

## Generation of high-order harmonics from inertially confined molecular ions

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We consider the generation of high-order harmonics from inertially confined diatomic molecular ions driven by strong short pulses of laser radiation. Using a simple analytically solvable model, we show that diatomic molecular ions can be a very efficient source of high-order harmonics. The sources of the strong nonlinear response are charge-resonant states of odd-charge molecular ions. We also discuss possibilities for quasi-phase-matching, which are given by the molecular ions and which have no analogies in atomic systems.

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### I. INTRODUCTION

Over the last decade there has been a considerable interest in studying high-order multiphoton processes in atoms and molecules. This interest was mainly due to advances in the experimental technique that now allows one to study interaction of atoms and molecules with laser pulses of intensities  $I \sim 10^{13} - 10^{16}$  W/cm<sup>2</sup> and pulse durations  $\tau \sim 100$  fsec and shorter. One of the most striking and potentially practical phenomena observed is the generation of very-high-order optical harmonics of incident light. This process has been studied in detail using atoms, for moderate laser intensities ( $\sim 10^{13}$  W/cm<sup>2</sup>) and comparatively long (tens of picoseconds) pulses; see, e.g., review [1]. Recently, analogous experiments [2-6] were performed with much higher intensities and shorter (sub-picosecond) pulse durations, and harmonics of order as high as 109 were reported [5].

It is important to note that, in some of these experiments, the laser intensity was significantly higher than the saturation intensity for ionization of neutral species. Under such conditions, the contribution of ions to the emission of high harmonics could be important. To our knowledge, there is only one theoretical paper [7] so far, analyzing ions as a source of high harmonics. According to Ref. [7], the contribution of ions to harmonic emission in typical multiphoton experiments could be significant, and the experimental data [6] show clear evidence for harmonic emission from ions. Harmonic generation from molecular ions will be discussed in this paper.

In general, a theoretical description of harmonic generation should involve two stages: (i) response of a single atom (molecule, ion), and (ii) propagation effects. Phase matching between the incident and the harmonic waves depends upon details of experimental design but, in general, free electrons are a problem. However, molecules introduce new means of overcoming this problem, and we will discuss them in Sec. V of the paper.

This paper, like most theoretical studies, focuses on the first problem, that is, the response of an isolated quantum system. In previous studies, harmonic emission was described using *ab initio* numerical simulations for a one-dimensional model atom [8] and realistic three-

dimensional potentials of complex atoms [9], as well as within the framework of more simple models allowing for an analytical treatment: essential-state [10] and short-range potential [11] models.

While most work has concentrated on atoms, in this paper we consider a simplified analytical model for harmonic production from odd-charge ions of diatomic molecules. Molecular ions, whose internuclear axis is aligned with the laser electric field, are assumed to be created by a strong short laser pulse and undergo further fragmentation. A second short laser pulse, coming during the fragmentation process, generates harmonics. The reason to study such a system is that molecular ions are more polarizable than atoms and so we might expect them to be a more intense source of harmonics.

Molecular ions possess a pair of states that can be very important for harmonic production, that is, any odd-charge homonuclear molecular ion has so-called charge-resonant (CR) states [12]. These are symmetric and antisymmetric states corresponding to the fragmentation of the odd-charge molecular ion  $A_2^{(2n+1)+}$  into  $A^{n+}$  and  $A^{(n+1)+}$ , say,  $H_2^+$  into H and  $H^+$ . The energy of these two states goes to the same limit at large  $R$ , but at small  $R$  the energy gap between them is significant.

Charge-resonant states are very strongly coupled, and the matrix element of the electronic transition  $\mu(R)$  between them increases with increasing separation  $R$  between the two nuclei:  $\mu \approx R/2$  [12,13]. Therefore one could expect that CR states coupled by a strong laser field could be an efficient source of high harmonics. It is important to point out here that recent experiments [14] have shown that, by using supershort laser pulses for producing (and probing) *inertially confined* molecular ions, one can control the internuclear separation  $R$  and, thus, the matrix element  $\mu(R)$ . They have also shown that the experimental angular dependence of dissociation products of  $I_2^{n+}$ , kinetic energy of fragments, and ionization rates of HCl or  $I_2$  can be understood assuming charge-resonant coupling to be the dominant coupling mechanism [14]. The same is true for bond-softening experiments [15]. Our simplified model, therefore, is also a realistic model.

Our model for harmonic emission includes only these

two charge-resonant electronic surfaces. Other transitions at large  $R$  are similar to multiphoton transitions in an atom (atomic ion) and are likely to be weaker at moderate laser intensities. As shown below, in the case of supershort laser pulses, the problem of harmonic generation from these two surfaces can be reduced to a local electronic two-level problem parametrically dependent on the internuclear separation  $R$ . This conclusion coincides with that of Ref. [16]. The transition frequency  $\omega_0(R)$  and matrix element  $\mu(R)$  of the local system have to be taken on the classical trajectory corresponding to the motion of the vibrational wave packet.

A two-level system is the simplest quantum system producing harmonics in a strong laser field. In Ref. [17], it was pointed out that harmonic emission from the two-level system is a direct consequence of the Floquet theorem and of the concept of quasienergies. Being a lovely theoretical model, the laser-driven two-level system has undergone continuous study throughout the whole history of laser-matter interaction (e.g., [18–22]). However, high-order harmonic emission from the two-level system was considered more closely only recently [23]. In Ref. [23], the problem was studied numerically and for a low-frequency case, that is, the laser frequency considered was less (four times) than the transition frequency. In this paper, we give the analytical description of high-order harmonic emission from a two-level system in the strong field limit. We consider the case when the Rabi coupling  $V = \mu(R)E(t)$  of the two levels in the laser field  $E = E(t)\cos\omega t$  exceeds the transition frequency  $\omega_0$  between the levels:  $V > \omega_0$ . The laser frequency  $\omega$  also is assumed not to be small:  $\omega_0 \leq \omega$ . These are the typical conditions for charge-resonant states of molecular ions, visible or near-IR laser frequency, and laser intensities about  $10^{14}$  W/cm<sup>2</sup>. No rotating-wave approximation is used, and results are obtained for an *arbitrary pulse envelope*  $E(t)$  with the only assumption that the duration  $\tau$  of the laser pulse is long compared to the laser period:  $\tau \gg 1/\omega$  [but short enough that the two-level approximation is valid, Eqs. (12) and (13)].

As in the numerical calculations for the low-frequency case [23], we find the long-familiar “plateau” in the harmonic spectrum. Plateaus seem to be a general feature of any strongly driven quantum system. Unlike the case of atoms and atomic ions, for CR states of molecular ions the plateau can be significantly (up to three orders of magnitude) higher than typical for atoms [9].

It is important to understand the difference between our case and that of Ref. [24], where the harmonic spectrum from H<sub>2</sub> was found to be very similar to that from H already at  $R \approx 2$  a.u. (the equilibrium distance for H<sub>2</sub> is  $R_e \approx 1.4$  a.u.). Any homonuclear odd-charge ion, e.g., H<sub>2</sub><sup>+</sup>, possesses CR states, whose contribution to harmonic emission is shown here to be very important when  $R$  is not too large. Analogous states in neutral hydrogen are charge-transfer states, leading to dissociation of H<sub>2</sub> either into H+H or into H<sup>+</sup>+H<sup>-</sup>. These states are also strongly coupled at small  $R$ , but the coupling turns to zero exponentially with increasing  $R$ . Therefore, unlike CR states, at large  $R$  they do not contribute to the generation of harmonics, leading to quantitatively the same

harmonic spectrum as from separate atoms.

