \end{bmatrix} \times \begin{bmatrix} \eta_1^{(1,0)}(R,t_0) & \eta_1^{(2,0)}(R,t_0) \\ \eta_2^{(1,0)}(R,t_0) & \eta_2^{(2,0)}(R,t_0) \end{bmatrix}^{-1} , \tag{7}$$

where $\eta_1^{(k,m)}(R,t)$ and $\eta_2^{(k,m)}(R,t)$ are the two components of the Floquet solution $\boldsymbol{\eta}^{(k,m)}$ ($k=1$ or 2), in a given Brillouin zone, which is indicated by the superscript $m \in \mathbb{Z}$. In the Schrödinger picture, the vector $\boldsymbol{\eta}^{(k,m)}(R,t)$ is a particular solution to the time-dependent Schrödinger equation (6) and is formed by the product of a dynamical phase factor $\exp\{-(i/\hbar)\varepsilon_{km}^{\mathrm{Fl}} t\}$ and a periodic vector-valued function $\tilde{\boldsymbol{\eta}}^{(k,m)}(R,t)$,

$$\boldsymbol{\eta}^{(k,m)}(R,t) = e^{-i/\hbar\varepsilon_{km}^{\mathrm{Fl}}(R)t}\tilde{\boldsymbol{\eta}}^{(k,m)}(R,t) . \tag{8a}$$

The quantity $\varepsilon_{km}^{\mathrm{Fl}}$ in the nonperiodic dynamical phase factor preceding the periodic vector $\tilde{\boldsymbol{\eta}}^{(k,m)}(R,t)$ is called quasienergy. The periodicity of $\tilde{\boldsymbol{\eta}}^{(k,m)}(R,t)$ implies that this vector can be written in the form of an infinite discrete Fourier series

$$\tilde{\boldsymbol{\eta}}^{(k,m)}(R,t) = \begin{bmatrix} \tilde{\eta}_1^{(k,m)}(R,t) \\ \tilde{\eta}_2^{(k,m)}(R,t) \end{bmatrix} = \sum_{n=-\infty}^{+\infty} e^{in\omega t} \begin{bmatrix} \eta_{1,n}^{(k,m)}(R) \\ \eta_{2,n}^{(k,m)}(R) \end{bmatrix} . \tag{8b}$$

The quantum number m labels the Brillouin zones in the frequency domain, which is the reciprocal space of the time domain, and $m=0$ denotes the first Brillouin zone. The vector $\tilde{\boldsymbol{\eta}}^{(k,m)}(R,t)$ is an eigenvector associated with the eigenvalue $\varepsilon_{km}^{\mathrm{Fl}}$ of the operator $(\underline{H} - i\hbar\partial_t)$ defined over the enlarged two-state linear space $[-\tau/2, +\tau/2] \otimes \mathbb{R}^2$ in which inner products are scalar products of two-dimensional time-dependent vectors averaged over the optical cycle $[-\tau/2, +\tau/2]$ of the field, $\tau \equiv 2\pi/\omega$. The time-independent Fourier components $\eta_{l,n}^{(k,m)}(R)$ and the quasienergy $\varepsilon_{km}^{\mathrm{Fl}}$ satisfy the following set of algebraic coupled equations:

$$[\varepsilon_1(R) + n\hbar\omega - \varepsilon_{km}^{\mathrm{Fl}}(R)]\eta_{1,n}^{(k,m)}(R) = \frac{V_{12}^0}{2}[\eta_{2,n+1}^{(k,m)}(R) + \eta_{2,n-1}^{(k,m)}(R)] , \tag{9a}$$

$$[\varepsilon_2(R) + n\hbar\omega - \varepsilon_{km}^{\mathrm{Fl}}(R)]\eta_{2,n}^{(k,m)}(R) = \frac{V_{12}^0}{2}[\eta_{1,n+1}^{(k,m)}(R) + \eta_{1,n-1}^{(k,m)}(R)] , \tag{9b}$$

where

$$V_{12}^0(R) = \boldsymbol{\mu}_{12}(R) \cdot \boldsymbol{\varepsilon} E_0 . \tag{10}$$

Note that Eqs. (9) can be read as the eigenvalue equation for the matrix $\underline{V}^d$ defined by

$$(\underline{V}^d)_{\nu\mu} = \left[(-1)^\nu \frac{(\varepsilon_1 - \varepsilon_2)}{2} + \nu\hbar\omega + \frac{(\varepsilon_1 + \varepsilon_2)}{2} \right] \delta_{\nu,\mu} - \frac{V_{12}^0}{2}(\delta_{\nu,\mu+1} + \delta_{\nu,\mu-1}) , \tag{11}$$

which is recognized as the dressed-molecule potential matrix in the diabatic electronic-field representation. Thus each column of the infinite matrix $\underline{C}$ which diagonalizes $\underline{V}^d$ is filled with the Fourier components of an eigenvector $\tilde{\boldsymbol{\eta}}^{(k,m)}$ of the Floquet Hamiltonian $(\underline{H} - i\hbar\partial_t)$. Because of the periodicity of $\underline{V}^d$ with respect to a translation by $2p\hbar\omega$, $p \in \mathbb{Z}$, i.e.,

$$\underline{V}^d \pm 2p\hbar\omega\underline{I} = \underline{V}^d , \tag{12}$$

the eigenvalues and eigenvectors of $\underline{V}^d$ satisfy

$$\varepsilon_{km}^{\mathrm{Fl}}(R) = \varepsilon_{k0}^{\mathrm{Fl}}(R) + m\hbar\omega , \tag{13a}$$

$$\eta_{l,\nu}^{(k,m)}(R) = \eta_{l,\nu-m}^{(k,0)}(R) \tag{13b}$$

or

$$\boldsymbol{\eta}^{(k,m)}(R,t) = e^{-im\omega t}\boldsymbol{\eta}^{(k,m)}(R,t) , \tag{13c}$$

with $m=2p$, $p\in\mathbb{Z}$, $l=1$ or 2, and $\nu\in\mathbb{Z}$. Thus the full quasienergy spectrum of the two-state system and the associated quasienergy states are generated once two independent eigenvectors associated with $m=0$, denoting the first Brillouin zone, are obtained. In addition to exhibiting the orthogonality properties with respect to the inner product defined above for the extended linear space, $[-\tau/2,+\tau/2]\otimes\mathbb{R}^2$,

$$\frac{1}{\tau}\int_{-\tau/2}^{+\tau/2}dt[\tilde{\boldsymbol{\eta}}^{(k,m)}(R,t)]^\dagger\tilde{\boldsymbol{\eta}}^{(k',m')}(R,t)=\delta_{kk'}\delta_{mm'}\;, \qquad (14)$$

which results from the fact that the two vectors $\tilde{\boldsymbol{\eta}}^{(k,m)}(R,t)$ and $\tilde{\boldsymbol{\eta}}^{(k',m')}(R,t)$ are two eigenvectors of the Hermitian operator $(\underline{H}-i\hbar\partial_t)$,

$$(\underline{H}-i\hbar\partial_t)\tilde{\boldsymbol{\eta}}^{(k,m,)}(R,t)=\varepsilon_{km}^{\mathrm{Fl}}(R)\tilde{\boldsymbol{\eta}}^{(k,m)}(R,t)\;, \qquad (15)$$

the two vectors $\tilde{\boldsymbol{\eta}}^{(k,0)}(R,t)$, $k=1$ or 2, lying within the first zone satisfy the stronger orthogonality condition [25]

$$\tilde{\boldsymbol{\eta}}^{(k,0)}(R,t)^\dagger\cdot\tilde{\boldsymbol{\eta}}^{(k',0)}(R,t)=\delta_{kk'}\;. \qquad (16)$$

It is this strong orthogonality of the vectors $\tilde{\boldsymbol{\eta}}^{(k,0)}(R,t)$, $k=1,2$ at all times and their definition as Floquet quasienergy states which permit the time-evolution operator $\underline{U}$ for the local two-state system to be expressed solely in terms of these two vectors, Eq. (7). Combining Eqs. (5), (7), and (8), the wave packets χ_1 and χ_2 supported by the coupled channels ε_1 and ε_2 are explicitly given by

$$\begin{aligned}\chi_1(R,t)&=e^{-i/\hbar(\hat{T}_N+\varepsilon_1)(t-t_0)}[U_{11}(R,t)\chi_1^0(R)+U_{12}(R,t)\chi_2^0(R)]\\&=e^{-i/\hbar(\hat{T}_N+\varepsilon_{10}^{\mathrm{Fl}})(t-t_0)}\{\tilde{\eta}_1^{(1,0)}(R,t)[\tilde{\eta}_1^{(1,0)}(R,t_0)]^*\chi_1^0(R)+\tilde{\eta}_1^{(1,0)}(R,t)[\tilde{\eta}_2^{(1,0)}(R,t_0)]^*\chi_2^0(R)\}\\&\quad+e^{-i/\hbar(\hat{T}_N+\varepsilon_{20}^{\mathrm{Fl})}(t-t_0)}\{\tilde{\eta}_1^{(2,0)}(R,t)[\tilde{\eta}_1^{(2,0)}(R,t_0)]^*\chi_1^0(R)\\&\qquad+\tilde{\eta}_1^{(2,0)}(R,t)[\tilde{\eta}_2^{(2,0)}(R,t_0)]^*\chi_2^0(R)\}+O(\delta t^2)\end{aligned} \qquad (17)$$

and

$$\begin{aligned}\chi_2(R,t)&=e^{-i/\hbar(\hat{T}_N+\varepsilon_2)(t-t_0)}[U_{21}(R,t)\chi_1^0(R)+U_{22}(R,t)\chi_2^0(R)]\\&=e^{-i/\hbar(\hat{T}_N+\varepsilon_{10}^{\mathrm{Fl}})(t-t_0)}\{\tilde{\eta}_2^{(1,0)}(R,t)[\tilde{\eta}_1^{(1,0)}(R,t_0)]^*\chi_1^0(R)+\tilde{\eta}_2^{(1,0)}(R,t)[\tilde{\eta}_2^{(1,0)}(R,t_0)]^*\chi_2^0(R)\}\\&\quad+e^{-i/\hbar(\hat{T}_N+\varepsilon_{20}^{\mathrm{Fl}})(t-t_0)}\{\tilde{\eta}_2^{(2,0)}(R,t)[\tilde{\eta}_1^{(2,0)}(R,t_0)]^*\chi_1^0(R)\\&\qquad+\tilde{\eta}_2^{(2,0)}(R,t)[\tilde{\eta}_2^{(2,0)}(R,t_0)]^*\chi_2^0(R)\}+O(\delta t^2)\;,\end{aligned} \qquad (18)$$

where $\chi_1^0(R)$ and $\chi_2^0(R)$ are the initial channel amplitudes, i.e., those defined at t_0. The $O(\delta t^2)$ error term in Eqs. (17) and (18) vanishes exactly when the two-channel potentials ε_1 and ε_2 are parallel and μ_{12} is independent of R. Its presence in the generic situation where $\partial_R(\varepsilon_1-\varepsilon_2)\neq 0$ and/or $\partial_R\mu_{12}\neq 0$ limits the validity of these formulas to a short-time interval. Thus Eqs. (17) and (18) are the basis for a stroboscopic wave-packet propagation algorithm in which a long propagation time must be divided up into shorter time slices over which these formulas can be applied. At all times, the wave packets χ_1 and χ_2 are seen to be the sum of two components. One component is propagated on the adiabatic potential-energy surface $V_{1,0}^{\mathrm{ad}}(R)$ defined by

$$V_{1,0}^{\mathrm{ad}}(R)\equiv\varepsilon_{10}^{\mathrm{Fl}}(R)\;, \qquad (19a)$$

while the other involves the propagator on the potential-energy surface $V_{2,0}^{\mathrm{ad}}(R)$, where

$$V_{2,0}^{\mathrm{ad}}(R)\equiv\varepsilon_{20}^{\mathrm{Fl}}(R)\;. \qquad (19b)$$

