Ultrafast control of vibrational states of polar molecules with subcycle unipolar pulses

Anton Pakhomov [1], Mikhail Arkhipov,[1] Nikolay Rosanov,[2] and Rostislav Arkhipov [1]

[1]*Faculty of Physics, St. Petersburg State University, Universitetskaya Naberezhnaya 7/9, St. Petersburg 199034, Russia*
[2]*Ioffe Institute, Politekhnicheskaya Street 26, St. Petersburg 194021, Russia*

We investigate theoretically the nonresonant excitation of vibrational levels in polar molecules by unipolar radiation pulses of duration much shorter than the characteristic period of the molecule's vibration. We consider several profiles of the potential of the interaction of atoms in a diatomic molecule and derive analytically the probabilities of the molecule's transition to excited vibrational states when driven by subcycle unipolar pulses. It is shown that the excitation efficiency is governed by the electric pulse area so that unipolar half-cycle pulses turn out to be the most efficient ones. We introduce the characteristic scale of the electric pulse area, which serves as a measure of the pulse action on the vibrational states of the molecule. The results are generalized to the interaction of excited vibrational and rotational states and it is shown that the behavior of the vibrational levels' populations versus the electric pulse area as well as the introduced characteristic scale stays valid.

I. INTRODUCTION

In recent times there has been great interest in the generation of few-cycle pulses in terahertz and especially optical frequency ranges [1–3]. The pulses of such ultrashort duration seem attractive in multiple applications, such as coherent control of ultrafast processes in matter or ultrafast optical data processing [2,4]. Of particular interest in ultrafast photonics are the half-cycle pulses containing just a half of a field oscillation and thus having a constant sign of the electric field. Such pulses, referred to as unipolar, can be more strictly defined as having nonzero values of the so-called electric pulse area [5–7]

$$\vec{S}_E = \int_{-\infty}^{+\infty} \vec{E}(\vec{r}, t)dt \neq 0, \qquad (1)$$

with the electric-field vector $\vec{E}(\vec{r}, t)$. Importantly, the electric pulse area (1) exhibits a fundamental conservation law, which directly follows from Maxwell's equations, namely, the electric pulse area is conserved, when an arbitrary ultrashort pulse propagates in a nonlinear dissipative medium in the one-dimensional case [8,9].

As can be easily inferred from Eq. (1), unipolar pulses, when interacting with charged particles, transfer a nonzero momentum to them. This fact makes it possible, for example, to much more efficiently ionize atoms or accelerate charges than usual bipolar pulses would [10–14]. It was also shown that unipolar pulses can efficiently excite electronic states in resonant media, even though they possess extremely broad spectra and therefore interact with media nonresonantly [15,16]. Besides that, the possibility of selective excitation of the levels in a hydrogen atom by varying the parameters of the unipolar pulse sequence was demonstrated [17].

Quite often in experiments it is much easier to produce not strictly unipolar pulses, but so-called quasiunipolar ones, which consist of an intense half-cycle burst and a much longer low-amplitude tail of the opposite sign of the electric field. The electric pulse area (1) in this case equals zero, which allows us to avoid some technical difficulties related to handling with the close to zero-frequency spectral components. Importantly, as it was recently demonstrated, such quasiunipolar pulses can act on quantum systems almost as strictly unipolar pulses would, provided the duration of their tail at the trailing edge is significantly longer than the duration of the leading burst [17].

Since subcycle unipolar pulses possess an ultrabroad spectrum extending up to zero frequency, specific approaches are needed for their production. So far, a number of methods for the generation of unipolar and quasiunipolar subcycle pulses have been suggested [5,18,19]. The most notable ones rely on the formation of terahertz unipolar precursor pulses in electro-optical crystals [20,21], excitation of a foil target by intense femtosecond pulses [22,23], or the control of the superradiant emission in a layer of a nonlinear resonant medium [24,25]. Also, the transformation of a bipolar pulse into a unipolar half-cycle pulse upon its linear reflection from thin metallic films was obtained in [26]. Besides that, the possibility of the unipolar half-cycle soliton formation in a nonlinear medium was demonstrated theoretically [27–32]. Recently, several approaches for the generation of attosecond [33] and terahertz [34] unipolar pulses in plasma were suggested. Transportation of unipolar pulses can be realized in coaxial waveguides having no cutoff frequency [35]. Finally, experimental determination of unipolarity and the electric pulse area of terahertz radiation emitted by filaments in water was recently performed [36].

Such subcycle pulses containing less than a single optical cycle were also studied for the control of molecular dynamics. In particular, subcycle unipolar pulses were used for effective molecular orienting and alignment [37–39]. Later, the selective control of the rotational levels with unipolar pulses was

demonstrated [40]. Several studies also addressed the issue of the transition of polar molecules to excited vibrational states upon interaction with few-cycle and subcycle pulses. The possible role of the electric pulse area (1) in nonresonant excitation of molecular vibrational levels by intense ultrashort pulses was noted in [41], but the investigation was only performed for bipolar pulses. In Ref. [42] the dissociation dynamics and angular distribution of the HF molecule interacting with intense half-cycle and few-cycle pulses was numerically analyzed. In particular, it was found that for sub-10-fs pulses the molecule has higher dissociation probabilities under half-cycle pulses than under other types of pulses. However, most papers so far studied only the vibration excitation and the molecule's dissociation under bipolar multicycle pulses with zero electric pulse area (1). At the same time, detailed studies of the excitation of the molecule's vibrational states by unipolar pulses are lacking.

In this paper we investigate theoretically the ultrafast excitation of vibrational states in polar molecules upon the interaction with unipolar subcycle pulses. We consider the pulses much shorter in duration than the characteristic vibrational period of the molecules. We obtain the efficient nonresonant excitation of higher vibrational states in polar molecules by unipolar pulses. The probabilities of the levels' excitation were analytically found for the simplest complemented Coulomb potential. Using a more advanced Morse potential profile, we demonstrate the molecule's dissociation by unipolar pulses with large enough electric pulse area. We also introduce a parameter of molecular scale of the electric pulse area which fully determines the influence of a subcycle unipolar pulse on the molecule's vibrational dynamics.

The paper is organized as follows. In Sec. II we describe the general model of the molecule's interaction with subcycle unipolar pulses and derive the general expression for the probability of transition to the excited states. In Sec. III we apply the derived expressions to the simplest model of the interatomic interaction in a polar molecule, namely, a complemented Coulomb potential, which allows for the analytical treatment. In Sec. IV we focus on a more advanced Morse potential and investigate the excitation and dissociation dynamics of polar molecules within this model. Section V is devoted to the mutual action of the excited rotational and vibrational levels and we examine how the excitation of the rotational states influences our findings for the molecule's transition to higher vibrational levels. The paper is summarized and concluding remarks are given in Sec. VI.

II. MODEL

We treat the interaction of an excitation pulse with a molecule using the standard time-dependent Schrödinger equation for the wave function ψ [43]:

$$i\hbar \frac{\partial \psi}{\partial t} = [\hat{H}_0 + \hat{V}(t)]\psi. \tag{2}$$

Here $\hat{H}_0$ is the intrinsic Hamiltonian of the molecule, which we expand as

$$\hat{H}_0 \psi = -\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi}{\partial r^2} + U(r)\psi + \hat{H}_{el}\psi, \tag{3}$$

with the reduced mass of the molecule μ, the potential energy of the interaction between atoms in the molecule $U(r)$ with the spacing between atoms or nuclei r, and the term $\hat{H}_{el}$ describing the electronic levels. The second term in Eq. (2) is the interaction potential $\hat{V}(t)$ of the molecule with the external electric field of the excitation pulse and can be represented within the dipole approximation as

$$\hat{V}(t) = -\vec{E}(t) \cdot \sum_i q_i \vec{r}_i, \tag{4}$$

with the summation performed over all charges q_i in the molecule and their radius vectors $\vec{r}_i$.