In Sec. II, we describe our model and show under what conditions harmonic generation from CR states of molecular ions can be reduced to a local electronic two-level problem with parametrical  $R$  dependence. In Sec. III, we describe the analytic theory for harmonic generation from this system. In Sec. IV, we discuss the results and the predicted harmonic spectrum for a number of special cases. In Sec. V, the role of free electrons produced together with molecular ions is commented upon. We show that molecules give us new possibilities for quasi-phase-matching that have no analogies in atomic systems.

## II. LOCAL ELECTRONIC SYSTEM IN A MOLECULE INTERACTING WITH A SHORT LASER PULSE

In this section, we show the conditions under which the molecular interaction with a short laser pulse can be described by the equations for a local electronic system taken at fixed internuclear distance  $R$ . This simplification was used in Ref. [15] to develop an effective numerical algorithm for studying the molecular wave-packet dynamics. In the present paper, by using a semi-classical approach, we derive the conditions under which the approximation of a local electronic system provides the adequate description of the interaction process. Since we take into account only two CR states in the model, the problem is then reduced to a local two-level system.

### A. Qualitative picture

We consider the physical process that occurs under the action of two successive laser pulses. First, a short strong laser pulse produces molecular ions, and then the second short laser pulse, delayed from the first one, generates harmonics. Consider a diatomic molecular  $A_2$  subjected to a short strong laser pulse with the duration much shorter than the typical time of nuclear motion. The molecule undergoes fast ionization and, if the laser intensity is sufficiently high, a number of differently charged ions  $A_2^{q+}$  are produced. If the duration of the laser pulse is short, the internuclear distance does not change much during the ionization process and is approximately given by the equilibrium distance  $R_e$  of the neutral molecule. In other words, a wave packet, spatially localized around  $R_e$ , is produced on the electronic surface corresponding to the ion  $A_2^{q+}$ ; see Fig. 1.

It is quite natural to assume that the ground electronic state  $|1\rangle$  of the ion  $A_2^{q+}$  is the one mostly populated. However, as was shown in Ref. [14], in a strong field this state is always strongly mixed with the corresponding charge-resonant state  $|2\rangle$  (which has the opposite parity). Therefore, after the end of the first laser pulse, one should consider at least two wave packets excited to the electronic surfaces  $|1\rangle$  and  $|2\rangle$  (see Fig. 2).

It is worth giving some typical values of the experimental parameters corresponding to the physical picture described above. In Ref. [14], a 30-fsec, 630-nm laser pulse was used to ionize the iodine molecule  $I_2$ , which has the typical vibrational period of the order of 150 fsec. The intensity  $I \sim 10^{14}$  W/cm<sup>2</sup> was enough to produce

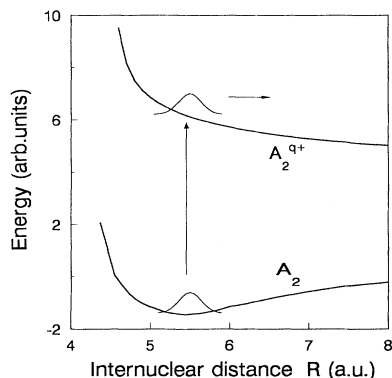


FIG. 1. Qualitative scheme of ionization of a diatomic molecule  $A_2$  and excitation of the vibrational wave packet in ion  $A_2^{q+}$  by a short laser pulse.

iodine ions up to  $I_2^{4+}$ . Fragmentation of the ions was mostly due to Coulomb repulsion. For such heavy species as iodine, the ion motion is only about 0.2 Å in 30 fsec, even for the fragmentation of  $I_2^{4+}$ . It is also important to point out that the experimental data [14] are consistent with significant excitation of both the ground state of the molecular ion and its charge-resonant state.

Consider the motion of the wave packet along, say, the potential surface  $|2\rangle$  of Fig. 2. This motion corresponds to the fragmentation of the iodine ion  $I_2^+$  into  $I^+$  and  $I$ . Let the second laser pulse be switched on when the center of the wave packet has a coordinate equal to  $R_0$  (Fig. 2). We assume the second laser pulse to be short, so that the coordinate  $R$  of the wave packet does not change much during the whole pulse; the concrete criterion will be given below. In this case, it is physically clear that the only transition that occurs during the laser pulse is the electronic transition between the states  $|1\rangle$  and  $|2\rangle$ ; the nuclear wave packet has not enough time to be changed and is simply transferred between the surfaces  $|1\rangle$  and  $|2\rangle$ . Thus, if the laser pulse is sufficiently short, the interaction process should reduce to local electronic transitions between the states  $|1\rangle$  and  $|2\rangle$  [15], with the internuclear separation corresponding to the classical coordinate of the wave packet.

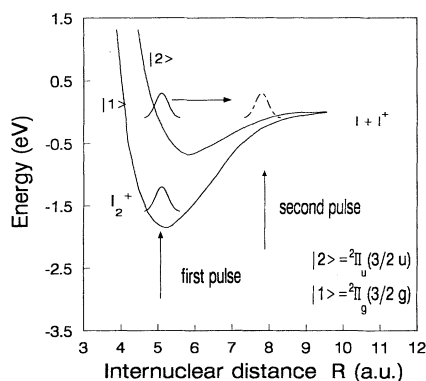


FIG. 2. Scheme of interaction of the  $I_2^+$  molecular ion with two successive laser pulses.

## B. Mathematical description

We now give the mathematical background supporting the intuitive physical picture described above. Starting from the Schrödinger equation for a system shown in Fig. 2, we derive the conditions for which this equation is reduced to a local two-level system. In the Born-Oppenheimer approximation, the wave function of our model system is

$$\Psi(r, R, t) = \psi_1(R, t)\phi_1(r, R) + \psi_2(R, t)\phi_2(r, R), \quad (1)$$

where  $\phi_{1,2}(r, R)$  are the stationary electronic wave functions of the states  $|1\rangle$  and  $|2\rangle$ , and  $\psi_{1,2}(R, t)$  are the time-dependent nuclear wave functions for the surfaces  $|1\rangle$  and  $|2\rangle$ , correspondingly.

Equations of motion for this system in the laser field  $E = E(t)\cos\omega t$  are ( $i, j = 1, 2; i \neq j$ ):

$$i\partial_t\psi_i(R, t) = \hat{H}_i\psi_i(R, t) + V(t, R)\psi_j(R, t), \quad (2)$$

where  $V(t, R) = \mu(R)E(t)\cos\omega t$ ,

$$\hat{H}_i = \hat{T} + \mathcal{E}_i(R) \quad (3)$$

is the field-free Hamiltonian of the nuclear motion with the electron in the state  $|i\rangle$ ,  $\mathcal{E}_i(R)$  is the electron energy in the state  $|i\rangle$ , and  $\hat{T}$  is the nuclear kinetic-energy operator. We assume that the molecule is aligned along the laser field. This condition is experimentally feasible [14] (see Sec. VI).

Let the second laser pulse be turned on at  $t=0$ , and consider the dynamics of the wave packet initially localized near  $R=R_0$  on the surface  $|2\rangle$  (Fig. 2). Our first approximation to Eq. (2) is to replace  $V(t, R)$  by  $V(t, R_0)$ . This approximation assumes that  $v\tau \ll R_0$ , where  $v$  is the wave-packet velocity and  $\tau$  is the laser-pulse duration. Thus, the first limitation to the duration of the second pulse is

$$\tau \ll R_0/v. \quad (4)$$

Let us show now that for a short laser pulse the solution of Eq. (2) can be found in the form

$$\psi_i(R, t) \approx a_i(t)\exp[i\mathcal{E}_i(R_0)t]\exp(-i\hat{H}_i t)\psi_0(R), \quad (5)$$

where  $\psi_0(R)$  is the initial wave packet on the surface  $|2\rangle$ ,  $\mathcal{E}_i(R_0)$  are the adiabatic electron energies, and the amplitudes  $a_i(t)$  are  $R$  independent.