The identification of the Floquet electronic quasienergy $\varepsilon_{k0}^{\mathrm{Fl}}(R)$ with the adiabatic PES's followed from the remark made above that Eqs. (9) are identical with the eigenvalue equation for $\underline{V}^d$, Eq. (11). These two components are not the initial wave packets $\chi_k^{(0)}(R)$ as such, but are obtained from these wave packets by a further transformation which involves the components of $\tilde{\boldsymbol{\eta}}^{(k,0)}$ at times t and t_0. At first sight, it may appear that an algorithm based on Eqs. (17) and (18) would suffer from the need to generate these quantities by solving Eqs. (9) for their Fourier components. However, as will be shown in Sec. III, the Floquet eigenvectors $\tilde{\boldsymbol{\eta}}^{(k,0)}$, as well as their associated eigenvalues $\varepsilon_{k,0}^{\mathrm{Fl}}$, can be obtained in a much more efficient manner by directly integrating the two-state time-dependent Schrödinger equation (6), exploiting the equivalence between this time integration and the diagonalization of the infinite matrix $\underline{V}^d$.

The mapping of the two-channel dynamics onto a set of local two-level dynamics using the approach of the Appendix yields the same picture if the new electronic basis introduced there is constructed such that it correlates with the field-free Born-Oppenheimer basis at the beginning of each time slice. In contrast, when this basis is a Floquet representation, Eqs. (17) and (18) are obtained for the first slice only. Essentially, this is due to the fact that the Floquet basis states do not correlate naturally to field-free states at the beginning of each slice. In fact, their correlation to the field-free states is determined once and for all at time $t=0$, which is considered to be the beginning of the whole excitation process. Hence, although time dependent, the Floquet electronic basis defined in the Appendix does not evolve, in the sense that it is not redefined at the beginning of each time slice.

B. Time-independent coupled-channel Floquet description

In the direct wave-packet description presented in the preceding section, no attempt was made to transform the time-dependent problem into time-independent coupled equations for the nuclear amplitudes, and the two-channel time-dependent Schrödinger equation was solved directly. The local two-state evolution operator was expressed in terms of Floquet vectors for convenience, mainly to bring out the role played by the dressed adiabatic potential-energy surfaces defined by Eqs. (19).

In an alternative formulation, more often used in studies of strong-field molecular dynamics, one directly searches for nuclear quasienergy states in a Floquet treatment of Eq. (1). Analogously to the definitions of the electronic quasienergy states, Eq. (8), the nuclear quasienergy wave functions are defined by

$$\begin{aligned}\chi^{(\gamma,m)}(R,t)&=\begin{bmatrix}\chi_1^{(\gamma,m)}(R,t)\\ \chi_2^{(\gamma,m)}(R,t)\end{bmatrix}\\ &=e^{-i/\hbar\mathcal{E}^{\text{Fl}}_{\gamma m}}\sum_{n=-\infty}^{+\infty}e^{in\omega t}\begin{bmatrix}\chi_{1,n}^{(\gamma,m)}(R)\\ \chi_{2,n}^{(\gamma,m)}(R)\end{bmatrix}\\ &=e^{-i/\hbar\mathcal{E}^{\text{Fl}}_{\gamma m}t}\tilde{\chi}^{(\gamma,m)}(R,t)\ . \end{aligned}\tag{20}$$

The Fourier components $\chi_{k,v}^{(\gamma,m)}$ must then satisfy the following set of coupled equations:

$$[\hat{T}_N+\varepsilon_1(R)+n\hbar\omega-\mathcal{E}^{\text{Fl}}_{km}]\chi_{1,n}^{(\gamma,m)}(R)=\frac{V_{12}^0(R)}{2}[\chi_{2,n+1}^{(\gamma,m)}(R)+\chi_{2,n-1}^{(\gamma,m)}(R)]\ ,\tag{21a}$$

$$[\hat{T}_N+\varepsilon_2(R)+n\hbar\omega-\mathcal{E}^{\text{Fl}}_{km}]\chi_{2,n}^{(\gamma,m)}(R)=\frac{V_{12}^0(R)}{2}[\chi_{1,n+1}^{(\gamma,m)}(R)+\chi_{1,n-1}^{(\gamma,m)}(R)]\ ,\tag{21b}$$

where γ is a multi-index denoting collectively both vibrational and electronic quantum numbers. In this case, the periodicity of $\underline{V}^d$ [Eq. (12)] implies

$$\mathcal{E}^{\text{Fl}}_{\gamma m}+\mathcal{E}^{\text{Fl}}_{\gamma 0}+m\hbar\omega\ ,\tag{22a}$$

$$\chi^{(\gamma,m)}(R,t)=e^{-im\omega t}\chi^{(\gamma,0)}(R,t)\ ,\tag{22b}$$

or

$$\chi_{l,v}^{(\gamma,m)}(R)=\chi_{l,v-m}^{(\gamma,0)}(R)\ .\tag{22c}$$

If the spectrum $\{\mathcal{E}^{\text{Fl}}_{\gamma m}\}$ is discrete then

$$\langle\langle\tilde{\chi}^{(\gamma,m)}(R,t)|\tilde{\chi}^{(\gamma',m')}(R,t)\rangle\rangle=\delta_{\gamma\gamma'}\delta_{mm'}\tag{23}$$

and in particular

$$\langle\tilde{\chi}^{(\gamma,0)}(R,t)|\tilde{\chi}^{(\gamma',0)}(R,t)\rangle=\delta_{\gamma\gamma'}\tag{24}$$

for all t. In fact, as shown by Okuniewicz [26], the set of Floquet solutions $\{\tilde{\chi}^{(\gamma,0)}(R,t)\}$ associated with a single Brillouin zone forms a complete basis if the quasienergy spectrum $\{\mathcal{E}^{\text{Fl}}_{\gamma m}\}$ is discrete. In this case, the general solution of Eq. (1) is

$$\chi(R,t)=\sum_{\gamma}\sum_{n}\langle\tilde{\chi}^{(\gamma,0)}(R,0)|\chi(R,0)\rangle e^{-i/\hbar(\mathcal{E}^{\text{Fl}}_{\gamma 0}-n\hbar\omega)t}\times\begin{bmatrix}\chi_{1,n}^{(\gamma,0)}(R)\\ \chi_{2,n}^{(\gamma,0)}(R)\end{bmatrix}\ .\tag{25}$$

For problems with continua, Eq. (25) would still be applicable if L^2 discretization is employed. Hence the dynamics of the two-channel system can be completely expressed in terms of Floquet states associates with a single Brillouin zone. The eventual L^2 discretization set aside, this conclusion is exact and does not imply that the Floquet description has been truncated to a single block: In principle, the first-zone nuclear amplitudes $\chi_{k,n}^{(\gamma,0)}(R)$, $k=1,2$ are to be obtained by solving the coupled equations (21) exactly.

At high field intensity, it is useful to introduce the adiabatic representation obtained by diagonalizing $\underline{V}^d$,

$$\underline{V}^{\text{ad}}=\underline{C}^{\dagger}\underline{V}^d\underline{C}\ ,\tag{26a}$$

$$(\underline{V}^{\text{ad}})_{ij}=\varepsilon_i^{\text{Fl}}(R)\delta_{ij},\quad i(j)=(k,m)\ .\tag{26b}$$

This corresponds to the transformation

$$\underline{X}_{\text{ad}}^{(\gamma,m)}=\underline{C}^{\dagger}\underline{X}_d^{(\gamma,m)}\tag{27}$$

of the nuclear amplitudes $\chi_{k,n}^{(\gamma,m)}(R)$ appearing in Eq. (21) which were gathered into an infinite vector $\underline{X}_d^{(\gamma,m)}$. Assuming that this representation is valid, then two classes of adiabatic solutions to Eqs. (21) can be defined.

(i) First class. These solutions are associated with vibrational states supported by the first adiabatic channel in a given Brillouin zone (the first one for instance) , i.e., by the adiabatic dressed potential $\varepsilon_{10}^{\text{Fl}}(R)$. Thus, defining $E_{1,v}^{\text{ad}},\chi_{1,v}^{\text{ad}}(R)$ through

$$[\hat{T}_N+\varepsilon_{10}^{\text{Fl}}(R)-E_{1,v}^{\text{ad}}]\chi_{1,v}^{\text{ad}}(R)=0\ ,\tag{28a}$$

the vector $\underline{X}_{\text{ad}}^{(\gamma,0)}$ contains a single nonzero element associated with $i=(1,0)$ and, in the original diabatic representation, the Floquet nuclear wave functions of this first class are given by

$$\chi_{1,n}^{(\gamma,0)}(R)=\tilde{\eta}_{1,n}^{(1,0)}(R)\chi_{1,v}^{\text{ad}}(R),\quad \gamma=(1,v)\tag{28b}$$

$$\chi_{2,n}^{(\gamma,0)}(R)=\tilde{\eta}_{2,n}^{(1,0)}(R)\chi_{1,v}^{\text{ad}}(R),\quad \gamma=(1,v)\tag{28c}$$

corresponding to a total (i.e., vibrational and electronic) quasienergy

$$\mathcal{E}^{\text{Fl}}_{(1,v),0}=E_{1,v}^{\text{ad}},\quad \gamma=(1,v)\ .\tag{28d}$$

Equations (28b) and (28c) were obtained by inverting Eq. (27) and by recalling that the columns of $\underline{C}$ are filled with the Fourier components of $\tilde{\eta}^{(k,m)}(R,t)$.

