

Carrier-envelope phase dependence of high-order harmonic spectra generated in non-resonant interaction of dipolar molecule system with ultrashort laser pulse

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The initial carrier-envelope phase dependence of dynamic process for an ultrashort laser pulse propagating non-resonantly in para-nitroaniline (pNA) molecule medium is investigated theoretically, by solving the full Maxwell-Bloch equations. The results show that when the laser pulse propagates with carrier frequency equal to the half of exciting frequency for the molecule's charge-transfer state, the laser pulse is modulated severely and the population distribution exceeds 1/2 because the two-photon absorption is a resonant process for the interaction of the laser pulse and the dipolar molecule medium. Higher and lower frequencies than carrier frequency occur in the spectrum and even high-order harmonic components approaching to 7th harmonic are produced, forming a continuous spectrum. The sensitivities of the carrier wave reshaping, the high-order harmonic spectrum and the temporal evolution of excited state population to the initial carrier-envelope phase are discussed in detail. It is found that for given pulse width, the phase dependence increases as the laser field grows intense; while for given laser intensity, it decreases when the pulse width becomes narrow. Due to the extra nonlinear effects introduced by the permanent dipole moments of the pNA molecule, the phase sensitivity in this molecule medium is more distinct than in the medium composed of pseudo-molecules without permanent dipole moments.

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The research of the laser-matter interaction has been taken into a microscopic and ultrafast regime, accompanying by the generation of few-cycle pulses from Ti: sapphire lasers by means of combining self-phase modulation with negative group velocity dispersion^[1]. Due to the short duration, laser pulses with low energy can have extremely intense peak power, high time resolution, broad spectrum bandwidth, and other excellent properties for application. It is known that an optical pulse can be described as an envelope superimposed on a serial of carrier waves. Although it is often ignored, there exists a relative phase shift between the peak of the envelope and maximum of the carrier, which is called carrier-envelope phase (CEP)^[2,3]. Especially for the pulses containing only a few cycles, the envelope amplitude and carrier frequency are not sufficient to characterize and control the laser radiation because the evolution of the light field is also influenced by CEP^[4]. Since the intense laser-matter interactions generally depend on the electric field, the CEP demonstrates its important role in a large number of nonlinear processes, e.g., atomic ionization^[5], populations on final energy state^[6], high-order harmonic and attosecond pulse generation^[7-9]. It is reported that CEP effects disappear completely as the pulse duration exceeding 8 fs in the experimental measurements^[10].

With good properties such as wide optical response band, good flexibility, high optical damage threshold, low cost, and easy combination or modification, numerous organic molecules have been designed and synthesized in different laboratories. Compared with inorganic molecule materials, the most outstanding virtue of organic molecule materials is that one can design their structures at molecule level for the purpose of attaining optimum optical response and other particular proper-

ties. The theoretical computations indicate that most of organic molecules have only one charge-transfer state in lower energy region from ultraviolet radiation to visible light^[11,12], and consequently one can take this kind of molecule as a two-level system in low energy range when investigating the interaction of the molecule medium with laser pulses. As a typical one-dimensional (1D) push-pull π -conjugated molecule, para-nitroaniline (pNA) receives much attention for its strong nonlinear optical response^[13-15]. It should be noticed that pNA is a dipolar molecule, which means a non-zero difference $\Delta\mu$ exists between the diagonal dipole matrix element (permanent dipole moments) of the initial state and that of the final state involved in the excited transition. The role of permanent dipoles is very significant for two-photon transitions, because the modified selection rule with $\Delta\mu \neq 0$ allows simultaneous two-photon excitation (a process forbidden for a two-level system if $\Delta\mu = 0$) to occur^[16,17].

In this letter, by solving the full Maxwell-Bloch equations, we investigate the phase dependence of dynamic behaviors for an ultrashort laser off-resonantly propagating in pNA molecule medium. These dynamic behaviors include the carrier wave reshaping, the population of the excited state and the generated spectrum for various laser intensities and pulse widths. The effect of permanent dipoles of pNA molecule on the phase sensitivity is illustrated by comparing with the dynamic process in the "fabricated" pseudo-pNA molecule medium without permanent dipoles.