In order to check the validity of Eq. (5), one should substitute it into Eq. (2). After simple arithmetic one can obtain the following equation for  $a_i(t)$ , which according to Eq. (5) has to be  $R$  independent:

$$i\partial_t a_i(t)\psi_0(R) = \mathcal{E}_i(R_0)a_i(t)\psi_0(R) + V(R_0, t)a_j(t)\hat{U}_{ji}(R, t)\psi_0(R). \quad (6)$$

However, the propagation operator  $\hat{U}_{ji}(R, t)$  in this equation

$$\hat{U}_{ji}(R, t) = \exp\{i[\mathcal{E}_j(R_0) - \mathcal{E}_i(R_0)]t\} \times \exp(i\hat{H}_i t)\exp(-i\hat{H}_j t) \quad (7)$$

is  $R$  dependent in the general case. The  $R$  dependence disappears in Eq. (6) only if the propagation operator is approximately equal to the identity operator  $\hat{I}$ . If so, Eq. (5) is justified. Obviously, for sufficiently short time,  $\hat{U} \approx \hat{I}$ . Using the semiclassical approach, we can estimate how short the time should be. The operator Eq. (7) is field-free and the semiclassical field-free dynamics of a wave packet is quite simple: the wave packet propagates along the trajectory of a classical particle that has the initial coordinate and the initial energy equal to those of the wave packet. Therefore, if the wave packet  $|\psi\rangle$  is initially localized near some point  $R^*$ :  $\psi(R) \equiv f(R, R^*)$ ,  $R^* = \langle \psi(R) | R | \psi(R) \rangle$ , and has the initial energy  $E(R^*)$ , in the semiclassical approximation, the propagator  $\exp(-i\hat{H}t)$  give

$$\exp(-i\hat{H}t)f(R, R^*) = \exp[-iE(R^*)t]f'(R, R_{cl}), \quad (8)$$

where  $R_{cl} = R_{cl}(t)$  is the classical trajectory. The function  $f'$  on the right-hand side of Eq. (8) describes the shape of the wave packet at the moment  $t$ , where the prime denotes that this shape can be different from that at  $t=0$ . Let us make one more remark, which is important for analyzing the action of the operator Eq. (7). Calculating the field-free energy  $E_i(R^*)$  of the wave packet  $|\psi\rangle$  localized near  $R^*$  on the surface  $|i\rangle$ :

$$\langle \psi | \hat{H}_i | \psi \rangle = E_i(R^*) = T_i(R^*) + \mathcal{E}_i(R^*), \quad (9)$$

one finds that the kinetic-energy operator  $\hat{T}$  is the same for both potential surfaces. Therefore, the kinetic energy of the wave packet on the potential surface  $|j\rangle$  is equal to its kinetic energy on the surface  $|i\rangle$ :  $T_i(R^*) = T_j(R^*)$ ,  $E_i(R^*) - E_j(R^*) = \mathcal{E}_i(R^*) - \mathcal{E}_j(R^*)$ .

Now one can analyze the conditions for the approximate equality

$$\hat{U}_{ji}(R, t)\psi_0(R) \approx \hat{I}\psi_0(R), \quad (10)$$

which is required to justify Eq. (5). Using Eq. (8) and the remark above, one can easily check that Eq. (10) is satisfied if the two conditions below are fulfilled.

First, the distance between two classical particles propagating with the same initial velocity and coordinate but along different potential surfaces  $\mathcal{E}_1(R)$  and  $\mathcal{E}_2(R)$  should remain small compared to the width of the wave packet:

$$R_{cl,1}(t) - R_{cl,2}(t) \approx \left[ \frac{\partial \mathcal{E}_1(R_0)}{\partial R} - \frac{\partial \mathcal{E}_2(R_0)}{\partial R} \right] \frac{t^2}{2M} \ll \Delta R \quad (11)$$

( $\Delta R$  the wave-packet width,  $M$  the reduced nuclear mass). Equation (11) gives the limit to the pulse duration  $\tau$  for a given molecule and  $R_0$ .

Second, the change in the transition frequency  $\omega_{21}(R_{cl}) = \mathcal{E}_2(R_{cl}) - \mathcal{E}_1(R_{cl})$  on the classical trajectory  $R_{cl}(t) \approx R_{cl,1}(t) \approx R_{cl,2}(t)$  during propagation of the wave packet should be negligible in the scale of the propagation time  $t$ :  $\omega_{21}(R_{cl}(t)) - \omega_{21}(R_0) \ll t^{-1}$ .

Note that in the case of parallel electronic surfaces, both requirements are fulfilled for any  $t$ , and for any  $t$ ,  $\hat{U}_{ij} = \hat{I}$ .

Thus, if the laser pulse is so short that the classical tra-

jectories  $R_{cl,1}(t)$ ,  $R_{cl,2}(t)$  on the potential surfaces  $\mathcal{E}_1(R)$  and  $\mathcal{E}_2(R)$  (with same initial conditions) do not diverge much during the laser pulse:

$$R_{cl,2}(\tau) - R_{cl,1}(\tau) \ll \Delta R \quad (12)$$

( $\Delta R$  the wave-packet width,  $M$  the reduced nuclear mass), and if the change of the transition frequency  $\omega_{21}(R)$  on the classical trajectory  $R_{cl}(t)$  is small:

$$\omega_{21}(R_{cl}(t)) - \omega_{21}(R_0) \ll \tau^{-1}, \quad t \leq \tau, \quad (13)$$

then the evolution of the nuclear wave packets  $\psi_{1,2}(R, t)$  is described by the following simple formula [see Eq. (5)]:

$$\psi_i(R, t) \approx a_i(t) \exp[i\mathcal{E}_i(R_0)t] \exp(-i\hat{H}_i t) \psi_0(R), \quad (14)$$

where the amplitudes  $a_i(t)$  are  $R$  independent and satisfy the following equation [see Eq. (6)]

$$i\dot{a}_i(t) = \mathcal{E}_i(R_0)a_i(t) + V(R_0, t)a_j(t). \quad (15)$$

This is the equation for a two-level system with transition frequency  $\omega_{21}$  and matrix element  $\mu(R)$  taken on the classical trajectory of the initial vibrational wave packet at the moment when the second laser pulse operates.

The physical picture corresponding to our mathematical analysis should now be clear. As far as the wave packets propagating along  $\mathcal{E}_1(R)$  and  $\mathcal{E}_2(R)$  are "in phase," i.e., have approximately equal coordinates  $R_{1,2}(t)$ , the interaction is reduced to vertical transitions in a local two-level system with parameters depending on the coordinate of the wave packet. As far as the pulse is short, these parameters do not change essentially during the laser pulse when the wave packets propagate along the potential surfaces  $\mathcal{E}_{1,2}(R)$ , and hence they can be taken at the initial point  $R_0$  of the classical trajectory.

Obviously, the analysis presented here can be easily generalized to a more complicated case of  $N$  electronic surfaces.

### C. Harmonic generation

The matter of our interest is the generation of harmonics by the system described by Eq. (2) and depicted in Fig. 2. We will focus on the response of a single quantum system and, as usual [7–11,24], calculate the time-dependent dipole moment  $d(t)$  and its Fourier spectrum.