(ii) Second class. Similarly, Floquet solutions of the second class are associated with vibrational states

$\chi_{2,v'}^{\text{ad}}(R)$ supported by $\varepsilon_{20}^{\text{Fl}}(R)$, the second adiabatic channel in the first Brillouin zone,

$$[\hat{T}_N+\varepsilon_{20}^{\text{Fl}}(R)-E_{2,v'}^{\text{ad}}]\chi_{2,v'}^{\text{ad}}(R)=0 \tag{29a}$$

and the diabatic, Floquet nuclear wave functions of this second class are given by

$$\chi_{1,n}^{(\gamma,0)}(R)=\tilde{\eta}_{1,n}^{(2,0)}(R)\chi_{2,v'}^{\text{ad}}(R),\quad \gamma=(2,v') \tag{29b}$$

$$\chi_{2,n}^{(\gamma,0)}(R)=\tilde{\eta}_{2,n}^{(2,0)}(R)\chi_{2,v'}^{\text{ad}}(R),\quad \gamma=(2,v') \tag{29c}$$

corresponding to a total quasienergy given by

$$\mathcal{E}_{(2,v'),0}^{\text{Fl}}=E_{2,v'}^{\text{ad}},\quad \gamma=(2,v')\ . \tag{29d}$$

Substitution of Eqs. (28) and (29) into Eq. (25) gives

$$\begin{aligned}\chi(R,t)=&\sum_v\left[\chi_{1,v}^{\text{ad}}\langle\chi_{1,v}^{\text{ad}}|\sum_n[\tilde{\eta}_{1,n}^{(1,0)*}|\chi_2^0\rangle+\tilde{\eta}_{2,n}^{(1,0)*}|\chi_2^0\rangle]e^{-i/\hbar E_{1,v}^{\text{ad}}(t-t_0)}\right]\sum_n e^{in\omega(t-t_0)}\begin{bmatrix}\tilde{\eta}_{1n}^{(1,0)}\\ \tilde{\eta}_{2,n}^{(1,0)}\end{bmatrix}\\ &+\sum_{v'}\left[\chi_{2,v'}^{\text{ad}}(R)\langle\chi_{2,v'}^{\text{ad}}|\sum_n[\tilde{\eta}_{1,n}^{(2,0)*}|\chi_1^0\rangle+\tilde{\eta}_{2,n}^{(2,0)*}|\chi_2^0\rangle]e^{-i/\hbar E_{2,v'}^{\text{ad}}(t-t_0)}\right]\\ &\times\sum_n e^{in\omega(t-t_0)}\begin{bmatrix}\tilde{\eta}_{1n}^{(2,0)}\\ \tilde{\eta}_{2,n}^{(2,0)}\end{bmatrix}\ .\end{aligned} \tag{30}$$

The closure over $(1,v)$ states and over $(2,v')$ states then gives

$$\begin{aligned}\chi(R,t)=&e^{-i/\hbar(\hat{T}_N+\varepsilon_{10}^{\text{Fl}})(t-t_0)}\sum_n[\tilde{\eta}_{1,n}^{(1,0)*}\chi_1^0(R)+\tilde{\eta}_{2,n}^{(1,0)*}\chi_2^0(R)]\sum_n e^{in\omega(t-t_0)}\begin{bmatrix}\tilde{\eta}_{1n}^{(1,0)}\\ \tilde{\eta}_{2,n}^{(1,0)}\end{bmatrix}\\ &+e^{-i/\hbar(\hat{T}_N+\varepsilon_{20}^{\text{Fl}})(t-t_0)}\sum_n[\tilde{\eta}_{1,n}^{(2,0)*}\chi_1^0(R)+\tilde{\eta}_{2,n}^{(2,0)*}\chi_2^0(R)]\sum_n e^{in\omega(t-t_0)}\begin{bmatrix}\tilde{\eta}_{1n}^{(2,0)}\\ \tilde{\eta}_{2,n}^{(2,0)}\end{bmatrix}\end{aligned} \tag{31}$$

or, as separate components

$$\begin{aligned}\chi_1(R,t)=&e^{-i/\hbar(\hat{T}_N+\varepsilon_{10}^{\text{Fl}})(t-t_0)}\{\tilde{\eta}_1^{(1,0)}(R,t)[\tilde{\eta}_1^{(1,0)}(R,t_0)]^*\chi_1^0(R)+\tilde{\eta}_1^{(1,0)}(R,t)[\tilde{\eta}_2^{(1,0)}(R,t_0)]^*\chi_2^0(R)\}\\ &+e^{-i/\hbar(\hat{T}_N+\varepsilon_{20}^{\text{Fl}})(t-t_0)}\{\tilde{\eta}_1^{(2,0)}(R,t)[\tilde{\eta}_1^{(2,0)}(R,t_0)]^*\chi_1^0(R)\\ &\qquad+\tilde{\eta}_1^{(2,0)}(R,t)[\tilde{\eta}_2^{(2,0)}(R,t_0)]^*\chi_2^0(R)\}\ ,\end{aligned} \tag{32a}$$

$$\begin{aligned}\chi_2(R,t)=&e^{-i\hbar(\hat{T}_N+\varepsilon_{10}^{\text{Fl}})(t-t_0)}\{\tilde{\eta}_2^{(1,0)}(R,t)[\tilde{\eta}_1^{(1,0)}(R,t_0)]^*\chi_1^0(R)+\tilde{\eta}_2^{(1,0)}(R,t)[\tilde{\eta}_2^{(1,0)}(R,t_0)]^*\chi_2^0(r)\}\\ &+e^{-i\hbar(\hat{T}_N+\varepsilon_{20}^{\text{Fl}})(t-t_0)}\{\tilde{\eta}_2^{(2,0)}(R,t)[\tilde{\eta}_1^{(2,0)}(R,t_0)]^*\chi_1^0(R)\\ &\qquad+\tilde{\eta}_2^{(2,0)}(R,t)[\tilde{\eta}_2^{(2,0)}(R,t_0)]^*\chi_2^0(R)\}\ .\end{aligned} \tag{32b}$$

These results are identical with those expressed by Eqs. (17) and (18). The same physical picture thus emerges from the two distinct approaches, the first one denoting a direct wave-packet generation, while the second describes the wave packets as superpositions of vibrational quasienergy states. The approximations made in obtaining the pair of expressions of the wave packets, as given by Eqs. (17) and (18) or (32a) and (32b), differ from one approach to another. In the direct wave-packet description, the mapping of the two-channel dynamics onto local two-level dynamics requires a short time scale, whereas the adiabatic approximation made in the above treatment of the time-independent coupled equations (21) for the nuclear Floquet amplitudes requires a rather different condition. This condition corresponds to a high-intensity regime, as it is commonly accepted that nonadiabatic couplings between the adiabatic Floquet electronic states tend to vanish at high field intensities. This behavior of the field-induced nonadiabatic couplings can easily be established when the diabatic matrix $\underline{V}^d$ of Eq. (12) is truncated to a finite number of Floquet blocks. In the context of a nontruncated, infinite Floquet matrix $\underline{V}^d$, the exact demonstration of this behavior, particularly when the transition dipole moment is strongly R dependent, is not yet available. The detailed analysis of the behavior of the nonadiabatic couplings with respect to the field intensity will be reported in a separate paper. In the present paper, we adopt the simple viewpoint offered by a finite representation of the Floquet $\underline{V}^d$ matrix, and consider the adiabaticity condition to require a high field intensity. A finite representation of the Floquet matrix is indeed implicitly evoked in the numerical calculations reported below, since the time evolution is discretized in all these calculations. The equivalence of the two approaches employed above in the derivation of Eqs. (17) and (18) indicates that at high field intensities, the dynamics of the two-channel system become more and more adiabatic (with respect to nuclear motion) and the time evolution of the system can be represented faithfully by these expressions of the wave packets over a longer time scale. This behavior is the main object of the numerical investigations described below.

III. COMPUTATIONAL DETAILS

A. Local Floquet states and adiabatic PES's

To implement Eqs. (32), the Floquet solutions to the local two-level Schrödinger equation are needed, as they furnish the quantities $\varepsilon_{10}^{\rm Fl},\varepsilon_{20}^{\rm Fl}$, i.e., the adiabatic potential-energy surfaces in the first Brillouin zone, and the components $\tilde{\eta}_j^{(k,0)}(R,t),\tilde{\eta}_j^{(k,0)}(R,0)$ $(j,k=1$ or $2)$ of the two Floquet vectors in this first zone, at time t and at an initial time $t=0$. It is useful to recall here that the Fourier components of these vectors fill two columns of the transformation matrix $\underline{C}$ of Eq. (26). To obtain these local two-state Floquet solutions, it is sufficient to note that Eq. (7) can be written in the form

$$\underline{U}(R,t)=\underline{F}(t)e^{-(i/\hbar)\underline{Q}t}\underline{F}^{\dagger}(0) \tag{33}$$

where $\underline{F}(t)$ denotes the square matrix whose columns are the periodic vectors $\tilde{\boldsymbol{\eta}}^{(k,0)}(R,t)$, $k=1,2$, defined in Eqs. (8), and $\underline{Q}$ is a diagonal square matrix containing the Floquet eigenvalues $\varepsilon_{k,0}^{\rm Fl}$. More precisely

$$\underline{Q}=\begin{bmatrix}\varepsilon_{1,0}^{\rm Fl} & 0\\ 0 & \varepsilon_{2,0}^{\rm Fl}\end{bmatrix} \tag{34a}$$

and

$$\underline{F}(t)\equiv(\tilde{\boldsymbol{\eta}}^{(1,0)}(R,t),\quad \tilde{\boldsymbol{\eta}}^{(2,0)}(R,t)) \tag{34b}$$

so that

$$\underline{F}(t)e^{-(i/\hbar)\underline{Q}t}=\begin{bmatrix}\eta_1^{10}(R,t) & \eta_1^{20}(R,t)\\ \eta_2^{10}(R,t) & \eta_2^{20}(R,t)\end{bmatrix} . \tag{34c}$$

Since $\underline{F}(t)$ is periodic, we obtain from Eq. (33)

$$\underline{U}(R,\tau)=\underline{F}(0)e^{-(i/\hbar)\underline{Q}\tau}\underline{F}^{\dagger}(0) , \tag{35}$$

where τ has been defined previously as the period of the field's oscillations. This result shows that the matrix $\underline{Q}$, and hence the Floquet eigenvalues $\varepsilon_{k,0}^{\rm Fl}$, $k=1,2$ can be obtained by diagonalizing $\underline{U}(R,\tau)$, the evolution operator for the local two-state system evaluated exactly for one period of the field. The diagonalization of $\underline{U}(R,\tau)$ also gives the matrix $\underline{F}(0)$, i.e., the Floquet vectors $\tilde{\boldsymbol{\eta}}^{(k,0)}(R,0)$ evaluated at an initial time, here written as $t=0$. The same vectors at an arbitrary time t are obtained from $\underline{F}(t)$, which can be extracted from the time-evolution operator $\underline{U}(R,t)$ by inverting Eq. (33),

$$\underline{F}(t)=\underline{U}(R,t)\underline{F}(0)e^{(i/\hbar)\underline{Q}t} . \tag{36}$$

