Low-frequency dipole response of a diatomic heteronuclear molecule on an intense ultrashort laser pulse

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Abstract. In the present work we analyze the dipole response of a diatomic heteronuclear molecule on the nonperturbative action of the external low-frequency laser field. Main results are obtained by numerical solution of the time-dependent Schrödinger equation for the nuclear subsystem of the molecule. We study the spectrum of polarization response and the influence of the coherent repopulation of the ro-vibrational states on it. Generally, we consider two cases: repopulation due to Raman-type transitions leading to the interference stabilization of the molecule and repopulation arising as a result of extremely short pulse action. We also study the transformation of a weak probe pulse propagating through the highly excited medium of the studied molecules.

1. Introduction
Laser research during last decades, both theoretical and experimental, revealed a number of new remarkable features of molecular and atomic media exposed to external electromagnetic fields. Vast part of the new fundamental properties is discovered by virtue of using laser setups with extremely high intensities of generated light [1-7]. From theoretician’s point of view, some of them can be described in terms of perturbation theory, but there are also a number of fundamental processes demonstrating essentially nonperturbative quantum-mechanical behavior [1-3], such as tunnel ionization of atoms, plasma formation in clusters, photostabilization[2-6] etc. Molecular media have a lot of properties similar to those of the atomic systems when one deals with electronic subsystem [8] and transitions between electronic states. But once the measurement time is comparable with ro-vibrational evolution times, there are several very important differences between atomic and molecular behavior in the external field. They arise as a result of the nuclear subsystem response on the external field. Molecular-specific phenomena are alignment control [9], optical centrifuging, photostabilization with respect to ro-vibrational transitions [10], and many others. One of the most fascinating effects of the nuclear subsystem dynamics is the interference stabilization with respect to dissociation. It is interesting not only as the pure quantum-mechanical effect that seems counter-intuitive at the first glimpse, but also as an instrument of coherent repopulation of the wide set of ro-vibrational states. Roughly speaking, photostabilization consists in dissociation suppression when the incident field intensity exceeds some critical value. In the case of interference mechanism [2], it results from the multiple coherent Raman-type transitions via lower lying-bound states (so-called V-type transitions),
and higher-lying ro-vibrational continuum states (Λ-type transitions). Hence, the additional effect accompanying the interference stabilization regime is the population of the coherent superposition of the molecular states, very wide with respect to initial wave-packet. Looking at the dipole moment of the molecule, one can see that the spectrum of the dipole response gains a variety of frequencies that correspond to different rotational and vibrational transitions and can be very low with respect to incident light frequency.

The theory [2,3], experimental evidence [11], and explanation of the stabilization regime was developed for quasimonochromatic radiation. It can be regarded as the long-pulse approximation. The other limiting case is the case of extremely short pulses [12]. In terms of nuclear subsystem shortness means that the pulse duration is much lower than the vibrational period of the molecule (but still much higher than the inverse frequencies of the electron transitions). The most interesting situation arises when the pulse is characterized by the non-zero integral of electric field over time (so-called half-cycle pulse). The action of such short pulse is remarkable in the sense that the positions of nuclei are nearly unchanged during the pulse, but the nuclear subsystem gains momentum, which determines its further evolution and the dipole response.

The present work is devoted to the numerical study of the dipole response of the molecular media on low-frequency electromagnetic field in these two cases. We intend to analyze spectral characteristics of the response in the non-perturbative regimes of the interference stabilization and extremely short action of monopolar pulses.

2. Numerical model

We consider nuclear subsystem of the heteronuclear molecule within the Born-Oppenheimer approximation using single potential energy surface. The time-dependent Schrödinger equation can be written in the dipole approximation for linearly polarized field as

$$i\hbar \frac{\partial \psi(r, \theta, \phi, t)}{\partial t} = -\frac{\hbar^2}{2\mu} \Delta \psi(r, \theta, \phi, t) + \left( V(r) - qrE(t)\cos\theta \right) \psi(r, \theta, \phi, t). \tag{1}$$

Here $r$ is the internuclear distance, $\theta$ and $\phi$ are ordinary spherical angles taken from the polarization direction. $V(r)$ denotes the vibrational potential energy of nuclei, $E(t)$ is incident field, $q$ is the effective charge included into the dipole moment of the nuclear subsystem. It is convenient to decompose full wave function over spherical harmonics as

$$\psi(r, \theta, \phi, t) = \sum_{j=-\infty}^{\infty} \sum_{m=-j}^{j} u_j^m(r, t) \frac{1}{r} Y_j^m(\theta, \phi). \tag{2}$$

