

Impact of electron ionization on the generation of high-order harmonics from molecules

S. Brener,¹ M. V. Ivanov,² and N. Moiseyev¹¹Department of Chemistry and Minerva Center for Non Linear Physics, Technion-Israel Institute of Technology, Haifa 32000, Israel²Institute of Precambrian Geology and Geochronology (IPGG), Nab. Makarova 2, St. Petersburg 199034, Russia

(Received 17 March 2003; published 11 August 2003)

When the laser frequency is tuned to be equal to the molecular electronic excitation, high-order harmonics are generated due to the electronic dipole transitions between the corresponding two potential-energy surfaces (PES). A natural, often taken, choice is the PES of the field-free molecular system. In this special choice the ionization phenomenon is not considered. Only the effect of the dissociation is considered. The method we developed enables one to remain within the framework of the 2-PES approximation and yet to include also the ionization effect in the calculations of molecular high-order harmonic generation spectra. In this approach the coupling between the electronic and nuclear motions is taken into consideration by using coupled complex adiabatic PES. As an illustrative numerical example, we calculated the high harmonic generation (HHG) spectra of H_2^+ in a 730-nm laser with the intensity of 8.77×10^{13} W/cm². The inclusion of the ionization in our approach not only enables the electrons to tunnel through the effective static potential barrier, but also apply an asymmetric force which accelerates the electron *before* ionization takes place. Therefore, indirectly the inclusion of the ionization by the laser field may lead eventually to an enhanced HHG spectra in comparison with the calculated one when the “natural” choice of the field-free 2PES is taken.

DOI: 10.1103/PhysRevA.68.023402

PACS number(s): 32.80.Rm, 42.50.Hz, 42.65.Ky

I. BACKGROUND AND MOTIVATION

High-order harmonic generation (HHG) by molecular gases interacting with strong linear polarized laser fields has been studied experimentally during the last decade [1–5]. Most of the experiments were carried out with diatomic molecules, e.g., O₂ or N₂. However, there are also measurements of the HHG spectra taken for organic molecules [6–9]. There has been no indication that the mechanism of the generation of high-order harmonics by molecules is different from the well-known Corkum-Kulander three-step mechanism of atomic HHG [10,11]. However, several theoretical works (see, e.g., Refs. [12,13]) predict that dissociating diatomic and linear triatomic molecules with large internuclear separations are capable of producing high-order harmonics with energies far beyond the atomic HHG cutoff. These ideas have not been confirmed yet by experiments. Another molecular effect on the HHG spectra is the alignment and orientation of the molecules inside the electromagnetic field. The molecular orientation dependence of the HHG spectra was the subject of theoretical [14,15] and experimental studies [16].

The theoretical studies and the numerical calculations for molecules in strong laser fields are complicated since both ionization and dissociation may happen simultaneously. Besides very limited number of calculations [17,18], most of the calculations so far have been carried out for the test-case model of H_2^+ in ac field while either the ionization or the dissociation phenomenon was ignored (see, for example, Refs. [19–22]). For example, only the coupling between the two lowest electronic states was taken into consideration. In Fig. 1 we show the two corresponding potential-energy curves (PEC) of the field-free H_2^+ .

The laser driven molecular Hamiltonian within the two-state Born-Oppenheimer approximation is given by

$$H(\mathbf{R}, t) = H_0(\mathbf{R}) - \varepsilon_0 \mu(R) \cos \theta \cos \omega t, \quad (1)$$

where H_0 is the field-free molecular Hamiltonian given by

$$H_0(\mathbf{R}) = T(\mathbf{R}) + V(R) \quad (2)$$

and $V(R)$ is a diagonal matrix with the two PEC shown above on the diagonal, θ is the angle between H_2^+ molecular axis and the laboratory z axis, $\mu(R)$ is the off-diagonal 2×2 matrix containing the dipole transition moments, and ε_0 is the maximum field amplitude.

The state vector of the system evolves in time as

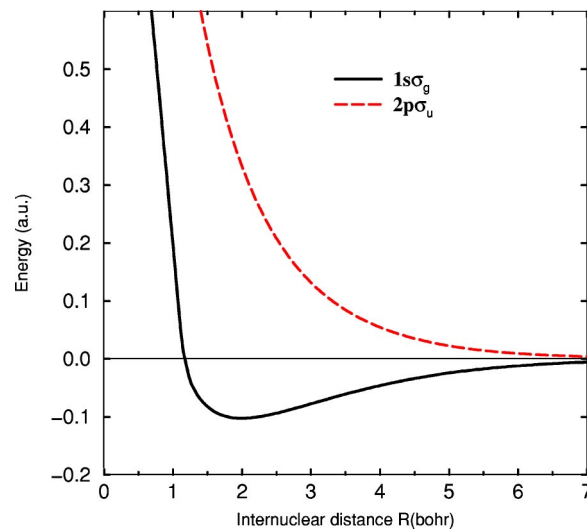


FIG. 1. The field-free potential-energy curves (PEC), $1s\sigma_g$ and $2p\sigma_u$, of H_2^+ which are coupled by the laser. The PEC are the electronic energies obtained by solving the time-independent Hermitian Schrödinger equation within the framework of the adiabatic (Born-Oppenheimer) approximation.