In the consideration below we make use of the assumption that the excitation pulse duration τ_p is much smaller than the typical period of molecular vibrations

$$\omega_V \tau_p \ll 1, \tag{5}$$

where ω_V is the characteristic vibration frequency. The assumption (5) dates back to the originals papers on the sudden perturbations of quantum systems [44]. Such an approximation was previously used in Refs. [15,16,45], and it was shown that the inequality (5) makes it possible to disregard the intrinsic Hamiltonian $\hat{H}_0$ when solving Eq. (2) for the molecule excitation by a driving pulse. If this driving pulse of the duration τ_p arrives at the time point t_0, the formal solution of Eq. (2) for the wave function after the pulse passage can be written as [15,45]

$$\psi(t_0 + \tau_p) = \psi(t_0) \exp\left(-\frac{i}{\hbar} \int_{t_0}^{t_0+\tau_p} [\hat{H}_0 + \hat{V}(t)]dt\right)$$

$$= \psi(t_0) \exp\left(-\frac{i}{\hbar} \int_{t_0}^{t_0+\tau_p} \hat{H}_0 dt\right)$$

$$\times \exp\left(-\frac{i}{\hbar} \int_{t_0}^{t_0+\tau_p} \hat{V}(t)dt\right). \tag{6}$$

The first exponential factor here can be estimated using the condition (5) as

$$\exp\left(-\frac{i}{\hbar} \int_{t_0}^{t_0+\tau_p} \hat{H}_0 dt\right) \sim e^{i\omega_V \tau_p} \approx 1$$

so that the expression (6) reduces to

$$\psi(t_0 + \tau_p) \approx \psi(t_0) \exp\left(\frac{i}{\hbar} \sum_i q_i \vec{r}_i \cdot \int_{t_0}^{t_0+\tau_p} \vec{E}(t)dt\right)$$

$$= \psi(t_0) \exp\left(\frac{i}{\hbar} \vec{S}_E \cdot \sum_i q_i \vec{r}_i\right). \tag{7}$$

Equation (7) yields that the final state of the system is fully determined by the electric area of the excitation pulse S_E defined by Eq. (1) [15,16,40,45].

In order to calculate the populations of the molecular excited states caused by the driving pulse, one has to expand the wave function of the system $\psi(t_0 + \tau_p)$ from Eq. (7) into a series of the respective eigenfunctions $\psi_n(\vec{r})$,

$$\psi(\vec{r}, t_0 + \tau_p) = \sum_n a_n \psi_n(\vec{r}),$$

so that the expansion coefficients

$$a_n = \int \psi_n^*(\vec{r})\psi(\vec{r}, t_0 + \tau_p)d\vec{r} \qquad (8)$$

provide the probability of transition to the excited states:

$$w_n = |a_n|^2. \qquad (9)$$

Let us now further simplify Eq. (7). We represent the radius vector $\vec{r}_i$ of each charge as the sum of the radius vector with respect to the center of the nearest atom $\vec{r}_i^o$ and the radius vector of this atom's center $\vec{R}_i^o$: $\vec{r}_i = \vec{r}_i^o + \vec{R}_i^o$. Since the radius vector $\vec{R}_i^o$ is the same for all charges coupled to each atom, for the second summation term we can get.

$$\sum_i q_i \vec{R}_i^o = \vec{R}_{12} \sum_j q_j = Q\vec{R}_{12}, \qquad (10)$$

with the index j running now over all charges of each atom, the radius vector $\vec{R}_{12}$ pointing between the centers of atoms in a diatomic molecule, and Q being the overall charge attributed to each atom. The nonzero value of Q hence means that the interatomic bonding in the molecule has to be at least partially ionic so that the expression (10) equals the permanent dipole moment of the molecule. Given that, the expression (7) reduces to

$$\psi(t_0 + \tau_p) \approx \psi(t_0) \exp\left(\frac{i}{\hbar}\vec{S}_E \cdot \sum_i q_i \vec{r}_i^o\right) \exp\left(\frac{i}{\hbar}\vec{S}_E \cdot Q\vec{R}_{12}\right). \qquad (11)$$

From Eq. (11) we can infer that in the first approximation we can suitably separate excitation of the electronic levels in the molecule on the one hand and the excitation of the molecular vibrational and rotational levels on the other hand. Indeed, the wave function $\psi(t_0 + \tau_p)$ is connected to the wave function $\psi(t_0)$ through two factors in Eq. (11), where the first factor describes only the electron states inside the molecule and the second factor only depends on the separation between the atoms and the molecule's orientation with respect to the driving electric field. If we neglect in the first approximation the influence of the excited electronic states on the parameters of the potential of the interatomic interaction in the molecule and on the permanent dipole moment of the molecule, we can treat the electronic and the vibrational or rotational levels separately.

In practice, such an assumption means that, when calculating the expansion coefficients using Eq. (8), we separate both exponential factors in Eq. (11) and use only the second factor to consider the vibrational and rotational states of the molecule. At the same time the first exponential factor in Eq. (11) is solely attributed to the excitation of the electronic states and should be coupled to the electronic part of the eigenfunctions $\psi_n(\vec{r})$ in Eq. (8). When considering only vibrational levels, this part related to the electronic states can be skipped within the approximation used. Thus, in what follows we will deal only with the second exponential factor in Eq. (11).

Below we study in detail two specific types of potential energy profile for the interatomic interaction, namely, the complemented Coulomb potential and the Morse potential. In the first step, we neglect the rotational motion of the molecule and focus on the vibrational levels. Then we extend our results
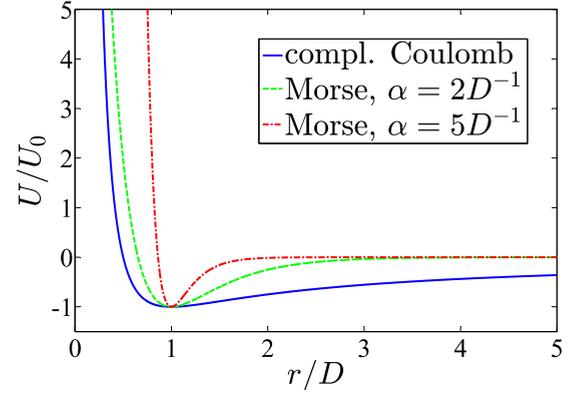
FIG. 1. Profile of the finite potential well as provided by the complemented Coulomb potential (13) and Morse potential (36) for $\alpha = 2D^{-1}$ and $5D^{-1}$.

to the case when the rotational levels are also involved and investigate the mutual action of the vibrational and rotational excited states.

III. COMPLEMENTED COULOMB POTENTIAL

We start with a Coulomb-type potential describing the attraction of differently charged atoms in a molecule of a polar dielectric. At the same time, in order to enable the formation of a stable molecule, the Coulomb attraction has to be balanced by the repulsive forces. For definiteness we take the simplest possible r^{-2} dependence of this repelling potential on the interatomic separation r in the molecule. Therefore, we end up with the potential energy $U(r)$,

$$U(r) = -\frac{C_1}{r} + \frac{C_2}{r^2}, \qquad (12)$$

with some positive constants $C_1 > 0$ and $C_2 > 0$. The first term on the right-hand side of Eq. (12) stands for the standard Coulomb attraction, while the second term corresponds to the repulsive forces that confront the attraction as the atoms get close enough to each other. For convenience, we rewrite Eq. (12) in the more suitable form

$$U(r) = U_0\left(-\frac{2D}{r} + \frac{D^2}{r^2}\right), \qquad (13)$$

where U_0 is the molecular binding energy and D is the equilibrium interatomic separation. Indeed, from Eq. (13) we easily find that the minimum of the potential energy corresponding to

$$\frac{dU(r)}{dr} = 0$$

is reached for $r = D$, while the respective value of the potential energy equals $-U_0$, as can be seen in Fig. 1.

The eigenstates of the potential (13) are given by the Schrödinger equation $\hat{H}_0\psi = E\psi$, with the energy value E, which attains the form

$$\frac{d^2\psi}{dr^2} + \frac{2\mu}{\hbar^2}\left(E + \frac{2DU_0}{r} - \frac{U_0D^2}{r^2}\right)\psi = 0. \qquad (14)$$

Equation (14) represents the so-called Whittaker equation. It seems convenient to convert Whittaker's equation to another form using the ansatz $\psi(r) = \rho^p e^{-\rho/2} u(\rho)$, where

$$\rho = 2\varepsilon r, \quad \varepsilon = \sqrt{-\frac{2\mu}{\hbar^2}E}, \quad p = \frac{1}{2} + \sqrt{\frac{1}{4} + \frac{2\mu U_0 D^2}{\hbar^2}}. \tag{15}$$

Now for the function $u(\rho)$ we obtain the equation

$$\rho \frac{d^2 u}{d\rho^2} + \frac{du}{d\rho}(2p - \rho) + u(\gamma - p) = 0, \tag{16}$$

with

$$\gamma = \frac{2\mu U_0 D}{\varepsilon \hbar^2}.$$

Equation (16) is the Kummer or confluent hypergeometric equation, whose solutions are confluent hypergeometric functions. In order to get a feasible solution for the wave function, we need the wave function $\psi(r)$ to be finite at $r = 0$ and go to zero as $r \to +\infty$. This condition is only obeyed when

$$\gamma - p = n, \tag{17}$$

with n a non-negative integer. In this case the solution of Eq. (16) is the generalized Laguerre polynomial $L_n^{(2p-1)}(\rho)$. The equality (17) allows us to find the energy values of the eigenstates

$$E_n = -\frac{2\mu U_0^2 D^2}{\hbar^2(p+n)^2}, \quad n = 0, 1, 2, \ldots. \tag{18}$$