If we assume that only states with $m = 0$ are populated initially, we can omit superscript $m$, since it is always zero, and rewrite TDSE as a system of partial differential equations for $u_j$:

$$i\hbar \frac{\partial u_j}{\partial t} = -\frac{\hbar^2}{2\mu} \frac{\partial^2 u_j}{\partial r^2} + \left( V(r) + \frac{\hbar^2 j(j+1)}{2\mu r^2} \right) u_j - qrE(t) \left( \beta_{j+1}^l u_{j+1} + \beta_{j-1}^l u_{j-1} \right). \tag{3}$$

Coefficients $\beta$ origin from the Clebsch-Gordan coefficients and are equal to

$$\beta_{j+1}^l = \frac{j}{\sqrt{(2j-1)(2j+1)}} \tag{4}$$
$$\beta_{j+1}^l = \frac{j+1}{\sqrt{(2j+1)(2j+3)}} \tag{4}$$
In order to provide the possibility of interference stabilization of the molecule we need to consider the molecule with dense vibrational spectrum and effective transitions to the vibrational continuum. Taking it into account we have chosen the system with properties close to the IBr ones. Potential energy surface was approximated by Morse potential curve with bound energy equal to 1.3 eV, steepness parameter $\alpha = 5$, equilibrium internuclear distance of 2.5 angstroms. Initially the molecule is assumed to occupy the highly excited vibrational state. The frequency of the laser radiation (except the case of extremely short action) was taken low enough to provide effective transitions to the vibrational continuum. In our calculations it was 0.1 eV. Laser pulse envelope was described using smoothed trapezoidal shape with equal durations of front and tail parts. The system (3) was solved numerically using finite difference method with iterating of the right part of equation. Having the time-dependent wavefunction of the system $\psi$, we can calculate the vibrational and rotational quantum number distributions over the bound states using ordinary formulae

$$W_j = \sum_v \left| \langle \psi | \varphi_{v,j} \rangle \right|^2,$$

$$W_v = \sum_j \left| \langle \psi | \varphi_{v,j} \rangle \right|^2.$$ 

Here $v$ is the vibrational quantum number, $j$ is the rotational quantum number, $\varphi_{v,j}$ stands for the corresponding stationary wavefunction. The time-dependent average dipole moment of the system can be obtained as

$$\langle d_z \rangle = \langle \psi | q r \cos \theta | \psi \rangle.$$

3. Results and discussion

While in the weak field regime the polarization response of the molecule to the external field action is perturbative and rather straightforward, in the strong-field regime, when the interference stabilization is present, the perturbation theory-based approach is non-applicable. There are two main characteristics that define discrepancy. First, strong-field dynamics assumes strong repopulation of the large set of ro-vibrational levels during the pulse. It destroys the proportionality between dipole moment of the molecule and electric field, and in the stabilization regime, when multiple Raman-type transitions take place, it also destroys the polynomial dependence usual for nonlinear optics. Second, the post-pulse dipole response is defined by the redistributed population over rotational-vibrational molecular levels. This redistribution is possible due to non-adiabaticity of the incident radiation. So, if the incident pulse is sufficiently long (and has slow-varying envelope), one won’t see any post-pulse dynamics, while in the case of short non-adiabatic pulse action the residual polarization signal can be observed in the after-pulse regime.

In our calculations we took a vibrationally excited molecule to provide pure stabilization regime with the single-photon bound state-continuum coupling. The bound state had dissociation energy of 0.082 eV, non-excited with respect to rotations. In experiment such excited molecule can be obtained in the field-induced ionization process. If one wants to take into account the thermal effects, he has to deal with non-coherent summation over a set of rotational states, but here we consider highly non-equilibrium system. The time-dependence of the dipole moment induced by the strong pulse interacting with vibrationally excited molecule is presented on the fig. 1.
Figure 1. Time dependence of the electric field of the incident pulse (top), and the corresponding dipole response of the molecular system (bottom). Intensity of the incident light was set to 2 TW/cm^2. Initial state of the molecule is described in the text. Dissociation during the pulse has not exceeded the value of 2 percent.

Here one can see that the response is not proportional to the laser field (even in terms of envelope) during the pulse, and moreover, the residual polarization signal is present. It should be noticed that frequencies much lower than the pulse carrier frequency can be distinguished. As it has been said, field-free dynamics is fully determined by the population distribution of different ro-vibrational states and the energy differences between populated levels. So we can divide the obtained response into several terms. First, rapidly changing near-resonant response is provided by the vibrational energy gaps. Second, the slowest term, arises as a result of rotational repopulation. Its characteristic time can be estimated as $\tau \sim \hbar / B$ where $B$ is the rotational constant. All these frequencies can be observed in the corresponding spectrum (fig. 2). Intermediate frequencies of the response are supressed. Hence, calculations predict possibility of the non-vanishing response at the rotational molecular frequencies in the case of multiple Raman-type transitions.
Figure 2. Spectrum of the dipole response shown on the fig.1.