$$\Phi(\mathbf{R}, t) = \begin{pmatrix} \Psi_1(\mathbf{R}, t) Y_{00}(\hat{\mathbf{R}}) \\ \Psi_2(\mathbf{R}, t) Y_{10}(\hat{\mathbf{R}}) \end{pmatrix}, \quad (3)$$

where the nuclear time-dependent function is the solution of the Schrödinger equation associated with the eigenfunction of the Floquet operator,

$$H_F(\mathbf{R}, t) \Phi_\alpha(\mathbf{R}, t) = \epsilon_\alpha \Phi_\alpha(\mathbf{R}, t), \quad (4)$$

where

$$H_F(\mathbf{R}, t) \equiv -i\hbar \frac{\partial}{\partial t} + H(\mathbf{R}, t). \quad (5)$$

In order to calculate the *resonance* state that controls the photoinduced dynamics, the complex scaling method [23,24] has been implemented in the calculations of the resonance quasienergy (QE) Floquet states and their corresponding eigenvalues. That is,

$$R \rightarrow R e^{i\theta_{cs}}, \quad (6)$$

The resonance *complex* QE eigenvalues are θ_{cs} invariant, where the photoionization decay rate is equal to minus twice the imaginary part of the eigenvalue of the complex-scaled Floquet operator.

The resonance photoinduced time-dependent dipole moment amplitude (a complex function of time) is given by

$$d^{res}(t) = \langle \Phi(R, t) | \mu(R) \cos \theta | \Phi(R, t) \rangle. \quad (7)$$

The high-order harmonic generation spectra are calculated according to

$$\sigma_{HG}(\Omega) \propto \left| \frac{1}{T} \int_0^T \Omega^2 e^{i\Omega t} d^{res}(t) dt \right|^2, \quad (8)$$

where $\hbar\Omega$ is the photon energy of the emitted radiation where $\Omega = n\omega, n = 1, 3, 5, 7, \dots$. The HHG spectra are obtained from the Fourier transform of the electron acceleration along the z direction (the electric field oscillates along the z axis), $\langle \dot{z} \rangle(t)$, rather than of the dipole $\langle z \rangle(t)$. This explains the multiplication by Ω^2 in Eq. (8). The HHG spectra for H_2^+ interacting with a laser with $\omega = 0.07382$ a.u. and laser intensity up to 8.51×10^{14} W/cm² were calculated for two electronic PEC, while the ionization is neglected by Moiseyev, Chrysos, Atabeck, and Lefebvre [19] using the complex coordinate method. In strong field, $I_0 \geq 9 \times 10^{14}$ W/cm², the H_2^+ molecule is unstable (see, e.g., the experimental results by Bucksbaum *et al.* [25]). For lower fields (e.g., we consider here $\epsilon_0 = 0.05$ a.u. which means that $I_0 = 8.77 \times 10^{13}$ W/cm²) the HHG is less pronounced, yet the ionization phenomenon is not negligible.

The open question is: How can one carry out photoinduced dynamical calculations with two electronic PEC and yet take into consideration the ionization phenomenon which was neglected above?

It is clear that the oscillations between the two PEC, which are coupled by the electric field, generate the high-

order harmonics. However, ionization does occur in such strong fields and has an effect on the probability to generate the high-order harmonics.

II. ALTERNATIVE APPROACH WHERE IONIZATION IS CONSIDERED

Within the framework of the conventional quantum mechanics (QM), it is hard and even often impossible to study the dynamics of molecular systems where the electronic and the nuclear coordinates are strongly coupled. Strong enough to break down the Born Oppenheimer approximation. In such a case the non-Hermitian quantum mechanics enables us to take into consideration the coupling between the channels that are open for dissociation and ionization in a simple way [26,27].

For the sake of clarity, let us explain it in some detail. In conventional (i.e., Hermitian) quantum mechanics, a resonance is associated with a wave packet [28]. In non-Hermitian quantum mechanics, however, each one of the resonances is associated with a single square-integrable quasienergy eigenstate of the complex scaled Hamiltonian [23,24]. The resonance eigenstates can be counted by their nodes and are square integrable in a very similar way to the bound states in Hermitian QM. The real parts of the complex eigenvalues of the complex-scaled Hamiltonian are the resonance energies, whereas the imaginary parts are the resonance widths (i.e., rates of decay; inverse of lifetimes of the intermediate complex). Using the adiabatic approximation where the nuclei are held fixed, the *complex adiabatic potential-energy surfaces*, $E_{ad}(R) - (i/2)\Gamma_{ad}(R)$, can be calculated. For simplicity of the representation, R stands for the internuclear distance in diatomic molecule. The coupling between the electronic and the nuclear motions have been introduced into the calculations by solving the nuclear equation of motion with *complex adiabatic potential-energy surfaces* [26,27]. Using this approach the Hamiltonian of the intermediate complex $[A-B]^*$ is described as $\hat{H}(R) = \hat{T}(R) + E_{ad}(R) - (i/2)\Gamma_{ad}(R)$. By solving the nuclear $[A-B]^*$ Schrödinger equation with the complex adiabatic potential-energy surface, the resonances associated with the vibrationally bound motion of the autoionizing $[A-B]^*$ complex are obtained.