One can easily see that within the same requirements as to the duration of the second laser pulse [Eqs. (12) and (13)], the dipole moment for the wave function Eq. (1) is reduced to that of the two-level system Eq. (15). Indeed, substituting in the general expression for  $d(t)$

$$\begin{aligned} d(t) &= \langle \Psi(r, R, t) | \hat{d} | \Psi(r, R, t) \rangle \\ &= \langle \psi_2(R, t) | \mu(R) | \psi_1(R, t) \rangle + \text{c.c.} \end{aligned} \quad (16)$$

the wave functions  $\psi_i(R, t)$  given by Eq. (14), one obtains

$$d(t) = \mu(R_0) a_2^*(t) a_1(t) \langle \psi_0(R) | \hat{U}_{12}(R, t) | \psi_0(R) \rangle + \text{c.c.} \quad (17)$$

Recalling that  $\hat{U}_{12}(R, t) \approx \hat{I}$ , Eq. (17) yields

$$d(t) = \mu(R_0) a_2^*(t) a_1(t) W + \text{c.c.}, \quad (18)$$

where

$$W = \langle \psi_0(R) | \psi_0(R) \rangle \quad (19)$$

is the initial population of the surface  $|2\rangle$ .

Therefore, the problem of calculating harmonic emission is reduced to the calculation of harmonics generated by the two-level system Eq. (15).

### III. TWO-LEVEL SYSTEM IN THE HIGH-INTENSITY LIMIT

#### A. General expressions

Let us rewrite Eq. (15) for the two-level system in the following way:

$$\begin{aligned} i\dot{a}_1(t) &= -\frac{1}{2}\omega_{21}a_1(t) + V(t)a_2(t), \\ i\dot{a}_2(t) &= \frac{1}{2}\omega_{21}a_2(t) + V(t)a_1(t). \end{aligned} \quad (20)$$

Here we shifted the zero energy level. It does not affect Eq. (18) for the dipole moment, and therefore we use the same notations for new probability amplitudes. We also omitted  $R_0$  in the transition frequency  $\omega_{21}(R)$  and coupling  $V(R, t) = V_0 f(t) \cos \omega t = \mu(R) E_0 f(t) \cos \omega t$ . The initial conditions corresponding to the wave packet initially on the potential surface  $|2\rangle$  are  $a_1(0) = 0$ ,  $a_2(0) = 1$ .

In this section, we consider the behavior of the system Eq. (20) in a very strong field

$$V_0 \gg \omega_{21}. \quad (21)$$

We also assume the transition frequency to be less than the laser frequency:

$$\omega_{21} \leq \omega. \quad (22)$$

The above relation between  $\omega_{21}$  and  $\omega$  is typical at comparatively large distances  $R \sim 7-8$  a.u. for both  $\text{H}_2^+$  and  $\text{I}_2^+$  (see Ref. [25] and Fig. 2), when  $\omega_{21}$  is of the order of  $10^{-1}$  eV. The first condition Eq. (21) is easily fulfilled at  $R \sim 7-8$  a.u. ( $\sim 2R_e$  for iodine) and intensity  $I \geq 10^{13}$  W/cm<sup>2</sup>.

One can hope to build a perturbation theory using the smallness of the transition frequency  $\omega_{21}$ . That is precisely what is done below.

One can easily obtain the zero-order approximation  $a_i^{(0)}(t)$ , corresponding to  $\omega_{21} = 0$  and initial conditions  $a_1(0) = 0$ ,  $a_2(0) = 1$ :

$$a_1^{(0)}(t) = -i \sin F(t), \quad a_2^{(0)}(t) = \cos F(t), \quad (23)$$

where we denoted

$$F(t) = \int^t V(t') dt' = V_0 \int^t f(t') \cos \omega t' dt'. \quad (24)$$

If the pulse envelope  $f(t)$  includes many field periods, the following approximate expression for  $F(t)$  is valid:

$$F(t) \approx \frac{V_0}{\omega} f(t) \sin \omega t. \quad (25)$$

However, one can also check that, in the zero approxima-

tion ( $\omega_{21} = 0$ ), the dipole moment  $d^{(0)}(t)$  is equal to zero. Moreover, the first-order correction to  $a_i^{(0)}(t)$  grows linearly with time. Hence, the perturbation approach is not straightforward.

It turns out to be more convenient to introduce new variables  $c_1(t)$  and  $c_2(t)$ :

$$\begin{aligned} c_1(t) &= \exp[iF(t)] [a_1(t) + a_2(t)], \\ c_2(t) &= \exp[-iF(t)] [-a_1(t) + a_2(t)]. \end{aligned} \quad (26)$$

Equations for  $c_i(t)$  are easily obtained from Eqs. (20):

$$\begin{aligned} \dot{c}_1(t) &= -i\frac{1}{2}\omega_{21}c_2(t) \exp[i2F(t)], \\ \dot{c}_2(t) &= -i\frac{1}{2}\omega_{21}c_1(t) \exp[-i2F(t)], \end{aligned} \quad (27)$$

and the initial conditions corresponding to  $a_1(0) = 0$ ,  $a_2(0) = 1$  are  $c_1(0) = c_2(0) = 1$ .

In terms of  $c_i(t)$ , the normalized dipole moment  $u(t) \equiv d(t) / \mu(R_0) W$  is

$$u(t) = \frac{1}{2} [ |c_1(t)|^2 - |c_2(t)|^2 ]. \quad (28)$$

The expression for the time derivative of the dipole moment is even more useful. Using Eq. (28) together with Eqs. (27), one can easily check that

$$\dot{u}(t) = i\frac{1}{2}\omega_{21}c_1(t)c_2^*(t) \exp[-i2F(t)] + \text{c.c.} \quad (29)$$

It is obvious from Eq. (29) that the first-order (in  $\omega_{21}$ ) approximation to  $\dot{u}(t)$  is given by zero-order values of  $c_i(t)$ . At the same time,  $\dot{u}(t)$  is equally useful for studying the emission spectrum.

#### B. First-order expression for the dipole moment in a very strong field

Consider the case of immediate turn-on of the pulse:  $f(t > 0) = 1$ . Recalling that  $F(t) = (V_0/\omega) \sin \omega t$ , it is clear from Eq. (29) and Eqs. (27) that high harmonics appear only if

$$2 \frac{V_0}{\omega} \gg 1. \quad (30)$$

With this strong inequality, the exponent in Eqs. (27) is a fast oscillating function. However, in spite of the fast oscillations, the Fourier decomposition of the exponent  $\exp[2i(V_0/\omega) \sin \omega t]$  contains the constant term given by the Bessel function  $J_0(2V_0/\omega)$ . It is this term that is responsible for the linear growth of the first-order correction to  $a_i^{(0)}$  mentioned above. The problem can be overcome if this term is taken into account exactly. For this purpose, let us rewrite Eqs. (27) in the following way:

$$\begin{aligned} \dot{c}_1(t) &= -i\frac{1}{2}\omega_{21} \{ c_2(t) \cos[2F(t)] + ic_2(t) \sin[2F(t)] \}, \\ \dot{c}_2(t) &= -i\frac{1}{2}\omega_{21} \{ c_1(t) \cos[2F(t)] - ic_1(t) \sin[2F(t)] \}. \end{aligned} \quad (31)$$

At  $\omega_{21} = 0$ ,  $c_i(t)$  are constants. As we shall see below, in strong fields the  $c_i(t)$ 's are very slowly varying functions. Therefore, the second term in the curly braces is both fast oscillating and lacking a constant component. It can be omitted *in the zero order*. The first term, however, con-

tains a slowly varying component and has to be taken into account exactly. By doing so, we obtain

$$c_1^{(0)}(t) = c_2^{(0)}(t) = \exp \left[ -i \frac{\omega_{21}}{2} \Phi(t) \right], \quad (32)$$

where

$$\Phi(t) = \int_0^t \cos[2F(t')] dt'. \quad (33)$$

Substituting this result into the general expression for  $\dot{u}(t)$  [Eq. (29)], we get

$$\dot{u}^{(1)}(t) = \omega_{21} \sin[2F(t)]. \quad (34)$$

In principle, Eq. (33) answers the question: “what harmonic emission is there from a strongly driven two-level system?” The spectrum of the harmonic emission is determined by the Fourier transform of  $\sin[2F(t)]$ .