It is important to emphasize that the potential (13) thus possesses an infinite number of energy levels in its discrete spectrum. The respective rescaled wave functions of the eigenstates are given as

$$\psi_n(r) = \sqrt{\frac{\varepsilon_n n!}{(n+p)\Gamma(n+2p)}}(2\varepsilon_n r)^p e^{-\varepsilon_n r} L_n^{(2p-1)}(2\varepsilon_n r), \tag{19}$$

with

$$\varepsilon_n = \frac{2\mu U_0 D}{\hbar^2(p+n)}.$$

The wave functions of the eigenstates (19) for $r \to 0$ behave as $\sim r^p$. It can be shown that such a power-law dependence for $r \to 0$ arises specifically for the repulsive potential energy term $\sim r^{-2}$ as in Eqs. (12) and (13). Indeed, let us assume that the repulsive potential energy term for small $r \to 0$ exhibits

$$U(r) = \frac{U_K}{r^K}, \quad K > 2.$$

Now the Schrödinger equation for small $r \to 0$ instead of Eq. (14) appears to be

$$r^K \frac{d^2 \psi}{dr^2} + \frac{2\mu U_K}{\hbar^2} \psi = 0.$$

It can be easily checked that the respective solution for small r is

$$\psi(r) = \text{const } e^{-(r/D)^{-s}}, \tag{20}$$

with $s = \frac{K}{2} - 1$. When $r \to 0$ the wave function (20) goes to zero faster than the power-law dependence $r^{n'}$ with an arbitrary large positive integer n', i.e., the slope of the wave function (20) for $r \ll D$ is smaller than for the power-law dependence $r^{n'}$. Such an extremely small amplitude of the wave function in the vicinity of $r = 0$ means that the area $r \ll D$ of the interatomic spacing is completely inaccessible for the molecule.

Next we move on to the calculation of the probability of transition to the excited vibrational states. Suppose that the molecular vibrations were not excited before the arrival of the excitation pulse, meaning that the molecule was in the eigenstate with $n = 0$. Since $L_0^{(2p-1)}(\rho) = 1$, the respective wave function ψ_0 from Eq. (19) is given as

$$\psi_0(r) = \sqrt{\frac{\varepsilon_0}{p\Gamma(2p)}}(2\varepsilon_0 r)^p e^{-\varepsilon_0 r}, \tag{21}$$

with

$$\varepsilon_0 = \frac{2\mu U_0 D}{\hbar^2 p}$$

and the respective energy value

$$E_0 = -\frac{2\mu U_0^2 D^2}{\hbar^2 p^2}.$$

Then, according to Eqs. (8) and (9), the probability of the excitation of the nth vibrational level is given as

$$w_n = |a_n|^2 = \left| \int_0^{+\infty} \psi_n^*(r)\psi_0(r) \exp\left(\frac{i}{\hbar} S_E Q r \cos\theta\right) dr \right|^2, \tag{22}$$

where θ is the angle between the permanent dipole moment of the molecule and the electric field.

Using Eqs. (19) and (21), Eq. (22) yields [46]

$$w_n = [4p(n+p)]^{2p} \frac{\Gamma(n+2p)}{\Gamma(2p)n!}$$
$$\times \frac{4p^4 b^2(n+p)^2[n^2 + b^2 p^2(n+p)^2]^{n-1}}{[(n+2p)^2 + b^2 p^2(n+p)^2]^{n+2p+1}}, \tag{23}$$

where we introduce the parameter

$$b = \frac{\hbar Q S_E \cos\theta}{2\mu U_0 D}. \tag{24}$$

Using Eq. (19) for the wave functions of the eigenstates, we can introduce the following spatial scale d_n corresponding to the spatial extension of the wave function in the nth eigenstate:

$$d_n = \frac{p}{\varepsilon_n} = \frac{\hbar^2 p(p+n)}{2\mu U_0 D}. \tag{25}$$

According to Eq. (23) for the probabilities of the excitation of the vibrational states, the efficiency of the unipolar pulse action on the molecule vibrational motion is determined by the value

$$bp(n+p) = \frac{S_E \cos\theta}{S_0},$$

where we define

$$S_0 = \frac{\hbar}{Q d_n}. \tag{26}$$

Following the notation proposed in [16,47], we call the quantity (26) the molecular scale of the electric pulse area. The molecular scale (26) represents the characteristic measure for the efficiency of the molecule's excitation by unipolar pulses. This means that only unipolar subcycle pulses with electric pulse area comparable to Eq. (26) can noticeably influence the populations of the vibrational levels of a polar molecule.

Let us estimate now the value of the parameter p for an exemplary molecule. The dissociation energy in diatomic molecules typically falls in the range $U_0 = 1$–10 eV and the equilibrium distance between atoms usually equals $D = 1$–2 Å. The reduced oscillator mass μ is mainly provided by the nuclear masses, so we can assume $\mu \sim 10 M_p$ with the proton mass M_p. Taking now, in Eq. (15), $U_0 = 3$ eV, $D = 1$ Å, and $\mu = 10 M_p$, we get $p \approx 120$. So a large value of the power degree indicates extremely slow growth of the wave function in the vicinity of $r = 0$. It should also be concluded that the introduced molecular scale of the electric pulse area (26) is therefore almost constant for all vibrational levels as long as $n \ll p$ and represents the characteristic feature of the molecular system.

It is now more convenient to rewrite Eq. (23) as

$$w_n = \left(\frac{4}{(2 + n/p)^2 + b^2(n+p)^2} \right)^{2p+1} \left(1 + \frac{n}{p} \right)^{2p+2}$$

$$\times \frac{\Gamma(n + 2p)}{\Gamma(2p)n!} \frac{b^2}{b^2(1 + n/p)^2 + n^2/p^4}$$

$$\times \left(\frac{n^2 + b^2 p^2 (n+p)^2}{(n+2p)^2 + b^2 p^2 (n+p)^2} \right)^n. \tag{27}$$

Since we are mainly interested in the lowest excited vibrational levels, we can reliably make an assumption

$$n \ll p. \tag{28}$$

In particular, the condition (28) allows us to reduce in Eq. (27)

$$\Gamma(n + 2p) \approx \Gamma(2p)(2p)^n,$$

$$\left(1 + \frac{n}{p} \right)^{2p+2} \approx \left(1 + \frac{n}{p} \right)^{2p} \approx e^{2n}. \tag{29}$$

Now we can analyze the transition probabilities using Eq. (27) in several limits depending on the value of the rescaled electric pulse area described by the parameter b Eq. (24).

In the limit $b \ll p^{-2}$ and $n \ll p$, we can set the first factor in Eq. (27) equal to unity and use the expressions (29) to turn Eq. (27) into

$$w_n \approx e^{2n} \frac{(2p)^n}{n!} \frac{b^2 p^4}{b^2 p^4 + n^2} \left(\frac{n}{2p} \right)^{2n}$$

$$= \left(\frac{n^2 e^2}{2p} \right)^n \frac{1}{n!} \frac{b^2 p^4}{b^2 p^4 + n^2}. \tag{30}$$

According to Eq. (30), the population of all levels with $n \geqslant 1$ is very small and turns to zero as $b \to 0$, while for the ground state $w_0 \approx 1$.

In the limit $b \sim p^{-1}$ and $n \ll p$, we can set the fourth factor in Eq. (27) equal to unity and it transforms into

$$w_n \approx \left(\frac{4}{4 + b^2 p^2} \right)^{2p+1} e^{2n} \frac{(2p)^n}{n!} \left(\frac{b^2 p^2}{4 + b^2 p^2} \right)^n. \tag{31}$$

In this case the population of the ground state is very small and high-energy levels primarily get populated. We can directly find the level with the largest population by calculating

$$\frac{w_n}{w_{n-1}} = \frac{2p \, e^2}{n} \frac{b^2 p^2}{4 + b^2 p^2}.$$

One can see that the most populated level is

$$n_m = \left[2p \, e^2 \frac{b^2 p^2}{4 + b^2 p^2} \right],$$

where $[\cdots]$ stands for the integer part of the value. This value is by an order of magnitude larger than p, meaning that for unipolar pulses with such a large electric pulse area our complemented Coulomb model predicts the molecule transfer to very high vibrational states. Such a prediction obviously does not meet realistic processes, meaning that our model fails to correctly describe the action of excitation pulses with a large electric pulse area.