The extension of the complex adiabatic approach described above, to time dependent Hamiltonians (e.g., when the molecular system interacts with time periodic electric field) is straightforward when the (t, t') approach is taken [29]. Within the framework of the (t, t') approach, time serves as an additional coordinate. Therefore, the resonances are associated with the eigenstates of the complex-scaled Floquet operator when the system is time periodic. When short pulsed lasers are used, the time periodic conditions are imposed by considering the duration of the laser pulse as the time period. For atoms the HHG spectra were calculated from the Fourier transform of the time-dependent complex dipole amplitude $d(t)$, assuming that a single resonance complex-scaled QE wave function controls the photoinduced dynamics [30]. More accurately, the HHG spectra are calculated from the Fourier transform of the electronic accelera-

tion expectation value, $\vec{d}(t)$ [31]. The expectation values are calculated by the use of the c product rather than the usual scalar product. See the definition of the inner product in non-Hermitian QM in Ref. [24] and references therein and in Ref. [32]. Assuming that the photoinduced dynamics is controlled by a *single* resonance quasienergy state, the harmonic generation spectra can be obtained as follows.

(a) The electronic coordinates in the adiabatic Hamiltonian are complex scaled. The Hamiltonian includes the laser field and is time periodic one. By solving the Floquet adiabatic eigenvalue problem, the adiabatic complex resonance QE surfaces, $E_{ad}^{(\alpha)}(R) - i/2\Gamma_{ad}^{(\alpha)}(R)$, and their correspondent complex-scaled Floquet states $\phi_{elec}^{(\alpha)}(\vec{r}, t, R)$ are calculated. The solutions which are needed for the next step of the calculations are associated with the initial state (the ground state of the field-free Hamiltonian). When the laser frequency is tuned to be in resonance with the electronic excitation, it is expected to have two QE Floquet electronic metastable (resonance) states which are populated by the initial state. The QE resonance functions $\phi_{elec}^{(\alpha)}(\vec{r}, t, R)$ are also functions of the scaling parameter $\exp(i\theta_{cs})$, although the resonance QE surfaces are θ_{cs} independent. The fact that $\phi_{elec}^{(\alpha)}$ are θ_{cs} dependent functions is important when expectation values are calculated using the inner product for non-Hermitian QM formalism (so-called the c product) [24,32].

(b) Using the QE Floquet electronic resonance states which are populated by the initial state, the nonadiabatic coupling Hamiltonian matrix elements $H_{\alpha',\alpha}^{non-ad}(R,t) = \langle \phi_{elec}^{(\alpha')}(\vec{r}, t, R, -\theta_{cs}) | d/dR | \phi_{elec}^{(\alpha)}(\vec{r}, t, R, +\theta_{cs}) \rangle_{\vec{r}}$ are calculated. The change of sign of θ_{cs} in the bra state is to satisfy the definition of the c product. When the complex-scaled electronic resonance wave functions are accurately calculated, $H_{\alpha',\alpha}^{non-ad}(R,t)$ would be θ_{cs} independent although the resonance wave functions are θ_{cs} dependent.

(c) The nuclear time-dependent Hamiltonian is given by $H_N(R,t) = H_{ad}(R) + [H^{non-ad}(R,t) \cdot \hat{p}_R + \hat{p}_R \cdot H^{non-ad}(R,t)] / 2M$, where $H_{ad}(R)$ is a diagonal matrix with the nuclear kinetic-energy operator and the complex adiabatic potential surfaces on the diagonal; $\hat{p}_R = -i\hbar d/dR$; and M is the reduced mass of the molecule (for simplicity of representation, we assume that the molecule is a diatomic one).

(d) By solving the nuclear Schrödinger equation with the time periodic Hamiltonian $H_N(R,t)$, the nuclear resonance QE states are obtained. To include the predissociation resonances, the nuclear coordinate R is complex scaled as the electronic coordinates in step (a) of the calculations. Using these resonance complex-scaled nuclear Floquet states, the complex time-dependent dipole is calculated.

(e) By carrying out a Fourier transform of the second time derivative of the dipole calculated in step (d), the HHG spectrum is obtained. When the basis set is far from being complete, the scaling parameter (i.e., rotational angle θ_{cs}) would be varied to provide stationary HHG spectra. It may be necessary to find different optimal values of θ_{cs} for every one of the high-order harmonics. That is, $\partial\sigma_{HG}(\Omega = n\omega) / \partial\theta_{cs} = 0$ for any value of n .