Although we obtained this result for immediate turn-on, using the same method one will get the same result for a smooth pulse envelope, with the corresponding expression for  $F(t)$  [see Eq. (24)]. However, the applicability conditions of Eq. (34) for a smooth pulse envelope will be different from those for the case of immediate turn-on.

Therefore, before discussing the harmonic spectrum, we still have to answer several questions. First, what is the *dimensionless* parameter of the perturbation expansion and under what conditions does the perturbation series converge? Second, under what conditions is the result Eq. (34) correct in the case of a smooth pulse envelope where the instantaneous value of the coupling amplitude  $V_0 f(t)$  can be not only large, but also small compared to  $\omega$  and  $\omega_{21}$ ?

### C. Applicability conditions of the perturbation theory in $\omega_{21}$

To answer the question of the perturbation series convergency, one has to calculate the first-order correction to Eq. (32). When doing so, one again has to be careful with the first term in the curly braces in Eq. (31), as was explained above. Using zero-order solutions Eq. (32) for the second term in the curly braces in Eqs. (31) and accounting for the first term exactly, one obtains the following first-order correction to  $c_i^{(0)}$  [Eq. (32)]:

$$\begin{aligned} c_1^{(1)}(t) &= \frac{\omega_{21}}{2} e^{i\omega_{21}\Phi(t)/2} \int_0^t \sin[2F(t')] e^{-i\omega_{21}\Phi(t')} dt', \\ c_2^{(1)}(t) &= -\frac{\omega_{21}}{2} e^{i\omega_{21}\Phi(t)/2} \int_0^t \sin[2F(t')] e^{-i\omega_{21}\Phi(t')} dt'. \end{aligned} \quad (35)$$

These values have to be small compared to  $|c_i^{(0)}| = 1$ .

First consider immediate turn-on of the pulse. In the case of our interest, that is,  $2V_0 \gg \omega$ , the integrals in Eq. (35) can be easily estimated by using the stationary-phase method:

$$|c_i^{(1)}(t)| = O(\epsilon), \quad \epsilon \equiv \frac{\omega_{21}}{\sqrt{V_0 \omega}}. \quad (36)$$

The correction is small if  $\epsilon \ll 1$ . Therefore, the two requirements that determine if the perturbation series converges in  $\omega_{21}$  are

$$2 \frac{V_0}{\omega} \gg 1, \quad \frac{\omega_{21}}{\sqrt{V_0 \omega}} \ll 1. \quad (37)$$

Note that if the conditions in Eq. (37) are fulfilled, the relation between laser frequency and transition frequency is not crucial: the solutions Eqs. (32), (34), (35) are valid not only for large laser frequencies  $\omega > \omega_{21}$ , but also for small frequencies  $\omega < \omega_{21}$  [if the requirements Eq. (37) are met].

In the case of a smooth turn-on, Eqs. (37) are not fulfilled at the pulse front. Therefore, in principle, for an arbitrary relation between  $\omega$  and  $\omega_{21}$  and an arbitrary pulse envelope, the result for  $\dot{u}(t)$  should be different from that given by Eq. (34). However, in our case the typical relation between  $\omega$  and  $\omega_{21}$  is  $\omega \gg \omega_{21}$ . One can easily check that, if  $\omega_{21} \ll \omega$ , the first-order correction Eq. (35) is small for any ratio of  $2V_0/\omega$ . Therefore, in the case of a smooth pulse envelope, the perturbation theory described above is applicable if

$$\omega \gg \omega_{21}. \quad (38)$$

Indeed, under this condition the second term in the curly braces in Eqs. (31) is fast oscillating and small both in the case of the strong field  $V_0 f(t) \gg \omega$  and in the case of the weak field  $V_0 f(t) \ll \omega$  (and resonance phenomena also are absent).

We can conclude that the normalized dipole moment  $u(t)$  is given by

$$\dot{u}(t) \approx \omega_{21} \sin[2F(t)]. \quad (39)$$

This result is valid both for abrupt turn-on of a strong pulse satisfying the conditions Eq. (37) and for an arbitrary pulse with sufficiently large frequency  $\omega \gg \omega_{21}$ .

## IV. THE SPECTRUM OF HARMONIC EMISSION FROM CR STATES

### A. Results

Using Eq. (25) and Eq. (39), the approximate expression for the dipole moment of our system can be written as

$$d(t) = \mu W \omega_{21} \int_0^t \sin \left[ \frac{2V_0}{\omega} f(t') \sin \omega t' \right] dt'. \quad (40)$$

The emission spectrum is given by the squared modulus of the corresponding Fourier component of  $d(t)$ .

Strictly speaking, in the case of finite interaction time, i.e., when the field is turned on and then turned off, one has to speak of the total energy emitted during the whole laser pulse [26]:

$$\mathcal{E}(\Omega) \propto \left| \int d(t) \exp(i\Omega t) dt \right|^2. \quad (41)$$

However, if the emission spectrum consists of well-separated and relatively narrow peaks centered near  $\Omega_N = N\omega$ , one can also talk about the *time-dependent* intensity of emission at the frequencies  $\Omega_N$ . This language is very useful, because the values usually measured in the experiment are average intensities of harmonics. Let us specify the time-dependent and average emission intensi-

ties in our case.

Returning to Eq. (40) and using the following relation:

$$\sin \left[ \frac{2V_0}{\omega} f(t) \sin \omega t \right] = i \sum_k \exp[-i(2k+1)\omega t] \times J_{2k+1} \left[ \frac{2V_0}{\omega} f(t) \right], \quad (42)$$

one can rewrite Eq. (40) in the equivalent form

$$d(t) = \mu W \omega_{21} i \sum_k \int_0^t \exp[-i(2k+1)\omega t'] \times J_{2k+1} \left[ \frac{2V_0}{\omega} f(t') \right] dt'. \quad (43)$$

Now, assuming the envelope  $f(t)$  to be a slowly varying function compared with the field oscillations, the dipole moment can be approximately written in the form

$$d(t) \approx \sum_k d_{2k+1}(t) \exp[-i(2k+1)\omega t], \quad (44)$$

where

$$d_{2k+1}(t) = -\mu W \frac{\omega_{21}}{(2k+1)\omega} J_{2k+1} \left[ \frac{2V_0}{\omega} f(t) \right] \quad (45)$$

are the time-dependent amplitudes of harmonics of the dipole moment.

Now we are able to define the time-dependent and average emission intensities at the frequencies  $\Omega_N = N\omega$ . If the laser intensity is constant, that is,  $f(t) = 1$ , then the values  $d_{2k+1}(t)$  in Eq. (45) are time independent. The dipole moment Eq. (44) is a purely  $\omega$ -periodic function and the emission occurs only at frequencies  $\Omega_N$  with intensities [27]

$$I_N \sim |d_N|^2 = \left[ \mu W \frac{\omega_{21}}{N\omega} \right]^2 J_N^2 \left[ \frac{2V_0}{\omega} \right], \quad (46)$$

where  $n$  is the density number of molecular ions and  $\mathcal{F}_N$  is the phase-matching factor. For further convenience, we will also put the initial population  $W$  of the upper CR state equal to unity, understanding  $n$  as the density of molecular ions initially in the state  $|2\rangle$ .