The semi-classical theory is applied here for treating the laser and medium interaction dynamics. That is to say, the laser field is considered as a classical electromagnetic field with definite amplitude and phase, and

can be described by Maxwell equations; while the pNA molecule medium is considered as a quantum system and described by Bloch equations. It is assumed that a few-cycle laser pulse propagates along the z axis from vacuum into an interface of a two-level medium at $z=0$. The electronic field E_x of the pulse is set to be polarized along the x axis and its magnetic field H_y polarized along the y axis. In this manner, the Maxwell equations take form as

$$\frac{\partial E_x}{\partial z} = -\mu_0 \frac{\partial H_y}{\partial t}, \quad (1)$$

$$\frac{\partial H_y}{\partial z} = -\frac{\partial P_x}{\partial t} - \varepsilon_0 \frac{\partial E_x}{\partial t}, \quad (2)$$

where ε_0 and μ_0 are the permeability and permittivity in vacuum, respectively. For the two-level system used here, the definition of the macroscopic nonlinear polarization P_x is

$$P_x = N(\mu_{x11}\rho_{11} + \mu_{x22}\rho_{22} + \mu_{x12}\rho_{21} + \mu_{x21}\rho_{12}), \quad (3)$$

where N is the molecular density of the medium, μ_{x11} and μ_{x22} are the diagonal dipole matrix elements (along the electronic field direction) of the ground and excited states, $\mu_{x12}(=\mu_{x21}=\mu)$ is the transition dipole moments between the two states, and $\rho_{ij}(i, j = 1, 2)$ is the density matrix elements equal to the population in the states.

For convenience, some denotations are introduced with the relations as follows. $\Delta\mu$ equals the difference of permanent dipole moments between the excited and ground states, i.e., $\Delta\mu = \mu_{22} - \mu_{11}$, d is the population difference between the two states $d = \rho_{22} - \rho_{11}$, and $u = \rho_{12} + \rho_{21}$, $v = i(\rho_{21} - \rho_{12})$. Therefore, the reduced expression from Bloch equations for the two-level medium can be written as

$$\frac{\partial u}{\partial t} = -\gamma_{12}u - \omega_0 v + \frac{\Delta\mu}{\hbar} E_x v, \quad (4)$$

$$\frac{\partial v}{\partial t} = -\gamma_{21}v + \omega_0 u + 2\frac{\mu E}{\hbar} d - \frac{\Delta\mu}{\hbar} E_x u, \quad (5)$$

$$\frac{\partial d}{\partial t} = -\gamma_{22}(d+1) - 2\frac{\mu E_x}{\hbar} v, \quad (6)$$

where ω_0 is the exciting frequency between the two states, γ_{22} and γ_{12} (γ_{21}) are the population and polarization relaxation constants, respectively.

The electronic structures and dipole moments of para-nitroaniline (pNA) molecule have been calculated by use of density functional theory at ab initio level^[18]. The results shows that in lower energy region, the molecule has only one charge-transfer (CT) state, i.e., the transition dipole moment is very large between the CT state and the ground state. It is well known that the CT state of a molecule determines its optical property, so that pNA molecule can be taken as a two-level system in low energy range when interacting with a laser pulse. The calculated molecular parameters are $\omega_0=5.85\times 10^{15}$ Hz, $\mu=1.621\times 10^{-29}$ C·m, and $\Delta\mu=1.728\times 10^{-29}$ C·m. Material parameters of the molecules in the medium are chosen as $N=7.0\times 10^{25}/\text{m}^3$, $\gamma_{12}=1.0\times 10^{12}/\text{s}$, and $\gamma_{22}=1.0\times 10^{12}/\text{s}$ ^[19], and all the molecules are supposed

to be at the ground state at the initial time. Besides, the electric field strength of the input laser pulse is determined as a hyperbolic-secant shape:

$$E_x(z, t = 0) = F \operatorname{sech} [1.76(z/c + z_0/c)/\tau_p] \cos [\omega_p(z/c + z_0/c) + \varphi], \quad (7)$$

where F is the field amplitude, τ_p is the full-width at half-maximum (FWHM) of the pulse envelope, ω_p is the carrier frequency, and φ is the CEP. The choice of z_0 ensures that the pulse penetrates negligibly into the medium at $t=0$. The coupled Maxwell-Bloch equations can be solved by using a standard finite-difference time-domain approach for the full-wave Maxwell equations, and predictor-corrector method for the Bloch equations^[20].