The above procedure of calculating the HG spectra is

computationally very demanding. Therefore we wish to propose a simple method that will enable to take into consideration the ionization effect on the HG spectra within the framework of the adiabatic approximation. The key point of our method is embedded in the answer to the following questions: (1) what optimal adiabatic electronic states of a diatomic molecule should be used as basis functions in the variational calculations? (2) Why in the study of the HG spectra of H_2^+ have the $1s\sigma_g$ and $2p\sigma_u$ adiabatic electronic wave functions been used to form the basis set?

When weak lasers are used as in spectroscopy measurements, the answers to this questions are straightforward. For weak lasers the natural zero-order Hamiltonian is clearly the field-free Hamiltonian. Since the $1s\sigma_g$ and $2p\sigma_u$ states are coupled by the laser, one should take them as the natural basis functions. Therefore these two adiabatic electronic states should be used as basis functions. However, this is not necessarily so when high intensity lasers are applied. In such a case the perturbation picture breaks down. When the laser frequency is sufficiently small such that the Keldysh parameter $\gamma = \sqrt{I_p/2U_p}$ (Ref. [33]) is less than 1, the ionization dynamics are dominated by tunneling. Here I_p is the ionization energy and $U_p = e_0^2/(4m\omega^2)$ is the pondermotive energy. In low laser frequency regime, where γ is sufficiently small, the mechanism of generation of atomic high-order harmonics is the well known three-step mechanism due to Corkum and Kulander and co-workers [10,11]. This mechanism, based on the recollision of the ionized electron with the core, explains the cutoff in atomic HHG spectra occurring at the photon energy of $I_p + 3.2U_p$. Following this discussion it seems that in strong laser fields where $\gamma < 1$, the selection of $H_{FF} + F_{dc}\sum_j \vec{r}_j \cdot \hat{e}_z$ Hamiltonian (where F_{dc} is the field amplitude) as the “zero-order” time-independent Hamiltonian is preferable on the selection of the field-free Hamiltonian H_{FF} . The strong-field dynamics of diatomic molecules (such as H_2^+) exhibits significant differences from rare-gas atoms due to the strong coupling between their ground and first excited states (e.g., the field couples the $1s\sigma_g$ and $2p\sigma_u$ states). In a way it is similar to the situation of HHG at long wave lengths from alkali-metal atoms [34] where the field couples the ground electronic state with the first excited state. The molecular case is, of course, more complicated due to couplings between the vibrational and rotational motions to the electronic one.

On the basis of the above analysis we assumed that the two adiabatic curves should be associated with the zero-order Hamiltonian

$$\hat{H}_{electron}^{dc} = \hat{H}(H_2^+; BO) + \varepsilon_0 f_{dc} \vec{e}_z \cdot \vec{r}, \quad (9)$$

where \vec{r} is the position vector of the electron in a molecular system axis and \vec{e}_z is a unit vector along the z axis of the laboratory (the electric field oscillates along the z axis). The dc-field amplitude is $F_{dc} = \varepsilon_0 f_{dc}$, where $-1 \leq f_{dc} \leq 1$ is a control parameter. The fact that the static field not only ionizes the molecule but also accelerates the electron is explored by carrying out the Kramers-Henneberger transformation where $\vec{r} \rightarrow [\varepsilon_0 f_{dc} \vec{e}_z \cdot \vec{r}] t^2/2$ [35].

The HHG spectra will be calculated as a function of f_{dc} and will be averaged in a way that will be explained below. The only reason that the HHG spectra depend on the control parameter f_{dc} is due to the use of incomplete electronic adiabatic functions as a basis set (e.g., two adiabatic PEC in H_2^+). To simplify the representation of our method, we use H_2^+ as an illustrative model Hamiltonian.

Let us first sketch our proposed method.

(1) *The electronic energies of H_2^+ in a dc field (i.e., static field) are calculated as function of R and f_{dc} (assuming that the transition is between $j=0$ and $j=1$ rotational states). The grid points for the control parameter are taken by varying $f_{dc} = \cos(\tau)$ as τ is linearly varied from 0 to $\pi/2$.*

The complex adiabatic PEC are obtained by scaling the electronic coordinates by $\exp(i\theta)$. In the case of H_2^+ the two complex adiabatic potential curves, PEC, which are θ independent and are given by

$$\begin{aligned} E_1(R, \tau) &= E_{1s\sigma_g}^{ad-dc}(R, \tau) - \frac{i}{2} \Gamma_{1s\sigma_g}^{ad-dc}(R, \tau), \\ E_2(R, \tau) &= E_{2p\sigma_u}^{ad-dc}(R, \tau) - \frac{i}{2} \Gamma_{2p\sigma_u}^{ad-dc}(R, \tau). \end{aligned} \quad (10)$$

The complex permanent dipole moments are

$$\mu_{1s\sigma_g}^{ad-dc}(R, \tau) \quad \text{and} \quad \mu_{2p\sigma_u}^{ad-dc}(R, \tau). \quad (11)$$

The complex transition dipole moment is

$$\mu_{1s\sigma_g, 2p\sigma_u}^{ad-dc}(R, \tau). \quad (12)$$

To calculate the resonance PEC and the corresponding dipole matrix elements, one does not have to use the complex-scaling approach [24]. For example, the accurate algorithms developed by Ivanov [36] can be used for our illustrative model Hamiltonian of H_2^+ .