If the field intensity changes in time, the peaks at  $\Omega_N$  are broadened and, strictly speaking, one has to talk about the total energy emitted at a given frequency  $\Omega$  [Eq. (41)]. However, it is convenient to use the time-dependent intensity

$$I_N(t) \propto |d_N(t)|^2 = \left[ \mu \frac{\omega_{21}}{N\omega} \right]^2 J_N^2 \left[ \frac{2V_0}{\omega} f(t) \right]. \quad (47)$$

Indeed, if the peaks in the emission spectrum are still well separated, one can determine the total energy emitted in the whole spectral interval under the  $N$ th peak:

$$\mathcal{E}_N = \int \mathcal{E}(\Omega) d\Omega, \quad \Omega \approx \Omega_N. \quad (48)$$

Using the Parseval theorem, which says that the norm in the Fourier domain is equal to that in the time domain,

$$\int |d_N(\Omega)|^2 d\Omega = \int |d_N(t)|^2 dt, \quad (49)$$

one can easily check that  $\mathcal{E}_N$  is related to  $I_N(t)$  as

$$\mathcal{E}_N = \int I_N(t) dt. \quad (50)$$

This equality justifies the use of  $I_N(t)$  and explains its physical meaning.

In experiments, the average intensity is usually measured as

$$\langle I_N \rangle = \frac{1}{T} \int I_N(t) dt \propto \frac{1}{T} \int |d_N(t)|^2 dt, \quad (51)$$

where  $T$  is the time of interaction. We will characterize the harmonic spectrum by the values

$$i(N) = \frac{1}{T} \int |d_N(t)|^2 dt = \left[ \mu \frac{\omega_{21}}{N\omega} \right]^2 \frac{1}{T} \int J_N^2 \left[ \frac{2V_0}{\omega} f(t) \right] dt. \quad (52)$$

This expression provides the complete description of the harmonic emission from CR states in the framework of our model, that is, under the action of very short laser pulses.

The values that are calculated in most papers are  $i(N)$  averaged either over the whole interaction time (e.g., [28]), or only over the time when the laser intensity is kept constant, i.e., excluding the turn-on of the laser pulse and corresponding transient effects (e.g., [29]). We will calculate both values of  $i(N)$ , i.e., for the peak intensity kept constant after fast turn-on and for the Gaussian laser pulse. Note that, with the turn-on time excluded,  $i(N)$  in our model is simply given by  $i(N) = |d_N|^2 = (\mu\omega_{21}/N\omega)^2 J_N^2(2V_0/\omega)$ . With it, our results can be compared directly with atomic calculations.

## B. Discussion

Let us now analyze the spectrum of harmonic emission. It is well known that Bessel functions attain their maximum values when their argument is close to the index. Hence, according to Eq. (52), for constant laser intensity [ $f(t) = 1$ ], the number of harmonics produced is

$$N_{\max} \approx 2V_0/\omega. \quad (53)$$

The same dependence on  $V_0$  and  $\omega$  was found in Ref. [23] in the case of laser frequency  $\omega$  small compared to  $\omega_{21}$ . The maximum frequency in the spectrum is  $\Omega_{\max} = N_{\max}\omega \approx 2V_0$  and is independent of the laser frequency.

Linear dependence of  $N_{\max}$  on the field amplitude is different from the dependence  $N_{\max} \propto E_0^2$  typical for atoms and atomic ions [7,29]. It is the peculiarity of the two-level system and, hence, of CR states of the diatomic molecular ions.

It is also known that Bessel functions are small and oscillate if their argument is much larger than the index. As a result, intensities of low-order harmonics, i.e., with numbers  $N \ll N_{\max} \approx 2V_0/\omega$ , are not higher than those of high-order harmonics, and some of the low-order har-

monics are strongly suppressed owing to the oscillations of Bessel functions (Fig. 3). Emission takes place almost equally at all frequencies up to  $\Omega_{\max} = N_{\max} \omega \sim V_0$  (Fig. 3). The plateau in a harmonic spectrum of a strongly driven quantum system is usually associated with the low-frequency field,  $\omega \ll \omega_{21}$ . In our case of  $\omega \sim \omega_{21}$ , or even  $\omega \gg \omega_{21}$ , the plateau appears when the laser frequency becomes small compared to the Rabi frequency  $V_0$ . Therefore, the field creates the low-frequency condition itself, making the laser frequency small compared to the Rabi frequency.

A laser pulse with a smooth envelope (it is always the case in experiments) destroys both the suppression of some low-order harmonics and the very-well-pronounced plateau because, on the leading and rear edges of the pulse, the field passes values optimal for all harmonics with  $N \leq N_{\max}$ :  $2V_0 f(t)/\omega \sim N$ . Figure 4 compares the spectrum emitted at  $V_0/\omega = 15.0$  in the case of two different pulses: with Gaussian envelope  $f(t) = \exp(-t^2/\tau^2)$  and with short front  $f(t) = 1 - \exp(-t/t_{\text{rise}})$ ,  $0 \leq t \leq \tau$  with the rise time  $t_{\text{rise}} = 0.2\tau$ . It is seen that the suppression of some harmonics survives in the case of a fast rise time, but disappears in the case of a Gaussian pulse.

Quantitative estimates can be obtained, for example, for the ground state and its charge-resonant state of the molecular ions  $I_2^+$  and  $I_2^{3+}$ . Using the potential curves calculated in Ref. [25], one can see that the transition frequency  $\omega_{21}(R)$  turns to zero at the internuclear separation  $R \approx 10$  a.u. (see also Fig. 2). Therefore, we take  $R$  around 7–8 a.u., so that the corresponding transition frequency is about  $\omega_{21}(R) \approx 0.2$ – $0.1$  eV, is still not too small. The typical laser intensities will be  $I \sim 10^{13}$ – $10^{14}$  W/cm<sup>2</sup>, depending on the concrete species. Recalling that  $\mu(R) \approx R/2$ , we can calculate all quantities determining the emission intensity  $i(N)$  for a given laser intensity.

Figure 5 shows the calculated values  $i(N) = \langle |d_N(t)|^2 \rangle$  for  $I_2^+$  at laser intensities  $I_1 = 4 \times 10^{13}$  W/cm<sup>2</sup>,  $I_2 = 6 \times 10^{13}$  W/cm<sup>2</sup> [Fig. 5(a)], and for  $I_2^{3+}$  at  $I_3 = 2 \times 10^{14}$  W/cm<sup>2</sup>,  $I_4 = 4 \times 10^{14}$  W/cm<sup>2</sup> [Fig. 5(b)]. The internuclear separation is  $R \approx 7$  a.u., and the laser frequency is  $\omega = 1$  eV.

There are several important peculiarities of harmonic emission from CR states, which are clear from Fig. 5.

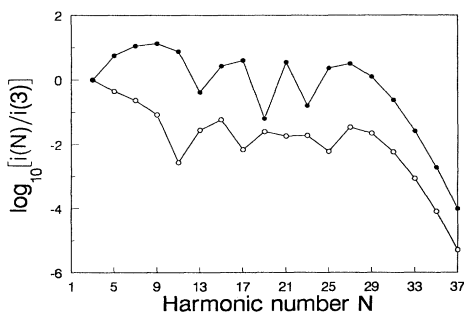


FIG. 3. Harmonic generation in a two-level system driven by a strong high-frequency field. Open circles— $V_0/\omega = 15.0$ ; closed circles— $V_0/\omega = 14.5$ .