Finally, let us focus on the intermediate case, when

$$p^{-2} \lesssim b \lesssim p^{-1}. \tag{32}$$

In this case the molecule is expected to be transferred mainly to the lowest excited states, so our model of the interatomic potential can be expected to provide satisfactory results for the molecule excitation. We investigate this intermediate case by the direct numerical calculation of Eq. (27). We suppose that the molecule is illuminated by a unipolar pulse of the Gaussian electric-field profile

$$E(t) = E_0 e^{-(t/\tau_p)^2}, \tag{33}$$

with the pulse amplitude E_0 and the pulse duration τ_p. The electric pulse area (1) is found to be

$$S_E = \sqrt{\pi} E_0 \tau_p. \tag{34}$$

The parameter values $E_0 = 10^{10}$ V/m, $\mu = 10 M_p$, $U_0 = 3$ eV, $D = 1$ Å, $Q = e$, and $\theta = 0$ are used in the calculations, while the pulse duration τ_p is taken as a variable parameter. Since frequencies of the vibrational transitions in diatomic molecules are typically around several tens of terahertz, the condition (5) requires a pulse duration up to several tens of femtoseconds. Specifically, for the parameter values above Eq. (18) yields, for the main transition frequency, $\omega_{01} = 7.4 \times 10^{13}$ Hz, which gives an oscillation period of 85 fs. Therefore, the unipolar pulse duration τ_p in our calculations has to satisfy the condition $\tau_p \ll 85$ fs.

The numerical results for the populations of the ground and four lowest excited vibrational levels are plotted in Fig. 2. Within the considered range of the pulse duration the product bp changes from zero to around 0.45, so we mostly stay in between the two limiting cases considered above. One can see that as the pulse duration increases the levels' populations shift towards higher states. Already for a pulse duration around 6 fs, the ground state ceases to be the most populated and thus the population inversion can be created. The respective range of values of the electric pulse area in Fig. 2 is

$$0 \leqslant S_E \leqslant 54.3 S_0, \tag{35}$$
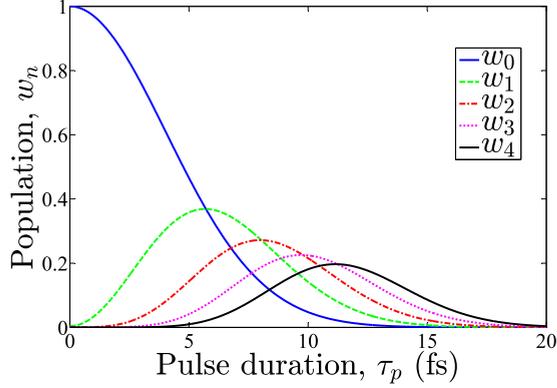
FIG. 2. Probabilities of the vibrational levels excitation for a polar molecule with the potential energy profile provided by the complemented Coulomb potential (13). The parameters are $E_0 = 10^{10}$ V/m, $\mu = 10 M_p$, $U_0 = 3$ eV, $D = 1$ Å, $Q = e$, and $\theta = 0$.

with the characteristic molecular scale S_0 from Eq. (26), so the introduced parameter S_0 acts as a measure of the efficiency of the vibrational levels' excitation by unipolar subcycle pulses.

The complemented Coulomb potential considered in this section allows us to derive a suitable analytical expression for the excitation probabilities of the vibrational levels. However, this model possesses certain restrictions, which limit its applicability. Specifically, the complemented Coulomb potential exhibits an infinite number of eigenstates and thus cannot predict the molecule dissociation under the action of an intense pulse. Instead, we obtain an unrealistic molecule transfer to the vibrational states with very large level indices. These results imply that the complemented Coulomb potential can only be used to describe the excitation of the lowest vibrational states by the subcycle unipolar pulses of a small enough electric pulse area, namely, of the order of the characteristic molecular scale (26). At the same time this potential becomes invalid when it comes to the excitation of higher vibrational levels and the molecule dissociation, so more advanced models are needed. In the next section we examine the Morse potential, which is expected to serve as such a model.

IV. MORSE POTENTIAL

We proceed with an alternative profile of the interaction between atoms in the molecule. For this reason we make use of the Morse potential, which is widely used for the description of real diatomic molecules,

$$U(r) = U_0(e^{-2\alpha(r-D)} - 2e^{-\alpha(r-D)}), \quad (36)$$

where again U_0 is the molecular binding energy, D is the equilibrium distance between the atoms or nuclei, and an additional parameter α controls the slope of the potential-well borders. Two profiles of the potential well given by the Morse potential are plotted in Fig. 1 for two different values of the parameter α.

The Schrödinger equation for the eigenstates yields

$$\frac{d^2\psi}{dr^2} + \frac{2\mu}{\hbar^2}(E - U_0 e^{-2\alpha(r-D)} + 2U_0 e^{-\alpha(r-D)})\psi = 0. \quad (37)$$

As shown in [43], this equation can be put into a convenient form through the change of variables

$$\xi = \frac{2\sqrt{2\mu U_0}}{\alpha\hbar}e^{-\alpha(r-D)}, \quad s = \frac{\sqrt{-2\mu E}}{\alpha\hbar},$$

$$n = \frac{\sqrt{2\mu U_0}}{\alpha\hbar} - \left(s + \frac{1}{2}\right), \quad (38)$$

$$\psi(\xi) = e^{-\xi/2}\xi^s u(\xi), \quad (39)$$

which turns Eq. (37) into the following equation for $u(\xi)$:

$$\xi\frac{d^2u}{d\xi^2} + (2s + 1 - \xi)\frac{du}{d\xi} + nu = 0. \quad (40)$$

For the sake of simplicity, we can assume that the potential energy as $r \to 0$,

$$U(r)|_{r\to 0} = U_0(e^{2\alpha D} - 2e^{\alpha D}),$$

is large enough, although finite, so we get that the new variable ξ changes from almost $+\infty$ to 0 as r runs from 0 to $+\infty$. Equation (40) is basically identical to Eq. (16), so we can conclude that the eigenstates correspond to positive integer values of n. The respective energy levels are

$$E_n = -U_0\left[1 - \frac{\alpha\hbar}{\sqrt{2\mu U_0}}\left(n + \frac{1}{2}\right)\right]^2, \quad n = 0, 1, 2, \dots \quad (41)$$

and the rescaled wave functions of the eigenstates

$$\psi_n(r) = \sqrt{\frac{2\alpha\, s_n n!}{\Gamma(n + 2s_n + 1)}}e^{-\xi/2}\xi^{s_n}L_n^{2s_n}(\xi), \quad (42)$$

with

$$s_n = \frac{\sqrt{2\mu U_0}}{\alpha\hbar} - \left(n + \frac{1}{2}\right). \quad (43)$$

In contrast to the complemented Coulomb potential considered in the preceding section, the Morse potential exhibits only a finite number of energy levels in the discrete spectrum. The total number of levels N is provided by the condition $E_n < 0$, which gives, according to Eq. (41),

$$N = \left[\frac{\sqrt{2\mu U_0}}{\alpha\hbar} - \frac{1}{2}\right] + 1, \quad (44)$$

where the square brackets denote again the integer part and we add 1 to take the ground state with $n = 0$ into account. For example, using the same parameters as in Fig. 2 and $\alpha = 4D^{-1}$, we get $N = 30$.

As in the preceding section, we assume the molecule to be in the ground state with $n = 0$ before the arrival of the excitation pulse and calculate the probability of transition to the excited vibrational levels. The wave function ψ_0 of the ground state from Eq. (42) is given as

$$\psi_0(r) = \sqrt{\frac{2\alpha\, s_0}{\Gamma(2s_0 + 1)}}e^{-\xi/2}\xi^{s_0}, \quad (45)$$

with

$$s_0 = \frac{\sqrt{2\mu U_0}}{\alpha\hbar} - \frac{1}{2}.$$

Now Eq. (22) for the excitation probabilities using the tabulated integral from [46] yields

$$w_n = \frac{2s_n}{n!} \frac{|\Gamma(2s_0 - n - i\gamma)|^2}{\Gamma(2s_0)\Gamma(2s_0 - n + 1)} \left| \frac{\Gamma(1 + i\gamma)}{\Gamma(1 - n + i\gamma)} \right|^2,$$

with the new parameter

$$\gamma = \frac{S_E Q \cos\theta}{\alpha\hbar}. \tag{46}$$

Since

$$|\Gamma(1 + i\gamma)|^2 = \frac{\pi\gamma}{\sinh\pi\gamma},$$

we end up with

$$w_n = \frac{2(s_0 - n)}{n!} \frac{|\Gamma(2s_0 - n - i\gamma)|^2}{\Gamma(2s_0)\Gamma(2s_0 - n + 1)} \\ \times \frac{\pi\gamma}{\sinh\pi\gamma |\Gamma(1 - n + i\gamma)|^2}. \tag{47}$$