(2) *Calculation of the two electronic PEC which are coupled due to the controlled static dc field.*

Since we used $\hat{\mathcal{H}}_{electron}^{dc}$ as the “zero-order” Hamiltonian for calculating of the two adiabatic resonance electronic states which serve as basis functions in our calculations, we have to subtract the dc term as we calculate the coupled PEC:

$$\begin{aligned} V_{11}(R, \tau) &= E_1(R, \tau) - \varepsilon_0 \cos(\tau) \mu_{1s\sigma_g}^{ad-dc}(R, \tau), \\ V_{22}(R, \tau) &= E_2(R, \tau) - \varepsilon_0 \cos(\tau) \mu_{2p\sigma_u}^{ad-dc}(R, \tau), \\ V_{12}(R, \tau) &= V_{21}(R, \tau) = -\varepsilon_0 \cos(\tau) \mu_{1s\sigma_g, 2p\sigma_u}^{ad-dc}(R, \tau). \end{aligned} \quad (13)$$

(3) *Calculation of the resonance Floquet eigenstates of the diatomic molecule in the strong laser field.*

The Floquet Hamiltonian is as defined above in Eq. (4). The 2×2 time-dependent dc-controlled potential matrix is equal to

$$\begin{aligned} V^{dc\text{-controlled}}(R, t; \tau) &= V[\text{calculated in step (2)}] \\ &+ \varepsilon_0 \cos(\omega t) V_{cup}(R; \tau), \end{aligned} \quad (14)$$

where the $2 \times 2 V_{cup}$ matrix is a matrix with the off-diagonal elements:

$$V_{cup}(R; \tau) = \mu_{1s\sigma_g, 2p\sigma_u}^{ad-dc}(R, \tau). \quad (15)$$

The coordinate R is scaled by a complex factor as described in Eq. (6). In the next step of the calculation, the photoinduced vibrational resonances are obtained via the complex scaling of R .

The complex eigenvalues and the corresponding vector eigenstates of the complex Floquet matrix operator were calculated by the (t, t') method developed by Peskin and Moiseyev [29]. The resonance solutions are associated with complex eigenvalues that are complex-scaling invariant (provided the scaling angle is sufficiently large). Not to be confused with t, t' notation and τ , let us remind that τ is an adiabatic controlled dc field parameter; t' is the time that serves as an additional coordinate in the propagation calculations where the resonance Floquet states are calculated; and t is time as appears in the (t, t') representation of the time-dependent Schrödinger equation with time-dependent Hamiltonians. The time evolution operator reads now as $\exp(-i\mathcal{H}_F t/\hbar)$, where $\mathcal{H}_F = -i\hbar d/dt' + T_R + V^{dc\text{-controlled}}(R, t'; \tau)$ and T_R is the complex-scaled nuclear kinetic-energy operator. The resonance complex-scaled periodic Floquet states $\Phi_{1,2}(R, t; \tau)$ are obtained at the $t' = t \text{ cut}$, i.e., $\Phi_{1,2}(R, t' = t, t; \tau)$ [29].

(4) *Calculation of the time-dependent photoinduced resonance dipole moment.*

From the results obtained from the calculations described in Eq. (3), we select the longest lived resonance state (associated with the smallest imaginary part of the complex eigenvalue of the Floquet operator). The state vector of the system evolves in time as

$$|\Psi(t; \tau)\rangle = \Phi_1(R, t; \tau) |\psi_{1s\sigma_g}^{ad-dc}\rangle + \Phi_2(R, t; \tau) |\psi_{2p\sigma_u}^{ad-dc}\rangle. \quad (16)$$

Using this state vector the resonance dipole moment is calculated:

$$\begin{aligned} d^{res}(t; \tau) &= \sum_{n, n'} e^{i\omega(n-n')t} \langle [\phi_1^{(n')}](R; \tau) | V_{cup}(R; \tau) | \phi_2^{(n)}(R; \tau) \rangle. \end{aligned} \quad (17)$$

Here $\phi_1^{(n')}(R; \tau)$ and $\phi_2^{(n)}(R; \tau)$ are the Fourier components of the time-periodic functions $\Phi_1(R, t; \tau)$ and $\Phi_2(R, t; \tau)$. The time period is $T = 2\pi/\omega$. The complex conjugate in the integration was taken due to the properties on the inner product in non-Hermitian quantum mechanics [24,32].