This method for calculating the eigenvalues and eigenvectors of $\underline{V}^d$, without actually diagonalizing this (infinite) Floquet matrix has previously been used by Muller [27]. It relies on the ability to generate the two-state time-evolution operator $\underline{U}(R,t)$ by an alternative method, which should be formally exact, at least. Such a method indeed exists and has been demonstrated elsewhere [20–22]. It was found that $\underline{U}(R,t)$ can be written exactly in the form

$$\underline{U}(R,t)=\begin{bmatrix} e^{-(i/\hbar)[\varepsilon_1 t+\int_0^t dt'\lambda_1(t')]}\cos\dfrac{\mathcal{A}}{2} & -e^{-(i/\hbar)[\varepsilon_1 t+\int_0^t dt'\lambda_1(t')-\hbar\varphi]}\sin\dfrac{\mathcal{A}}{2}\\ e^{-(i/\hbar)[\varepsilon_2 t+\int_0^t d'\lambda_2(t')+\hbar\varphi]}\sin\dfrac{\mathcal{A}}{2} & e^{-(i/\hbar)[\varepsilon_2 t+\int_0^t dt'\lambda_2(t')]}\cos\dfrac{\mathcal{A}}{2}\end{bmatrix} , \tag{37}$$

where $\mathcal{A}$ is an effective field-area function, defined by

$$\mathcal{A}(t)\equiv\frac{2}{\hbar}\int_0^t\boldsymbol{\mu}_{12}\cdot\mathbf{E}(t')\sin(\varphi-\omega_{12}t')dt' , \tag{38}$$

and φ is a phase angle coupled to $\mathcal{A}$ through

$$\dot{\varphi}\tan\mathcal{A}(t)=\frac{2}{\hbar}\boldsymbol{\mu}_{12}(R)\cdot\mathbf{E}(t)\cos(\varphi-\omega_{12}t) . \tag{39}$$

In these expressions, $\omega_{12}=(\varepsilon_1-\varepsilon_2)\hbar$ is the Bohr frequency for the vertical transition from state 1 to state 2 at the nuclear configuration R, and

$$\lambda_1(t)=\boldsymbol{\mu}_{12}\cdot\mathbf{E}(t)\sin\mathcal{A}(t)\cos[\varphi(t)-\omega_{12}t]\\ \times[1-\cos\mathcal{A}(t)]/2=-\lambda_2(t) . \tag{40}$$

This formally exact solution to the two-state Schrödinger equation was used previously in an algorithm for the wave-packet propagation in two-channel laser-driven systems. The only remaining difficulty in using this exact representation is the integration of the nonlinear integro-differential equation (39). A numerical iterative procedure to integrate this equation by linearization over a short-time scale has been presented and tested in Ref. [20]. Here, it is used to generate the quantities needed to construct the evolution operator $\underline{U}(R,t)$ according to Eq. (37); the phase angle $\varphi(t)$, the area function $\mathcal{A}(t)$, and the Berry phase integral containing the quantities λ_i, $i=1,2$. These quantities depend on R, as do ω_{12} and $\boldsymbol{\mu}_{12}$.

We considered a two-channel model for the photodissociation of $H_2{}^+$ employing the potential energy and transition dipole functions given by Bunkin and Tugov [28]. The cw field is assumed to have the form given in Eq. (3), with $\omega=0.27639$ a.u., corresponding to a wavelength $\lambda=164.85$ nm. Five values of the field intensity were considered, namely $I=10^{12}$, 1.4×10^{13}, 4×10^{13}, 10^{14}, and 3.52×10^{14} W/cm^2. For each intensity, the operator $\underline{U}(R,t)$ was evaluated at the grid points of a temporal grid obtained by dividing a field period τ into 64 slices. Once this is done, diagonalization of $\underline{U}(R,\tau)$ gives the Floquet eigenvalues $\varepsilon_{k,0}^{\mathrm{Fl}}(R)$, $k=1,2$, which represent the two adiabatic dressed potential-energy surfaces associated with the first Brillouin zone. The surfaces associated with other zones are obtained by a simple translation of these first-zone potential-energy curves, according to (13a). As noted above, the diagonalization of $\underline{U}(R,\tau)$ also gives $\underline{F}(0)$, i.e., the Floquet vectors $\tilde{\boldsymbol{\eta}}^{(k,0)}(R,0)$ evaluated at $t=0$. The same vectors at other grid points, corresponding to times t lying within a single field period, are contained in $\underline{F}(t)$, which is calculated using Eq. (36). As noted before,the discrete representation of the time-evolution operator $\underline{U}$ on a temporal grid containing 64 grid points corresponds to the truncation of the Floquet diabatic potential matrix $\underline{V}^d$ to 64 blocks. Figure 1 shows the adiabatic dressed potential-energy curves obtained for the five values of I given above, and for a single Brillouin zone, the central zone, for instance. Figure 2 illustrates the way these PES's are repeated in the other zones as a result of the periodicity of the time-dependent problem.

B. Wave-packet computations

Starting, at $t=0$, from an initial wave packet denoting the $v=0$ vibrational ground state supported by the $1\sigma_g$ electronic ground-state manifold, Eqs. (17) and (18) were used to generate the wave packet at a future time $t>0$. In view of the short-time or adiabatic approximation involved in obtaining Eqs. (17) and (18), these equations can be used over a sufficiently short-time scale only. Thus a long total excitation time must be divided into short time slices over which these equations apply. The time t_0 in these expressions then denotes the beginning of a time slice, and the initial wave packets must be redefined at the beginning of each time slice. Time slices of extension $\delta t=n\tau/64$, with $n=1-15$, were used in a systematic study of the convergence of the wave-packet calculations using Eqs. (17) and (18). To test the adiabatic approximation at high field intensities, we have also carried out single-step propagations using a large time step of 1.0–11.0 fs. These single-step propagations make use of the representation given by Eqs. (A18) of the Appendix instead, as this denotes more transparently a wave-packet propagation on uncoupled adiabatic dressed PES's. Insofar as the results of these long single-step propagations confirm the validity of the adiabatic approximation, i.e., the weakness of the residual nonabiabatic couplings, there should be no numerical difference between Eqs. (17), (18), and Eqs. (A18).

The wave packets generated with Eqs. (17) and (18) are compared with those obtained by a direct application of the third-order split-operator method using a fixed time step $\delta t=\tau/64$ over which the field is considered constant. In applying the adiabatic Floquet propagation procedure described by Eqs. (17) and (18), the split-operator formula is also used to represent the propagators $\exp[-(i/\hbar)(T_N+\varepsilon_{k,0}^{\mathrm{Fl}})\delta t]$ associated with the adiabatic dressed channels $\varepsilon_{k,0}^{\mathrm{Fl}}$, $k=1,2$. In implementing this split-operator formula, all potential terms are evaluated in the coordinate representation, while the kinetic-energy factor is evaluated in the momentum representation. Passage from one representation to another is achieved by a fast Fourier transform (FFT) algorithm, and the wave packets are discretized on a spatial grid containing 1024 points with step size $\delta R=4.075\times10^{-2}$ a.u.

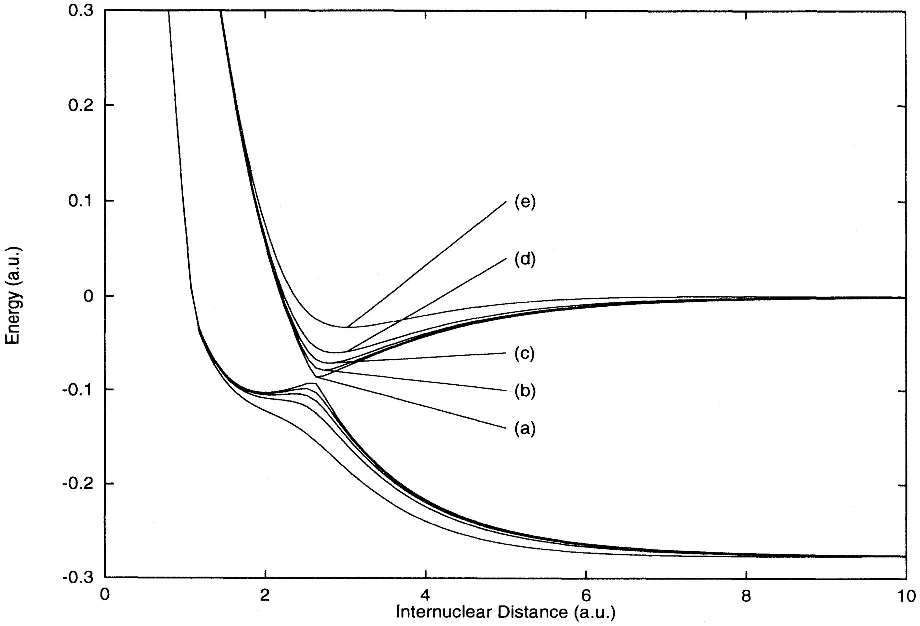

FIG. 1. The two adiabatic dressed potential-energy surfaces, $\varepsilon_{k,0}^{\mathrm{Fl}}(R)$, $k=1,2$, associated with the first Brillouin zone, are shown for (a) $I=10^{12}$ W/cm^2, (b) $I=1.4\times10^{13}$ W/cm^2, (c) $I=4\times10^{13}$ W/cm^2, (d) $I=10^{14}$ W/cm^2, and (e) $I=3.52\times10^{14}$ W/cm^2. These surfaces are obtained by diagonalizing $\underline{U}(R,\tau)$ for a two-state model of $H_2{}^+$ involving the $^2\Sigma_g^+$ ground state and the $^2\Sigma_u^+$ first excited state of the molecular ion coupled by a cw laser field ($\lambda=164.85$ nm).

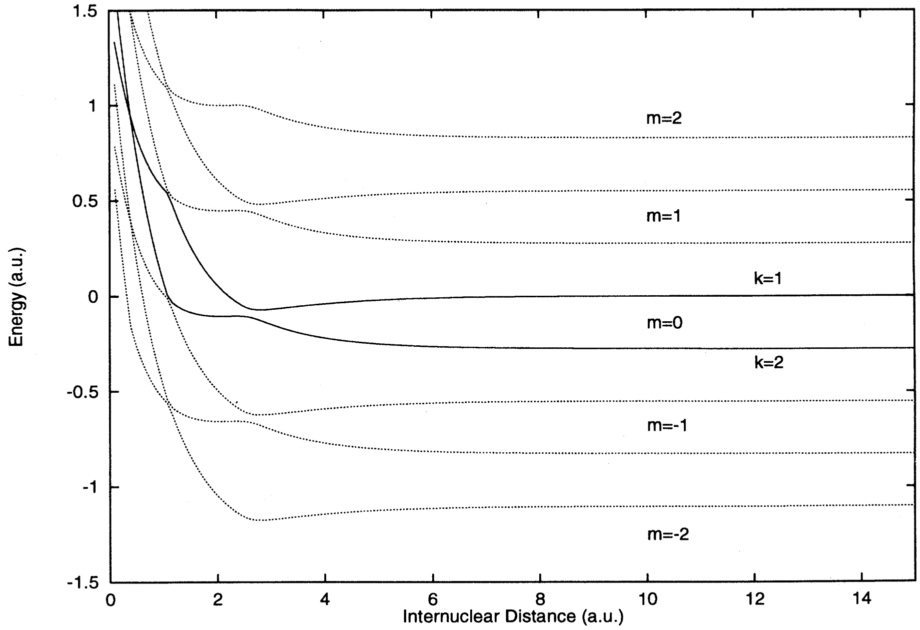

FIG. 2. For $I=4\times10^{13}$ W/cm^2, the adiabatic dressed potential-energy surfaces, $\varepsilon^{\mathrm{Fl}}_{k,m}(R)$, $k=1,2$ for the two-state model of $H_2{}^+$ are shown for five Brillouin zones corresponding to $m=\pm2,\pm1,0$.