In particular, for the population of the ground state with $n = 0$ we get

$$w_0 = \frac{|\Gamma(2s_0 - i\gamma)|^2}{[\Gamma(2s_0)]^2}, \tag{48}$$

while for the first excited state with $n = 1$,

$$w_1 = 2\gamma^2(s_0 - 1)\frac{|\Gamma(2s_0 - 1 - i\gamma)|^2}{[\Gamma(2s_0)]^2}, \tag{49}$$

Finally, for the excited states with $n \geqslant 2$, we can simplify Eq. (47) using the relations

$$|\Gamma(-n + i\gamma)|^2 = \frac{\pi}{\gamma\sinh\pi\gamma}\prod_{k=1}^{n}(k^2 + \gamma^2)^{-1}$$

for positive integer n and

$$|\Gamma(a + ib)|^2 = |\Gamma(a)|^2 \prod_{k=0}^{+\infty} \frac{1}{1 + \frac{b^2}{(a+k)^2}}$$

for the complex-valued argument. Thus Eq. (47) for $n \geqslant 2$ finally reduces to

$$w_n = \frac{2(s_0 - n)}{2s_0 - n} \frac{\Gamma(2s_0 - n)}{\Gamma(2s_0)n!}\gamma^2 \frac{\prod_{k=1}^{n-1}(k^2 + \gamma^2)}{\prod_{k=0}^{+\infty}\left(1 + \frac{\gamma^2}{(2s_0 - n + k)^2}\right)}. \tag{50}$$

Equation (50) yields that if $\gamma \ll \sqrt{2s_0 - n}$, we get

$$w_n \sim \gamma^2(1 + \gamma^2)(4 + \gamma^2)\cdots[(n-1)^2 + \gamma^2].$$

Specifically, in the limit $\gamma \ll 1$, we obtain, for all excited levels, $w_n \sim \gamma^2$. It is of certain interest to find the condition for the creation of the population inversion in the lowest vibrational transition from the ground state $n = 0$ to the first excited state $n = 1$. Using Eqs. (48) and (49) and the basic property of the Gamma function $\Gamma(z + 1) = z\Gamma(z)$, we find

$$\frac{w_1}{w_0} = \frac{2\gamma^2(s_0 - 1)}{\gamma^2 + (2s_0 - 1)^2}.$$

The population inversion therefore arises, as long as the following inequality is obeyed:

$$\gamma \geqslant \frac{2s_0 - 1}{\sqrt{2s_0 - 3}}. \tag{51}$$
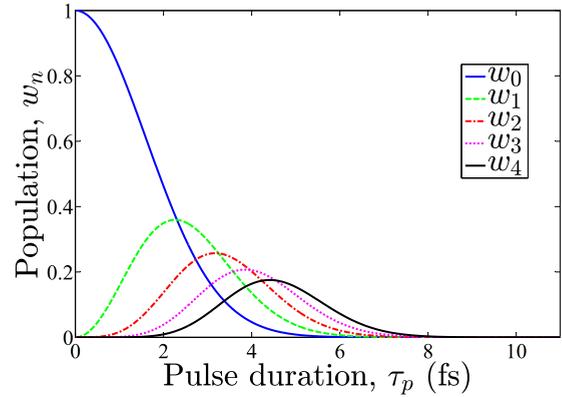
FIG. 3. Probabilities of the vibrational levels excitation for a polar molecule with the potential energy profile provided by the Morse potential (36). The parameters are $E_0 = 5\times10^{10}$ V/m, $\mu = 10M_p$, $U_0 = 3$ eV, $D = 1$ Å, $\alpha = 4D^{-1}$, $Q = e$, and $\theta = 0$.

Similar to Eq. (26), we can introduce the characteristic molecular scale of the electric pulse area as

$$S_0 = \frac{\hbar}{Qd}, \tag{52}$$

with the characteristic spatial size of the Morse potential well $d = \frac{1}{\alpha}$, so that the parameter (49) describing the efficiency of the unipolar pulse action on the oscillating molecule within the Morse potential is given as

$$\gamma = \frac{S_E \cos\theta}{S_0}. \tag{53}$$

Figure 3 shows an example of the vibrational level population calculated using Eq. (47) for the driving unipolar pulse (33) and (34) with the amplitude $E_0 = 5\times10^{10}$ V/m and the same molecule parameters as in Fig. 2 and $\alpha = 4D^{-1}$. The frequency of the lowest transition in this case according to Eq. (41) is $\omega_{01} = 2.9\times10^{14}$ Hz, so the oscillation period is 21.4 fs, which limits the unipolar pulse duration τ_p. For these parameters the condition (51) for the creation of the population inversion in the lowest vibrational transition from the ground state $n = 0$ to the first excited state $n = 1$ yields $\gamma \geqslant 7.76$, corresponding to the unipolar pulse duration $\tau_p \geqslant 2.3$ fs, which indeed can be seen in Fig. 3. In general, the parameter γ from Eqs. (49) and (53) runs in Fig. 3 from zero until 37. The population of the ground state correspondingly decreases from one to zero, while the populations of the excited levels first increase from zero with the pulse duration, then reach a maximum, and eventually decrease again towards zero in favor of higher excited levels.

From a comparison of Figs. 2 and 3, one can see that a longer pulse duration and larger electric pulse area are needed for the excitation of vibrational levels in a polar molecule with the Morse potential profile. This finding seems to be related to the larger value of the energy-level separation within the Morse potential. With decreasing the value of the parameter α and therefore the energy-level separation according to Eq. (41), the maxima of the excited level population in Fig. 3 shift towards smaller pulse durations, thus approaching the curves in Fig. 2 for the complemented Coulomb potential in terms of the electric pulse area.
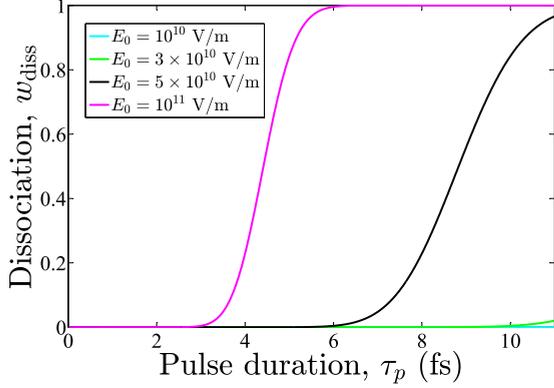
FIG. 4. Dissociation probability of a polar molecule with the potential energy profile provided by the Morse potential (36) vs the pulse duration for several values of the unipolar pulse amplitude E_0. The other parameters are the same as in Fig. 3.

An important advantage of the Morse potential as compared to the complemented Coulomb potential is its ability to describe the molecule dissociation. This property results from the finite number of energy levels in the discrete spectrum. The dissociation probability of a polar molecule can be obtained as

$$w_{\text{diss}} = 1 - \sum_{n=0}^{N-1} w_n, \qquad (54)$$

with the levels' population given by Eq. (47). Figure 4 illustrates the dissociation probability (54) as a function of the unipolar pulse duration for several values of the pulse amplitude E_0, while all other parameters are the same as in Fig. 3. For the pulse amplitude $E_0 = 10^{10}$ V/m the dissociation probability turns out to be negligibly small within the considered range of the electric pulse area, while for $E_0 = 10^{11}$ V/m the dissociation probability approaches 1 already for the pulse duration $\tau_p \approx 6$ fs. These results therefore demonstrate that the molecule's excitation by subcycle unipolar pulses not only can transfer the molecule to higher vibrational levels, but also leads to the molecule dissociation provided the electric pulse area is large enough, namely, with respect to the molecular scale (52).

V. COUPLING OF ROTATIONAL AND VIBRATIONAL MODES

The treatment in the previous sections was solely focused on the vibrational dynamics of a polar molecule while completely neglecting the molecule's rotational motion. However, as Eq. (11) yields, the molecule's wave function after the action of a driving unipolar pulse depends not only on the distance between atoms or nuclei in the molecule, but also on the angle between the molecule's axis and the electric-field direction of the driving pulse, i.e., on the orientation of the molecule. Hence, the interaction of a polar molecule with a unipolar pulse will also result in the excitation of rotational levels. Such excitation was recently studied for a rigid polar molecule in [40] for the case of a fully symmetric rotator. In this section we aim to generalize the findings of the previous

sections and take into account the rotational dynamics as well. Besides that, in contrast to the treatment of a fully symmetric rotator in Ref. [40], we consider a diatomic molecule, which possesses an asymmetry in the parameters of its rotational motion.