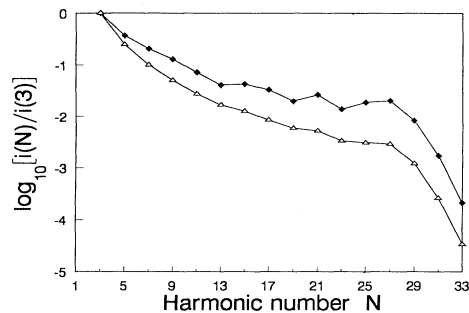


FIG. 4. Same as in Fig. 3, but for a smooth pulse envelope.  $V_0/\omega = 15.0$ , triangles—Gaussian laser pulse; diamonds—pulse with envelope  $f(t) = 1 - \exp(-t/t_{\text{rise}})$ ,  $0 < t < \tau$ ,  $t_{\text{rise}} = 0.2\tau$ .

First, the spectrum in Fig. 5 has the familiar features expected from the harmonic spectrum in a strong field: plateau and cut-off. Second, in the case of CR states of odd-charge molecular ions, the plateau is shorter than in the case of atoms, atomic ions, or neutral molecules [7,24,28]. Indeed, in the case of atoms, the plateau is long and quite pronounced already at intensities  $I \sim 3$ – $5 \times 10^{13}$  W/cm<sup>2</sup> [28], whereas in the case of CR states, the intensities  $I \sim 10^{14}$  W/cm<sup>2</sup> are required.

On the other hand, in the case of CR states, the values

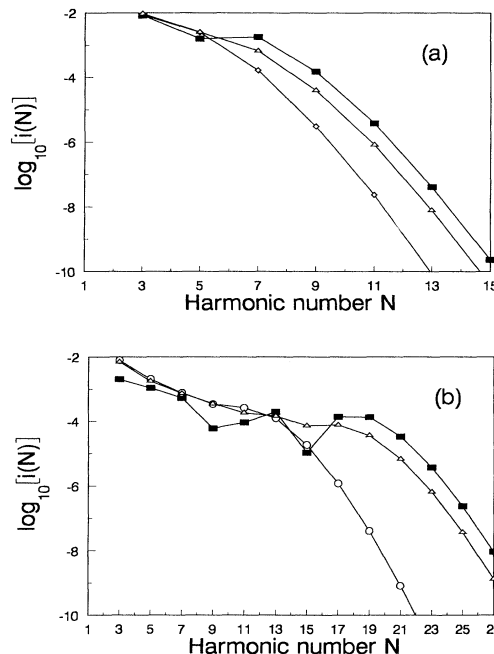


FIG. 5. (a) Harmonic emission from  $I_2^+$  for laser frequency  $\omega = 1$  eV and internuclear distance  $R \approx 7$  a.u. (1) Open diamonds,  $I = 4 \times 10^{13}$  W/cm<sup>2</sup>, Gaussian laser pulse; (2) open triangles,  $I = 6 \times 10^{13}$  W/cm<sup>2</sup>, Gaussian laser pulse; (3) closed squares,  $I = 6 \times 10^{13}$  W/cm<sup>2</sup>, constant peak intensity. (b) Harmonic emission from  $I_2^{3+}$  for laser frequency  $\omega = 1$  eV and internuclear distance  $R \approx 7$  a.u. (1) Open circles,  $I = 2 \times 10^{14}$  W/cm<sup>2</sup>, Gaussian laser pulse; (2) open triangles,  $I = 4 \times 10^{14}$  W/cm<sup>2</sup>, Gaussian laser pulse; (3) closed squares,  $I = 4 \times 10^{14}$  W/cm<sup>2</sup>, constant peak intensity.



$i(N) = \langle |d_N|^2 \rangle$  can be considerably higher than typical values for atoms or neutral molecules. According to Fig. 5, at sufficiently high intensities  $I \sim 10^{14}$  W/cm<sup>2</sup>,  $i(N) = \langle |d_N|^2 \rangle \sim 10^{-3}$  for  $N < N_{\max}$ , which is two to three orders of magnitude higher than typical in atoms [24,29] or atomic ions [7]. Unfortunately, there are no data on harmonic generation from I atoms, but the direct comparison can be done between the known data for H and H<sub>2</sub> [24] and those for the stretched H<sub>2</sub><sup>+</sup> “frozen” at the internuclear distance  $R \sim 7-8$  a.u. In the region  $R \geq 7-8$  a.u., CR states of H<sub>2</sub><sup>+</sup> are very similar to those of I<sub>2</sub><sup>+</sup>, and harmonic intensities due to CR states in our model are similar to those for I<sub>2</sub><sup>+</sup>. There are also data of recent *ab initio* numerical simulations of the Schrödinger equation for stretched H<sub>2</sub><sup>+</sup> [30], which agree well with our data for  $N < N_{\max} \approx 2V_0/\omega$ . Both data give the typical values  $|d_N|^2 \sim 10^{-3}$  at  $I \approx 6 \times 10^{13}$  W/cm<sup>2</sup>,  $\omega \approx 1$  eV, and  $N \leq 9$ , whereas Ref. [24] gives  $|d_N|^2 \sim 10^{-5}-10^{-6}$  for H and  $|d_N|^2 \sim 10^{-6}-10^{-7}$  for H<sub>2</sub> frozen at the equilibrium distance  $R = 1.4$  a.u.

The situation is also promising in the case of smaller laser frequencies. Figure 6 shows the spectrum of high harmonics at the intensity  $I = 6 \times 10^{13}$  W/cm<sup>2</sup>, internuclear distance  $R = 8$  a.u. [transition frequency  $\omega_{21}(R) \approx 0.1$  eV], and laser frequencies  $\omega = 0.5$  eV and  $\omega = 0.33$  eV. As seen in Fig. 6, at smaller frequencies the plateau is much longer and its level is high. We would like to point out again that the maximum harmonic frequency  $\Omega_{\max} = N_{\max}\omega \approx 2V_0$  is approximately  $\omega$  independent. From Figs. 5 and 6, it is also clear that the intensity of the maximum harmonic also is approximately  $\omega$  independent.

Hence, the strong coupling of CR states can be a very efficient source of harmonics, able to compete with the emission from separate atoms or atomic ions. On the other hand, when dealing with ions, one has to worry about the propagation effects, that is, the influence of free electrons created in the ionization process on phase matching. However, the use of molecular ions brings several possibilities to solve the problem, and we will discuss them in Sec. V.

Concluding this section, we would like to make one

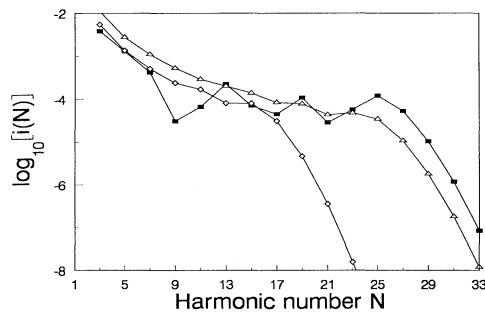


FIG. 6. Harmonic emission from I<sub>2</sub><sup>+</sup> for different laser frequencies, internuclear distance  $R \approx 8$  a.u., and peak laser intensity  $I = 6 \times 10^{13}$  W/cm<sup>2</sup>. (1) Open diamonds,  $\omega = 0.5$  eV, Gaussian laser pulse; (2) open triangles,  $\omega = 0.33$  eV, Gaussian laser pulse; (3) closed squares,  $\omega = 0.33$  eV, constant peak intensity.

more remark. As was already mentioned in Sec. I, there are, in zero approximation, two main mechanisms of harmonic production in the process of fragmentation of molecular ions: that due to strong coupling of CR states and that due to the emission from two separate ions. Qualitatively, the total emission spectrum is given by the superposition of the emission spectra due to these two different mechanisms. As far as the spectrum due to CR states exhibits a shorter but higher plateau, under appropriate conditions one can hope to get a *double-plateau structure* in the total harmonic spectrum. It is indeed observed in numerical simulations [30] for H<sub>2</sub><sup>+</sup> frozen at  $R \approx 7$  a.u..