Here we consider the off-resonant propagation process of an ultrashort pulse laser in the pNA molecule medium. In this case, the laser carrier frequency ω_p is chosen as half of exciting frequency ω_0 of the molecule's charge-transfer state. In order to investigate the effects of pNA molecule's permanent dipoles on the interaction dynamics, we "fabricate" a pseudo-pNA molecule without permanent dipoles^[18,21]. Except for this parameter $\Delta\mu=0$, other parameters of the pseudo-molecule is the same as those of pNA molecule.

The temporal evolutions of carrier waves at a certain propagation distance for different laser field strengths and different carrier-envelope phases are presented in Fig. 1. For the resonant case discussed in Refs. [18,21], the area theorem can still approximately predict the evolution profile of the few-cycle pulse area, i.e., the $2n\pi$ (n is an integer) pulse split up into $n\times 2\pi$ pulses as propagating further in the medium. However, the area theorem cannot describe the laser evolution in the non-resonant case studied here. For example, the 4π pulse (with $F=2.290\times 10^{10}$ V/m and $\tau_p=2$ fs, according to the definition of pulse area in resonant propagation

as $\Omega(z) = \frac{\mu}{\hbar} \int_{-\infty}^{+\infty} E_0(z, t') dt' = \frac{\mu F \tau_p \pi}{1.76\hbar}$ ^[22]) in Fig. 1(b) dose

not split up, only being modulated severely. It is because that a strong pulse laser propagating in a medium may make the refractive index of the medium vary with the laser intensity, and the medium echoes to inflict a phase modification (SPM) on the pulse, resulting in the carrier field reshaped sharply.

The Rabi-Flopping for the population distribution of the molecules is still closely connected with the carrier oscillations (see Fig. 2). Compared with the resonant case in Ref. [18], there are two different features occurring in the non-resonant case. Firstly, the laser field cannot invert the populations in the two state levels completely. As illustrated in Fig. 2(a), the population difference is below -0.7 under the excitation of weaker 2π laser field. Only for more intense laser field such as 6π pulse, the population difference can exceed 0.5. Secondly, the population profile rises and falls more evidently, but the flattening of the population profile where

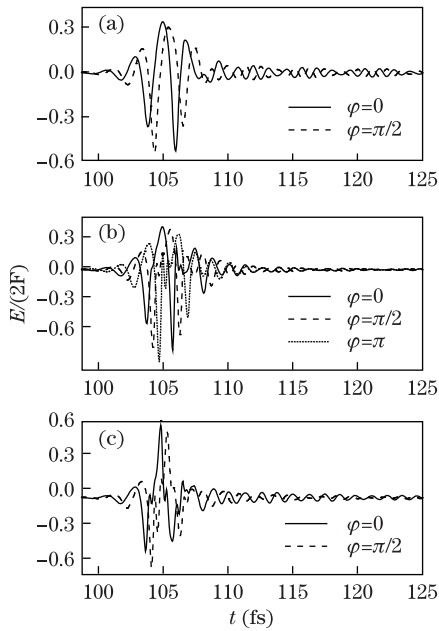


Fig. 1. Pulse carrier in pNA molecule medium at the propagation distances $z=26.4 \mu\text{m}$. The field parameters are $\tau_p=2 \text{ fs}$, $\omega_p=\omega_0/2=2.925 \times 10^{15} \text{ Hz}$. (a) $F=1.145 \times 10^{10} \text{ V/m}$, (b) $F=2.290 \times 10^{10} \text{ V/m}$, and (c) $F=3.436 \times 10^{10} \text{ V/m}$; with $\varphi=0$ (—), $\varphi=\pi/2$ (---), $\varphi=\pi$ (···).