The intrinsic Hamiltonian describing the rotation of an arbitrary molecule can be written as

$$\hat{H}_R = \frac{\hbar^2}{2}\left(\frac{\hat{L}_x^2}{I_A} + \frac{\hat{L}_y^2}{I_B} + \frac{\hat{L}_z^2}{I_C}\right), \qquad (55)$$

where I_A, I_B, and I_C are the principal moments of inertia of the molecule and $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ are the operators of the angular momentum about axes in the principal coordinate system. In the general case, when $I_A \neq I_B \neq I_C$, there is no analytical solution for the eigenfunctions of such a three-dimensional rotator. However, for the case of a diatomic molecule it seems natural to assume two principal moments of inertia corresponding to two rotational axes orthogonal to the molecule's intrinsic axis to be equal $I_A = I_B = I_0 \neq I_C$, where I_C is attributed to the rotation about the molecule's axis. Moreover, we can expect $I_C \ll I_0$ due to relatively small transverse spatial extension of diatomic molecules. The rotational Hamiltonian (55) then reduces to the form

$$\hat{H}_R = \frac{\hbar^2}{2I_0}\hat{L}^2 + \frac{\hbar^2}{2}\left(\frac{1}{I_C} - \frac{1}{I_0}\right)\hat{L}_z^2, \qquad (56)$$

where we introduce the operator of the full angular momentum $\hat{L}$. Both operators $\hat{L}^2$ and $\hat{L}_z^2$ possess the same eigen wave functions, which have the form, in spherical coordinates,

$$\psi_{lm}(\theta, \varphi) = (-1)^m \sqrt{\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}} P_l^m(\cos\theta)e^{im\varphi}, \quad (57)$$

where P_l^m are the associated Legendre polynomials. The respective energy eigenvalues E_{lm} are given as

$$E_{lm} = \frac{\hbar^2 l(l+1)}{2I_0} + \frac{\hbar^2}{2}\left(\frac{1}{I_C} - \frac{1}{I_0}\right)m^2,$$
$$l = 0, 1, 2, \dots, \quad |m| \leqslant l. \qquad (58)$$

Equations (56) and (58) are only valid for a rigid rotator. Since we are dealing with molecular vibrations, we have to extend the principal moment of inertia I_0 as

$$I_0 = \mu r^2, \qquad (59)$$

with the interatomic or internuclei distance r. Since $I_C \ll I_0$, much higher energy is required to excite the diatomic molecule's rotation around its axis as compared with two orthogonal directions. Therefore, we can reliably skip the second term in Eq. (56) so that it reduces to

$$\hat{H}_R = \frac{\hbar^2 l(l+1)}{2\mu r^2}. \qquad (60)$$

The obtained term (60) has to be summed with the potential energy of the interatomic interaction in a molecule. Since the term (60) has a power dependence $\sim r^{-2}$, it is especially suitable to examine the coupling of vibrational and rotational modes using the complemented Coulomb potential proposed in Sec. III. According to the definition (13), in this case we

only need to replace the parameters U_0 and D with their modified values $\tilde{U}_0$ and $\tilde{D}$ as

$$\tilde{D} = D\left(1 + \frac{\hbar^2 l(l+1)}{2\mu U_0 D^2}\right),$$

$$\tilde{U}_0 = U_0\left(1 + \frac{\hbar^2 l(l+1)}{2\mu U_0 D^2}\right)^{-1}. \quad (61)$$

In fact, for the parameters from Fig. 2 and $l = 1$ the second term in large parentheses in Eq. (61) equals 1.39×10^{-4}, so the difference between U_0 and D and between $\tilde{U}_0$ and $\tilde{D}$ is negligible.

According to Eq. (11), the wave function after the pulse passage when skipping the electronic factor can be written as

$$\psi(r, \theta, \varphi, t_0 + \tau_p) = \psi(r, \theta, \varphi, t_0)\exp\left(\frac{i}{\hbar}QS_E r\cos\theta\right), \quad (62)$$

where the polar angle θ is measured from the direction of the electric field. Since the obtained term (60) is identical to the rotational Hamiltonian of a symmetric rotator, we can make use of the eigenfunctions (57), but assuming the fixed-in-space coordinate system instead of the molecule's principal coordinate system. Specifically, we fix the polar axis of our spherical coordinate system along the direction of the driving electric field, so the polar angle θ is measured from this direction. Now for the expansion coefficients a_{nlm} with index n denoting the vibrational levels and indices l and m standing for the rotational states, we find from Eq. (8)

$$a_{nlm} = \int_0^{+\infty} dr \int_{-\pi}^{\pi} d\varphi \int_0^{\pi} [\psi_n^V(r)]^*[\psi_{lm}^R(\theta, \varphi)]^*$$

$$\times \psi(r, \theta, \varphi, t_0)\exp\left(\frac{i}{\hbar}QS_E r\cos\theta\right)\sin\theta\, d\theta. \quad (63)$$

It seems appropriate to calculate first the angular part of the expression (63). Let us for definiteness suppose that the molecule was in a certain rotational state before the excitation with the indices m_0 and l_0. It could be easily seen from Eq. (63) that only rotational modes with $\Delta m = 0$ can be excited. Now the angular integration part of Eq. (63) reduces to

$$C_{lm} = \int_{-\pi}^{\pi} d\varphi \int_0^{\pi} [\psi_{lm}^R(\theta, \varphi)]^*\psi(r, \theta, \varphi, t_0)$$

$$\times \exp\left(\frac{i}{\hbar}QS_E r\cos\theta\right)\sin\theta\, d\theta = \frac{\sqrt{(2l_0+1)(2l+1)}}{2}$$

$$\times \delta_{m_0 m}\int_{-1}^{1} P_l^m(x)\exp\left(\frac{i}{\hbar}QS_E rx\right)P_{l_0}^{m_0}(x)dx, \quad (64)$$

with the variable $x = \cos\theta$. The coefficients C_{lm} from Eq. (64) provide the probabilities of the excitation of the respective rotational states: $w_{lm} = |C_{lm}|^2$. The integral in Eq. (64) cannot be calculated analytically for the general case of an arbitrary l; thus we explicitly solve it for several lowest values of l. Specifically, if the molecule was initially in the ground state, i.e., $m_0 = 0$ and $l_0 = 0$, for the lowest rotational levels we

obtain [40]

$$C_{00} = \sin\left(\frac{QS_E r}{\hbar}\right)\left(\frac{QS_E r}{\hbar}\right)^{-1},$$

$$C_{10} = i\sin\left(\frac{QS_E r}{\hbar}\right)\left(\frac{QS_E r}{\hbar}\right)^{-2} - i\cos\left(\frac{QS_E r}{\hbar}\right)\left(\frac{QS_E r}{\hbar}\right)^{-1}. \quad (65)$$

As the electric pulse area increases, the populations of the rotational states shift towards higher levels [40]. It seems interesting to consider the rotational motion of a rigid rotator with the permanent dipole moment $p_0 = Qr$ in the limit $\hbar \ll S_E p_0$, which would correspond to the transition of the quantum-mechanical treatment in classical mechanics for our problem [43]. Based on the findings in Ref. [40], we can estimate that the levels with the orbital quantum numbers $l \sim \frac{S_E p_0}{\hbar}$ will be mainly excited and have the largest populations w_{lm}. Therefore, the overall energy of the rotational motion is estimated as

$$E = \sum_{l=0}^{l=+\infty} \frac{\hbar^2 l(l+1)}{2I_0}w_{lm} \sim \frac{(S_E p_0)^2}{I_0},$$

i.e., closely matches the continuous spectrum of the rotational energy values of a classical rotator, since the classical rotator would gain the angular momentum $S_E p_0$ under a subcycle pulse action.