By introducing the dc field in our zero-order Hamiltonian we break the dynamical symmetry properties of the solutions (the dynamical symmetry analysis is based on the fact that time serves as additional coordinate in the Floquet operator, see Ref. [37] on the dynamical symmetry approach). To overcome this difficulty, we define a modified photoinduced resonance dipole moment, which is given by

$$d^{modified}(t, \tau) = d^{res}(t; \tau) + d^{res}(t; \tau + T/2). \quad (18)$$

The modified time-dependent complex dipole amplitude satisfies the dynamical symmetry property of the Floquet operator since we treat here the adiabatic parameter τ as a time variable. The physics behind Eq. (18) is as follows: the representation of the photoinduced electric field as a static one breaks the dynamical symmetry of the Hamiltonian. In the dc-field representation the electrons are ionized to the “right” direction when $f_{dc} = \cos(\tau)$ gets positive values, and are ionized to the “left” direction when f_{dc} is negative. Only when the interference between two cases is taken into consideration, the dynamical symmetry properties are conserved. The interference between the electrons, which are ionized to the two different directions, is included by calculating the time-dependent dipole moments for the two cases where f_{dc} gets either negative or positive values. Since $\cos(\tau + T/2) = -\cos(\tau)$, it is obvious that Eq. (18) satisfies the desired condition of $d^{modified}(t, \tau) = d^{modified}(t, \tau + T/2)$.

(5) *Calculation of the high-order generation spectra when ionization by the field is considered.*

The probability of getting the n th-order harmonic (emitted coherent radiation with the photon energy $n\hbar\omega$) is proportional to the Fourier transform of the acceleration probability amplitude [defined as the second time derivative of $d^{modified}(t, \tau)$],

$$\sigma_{HG}(n; \tau) = \left| \frac{(n\omega)^2}{T} \int_0^T dt e^{in\omega t} d^{modified}(t, \tau) \right|^2. \quad (19)$$

The variation of $\sigma_{HG}(n, \tau)$ with τ shows of the effect of the inclusion the dc field (and thereby, the inclusion of the ionization phenomenon) in the calculations of the two adiabatic PEC on the HHG spectra.

(6) *Calculation of the effective averaged HG spectra when the coupling between the molecular ionization and dissociation is considered.*

The probability that the oscillating electric field is in a given phase $\tau = \omega t$ is proportional to $d\tau/dx$, where $x \sim \cos(\tau)$ is the position of the electron in scaled time τ due to the oscillating electric field. Since $d\tau/dx \sim 1/\sin(\tau)$, therefore

$$\sigma_{HG}^{av}(n) = \frac{1}{2\pi} \int_0^{2\pi} d\tau \sigma_{HG}(n; \tau). \quad (20)$$

The effect of the ionization on the HHG spectra is introduced indirectly via the widths of the adiabatic 2 PEC and also via the nonzero imaginary parts of the permanent and transition dipole matrix elements.

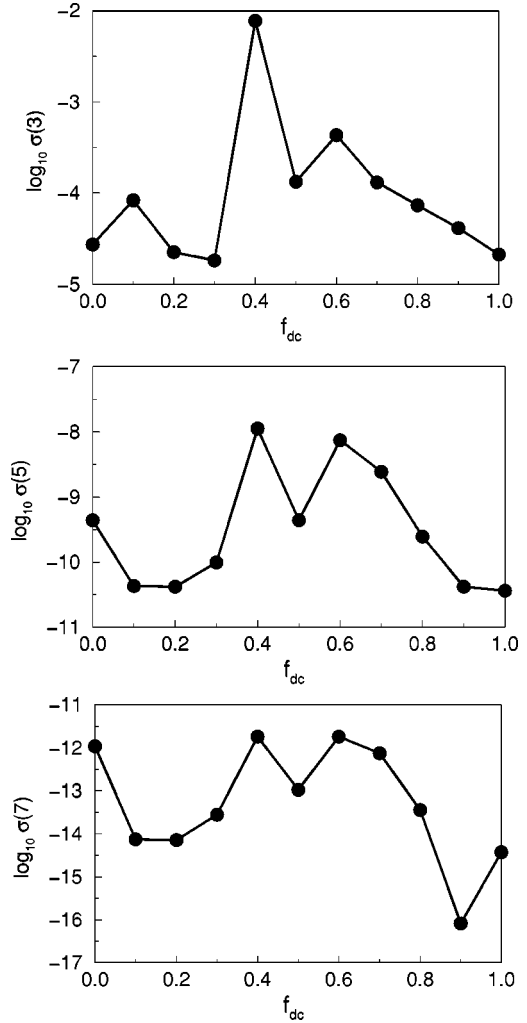


FIG. 2. Ionization effect on the third, fifth, and seventh harmonic generation spectra (HGS) of H_2^+ . The HGS are calculated as function of the dc-field strength controlled parameter $F_{dc} = 0.05f_{dc}$ a.u. For each value of f_{dc} , a different set of two adiabatic complex potential-energy curves (PEC) has been used in the calculations of the HGS. The imaginary parts of the complex PEC is the rate of ionization. The adiabatic PEC were obtained by solving the non-Hermitian Schrödinger equation of H_2^+ in a static electric field within the framework of the adiabatic approximation.