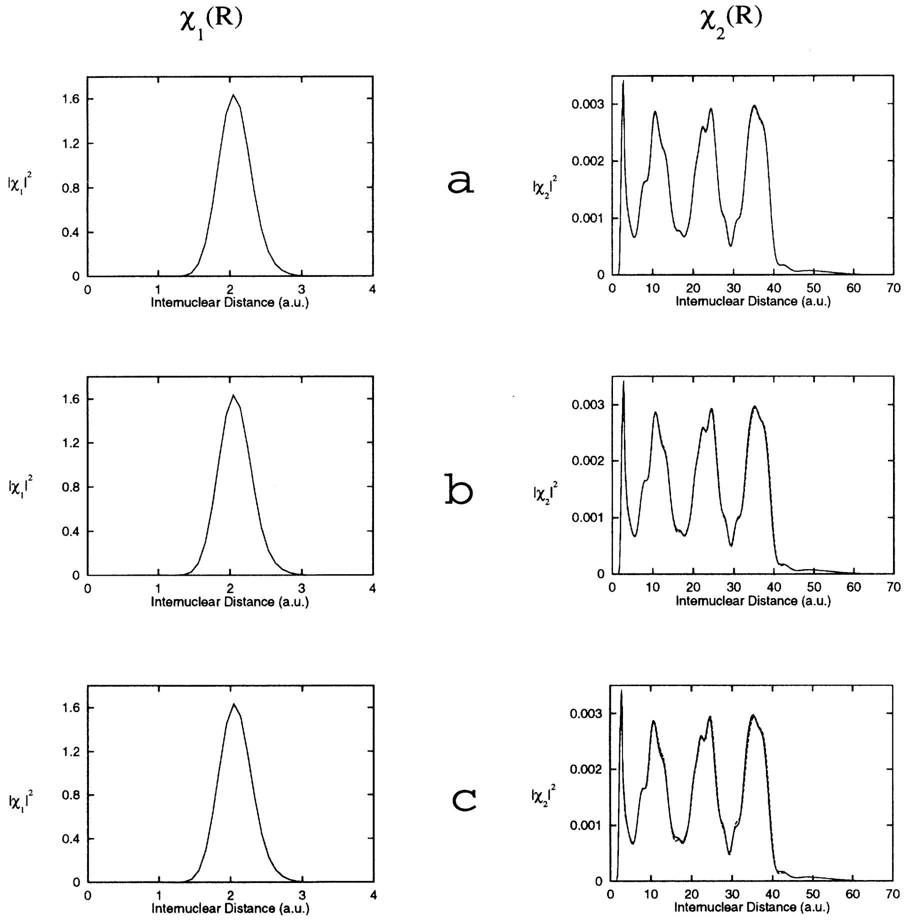

FIG. 3. Wave packets generated by a low-intensity laser field ($I=10^{12}$ W/cm^2), at $t=50$ fs, on the two diabatic (Born-Oppenheimer, field-free) electronic states of $H_2{}^+$. The results of the wave-packet propagation using the split-operator formula (solid lines) are compared with those obtained by applying Eqs. (17) and (18) over time slices $\delta t=n\tau/64$, with (a) $n=1$, (b) $n=8$, (c) $n=15$ (dashed lines). Note that only the square moduli of the wave packets are shown.

C. Results and discussions

The results of the wave-packet calculations described above using Eqs. (17) and (18) are shown in Fig. 3 for $I=10^{12}$ W/cm^2 corresponding to a low-intensity regime and in Fig. 4 for $I=3.52\times10^{14}$ W/cm^2 denoting a high-intensity regime. In each figure, the wave packets χ_1 and χ_2, which are supported by the Born-Oppenheimer, field-free ground- and excited-state manifolds at $t=50$ fs, and are generated using Eqs. (17) and (18) over time slices of extension $\delta t=n\tau/64$, $n=1$, 8, and 15, are compared with corresponding convergent split-operator results. At the lowest intensity, the wave packet supported by the ground-state manifold remains localized near the equilibrium configuration R_e, and the wave packet associated with the excited-state manifold represents a very small fraction of the initial population. Thus, in this case, the agreement between the description using Eqs. (17) and (18) and that using a straight split-operator formula is not surprising, and does not suffice to convincingly establish the accuracy of the new wave-packet propagation algorithm based on Eqs. (17) and (18). The results associated with the higher intensities, such as illustrated in Fig. 4. for $I=3.52\times10^{14}$ W/cm^2, confirm that this algorithm is indeed reliable. At these intensities, the initial wave packet is depleted at a much larger rate, creating an appreciable population on the excited manifold. Initially localized, the promoted population quickly spread out under the accelerating action of the repulsive wall of the excited PES. The continuous action of the intense field causes a population transfer back to the ground-state manifold at large R. The wave packets generated using Eqs. (17) and (18), i.e., by propagation on the dressed adiabatic PES's, for $I=3.52\times10^{14}$ W/cm^2, Fig. 4, agree reasonably well with those propagated with the split-operator formula. Both Figs. 3 and 4 indicate that the propagation of wave packets initially prepared on the dressed-molecule adiabatic PES's according to Eqs. (17) and (18) is remarkably efficient, as it requires a time step that is relatively long ($\delta t=15\tau/64$) in comparison to that required for a convergent propagation using the third-order split-operator formula ($\delta t=\tau/64$).

Even though wave-packet propagation using Eqs. (17) and (18) allows for the use of a relatively long time step, it is still only a numerical technique. However, it presents the advantage of offering, for each time step, a relatively simple physical picture of the wave-packet dynamics as occurring on adiabatic dressed PES's, thereby furnishing the link between the Floquet, i.e., time-independent concepts, and time-dependent wave-packet concepts. Insofar as this physical picture is concerned, it is interesting to assess the extent to which the wave-packet evolution in

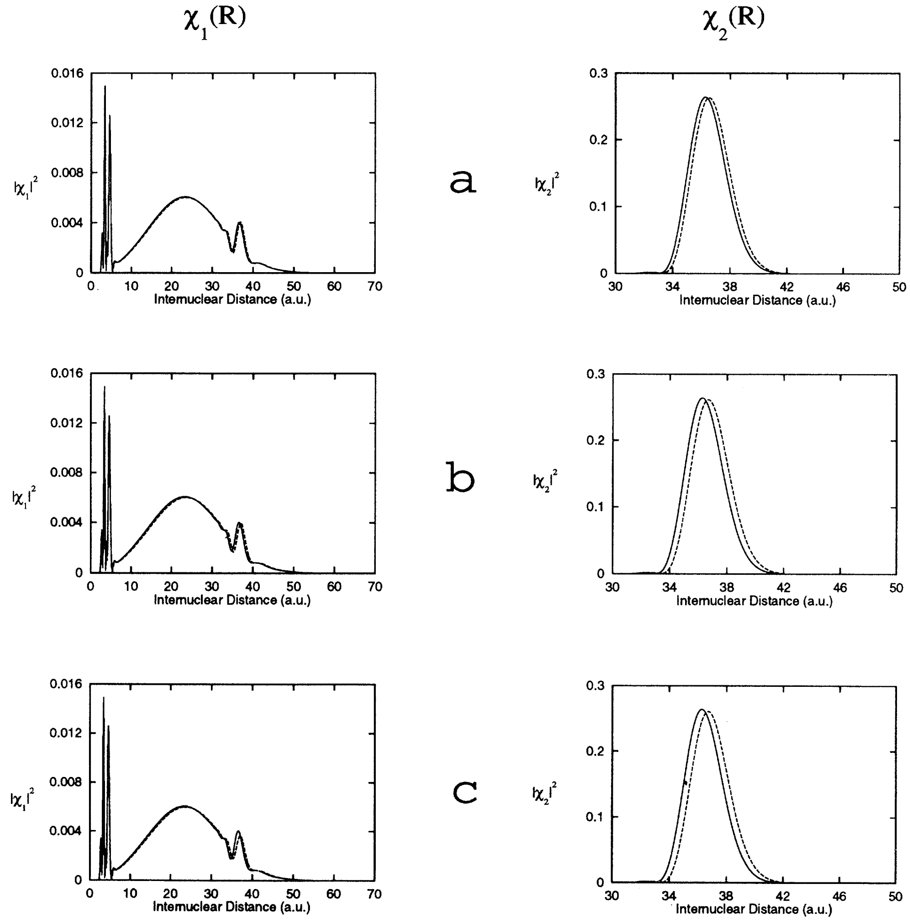

FIG. 4. Same as Fig. 3, but for a high-intensity regime ($I=3.52\times10^{14}$ W/cm^2).

the dressed or Floquet representation is indeed adiabatic. Figures 5 and 6 show results of single-step wave-packet propagations at various intensities, using Eqs. (A18) of the Appendix, with a single long step $\delta t = 5.5$ fs, Fig. 5 and $\delta t = 11$ fs, Fig. 6. A quantitative agreement with the results of the corresponding reference split-operator calculations (using a much smaller time step, $\delta t = \tau/64 = 8.59 \times 10^{-3}$ fs) is no longer obtained, but the wave packets generated in these single-step propagations do exhibit qualitatively the same behavior as these reference results. This qualitative agreement generally improves at higher field intensities, which can be seen in Fig. 7, where a measure of the deviation of the single-step propagation results from the reference ones is shown as a function of the field intensity for five values of the time step δt. The measure used for this deviation is defined by

$$\|\Delta\Psi\| = \int dR\,(|\Delta|\chi_1|^2/\langle\chi_1|\chi_1\rangle| + |\Delta|\chi_2|^2\langle\chi_2|\chi_2\rangle|)\,, \tag{41}$$

where $\Delta|\chi_k|^2$ denotes the difference between the value of $|\chi_k|^2$ obtained by the single-step propagation and that of the reference calculation. Clearly, $\|\Delta\Psi\|$ depends less strongly on δt at high field intensities than at low intensities, where it increases monotonously with δt, as expected. For all δt, $\|\Delta\Psi\|$ decreases monotonically as the field intensity increases. The results shown in Figs. 5–7 thus give a clear indication that the wave-packet dynamics in the two-channel system becomes more and more adiabatic as the field intensity increases, and that nonadiabatic coupling between Floquet adiabatic dressed channels is indeed negligible at high intensity.