Using Eqs. (65), we can now find the probability of transition to the vibrational levels from Eq. (63). In order to get the results in a convenient analytical form, we proceed here with the complemented Coulomb potential for the description of the vibrational motion. Therefore, the required transition probabilities are calculated by substituting the wave functions of the eigenstates (19) into Eq. (63), with the angular integration part given by Eqs. (65) and keeping in mind the relations (61). Specifically, for the ground rotational state with $m = 0$ and $l = 0$ using the first expression in Eq. (65) we get [46]

$$w_{n00} = |a_{n00}|^2 = \frac{\varepsilon_0 \varepsilon_n}{p(n+p)}\frac{\Gamma(n+2p)}{\Gamma(2p)n!}\left(\frac{\varepsilon_0}{\varepsilon_n}\right)^{2p}$$

$$\times \left(\frac{1}{2\beta_n\varepsilon_n}\right)^2 \text{Im}^2\left[\frac{(-1/2 + \varepsilon_0/2\varepsilon_n - i\beta_n)^n}{(1/2 + \varepsilon_0/2\varepsilon_n - i\beta_n)^{n+2p}}\right], \quad (66)$$

with

$$\beta_n = \frac{QS_E}{2\hbar\varepsilon_n} \quad (67)$$

and the imaginary part of the value Im. For the ground vibrational state $n = 0$ we get the simple expression

$$w_{000} = \left(\frac{1}{2p\beta_0}\right)^2 \text{Im}^2[(1 - i\beta_0)^{-2p}]. \quad (68)$$

We can easily check that the molecular scale (26) stays valid in the case of coupling with the rotational modes. Indeed, it can be inferred from Eqs. (66)–(68) that the outcome of the unipolar pulse action on the molecule is mainly determined by the product

$$p\beta_n = \frac{\hbar QS_E p(p+n)}{4\mu U_0 D} = \frac{S_E}{2S_0},$$

so the molecular scale (26) appears again.
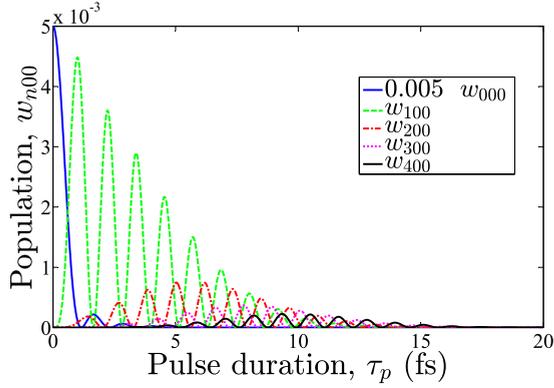
FIG. 5. Probabilities of the transition of a polar molecule to different vibrational levels n while staying in the ground rotational state with $m = 0$ and $l = 0$ upon a unipolar pulse action. The potential energy profile of the molecule is given by the complemented Coulomb potential (13). The other parameters are the same as in Fig. 2.

The transition probabilities obtained with Eq. (66) are plotted in Fig. 5 for the same parameters of the complemented Coulomb potential as used in Fig. 2. A few significant differences are worth addressing in Fig. 5 in comparison to Fig. 2. First, the dependence of the probability of transition to the vibrational states on the electric pulse area in Fig. 5 becomes oscillating, instead of the smooth curves in Fig. 2. At the same time the location of the maximum of the population for each specific vibrational level shifts towards a smaller electric area from Fig. 2 to Fig. 5. Second, in the considered range of the electric pulse areas the populations of the vibrational levels in Fig. 5 are at least for an order of magnitude smaller. This follows from the low population of the ground rotational state $m = 0$ and $l = 0$. Indeed, as it was shown in Ref. [40], the population inversion between the ground rotational state and the first excited one arises for the electric pulse area $\frac{S_E}{S_R} \sim 1$–2, where we define the characteristic scale of the electric pulse area for the rotational motion

$$S_R = \frac{\hbar}{p_0}, \qquad (69)$$

with the permanent dipole moment of the polar molecule p_0. In our case we have $p_0 = QD$. We can easily check that in Eq. (14) $d_n \approx D$ for $n \ll p$, so the characteristic molecular scales of the electric pulse area for the vibrational motion (26) and for the rotational motion (69) are very close to each other. At the same time, as Fig. 2 yields, the population inversion between the ground vibrational state and the first excited one arises for the electric pulse area:

$$\frac{S_E}{S_0} \sim 15\text{–}16. \qquad (70)$$

Therefore, the molecular rotational states get populated much faster with the electric pulse area, and for the electric pulse areas (70) needed to excite the lowest vibrational states, we already get the high rotational levels excited.

In a similar way we can find the probability of transition to the lowest excited rotational states. So, for the first excited rotational state with $m = 0$ and $l = 1$, using the second
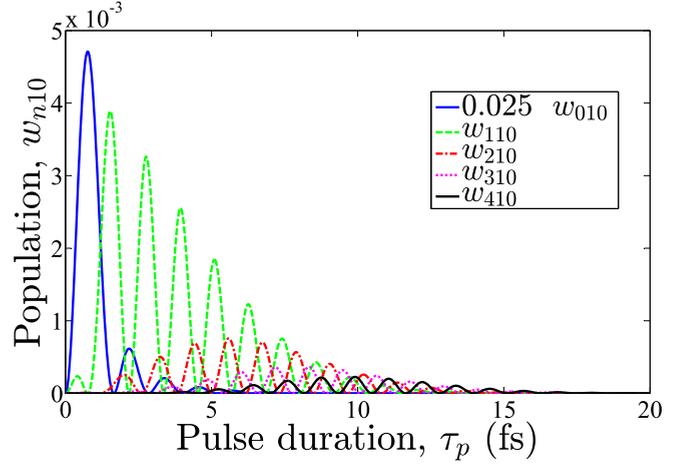
FIG. 6. Probabilities of the transition of a polar molecule to different vibrational levels n for the fixed excited rotational state with $m = 0$ and $l = 1$ upon a unipolar pulse action. The potential energy profile of the molecule is given by the complemented Coulomb potential (13). The other parameters are the same as in Fig. 2.

expression in (65) we obtain

$$
\begin{aligned}
a_{n10} = {}& \sqrt{\frac{\varepsilon_0 \varepsilon_n}{p(n+p)} \frac{\Gamma(n+2p)}{\Gamma(2p)n!}} \left(\frac{\varepsilon_0}{\varepsilon_n}\right)^p \frac{i}{2\beta_n \varepsilon_n} \\
& \times \left\{ -\mathrm{Re}\left[\frac{(-1/2 + \varepsilon_0/2\varepsilon_n - i\beta_n)^n}{(1/2 + \varepsilon_0/2\varepsilon_n - i\beta_n)^{n+2p}} \right] + \frac{n!}{\beta_n(2p-1)} \right. \\
& \times \frac{\Gamma(2p)}{\Gamma(2p+n)} \mathrm{Im}\left[\frac{1}{(1/2 + \varepsilon_0/2\varepsilon_n - i\beta_n)^{2p-1}} \right. \\
& \left. \left. \times P_n^{(2p-1,-1-n)}\left(1 - \frac{2}{1/2 + \varepsilon_0/2\varepsilon_n - i\beta_n} \right) \right] \right\}, \quad (71)
\end{aligned}
$$

where $P_n^{(\alpha,\beta)}(x)$ are Jacobi polynomials and Re stands for the real part of the value. In particular, for the ground vibrational state $n = 0$, Eq. (71) simplifies to

$$
\begin{aligned}
a_{010} = {}& \frac{i}{2p\beta_0} \left(-\mathrm{Re}[(1 - i\beta_0)^{-2p}] \right. \\
& \left. + \frac{1}{\beta_0(2p-1)} \mathrm{Im}[(1 - i\beta_0)^{-2p+1}] \right).
\end{aligned}
$$

Figure 6 shows the transition probabilities obtained with Eq. (71) for the same parameters of the complemented Coulomb potential as in Figs. 2 and 5. The observed behavior of the levels' populations vs the electric pulse area in Fig. 6 appears to be very similar to Fig. 5. The excitation probabilities for all considered vibrational levels stay well below 1%, which indicates again that high rotational states are mainly excited. At the same time the excited vibrational levels get sequentially populated as the electric pulse area increases, which confirms the main findings of the previous sections.

VI. CONCLUSION

The possibility of the efficient nonresonant excitation of the vibrational levels in polar molecules was demonstrated upon their interaction with subcycle unipolar pulses. Our

treatment was performed using an approximate analytical solution of the time-dependent Schrödinger equation in the limit when the duration of the excitation pulse is much smaller than the characteristic transition periods in a molecule. Despite the ultrabroad spectrum of unipolar subcycle pulses, it was shown that they enable an ultrafast transfer of polar molecules to the higher vibrational levels. Of crucial importance in this process is the nonzero value of the electric pulse area, which was shown to fully determine the efficiency of the excitation for all vibrational states.

These findings stand in marked contrast to other approaches for the optical control of the rovibrational states in molecules. Indeed, known control strategies make use of long multicycle bipolar pulses, e.g., chirped pulses or π pulses [48]. However, as we have demonstrated, in the limit of subcycle excitation pulses, bipolar pulses are no more efficient due to their zero electric pulse area. Therefore, unipolar pulses should be used when it comes to the control of the molecules' dynamics by pulses of the duration of tens of femtoseconds or shorter. Another important advantage of unipolar pulses for the molecules' excitation, which directly follows from our treatment, is their universal applicability. This means that one generally does not need to adjust unipolar pulse parameters when exciting different polar molecules with different transition frequencies. Indeed, the pulse action on each molecule is fully determined by the electric pulse area. At the same time, other control strategies using bipolar pulses require, for example, adjusting the pulse carrier frequency to the resonant frequency of each specific molecule.