III. ILLUSTRATIVE NUMERICAL APPLICATION TO H_2^+ IN A STRONG LASER FIELD

We study the HHG by ionic hydrogen molecule in 8.77×10^{13} W/cm² oscillating field with the frequency $\omega = 0.07382$ a.u. The maximum field amplitude in this case is $\varepsilon_0 = 0.05$ a.u. The calculations were carried out following the method described above. In Fig. 2 the results obtained by the method described in the preceding section, for the probability of getting the third-, fifth-, and seventh-order harmonics as functions of the strength of the dc field, $f_{dc} = \cos(\tau)$, are introduced. The probability has been normalized to have

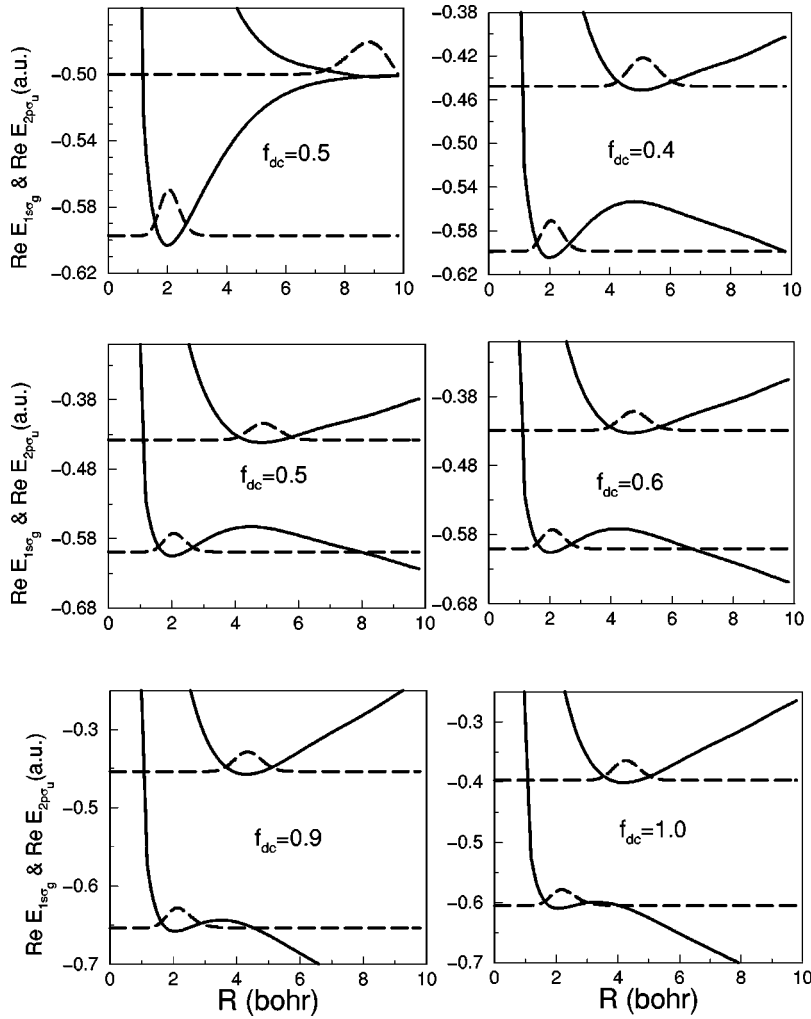


FIG. 3. The real parts of the $1s\sigma_g$ (lower solid line) and $2p\sigma_u$ (upper solid line) electronic energies of H_2^+ in a dc field as a function of the internuclear distance R and the dc-field amplitude $F_{dc} = 0.05f_{dc}$, where $f_{dc} = \cos(\tau)$. The dashed lines stand for the ground vibrational states' wave functions, $|Y_{0,0}\Phi_{1s\sigma_g}(R)|^2$ and $|Y_{1,0}\Phi_{2p\sigma_u}(R)|^2$ (are given in arbitrary units) of the $1s\sigma_g$ and $2p\sigma_u$ potentials.

$\sigma_{HG}(n=1; \tau) = 1$ for any given τ .