In view of this adiabaticity, it is possible to interpret the results shown in Figs. 5 and 6 for high intensities in terms of properties of the dressed PES's. It is tempting to interpret the oscillatory structure in χ_2, Fig. 6(b), or in χ_1, Fig. 6(c), as reflecting nodal structures of bound quasienergy states supported by the potential well newly created on the upper adiabatic PES at the one-photon avoided crossing. In this interpretation, the fact that this structure appears in χ_2 for $I = 4 \times 10^{13}$ W/cm^2, and in χ_1 for $I = 3.52 \times 10^{14}$ W/cm^2 can be rationalized by evoking the different barrier height found on the lower adiabatic PES in the two cases. For $I = 4 \times 10^{13}$ W/cm^2, this barrier is still sufficiently high to prevent the wave packet initially prepared on this adiabatic channel from moving toward the dissociation region. This wave packet would have mainly the character of the diabatic bound channel. The wave packet prepared on the upper adiabatic channel would then be associated with the diabatic open channel. In contrast, for $I = 3.52 \times 10^{14}$ W/cm^2, the barrier on the lower adiabatic PES is completely depleted and

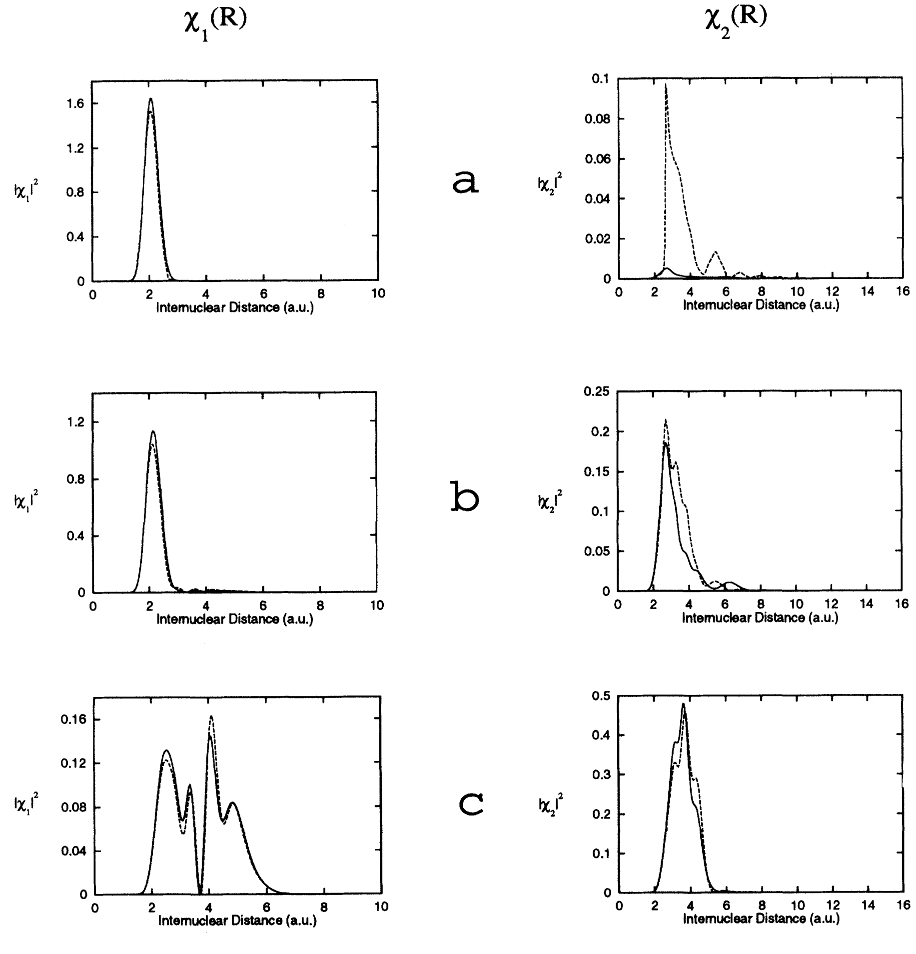

FIG. 5. The results of the wave-packet propagation using Eq. (A18) over a single long step $\delta t = 5.5$ fs $= t_f$ (dashed lines) are compared with those obtained with the split-operator formula for (a) $I = 10^{12}$ W/cm^2, (b) $I = 4 \times 10^{13}$ W/cm^2, and (c) $I = 3.52 \times 10^{14}$ W/cm^2.

the promoted wave packet therein would become dissociative and would be affected by a portion of the adiabatic PES which corresponds to the repulsive diabatic PES. This wave packet would then be χ_2, and the nodal structure of the vibrationally "trapped" states would appear in χ_1. Unfortunately, this attractive scheme is wrong. By recalculating the wave packets according to Eq. (A18), but without the final multiplication by $\underline{F}(R,t)$, we found that, at both intensities, the promoted population is larger on the upper adiabatic PES, rather than on the lower one, as implicitly assumed in the above scheme. Thus, the dissociation at high field intensity occurs on the upper adiabatic dressed PES, contrary to the assumed bond-softening mechanism. Moreover, the further propagation of these promoted wave packets on the uncoupled adiabatic PES's gives no oscillatory structure as in Figs. 6(b) and 6(c). Clearly, the oscillatory structure in these figures cannot arise from the excitations of laser-induced vibrational states. They are due to interferences between the adiabatic amplitudes $\exp[-i(T_N+V_k^{\mathrm{ad}})t]\xi_k(R,0)$ which are further redistributed between the diabatic channels 1 and 2 under the action of $\underline{F}(R,t)$.

IV. SUMMARY AND CONCLUSIONS

We have shown that in the Floquet or dressed-molecule representation, the time-resolved dynamics in a two-channel molecular system, such as $H_2{}^+$ driven by a cw laser field, can be analyzed in terms of propagation of wave packets on the two adiabatic dressed channels associated with a single Brillouin zone. The precise way an initial state is transported onto the adiabatic PES's and propagated thereupon is described by Eqs. (17) and (18). In a direct time-dependent approach, these equations were obtained by a mapping of the two-channel dynamics onto those of a set of two-level systems, which is continuously parametrized by the nuclear coordinate R. This mapping is achieved either by the Dirac transformation of Eq. (4) or by the construction of the new, time-dependent, electronic basis of the Appendix. This electronic basis is adiabatic with respect to nuclear motions on a sufficiently short time scale. Thus a condition for Eqs. (17) and (18) to apply is a short propagation time. In this sense, Eqs. (17) and (18) are viewed as the basis of a short-time algorithm for the propagation of wave packets in a two-channel system driven by a periodic field. In comparison with other numerical techniques currently in use, such as the split-operator formula applied over time slices sufficiently short so as to justify the replacement of the actual fluctuating field by an average, constant field, the present algorithm is distinguished by the explicit use of adiabatic dressed potentials. The algorithm was tested on the propagation of wave packets denoting the photodissociation of $H_2{}^+$. The numerical results reported es-

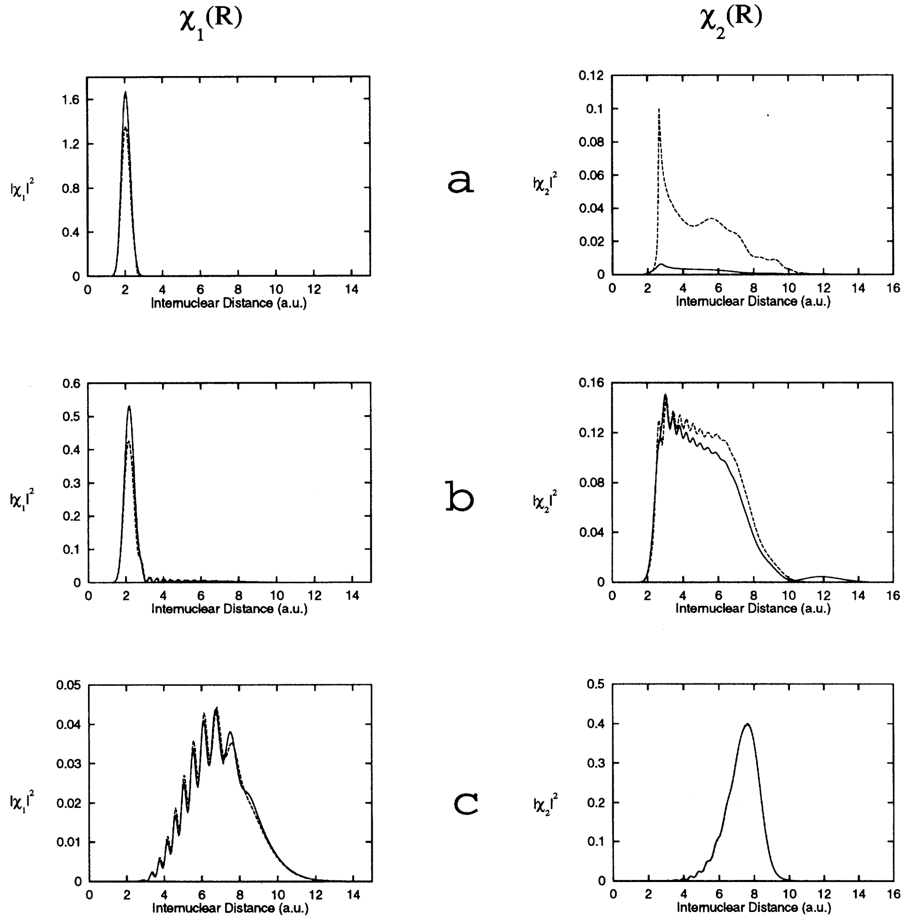

FIG. 6. Same as Fig. 5, but for $\delta t=11\ \mathrm{fs}=t_f$.

tablish the reliability of this algorithm. Moreover, these results indicate that the algorithm is more efficient than other techniques, since the time scale over which it can be directly applied is an order of magnitude larger than that required for the application of the split-operator algorithm alluded to previously.

The expressions for the wave packets in the adiabatic dressed representation, Eqs. (17) and (18), are also obtained within the so-called time-independent Floquet representation of nuclear motions. In this representation, nuclear, i.e., vibrational quasienergy states are governed by the set of time-independent coupled Schrödinger equations (21). By diagonalizing the diabatic dressed potential matrix, the adiabatic dressed representation is obtained. Nuclear amplitudes supported by the adiabatic channels are coupled by intensity-dependent nonadiabatic interactions which are believed to vanish as the field intensity increases. It is in this adiabatic, high-field-intensity limit that Eqs. (17) and (18) have been rederived. The validity of this adiabatic approximation is here indirectly assessed through single-step wave-packet calculations reported in the preceding section. The results of this numerical experiment confirm the hypothesis that the field-induced nonadiabatic couplings tend to vanish as the field intensity increases, and the wave-packet dynamics become more adiabatic. Without this adiabatic approximation, the general expression of the wave packets is of course Eq. (25), which represents the decomposition of the wave packets in the basis of the Floquet vibrational states within a single zone. A similar expression had also been derived previously in the context of a wave packet, time-resolved description within a dressed-molecule picture using a fully quantized field [29,30]. However, no attempt was made to reduce this description to a simple picture such as the one obtained in the present work in terms of the adiabatic dressed PES's associated with a single zone. It is interesting to note that, even at low intensity, where it is generally believed that an initial eigenstate of the field-free Hamiltonian would simply be transported onto the closest-lying resonance state, and where the rotating wave approximation (RWA) is valid, many Floquet states should be included in the sum appearing on the right-hand side of Eq. (25) in order to obtain a correct picture of the wave packets' motions. Indeed if the sum over γ in this equation is restricted to a single Floquet state, namely, the resonance state which offers the strongest overlap with the initial state, and the RWA is invoked, reducing the sum over n to a single term also, then the wave packets would not be moving at all, i.e., they are almost stationary, except for a monotonous de-