Our results were obtained for several models of the interatomic interaction in a diatomic molecule. First, we considered the simplest model of the Coulomb attractive potential complemented with an extra power term $\sim r^{-2}$ for the repulsive potential. Such a model allows for a particularly suitable

analytical treatment and yields convenient analytical expressions for the excitation probabilities of the vibrational levels but fails to describe the dissociation of molecules. Second, we studied a more advanced Morse potential, which can also be treated analytically, though in a less convenient form, but is able to predict the molecule dissociation for a large enough electric pulse area of the driving pulse. These results were shown to persist when the rotational states are taken into account as well, even though rotational levels get rapidly excited for smaller values of the electric pulse area. Hence, our findings clearly show that subcycle unipolar pulses can provide ultrafast all-optical control of the molecular systems.

For both considered models we have managed to introduce the characteristic measure of the electric pulse area, which we call the molecular scale of the electric pulse area. This quantity was shown to depend solely on the spatial size of the range of the interatomic separation values in the molecule's vibrational states. The introduced quantity determines the efficiency of the unipolar subcycle pulse action on the vibrational motion of a polar molecule. To excite the vibrational states one therefore needs a driving pulse with the electric pulse area comparable to or larger than this molecular scale.

We have also demonstrated the possibility of selective excitation of vibrational states through controlling the value of the electric pulse area of the excitation pulse. The most interesting consequence of this finding worth mentioning is the possibility of creating the population inversion and thus lasing on the vibrational transitions in polar molecules pumped by unipolar pulses.

[1] T. Brabec and F. Krausz, Rev. Mod. Phys. **72**, 545 (2000).

[2] F. Krausz and M. Ivanov, Rev. Mod. Phys. **81**, 163 (2009).

[3] U. Keller, Appl. Phys. B **100**, 15 (2010).

[4] F. Calegari, G. Sansone, S. Stagira, C. Vozzi, and M. Nisoli, J. Phys. B **49**, 062001 (2016).

[5] R. M. Arkhipov, A. V. Pakhomov, M. V. Arkhipov, I. Babushkin, Y. A. Tolmachev, and N. N. Rosanov, JETP Lett. **105**, 408 (2017).

[6] R. M. Arkhipov, M. V. Arkhipov, and N. N. Rosanov, Quantum Electron. **50**, 801 (2020).

[7] R. Arkhipov, M. Arkhipov, A. Pakhomov, I. Babushkin, and N. Rosanov, Laser Phys. Lett. **19**, 043001 (2022).

[8] N. Rosanov, Opt. Spectrosc. **107**, 721 (2009).

[9] N. N. Rosanov, R. M. Arkhipov, and M. V. Arkhipov, Phys. Usp. **61**, 1227 (2018).

[10] K. Ramasesha, S. R. Leone, and D. M. Neumark, Annu. Rev. Phys. Chem. **67**, 41 (2016).

[11] A. Wetzels, A. Gürtler, L. D. Noordam, F. Robicheaux, C. Dinu, H. G. Muller, M. J. J. Vrakking, and W. J. van der Zande, Phys. Rev. Lett. **89**, 273003 (2002).

[12] M. T. Hassan, T. T. Luu, A. Moulet, O. Raskazovskaya, P. Zhokhov, M. Garg, N. Karpowicz, A. M. Zheltikov, V. Pervak,

F. Krausz, and E. Goulielmakis, Nature (London) **530**, 66 (2016).

[13] X. Chai, X. Ropagnol, S. M. Raeis-Zadeh, M. Reid, S. Safavi-Naeini, and T. Ozaki, Phys. Rev. Lett. **121**, 143901 (2018).

[14] N. Rosanov and N. Vysotina, J. Exp. Theor. Phys. **130**, 52 (2020).

[15] R. M. Arkhipov, A. V. Pakhomov, M. V. Arkhipov, I. Babushkin, A. Demircan, U. Morgner, and N. N. Rosanov, Opt. Lett. **44**, 1202 (2019).

[16] N. Rosanov, D. Tumakov, M. Arkhipov, and R. Arkhipov, Phys. Rev. A **104**, 063101 (2021).

[17] R. Arkhipov, A. Pakhomov, M. Arkhipov, A. Demircan, U. Morgner, N. Rosanov, and I. Babushkin, Opt. Express **28**, 17020 (2020).

[18] R. M. Arkhipov, M. V. Arkhipov, A. A. Shimko, A. V. Pakhomov, and N. N. Rosanov, JETP Lett. **110**, 15 (2019).

[19] H. Leblond and D. Mihalache, Phys. Rep. **523**, 61 (2013).

[20] E. S. Efimenko, S. A. Sychugin, M. V. Tsarev, and M. I. Bakunov, Phys. Rev. A **98**, 013842 (2018).

[21] M. V. Tsarev and M. I. Bakunov, Opt. Express **27**, 5154 (2019).

[22] H.-C. Wu and J. Meyer-ter-Vehn, Nat. Photon. **6**, 304 (2012).

[23] J. Xu, B. Shen, X. Zhang, Y. Shi, L. Ji, L. Zhang, T. Xu, W. Wang, X. Zhao, and Z. Xu, Sci. Rep. **8**, 2669 (2018).

[24] A. V. Pakhomov, R. M. Arkhipov, I. V. Babushkin, M. V. Arkhipov, Y. A. Tolmachev, and N. N. Rosanov, Phys. Rev. A **95**, 013804 (2017).

[25] A. V. Pakhomov, R. M. Arkhipov, M. V. Arkhipov, A. Demircan, U. Morgner, N. N. Rosanov, and I. V. Babushkin, Sci. Rep. **9**, 7444 (2019).

[26] M. V. Arkhipov, R. M. Arkhipov, A. V. Pakhomov, I. V. Babushkin, A. Demircan, U. Morgner, and N. N. Rosanov, Opt. Lett. **42**, 2189 (2017).

[27] V. P. Kalosha and J. Herrmann, Phys. Rev. Lett. **83**, 544 (1999).

[28] A. Parkhomenko and S. Sazonov, J. Exp. Theor. Phys. **87**, 864 (1998).

[29] X. Song, W. Yang, Z. Zeng, R. Li, and Z. Xu, Phys. Rev. A **82**, 053821 (2010).

[30] V. V. Kozlov, N. N. Rosanov, C. De Angelis, and S. Wabnitz, Phys. Rev. A **84**, 023818 (2011).

[31] S. Sazonov, JETP Lett. **114**, 132 (2021).

[32] S. Sazonov, Laser Phys. Lett. **18**, 105401 (2021).

[33] Y. Shou, R. Hu, Z. Gong, J. Yu, J.-E. Chen, G. Mourou, X. Yan, and W. Ma, New J. Phys. **23**, 053003 (2021).

[34] A. V. Bogatskaya, E. A. Volkova, and A. M. Popov, Phys. Rev. E **104**, 025202 (2021).

[35] N. N. Rosanov, Opt. Spectrosc. **127**, 1050 (2019).

[36] M. V. Arkhipov, A. N. Tsypkin, M. O. Zhukova, A. O. Ismagilov, A. V. Pakhomov, N. N. Rosanov, and R. M. Arkhipov, JETP Lett. **115**, 1 (2022).

[37] C. Dion, A. Keller, and O. Atabek, Eur. Phys. J. D **14**, 249 (2001).

[38] A. Matos-Abiague and J. Berakdar, Phys. Rev. A **68**, 063411 (2003).

[39] D. Sugny, A. Keller, O. Atabek, D. Daems, C. M. Dion, S. Guérin, and H. R. Jauslin, Phys. Rev. A **69**, 033402 (2004).

[40] R. M. Arkhipov, A. V. Pakhomov, M. V. Arkhipov, and N. N. Rosanov, Laser Phys. Lett. **17**, 105301 (2020).

[41] E. M. Belenov, V. A. Isakov, and A. V. Nazarkin, Quantum Electron. **23**, 911 (1993).

[42] J. T. Lin, S. H. Lin, and T. F. Jiang, Phys. Rev. A **61**, 033407 (2000).

[43] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Oxford, 1974).

[44] A. Migdal, Zh. Eksp. Teor. Fiz. **9**, 1163 (1939).

[45] N. N. Rosanov, Opt. Spectrosc. **124**, 72 (2018).

[46] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic Press, New York, 1965).

[47] R. M. Arkhipov, M. V. Arkhipov, A. V. Pakhomov, and N. N. Rosanov, JETP Lett. **114**, 129 (2021).

[48] A. Devolder, M. Desouter-Lecomte, O. Atabek, E. Luc-Koenig, and O. Dulieu, Phys. Rev. A **103**, 033301 (2021).