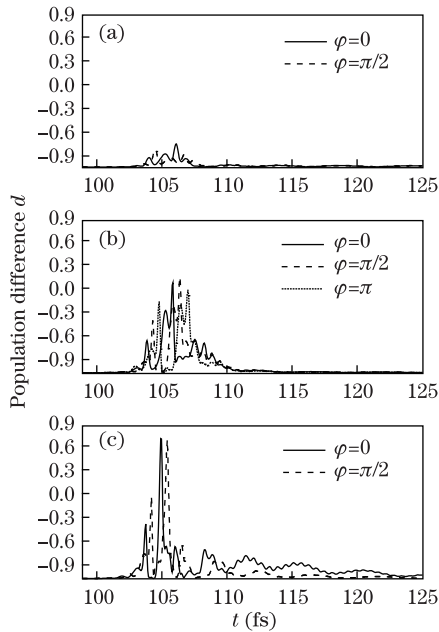


Fig. 2. Population difference in pNA molecule medium at $z=26.4 \mu\text{m}$. The field parameters are as in Fig. 1.

the time-derivative of the electric field is maximized at the null-field points disappears.

We can see from Fig. 3 that higher and lower frequencies than the carrier frequency occur in the spectrum. Upon increasing the laser intensity, the power of high-order harmonic components increases and the harmonics range broadens, forming a continuous spectrum. Harmonic components approaches to 7th order are visible at the higher laser intensities. It can be explained as follows. The intense laser has more energy to excite the molecule from the ground state to the charge-transfer state, so

that the probability of population inversion increase and it oscillates faster, resulting to the laser carrier be reshaped more sharply. In this way more complex spectral components are produced. Apart from the fundamental frequency, the frequency component around $2\omega_p$ is pronounced among the spectrum and displays an oscillatory feature even if the field strength is weaker, as shown in Fig. 3(a-i) and (a-ii). The frequency $2\omega_p$ corresponds to the resonant frequency for the two-level molecule, and it is mainly generated from the two-photon resonant transition which is allowed for the pNA molecule with the permanent dipoles by the selection rules^[16]. Its ground and excited states have no definite symmetry, so that not only the one-photon but also two-photon transition appears between two states of the dipolar molecule ($\Delta\mu \neq 0$), which contributes to the frequency component $2\omega_p$. In addition, the second-order nonlinear polarizability of the pNA molecule is not zero^[13], so the second-harmonic generation (SHG) process contributes to the $2\omega_p$ generation, too. From this point of view, the distinct $2\omega_p$ component in the spectrum indicates the preferable two-photon absorption properties of the pNA molecule.

It is indicated that the largest variation of the pulse energy appears when CEP φ is equal to zero and $\pi/2$ ^[23]. Therefore, we compare the spectrum with $\varphi=0$ and $\varphi=\pi/2$, which are respectively illustrated in Fig. 3. It is shown that whether in pNA molecule medium or in the pseudo-pNA molecule medium, the spectrum depends sensitively on the CEP. Moreover, by comparing Fig. 3(i), Fig. 3(ii), and Fig. 3(iii), the phase dependence of the corresponding spectra is found to rise as the field strength increases for fixed pulse width τ_p . The reasons are as follows. When the laser intensity is strong enough, the Rabi frequency $\Omega_R = \mu_{12}E/\hbar$ ^[22] can be comparable to the carrier frequency. And then accompanied by strong reshaping of the individual optical carriers, intense population oscillation takes place which is called carrier wave Rabi Flopping (CWRF)^[24]. The Rabi Flopping is not driven by the pulse envelope but by the laser carrier wave, or definitely by the electric-field time-derivative effects implicated in the Maxwell-Bloch (M-B) equations. Subsequently, the CWRF leads to the high-order frequency formation within the propagating laser pulse. Since few-cycle pulses with different initial phases have definitely different carrier waves, it is easy to understand that they have great differences in carrier reshaping and the corresponding spectra. With the same pulse width, stronger laser field has larger time-derivative, resulting in more severe carrier reshaping. The time-derivatives of the stronger field differ from each other more widely for different initial phases, and finally the laser-medium interaction manifests a more sensitivity to the initial CEP.