## V. PHASE-MATCHING PROBLEM

As we have shown in Sec. IV, CR states of molecular ions can provide a significant contribution to the emission of high harmonics. The main reason why CR states would become an important source of harmonics is a very high level of plateau in the harmonic spectrum. On the other hand, the use of molecular ions poses the important problem of the effect of free electrons on the phase-matching condition. In this section, we discuss the ways to exploit the significant difference between the polarizability (susceptibility) of molecular and atomic ions to solve this problem.

First, if we wish to overcome this problem, we could lower the gas density. For example, one can have the same number of free electrons when using I<sub>2</sub><sup>+</sup> as when using a 30% ionized medium of initially neutral atoms with 3.3 times higher density. Lowering the density 3.3 times will lead to the order of magnitude decrease in harmonic intensities. However, according to our calculations, the individual susceptibility of CR states can be  $10^2-10^3$  orders of magnitude higher than that of atoms or first atomic ions at the same intensities  $I \sim 10^{14}$  W/cm<sup>2</sup>.

Second, there is a much more important opportunity: using the difference in polarizabilities of atomic and molecular ions, one can modulate the energy transfer from the incident wave to the harmonic wave by a process analogous to quasi-phase-matching. In the absence of exact phase matching between the incident wave and the wave of the  $N$ th harmonic ( $\Delta k_N \neq 0$ ), the energy is transferred from the incident wave to the harmonic wave over the length of coherence  $L_N = \pi/\Delta k_N$ . Then the energy flow reverses its direction and the energy is transferred back to the incident wave over the next length of coherence  $L_N$  to  $2L_N$ . However, if the susceptibility of the medium is modulated in such a way that it is turned off at  $L_N$  to  $2L_N$ ,  $3L_N$  to  $4L_N$ , ..., but is turned on at 0 to  $L_N$ ,  $2L_N$  to  $3L_N$ , ..., then the energy flow will take place only in one direction. This idea of modulating the nonlinearity of the medium was suggested in Ref. [31] for harmonic generation in relativistically driven plasma. There the nonlinearity depends on the density, and so it is possible to achieve the desired modulation by modulating the plasma density. The use of CR states and the fact that their susceptibility can be much higher than that of atomic ions gives another means of modulating the nonlinear polarization of the medium.

The idea is to take the gas of, say,  $I_2$  molecules and dissociate them in chosen regions. In this way, we prepare a “sandwich” of molecules and atoms (see Fig. 7). UV radiation from a standard eximer laser would suffice in the case of  $I_2$ . Using a nanosecond pulse, one can neglect the motion of both molecules and atoms. That is, diffusion from one “sandwich” layer to another can be ignored. Then a short laser pulse ionizes the medium, creating the successive layers of atomic and molecular ions with rather different nonlinear polarizabilities (much higher for molecular ions). The second pulse, coming with some delay  $\Delta t$ , generates harmonics (see Fig. 7). The whole idea is based on the fact that nonlinear susceptibilities of atomic and molecular ions (even if the latter are stretched) are rather different owing to the presence of CR states in the molecular-ion spectra.

In general, the presence of the vibrational degree of freedom in molecules, together with the possibility to freeze a diatomic molecule at a fixed internuclear separation by using a supershort laser pulse, opens rich possibilities for using molecules as a nonlinear medium. Indeed, creating the vibrational wave packet and varying the time delay between the first and the second supershort laser pulses (see Fig. 2), one can obtain the nonlinear response from *different local electronic spectra* corresponding to different internuclear distances  $R$ . Obviously, the modulus and the phase of the polarization induced by the second pulse will depend on the details of the local electronic spectrum. In other words, the phase of short-pulse-induced polarization will depend on the concrete value of the internuclear distance, that is, on the time delay  $\Delta t$  between the two successive pulses. The principal possibility of controlling the phase of the nonlinear polarization of the medium by controlling  $\Delta t$  will be very important for the phase-matching problem, and will be discussed elsewhere. One can imagine, for example, preparing the vibrational wave packets in different regions of the medium at different times. The second pulse, which induces the polarization, will thus have a different delay time from the first pulse while propagating through different regions in the medium. Therefore, the polarization will change its phase along the length of the medium.

In summary, the very high polarizability of diatomic molecular ions opens several ways to solve the phase-

matching problem in spite of the presence of many free electrons.

## VI. CONCLUSION

In this paper, we have considered the nonlinear response of a single odd-charge ion of a homonuclear diatomic molecule to a strong short laser pulse. We described the conditions under which the use of a femtosecond laser pulse allows one to freeze the ion of a heavy molecule at a certain internuclear distance  $R$ . Under these conditions, the emission spectrum is determined by the local electronic spectrum corresponding to this particular internuclear distance  $R$ . We have shown that, at large values of  $R$ , the charge-resonant states of a molecular ion can be a very efficient source of high harmonics. At a high laser intensity, the harmonic spectrum has a plateau, which is probably typical for any strongly driven quantum system. Intensities of harmonics due to CR states can be several orders of magnitude higher than those due to atoms or atomic ions. However, the length of the plateau is shorter than in the case of atoms.

The presence of an additional—vibrational—degree of freedom, the very high susceptibility of molecular ions relative to atomic ions, and the use of supershort laser pulses opens possibilities of controlling the phase of the nonlinear polarization of the medium and of solving the phase-matching problem even if there are many free electrons in the medium. The phase of polarization can be controlled by controlling the internuclear separation, and we will discuss this issue in more detail in a subsequent paper [32]. The use of quasi-phase-matching allows one to handle the deleterious role of free electrons in harmonic emission.

It is important to note that, in this paper, we assumed that all ions of diatomic molecules are aligned along the linearly polarized laser field. Experiments [14,15] show that when such molecular ions are produced via multiphoton ionization of neutral molecules, they experience a torque which tends to align them along the electric field during the fragmentation process. Such a torque also exists in neutral molecules. It is likely that an appropriately shaped alignment pulse could be used to orient the molecules. The physics of the process is the same as in the long-familiar optical Kerr effect. Therefore our assumption is reasonable and the situation considered in the paper is experimentally feasible.

In summary, we think the use of molecular wave packets and supershort laser pulses opens a rich spectrum of possibilities for inducing and controlling the nonlinear polarization of the medium, including such possibilities as modulating the nonlinear susceptibility of the medium, controlling the phase of nonlinear polarization, and efficient generation of high harmonics of the incident light.

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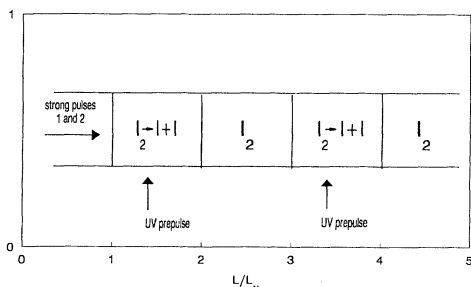


FIG. 7. Qualitative scheme of modulating the medium nonlinearity.

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