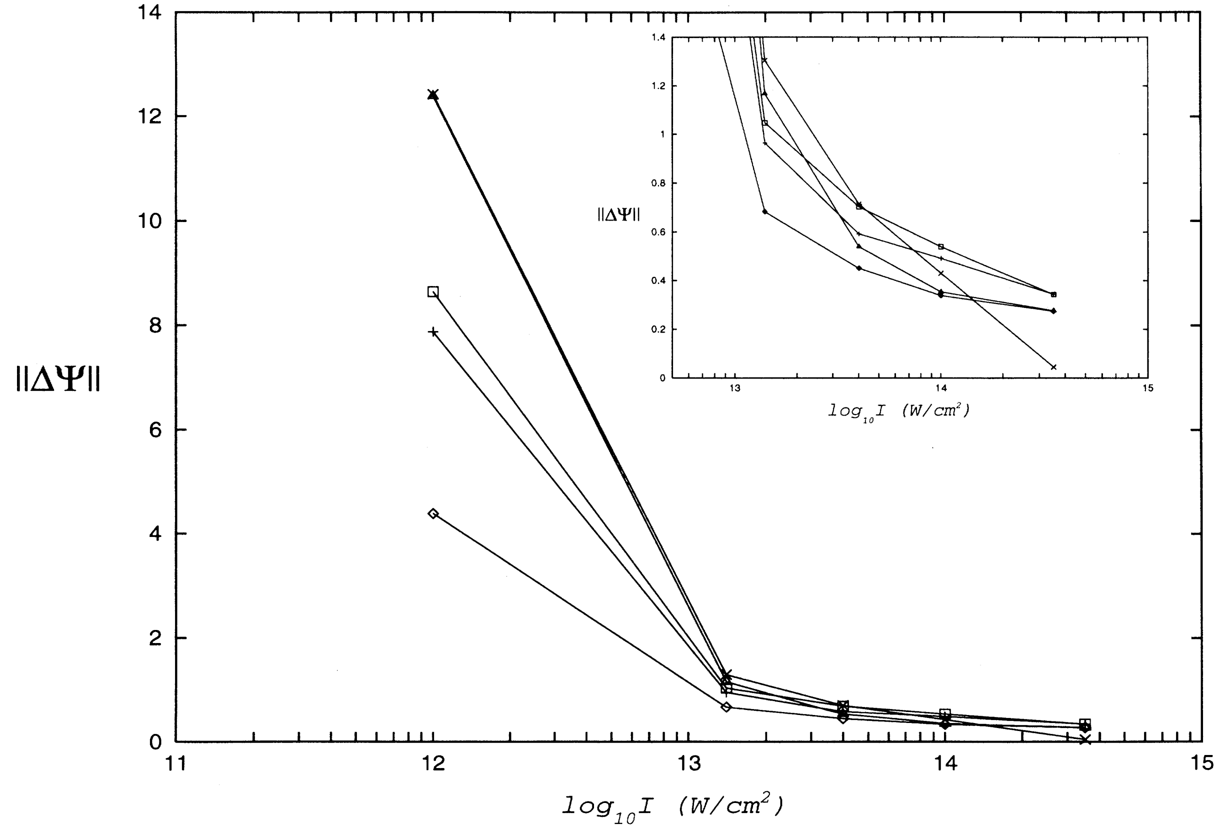

FIG. 7. The deviation of the single-step wave-packet propagation results from these of the reference split-operator calculations is shown as a function of the field intensity, for five values of $\delta t = t_f$, namely, $\delta t = 1.1$ fs (◇), 2.2 fs (+), 3.3 fs (□), 4.4 fs (×), and 5.5 fs (△). The deviation is measured by the function $\|\Delta\Psi\|$ defined in Eq. (41). The detailed behavior of $\|\Delta\Psi\|$ in the high-intensity region is shown in the inset.

cay of their amplitudes due to the imaginary part of the resonance energy. Clearly, inclusion of other Floquet states, more precisely of the nonresonance states which more closely resemble field-free continuum states, is necessary.

The present paper deals strictly with excitation of a two-channel molecular system by a cw, periodic field. An extension of this work to a pulsed laser field may be made either by assuming an adiabatic transport of Floquet states [31], or by using a two-time-scale approach, such as the one proposed by Peskin and Moiseyev [32]. However, this extension would appear most direct, requiring only certain parameter changes, if an artificial periodic repetition of the pulse can be introduced. This relies on the fact that the Floquet ansatz gives a complete description of the time evolution within a single period, so that, if the pulsed excitation is repeated with a period $T=\tau_{\text{pulse}}$, where τ_{pulse} is the actual duration of the pulse and if this period is an integer multiple of the period $2\pi/\omega$ of the carrying wave, then the Floquet construction with $\Omega=2\pi/T$ would describe correctly the detailed dynamics over the total duration of the physical pulse, i.e., at all times t within the period T. A picture of the wave-packet motions on the adiabatic dressed PES's associated with the repetition frequency Ω similar to that described by Eqs. (17) and (18) will be valid at high peak intensity, and can be used to investigate pulse shape effects on the molecular dynamics, as well as to assess the degree of control that can be exerted on the dynamics by varying the pulse shape and duration. This avenue, which can be described as a mapping of a pulsed excitation onto an equivalent periodic one, is being explored in our laboratories.

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APPENDIX

In the Schrödinger equation (1), $\chi_1(R,t)$ and $\chi_2(R,t)$ are the nuclear wave functions associated with two field-free, electronic eigenfunctions defined within the Born-Oppenheimer approximation. Thus, denoting these by $\varphi_1^d(r{:}R)$ and $\varphi_2^d(r;R)$, we have

$$\hat{H}_{\text{el}}(r;R)\varphi_i^d(r;R)=\varepsilon_i(R)\varphi_i^d(r;R) \tag{A1}$$

and the total wave function is given by

$$\Psi(r,R,t)=(\varphi_1^d(r;R)\;\;\varphi_2^d(r;R))\begin{bmatrix}\chi_1(R,t)\\ \chi_2(R,t)\end{bmatrix} . \tag{A2}$$

The time evolution of $\Psi(r,R,t)$ is governed by the total Schrödinger equation

$$i\hbar\partial_t\Psi(r,R,t)=\hat{H}(r,R,t)\Psi(r,R,t) , \tag{A3}$$

where

$$\hat{H}(r,R,t)=\hat{T}_N+\hat{H}_{\text{el}}(r;R)+\hat{V}(r,R,t) . \tag{A4}$$

In order to account for the field-induced coupling $\hat{V}$, which is assumed to operate only between the two electronic states $\varphi_1^d(r;R)$ and $\varphi_2^d(r;R)$, it is useful to express the time evolution in a new electronic basis which incorporates the mixing effect of $\hat{V}$, and is necessarily time dependent. The new electronic basis states are defined by a pair of orthonormal solutions of the electronic time-dependent Schrödinger equation

$$i\hbar\partial_t\varphi_i^{\text{ad}}(r,t;R)=[\hat{H}_{\text{el}}(r;R)+\hat{V}(r,t;R)]\times\varphi_i^{\text{ad}}(r,t;R) . \tag{A5}$$

Defining $\underline{T}$ to be the transformation matrix linking the two electronic bases, i.e., writing

$$(\varphi_1^{\text{ad}}(r,t;R)\;\;\varphi_2^{\text{ad}}(r,t;R))=(\varphi_1^d(r;R)\;\;\varphi_2^d(r;R))\underline{T}(t;R) , \tag{A6}$$

then Eqs. (A2) and (A5) imply

$$i\hbar\partial_t\underline{T}(t;R)=\begin{bmatrix}\varepsilon_1(R) & V_{12}(t;R)\\ V_{12}(t;R) & \varepsilon_2(R)\end{bmatrix}\underline{T}(t;R) , \tag{A7}$$

where $V_{12}(t,R)$ is a matrix element of $\hat{V}(r,t;R)$ in the two-state diabatic basis of Eq. (A1). Obviously the precise form of $\underline{T}$ depends on the initial conditions imposed upon the two orthogonal solutions of Eq. (A5). In the Floquet construction, the initial conditions are replaced by the requirement that $\underline{T}$ be of the form

$$\underline{T}(t;R)=\underline{F}(t;R)e^{-(i/\hbar)\underline{Q}(R)t} , \tag{A8}$$

where $\underline{F}$ is periodic and $\underline{Q}$ is the diagonal matrix of Floquet exponents. These matrices have previously been defined in Eqs. (34).

Substitution of Eq. (A6) into the Schrödinger equation (A3) for the total wave function gives

$$i\hbar\partial_t\left[(\varphi_1^{\text{ad}}(r,t;R)\;\;\varphi_2^{\text{ad}}(r,t;R))\underline{T}^{-1}(t;R)\begin{bmatrix}\chi_1(r,t)\\ \chi_2(R,t)\end{bmatrix}\right]$$

$$=[\hat{T}_N+\hat{H}_{\text{el}}(r;R)+\hat{V}(r,R,t)](\varphi_1^{\text{ad}}(r,t;R)\;\;\varphi_2^{\text{ad}}(r,t;R))\underline{T}^{-1}(t;R)\begin{bmatrix}\chi_1(R,t)\\ \chi_2(R,t)\end{bmatrix} . \tag{A9}$$

From the definition of the adiabatic basis states $\varphi_k^{\text{ad}}(r,t;R), k=1,2$, Eq. (A5), and from Eq. (A8), which expresses the choice of these basis states to be Floquet states of the two-level electronic system, Eq. (A9) can be rewritten in the form

$$\left\{(\varphi_1^{\mathrm{ad}} \quad \varphi_2^{\mathrm{ad}})e^{(i/\hbar)\underline{Q}(R)t} i\hbar\partial_t \left[\underline{F}^{-1}(t;R)\begin{bmatrix}\chi_1(R,t)\\ \chi_2(R,t)\end{bmatrix}\right]\right\}$$
$$=[\hat{T}_N(\varphi_1^{\mathrm{ad}} \quad \varphi_2^{\mathrm{ad}})+(\varphi_1^{\mathrm{ad}} \quad \varphi_2^{\mathrm{ad}})\underline{Q}(R)]e^{(i/\hbar)\underline{Q}(R)t}\underline{F}^{-1}(t;R)\begin{bmatrix}\chi_1(R,t)\\ \chi_2(R,t)\end{bmatrix} . \qquad \text{(A10)}$$

Define

$$\begin{bmatrix}\xi_1(R,t)\\ \xi_2(R,t)\end{bmatrix}=\underline{F}^{-1}(t;R)\begin{bmatrix}\chi_1(R,t)\\ \chi_2(R,t)\end{bmatrix} \qquad \text{(A11)}$$

to represent nuclear wave functions associated with the time-dependent electronic states $\varphi_k^{\mathrm{ad}}(r,t;R)$. Using Eq. (A6) to reexpress the dual vector $(\varphi_1^{\mathrm{ad}} \quad \varphi_2^{\mathrm{ad}})$ in terms of the diabatic, time-independent vector $(\varphi_1^d \quad \varphi_2^d)$, we obtain, after projecting Eq. (A10) onto these electronic diabatic basis states,

$$i\hbar\partial_t\begin{bmatrix}\xi_1(R,t)\\ \xi_2(R,t)\end{bmatrix}=[\underline{F}^{-1}(t;R)\hat{\underline{D}}\underline{F}(t;R)+\underline{Q}(R)] \times \begin{bmatrix}\xi_1(R,t)\\ \xi_2(R,t)\end{bmatrix} , \qquad \text{(A12)}$$

where

$$\hat{\underline{D}}=\int dr\begin{bmatrix}\varphi_1^{d*}(r;R)\\ \varphi_2^{d*}(r;R)\end{bmatrix}\hat{T}_N(\varphi_1^d(r;R) \quad \varphi_2^d(r;R)) . \qquad \text{(A13)}$$