Now consider the dipole response of the molecule on the action of the extremely short pulse referred to as “half cycle pulse”. This means that duration of the pulse is much lower than the vibrational period of the molecule. In addition the only physical property that characterizes the post-pulse evolution of the quantum-mechanical wave packet is the momentum transferred to the nuclear subsystem of the molecule. In order for this quantity to have nonzero values, the corresponding laser pulse must have non-vanishing integral of the electric field over time. It can be achieved experimentally from the single-cycle optical pulse using nonlinear saturating media [13]. Questions of repopulation under action of this pulse are discussed in detail in [14].

The dynamics of the dipole moment of the model molecule under such an action is presented on the fig. 3. We consider two cases, namely relatively weak pulse (fig. 3a), and relatively strong one (fig. 3b). The difference between these two cases consists in the number of ro-vibrational states involved in the post-pulse dynamics. It is seen that the dominating part of the dipole response is provided by the molecular rotations. When the incident pulse is weak, the population distribution over rotational states is not significantly wide. Hence, in the post-pulse dynamics one can mainly see the slow-varying dipole moment, corresponding to the matrix element between $j = 0$ and $j = 1$ states. The vibrational quantum number is nearly unchanged. Low repopulation of vibrational states affects the weak response at relatively high frequency, which can be seen on both pictures. As for the strong field case, the distribution over rotational quantum number is much broader. Since the energy gap between states with rotational quantum numbers $j - 1$ and $j$ is roughly proportional to $j$, the higher excitation of rotations assumes the higher frequencies involved and more rapid evolution of the dipole moment. So in general, we have quasiperiodic response at rotational frequencies which can be controlled by the momentum transferred to the system. One can notice the high-frequency oscillations on the time dependence. They arise from the molecular vibrational motion, and low amplitude is a consequence of low vibrational repopulation during the ultrashort pulse.
Figure 3. Post-pulse dipole response on the extremely short pulse action. Total momentum transferred to the molecule was set to 1 (a) and 5 (b) inverse angstroms correspondingly. Initial molecular state is chosen to be the highly excited vibrational one (see the text).

We only considered the situation when the initial state is one of the ro-vibrational eigenstates of the molecular Hamiltonian (highly excited one). From the experimental point of view it is more natural to study the behavior of the wide superposition of the states. This situation makes the dipole response analysis more complicated. However, the qualitative conclusions about the polarization dynamics obtained earlier remain valid. Such a scheme can be realized as follows. First, the molecule is exposed to the strong laser radiation. Dipole response on the pulse of this sort was discussed above. Strong pulse forms ro-vibrational wave packet and induces residual dipole response. Second, during the evolution of the residual response, the second (probe) pulse comes. It is weak, and the corresponding repopulation of the molecular ro-vibrational levels is rather low. But it causes additional dipole response. This response, in turn, can affect the probe pulse propagation and can have additional components of the spectrum in comparison with the case of the only strong pump pulse action.

Dipole response here consists of the part caused by the first pulse, and weak response to the second one which strongly depends on the medium excitation provided by the first pulse. It is interesting to extract the probe-field response. Time dependence extracted from our calculations is presented on fig. 4.
Figure 4. Time dependence of the electric field of the weak probe pulse (top), and the corresponding dipole response of the molecular system (bottom). Pump pulse had intensity 2TW/cm² and total duration of 20 optical cycles with the carrier frequency of 0.1eV. The intensity of the probe pulse was 0.2MW/cm². Dipole response on the first pulse has been subtracted.

And the fig. 5 presents its spectrum. As it has been expected, the response of the excited molecule strongly differs from ordinary linear response. Again we see the near-resonance component of the vibronic transitions, but at the same time the low frequency components are seen to be strongly enhanced though the probe pulse itself cannot provide neither stabilization, nor the high-order transitions. According to our model, these frequencies can be matched with non-uniform (with respect to $j$) quasi-resonant population and “de-population” of the rotational states.
4. Conclusions

We presented numerical data on the dipole response of diatomic heteronuclear molecule on the external laser field action investigated by “ab initio” TDSE calculations. If the incident pulse is strong enough the formation of wide rotational distribution can be achieved due to interference stabilization phenomenon and multiple Raman-type Λ and V transitions. In this case the population response reveals efficient low-frequency spectral components arising from rotational excitation of the molecule. These low-frequency components can be significantly enhanced if the molecular medium is pre-excited by a strong pump pulse providing a wide coherent population of rotational states. Such a possibility of quantum control of the low-frequency dipole response of the molecular medium is of great importance especially for problems of generation and amplification of the terahertz radiation.

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