By comparing Fig. 3(a) with Fig. 3(b), it is found that the spectrum depends more sensitively on the CEP in pNA molecule medium than in the pseudo-pNA-molecule medium. Particularly, when the CEP φ is zero and π , the energy of the two input pulses are entirely the same, although the field evolutions of the pulses are distinctly different. When the laser pulse with $\varphi=0$ and $\varphi=\pi$ propagating in the pseudo-pNA-molecule medium, the corresponding spectra are also just the same for the two

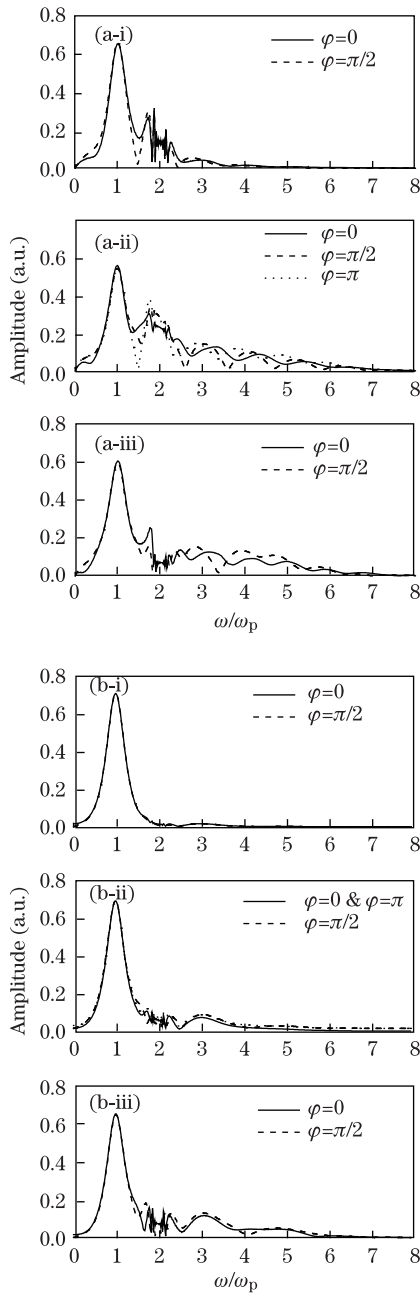


Fig. 3. Spectra in (a) pNA molecule and (b) pseudo-molecule medium at $z=26.4 \mu\text{m}$. The field parameters are as in Fig. 1.

different CEPs (Fig. 3(b-ii)). However, one can find in Fig. 3(a-ii) that the corresponding spectra for $\varphi=0$ depart from those of $\varphi=\pi$ for the pNA molecule medium. It is clearly due to the extra nonlinear effects introduced by the permanent dipole moments of pNA molecule.

Figure 4 presents the generated spectra when the laser pulse with fixed field strength propagates to $z=26.4 \mu\text{m}$. Whether in pNA molecule medium or in the pseudo-pNA-molecule medium, the phase dependence of the spectra decreases as the pulse width τ_p increases. We explain it from the following three aspects. Firstly, when τ_p decreases to the carrier oscillation period $T_0=2\pi/\omega_p$ or even shorter than T_0 , the peak of the pulse envelope and that of the carriers cannot fit well with each other at the initial time if CEP $\varphi \neq 2n\pi$. The lower frequency components vary with the CEP (see the inset figure in Fig. 4(b-i) and

then play an important role in the phase dependence of the frequency-barycenter. The calculations in Ref. [23] indicate that the barycenter of carrier frequency and the energy of the pulse have their maximum and minimum when φ equals zero and $\pi/2$, respectively. That is to say, the pulse energy changes with CEP φ . However if the pulse width τ_p is far longer than T_0 , the maximum of the field strength $E_{\text{max}} = F \text{sech}[1.76\varphi/(\omega_p\tau_p)]$ approaches to the field amplitude F which is a constant in Eq. (7), so that the maximum field strength becomes independent of CEP^[23]. The effect of CEP on the pulse energy is negligible, too. Secondly, even if the field strength remains unchanged, the shorter the pulse width is, the larger the time-derivatives of the