Using

$$\hat{T}_N(\varphi_1^d \quad \varphi_2^d)\underline{F}(t;R)=(\varphi_1^d \quad \varphi_2^d)\underline{F}(t;R)\hat{T}_N + [\hat{T}_N,(\varphi_1^d \quad \varphi_2^d)\underline{F}(t;R)] , \qquad \text{(A14)}$$

Eq. (A11) can be rearranged into the form

$$i\hbar\partial_t\begin{bmatrix}\xi_1(R,t)\\ \xi_2(R,t)\end{bmatrix}=[\hat{T}\underline{I}+\underline{Q}(R)+\underline{\hat{W}}(t;R)] \times \begin{bmatrix}\xi_1(R,t)\\ \xi_2(R,t)\end{bmatrix} , \qquad \text{(A15)}$$

where

$$\underline{\hat{W}}(t;R)=\int dr\,\underline{F}^{-1}(t;R)\begin{bmatrix}\varphi_1^{d*}(r;R)\\ \varphi_2^{d*}(r;R)\end{bmatrix} \times[\hat{T}_N,(\varphi_1^d(r;R) \quad \varphi_2^d(r;R))\underline{F}(t;R)] .$$

It is thus seen that the nuclear amplitudes $\xi_i(R,t)$ define wave packets which would be moving independently on the two Floquet PES's, if not for the coupling matrix $\underline{\hat{W}}(t;R)$ which represents nonadiabatic interactions between the two wave packets. As is seen in the rearrangement in Eq. (A14), this term results from the noncommutativity of $(\varphi_1^d \quad \varphi_2^d)$ and $\underline{F}(t;R)$ with $\hat{T}_N$. It is instructive to further expand this nonadiabatic coupling term and to decompose it into natural and field-induced nonadiabatic interactions

$$\underline{\hat{W}}(t;R)=-\frac{\hbar^2}{2\mu}\left\{\underline{F}^{-1}(t;R)\int dr\begin{bmatrix}\varphi_1^{d*}(r;R)\\ \varphi_2^{d*}(r;R)\end{bmatrix}\frac{\partial^2}{\partial R^2}(\varphi_1^d(r;R) \quad \varphi_2^d(r;R))\underline{F}(t;R)\right.$$
$$+2\underline{F}^{-1}(t;R)\int dr\begin{bmatrix}\varphi_1^{d*}(r;R)\\ \varphi_2^{d*}(r;R)\end{bmatrix}\frac{\partial}{\partial R}(\varphi_1^d(r;R) \quad \varphi_2^d(r;R))\underline{F}(t;R)\frac{\partial}{\partial R}$$
$$+2\underline{F}^{-1}(t;R)\int dr\begin{bmatrix}\varphi_1^{d*}(r;R)\\ \varphi_2^{d*}(r;R)\end{bmatrix}\frac{\partial}{\partial R}(\varphi_1^d(r;R) \quad \varphi_2^d(r;R))\frac{\partial}{\partial R}\underline{F}(t;R)$$
$$\left.+\underline{F}^{-1}(t;R)\frac{\partial^2}{\partial R^2}\underline{F}(t;R)+2\underline{F}^{-1}(t;R)\frac{\partial}{\partial R}\underline{F}(t;R)\frac{\partial}{\partial R}\right\} . \qquad \text{(A16)}$$

The first two terms of Eq. (A16) are natural nonadiabatic couplings, i.e., they arise already in the field-free Born-Oppenheimer approximation. Since they are not amplified by the presence of the field, they can be considered negligible. The other three terms are purely nonadiabatic couplings due to the transformation from the time-independent electronic basis ($\varphi_1^d \quad \varphi_2^d$) to the Floquet basis. As mentioned in Sec. II, those coupling terms are believed to vanish at high field intensity. Otherwise, they can be neglected on a short-time scale. Within either of these two approximations, the solution of (A14) is

$$\begin{bmatrix}\xi_1(R,t)\\ \xi_2(R,t)\end{bmatrix}=e^{-(i/\hbar)[\hat{T}_N\underline{I}+\underline{Q}]t}\begin{bmatrix}\xi_1(R,0)\\ \xi_2(R,0)\end{bmatrix}. \tag{A17}$$

Using Eq. (A11), we finally obtain

$$\begin{aligned}\begin{bmatrix}\chi_1(R,t)\\ \chi_2(R,t)\end{bmatrix}&=\underline{F}(t;R)\begin{bmatrix}\xi_1(R,t)\\ \xi_2(R,t)\end{bmatrix}\\ &=\underline{F}(t;R)e^{-(i/\hbar)[\hat{T}_N\underline{I}+\underline{Q}]t}\begin{bmatrix}\xi_1(R,0)\\ \xi_2(R,0)\end{bmatrix}\\ &=\underline{F}(t;R)e^{-(i/\hbar)[\hat{T}_N\underline{I}+\underline{Q}]t}\\ &\quad\times\underline{F}^{-1}(0;R)\begin{bmatrix}\chi_1(R,0)\\ \chi_2(R,0)\end{bmatrix}.\end{aligned} \tag{A18}$$

Recalling the definition of $\underline{F}$ in terms of the Floquet vector $\tilde{\eta}(R,t)$ for the two-state system, Eq. (34b), this final result is seen to differ from that embodied in Eqs. (17) and (18) by the permutation of the operator $e^{-i/\hbar\hat{T}_N t}$ with the multiplicative matrix $\underline{F}(t;R)$. Insofar as the field-induced nonadiabatic couplings in Eqs. (A16) are negligible, Eq. (A18) can be considered to be equivalent to Eqs. (17) and (18), as the commutator between $e^{-i/\hbar\hat{T}_N t}$ and $\underline{F}(t;R)$ is of the same order of magnitude as these neglected nonadiabatic couplings.

[1] P. H. Bucksbaum, A. Zavriyev, H. G. Muller, and D. W. Schumacher, Phys. Rev. Lett. **64**, 1883 (1990).

[2] B. Yang, M. Saeed, L. F. DiMauro, A. Zavriyev, and P. H. Bucksbaum, Phys. Rev. A **44**, 1458 (1991).

[3] C. Cohen-Tannoudji and S. Reynaud, in *Multiphoton Processes,* edited by J. Eberly and P. Lambropoulos (Wiley, New York, 1978).

[4] T. F. George, J. Phys. Chem. **86**, 10 (1982); T. F. George, I. H. Zimmerman, I. H. Yuan, J. M. Laing, and J. R. DeVries, Acc. Chem. Res. **10**, 449 (1977).

[5] N. M. Kroll and K. M. Watson, Phys. Rev. A **13**, 1018 (1976).

[6] A. M. Lau and C. K. Rhodes, Phys. Rev. A **16**, 2392 (1977); A. M. F. Lau, *ibid.* **13**, 139 (1976).

[7] A. D. Bandrauk and M. L. Sink, J. Chem. Phys. **74**, 1110 (1981); Chem. Phys. Lett. **57**, 569 (1978); A. D. Bandrauk and J. F. McCann, Comments At. Mol. Phys. **22**, 325 (1989).

[8] T. T. Nguyen-Dang and A. D. Bandrauk, J. Chem. Phys. **79**, 3256 (1983); **80**, 4926 (1984).

[9] G. Floquet, Ann. Ec. Norm. Super. **12**, 47 (1883).

[10] S. I. Chu, J. Chem. Phys. **75**, 2215 (1981).

[11] S. I. Chu, in *Lasers, Molecules and Methods,* Advances in Chemical Physics Vol. LXXIII, edited by J. O. Hirschfelder, R. Wyatt, and R. D. Coalson (Wiley, New York, 1989).

[12] X. He, O. Atabek, and A. Giusti-Suzor, Phys. Rev. A **38**, 5586 (1988); **42**, 1585 (1990); X. He, Ph.D. thesis, Université de Paris–Sud, 1989.

[13] A. Giusti-Suzor, X. he, O. Atabek, and F. H. Mies, Phys. Rev. Lett. **64**, 515 (1990).

[14] S. Miret-Artes, O. Atabek, and A. D. Bandrauk, Phys. Rev. A **45**, 8056 (1992).

[15] T. T. Nguyen-Dang and S. Manoli, Phys. Rev. A **44**, 5841 (1991); S. Manoli and T. T. Nguyen-Dang, *ibid.* **48**, 4307 (1993).

[16] A. Zavriyev, P. H. Bucksbaum, J. Squier, and F. Saline, Phys. Rev. Lett. **70**, 1077 (1993).

[17] O. Atabek and G. Jolicard, Phys. Rev. A **46**, 5845 (1992).

[18] A. Giusti-Suzor and F. Mies, Phys. Rev. Lett. **68**, 3869 (1992).

[19] A. D. Bandrauk, E. Aubanel, and J. M. Gauthier, Laser Phys. **3**, 381 (1993).

[20] T. T. Nguyen-Dang and H. Abou-Rachid, Phys. Rev. A **45**, 4752 (1992).

[21] T. T. Nguyen-Dang and H. Abou-Rachid, J. Chem. Phys. **96**, 256 (1992).

[22] H. Abou-Rachid, T. T. Nguyen-Dang, R. K. Chaudhury, and X. He, J. Chem. Phys. **97**, 5497 (1992).

[23] T. T. Nguyen-Dang, S. Manoli, and H. Abou-Rachid, Phys. Rev. A **43**, 5012 (1991).

[24] J. H. Shirley, Phys. Rev. B **138**, 979 (1965).

[25] H. Sambe, Phys. Rev. A **7**, 2203 (1973).

[26] J. M. Okuniewicz, J. Math. Phys. **15**, 1587 (1974).

[27] H. G. Muller, in *Coherence Phenomena in Atoms and Molecules in Laser Fields,* Vol. B287 of *NATO Advanced Study Institute, Series B: Physics,* edited by A. D. Bandrauk and S. C. Wallace (Plenum, New York, 1992).

[28] F. V. Bunkin and I. I. Tugov, Phys. Rev. A **8**, 601 (1973).

[29] F. H. Mies and A. Giusti-Suzor, Phys. Rev. A **44**, 7547 (1991).

[30] T. L. DeVries and T. F. George, Phys. Rev. A **26**, 1419 (1982).

[31] H. P. Breuer and M. Holthaus, Z. Phys. D **11**, 1 (1989); H. P. Breuer, K. Dietz, and M. Holthaus, J. Phys. B **24**, 1343 (1991); M. Holthaus, Phys. Rev. Lett. **69**, 1596 (1992).

[32] U. Peskin and N. Moiseyev, J. Chem. Phys. **99**, 4590 (1993).