In these calculations we used two types of effective PEC. For $f_{dc} = 0$, the calculations were carried out with the field-free $1s\sigma_g$ and $2p\sigma_u$ potential curves described in Fig. 1. For $f_{dc} = 1$, the complex adiabatic PEC were obtained by calculating the electronic resonances of the molecular ion which interacts with a dc field with the maximum field amplitude of $\varepsilon_0 = 0.05$ a.u. In Fig. 3 we represent the shape of the two adiabatic dc-controlled PEC (i.e., the real part of the complex electronic adiabatic resonance eigenvalues as function of R) for different values of the dc-controlled parameter f_{dc} . The two complex electronic adiabatic PEC and the corresponding wave functions were obtained by solving numerically exact the time-independent Schrödinger equation for the Stark effect on the three-dimensional (3D) molecular hydrogen ion Coulombic potential [36].

The results presented in Fig. 2 clearly indicate that including the static field in the generation of the two PEC has an enormously strong effect on the probability of generating high-order harmonics. As a matter of fact, when ionization is ignored (no static field), the HG probabilities get minimal values. Moreover, there is an optimal value of f_{dc} (around 0.4) where the HHG spectra are enhanced by *many orders of magnitude*.

An explanation to it can be deduced from the PEC and

resonance vibrational QE density probabilities presented in Fig. 3. As the dc field is introduced into the calculations beside the electron ionization, the dissociation of the molecule on the repulsive upper PEC is suppressed. Moreover, as the static field parameter is increased, the centers of the two resonance vibrational wave-function components approach one another. On the other hand, the increasing of the dc field reduces the amplitude of the ionized vibrational component of the wave function, which is localized on the lower PEC due to the tunneling (dissociation) through the potential barrier (induced by the dc field). Therefore, the overlap between the complex-scaled resonance wave-function components, which are localized on the two different PEC, gets a maximal value for a specific dc field intensity due to these two counteractive effects. As the overlap between these two components becomes larger, the transition dipole matrix element gets larger values, which implies higher probabilities of generating high-order harmonics.

The final values for the probabilities of generating high-order molecular harmonics are obtained by carrying out the averaging over the HHG spectra obtained from the different adiabatic dc-controlled PEC. Applying the averaging procedure given in Eq. (20), the HHG spectra presented in Fig. 4 were obtained. Although Eq. (19) can be used for calculating also the very high harmonics (see, for example, Fig. 1 in Ref.

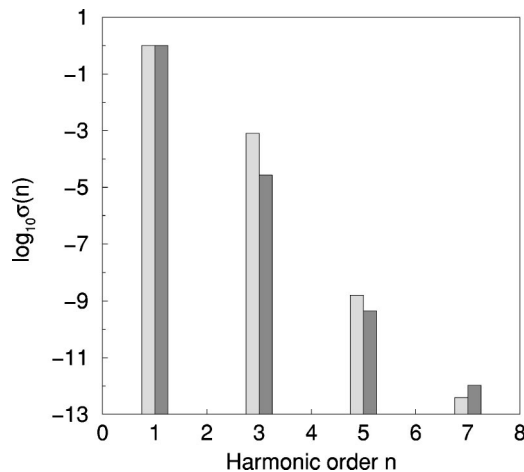


FIG. 4. The third, fifth, and seventh harmonic generation spectra of H_2^+ . The dark histograms stand for the results obtained after averaging over the different complex adiabatic PEC, which were used to introduce the ionization effect into the calculations of the HHG spectra. The bright histograms stand for the results obtained for the field-free PEC, where ionization has not been considered. Both histograms were normalized to give a unit cross section for the generation of the fundamental harmonic $n=1$.

[13]), here we concentrated on the low end of the HHG spectra. For comparison, we show also the HHG spectra that are obtained when the field-free molecular ion, $1s\sigma_g$ and $2p\sigma_u$ PEC have been used. As one clearly sees, the inclusion of ionization into the HHG calculations enhance the probability of generating the high-order harmonics.

IV. CONCLUSIONS

The ionization occurs in our model due to the introduction of the dc field (this is, indeed, a good description of the ionization process when the laser frequency is smaller than the frequency of the motion of the electron in the ground state). The dc field not only ionizes the molecule but also accelerates the electron before ionization takes place. The ionization (note that free electron in oscillating field does not produce high harmonics) and the acceleration (accelerated electron emit high frequency radiation) have two counteractive effects on the generation of high-order harmonics. Therefore, one should find the optimal dc-field strength control parameter f_{dc} , at which the harmonic intensity is maximal. This requires taking into consideration the coupling between the nuclear and electron motions in the numerical calculations.

ACKNOWLEDGMENTS

This work was supported in part by the U.S.-Israel Binational Science Foundation, by the Basic Research Foundation administered by the Israeli Academy of Sciences and Humanities, and by the Fund for the Promotion of Research at Technion. One of us (S.B.) acknowledges the Center of Immigrant Absorption in Science, Ministry of Immigrant Absorption, State of Israel, for partial support. Dr. Peter Schmelcher from the University of Heidelberg and Dr. Manfred Lien from the Max Planck Institute for Nonlinear Physics of Complex Systems in Dresden are acknowledged for fruitful discussions.

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