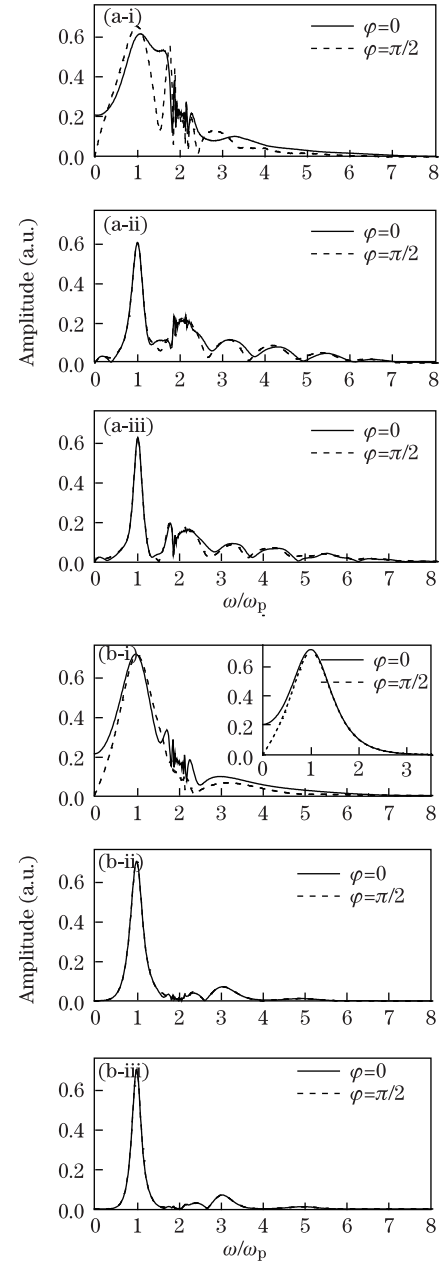


Fig. 4. Spectra in (a) pNA molecule and (b) pseudo-molecule medium at $z=26.4 \mu\text{m}$. The field parameters are $F=2.290 \times 10^{10} \text{ V/m}$, $\omega_p=\omega_0/2=2.925 \times 10^{15} \text{ Hz}$, with (i) $\tau_p=1 \text{ fs}$ (ii) $\tau_p=3 \text{ fs}$ (iii) $\tau_p=4 \text{ fs}$. The inset in (b-i) is the spectra of the input pulse at $z=0$.

laser filed are, resulting in more severe carrier reshaping. Further, if the CEP is different, the filed time-derivatives derive from each other more violently, and this difference leads to a more distinct sensitivity of the laser-medium interactions to the initial CEP, as shown in Fig. 4. Thirdly, as the pulse duration increases, it is clear that the number of optical cycles included in the pulse envelope rises, and then the wings (weak field region) of the pulse contains a greater number of optical periods. Just as discussed above, the phase effect on the interaction is very small if the laser field is weak. Accordingly, the absence of CEP effect can be expected when the number of optical periods in the weak field region grows up. In the middle of the pulse envelope (strong field region), however, the interaction dynamics still retains dependent of CEP. Hence force, it is relatively easy to understand why the phase effect is more pronounced for short pulses than long pulses.

By comparing Fig. 4(a) with Fig. 4(b), we can see that the phase dependence in the pseudo-pNA-molecule medium is less than that of in the pNA molecule medium, just as presented in Fig. 3(a) via Fig. 3(b). In Fig. 4(b), the difference of the spectra for $\varphi=0$ and $\varphi=\pi/2$ has been invisible when the pulse width τ_p broadens to 3 fs, while in Fig. 4(a), this kind of difference begins to disappear until τ_p increases to 4 fs. No doubt, it is also attributed to the extra nonlinear effects introduced by the permanent dipole moments of pNA molecule.

In conclusion, the initial carrier-envelope phase dependence of high harmonic spectra generated in the non-resonant dynamics process of an ultrashort pulse laser propagating in a pNA molecule medium is investigated by solving the full M-B equations, including the effects of permanent dipoles. When the laser pulse propagates with carrier frequency equal to half of exciting frequency of the molecule's charge-transfer state, it is found that the sensitivities of the carrier wave reshaping, the high harmonic spectrum and the temporal evolution of excited state population to the initial carrier-envelope phase increase as the laser field grows intense for given pulse width; while for given laser intensity, the phase dependence decreases when the pulse width becomes narrow. Due to the extra nonlinear effects introduced by the permanent dipole moments of pNA molecule, the sensitivity to the initial phase in pNA molecule medium is more pronounced than in the medium constituted by pseudo-molecules without permanent dipole moments. Another phenomenon should be noticed is that the second harmonic spectral component oscillates more sharply and depends more crucially on the initial phase than other harmonic components. It is because the second harmonic component is sourced from the intensely resonant two-photon absorption process, while the occurrence probability of the latter process is sensitive to the laser field evolution affected by the initial carrier-envelope phase. Moreover, the distinct second harmonic component in the spectrum also indicates the preferable two-photon absorption properties of the pNA molecule.

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