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The effect of light-induced conical intersections on the alignment of diatomic molecules

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ABSTRACT

It has already been shown that dressing of diatomic molecules by standing or by running linearly polarized laser waves gives rise to conical intersections (CIs). Due to the presence of such light-induced CIs (LICI), the rovibronic molecular motions are strongly coupled. Here we investigate an impact of LICI on molecular alignment. We show that the degree of alignment of a diatomic molecule as a function of time as obtained from the rigid rotor calculations (where the LICI is ignored) is very different from the exact calculations (where the LICI is taken into consideration). This claim is valid under an assumption that the initially prepared wavepacket has a significant amplitude at the nuclear geometry where the LICI is located. Moreover, our results clearly show that the LICI increases the electronic excitation of the diatom. In particular for weak laser fields this effect is very significant. Our prediction of the LICI's effect on the alignment of diatomic molecules can be confirmed by a two-laser experiment. Here, the first laser should have weak intensity and its duration should be sufficiently long as to align the molecules. The wavelength should be tuned in such a way as to ensure that the initial nuclear wavepacket has a significant amplitude at the internuclear distance corresponding to the LICI. The second laser pulse should be strong to produce measurable high-order harmonics. The high-order harmonic generation spectra should be measured as a function of the time delay between the two laser pulses, and are predicted to give an experimental evidence for the LICI effect on the alignment.

1. Introduction

Conical intersections (CIs) between electronic potential energy surfaces play a crucial role in various basic molecular processes [1–4]. For nuclear geometries in the vicinity of a CI, the Born–Oppenheimer separation between the electronic and the nuclear motions breaks down, and the non-adiabatic coupling effects become fundamentally important. *For conceptual reasons, diatomic molecules in free space cannot possess any CIs, since the formation of a CI requires at least two nuclear degrees of freedom whose change influences the electronic wavefunction.* Although CIs do not exist in free diatomic molecules, we have recently demonstrated that *CIs do appear in diatomic molecules dressed by a linearly polarized laser light* [5]. The focus of Ref. [5] was on the effect of the light-induced conical intersection (LICI) on the molecular optical lattices produced when diatoms interact with standing laser waves. In Ref. [6] we studied an effect of the *LICI* on the absorption spectra of m Na_2 when the diatom interacts with a linearly polarized light (running waves). More recently we calculated the topological (Berry) phase of the LICI in the m Na_2 molecule [7] and the effect of the polarization of the laser field on the LICI phenomenon [8]. In this paper we concentrate on the effect of LICIs on the time-dependent alignment of diatomic molecules (m Na_2 is chosen as an illustrative example) initially prepared in their ground electronic, vibrational, and rotational state. Before proceeding let us summarize first the conditions for a LICI and then summarize our finding.

A LICI appears if one has a sufficiently large laser frequency such that the ground electronic state potential energy curve (PEC) $E_1(R)$ and the shifted electronically excited PEC $E_2(R)$ cross at an internuclear distance $R = R_0$ where

$$E_1(R_0) = E_2(R_0) - \hbar\omega_L. \quad (1)$$

An impact of this LICI on the dynamics is large provided that the initial wavepacket has a significantly large amplitude at $R = R_0$. See the dependence of the LICI crossing points, $R = R_0$, on the laser frequency as presented in Fig. 1. Since the LICI induces strong

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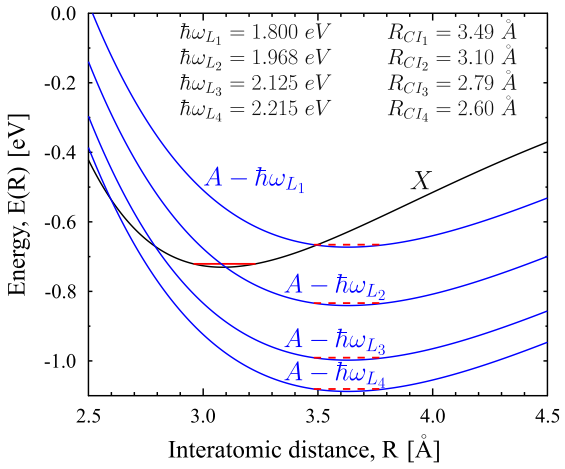

Fig. 1. The potential energy curve (PEC) of $m\ Na_2$ in the ground electronic state (denoted by X), and the PEC of the first excited electronic state shifted by one-photon energy, plotted as functions of the internuclear distance R. The light-induced conical intersections (LICI) are obtained for the values of R where the two PECs cross, provided that the molecules are oriented perpendicularly to the light polarization axis (i.e., $\theta = \pi/2$).

couplings between different vibrational and rotational field free states of the diatom, all the molecular degrees of freedom should be taken into consideration in the numerical calculations. This is however not the case of the rigid rotor approximation which is frequently used in theoretical treatments of molecular alignment. Rigid rotor approximation implies that molecular vibrations are frozen and thereby no LICI can be formed.

Our main findings are as follows:

(1) As expected there is no effect of the LICI in the off-resonance regime where the laser frequency is too small to have crossings between the two PECs at values of $R = R_0$ at which the initial wavepacket posseses a significantly large amplitude. For such off-resonance conditions the alignment can be calculated within the rigid rotor approximation. Moreover, the population of the excited electronic PEC is negligible in comparison to the population of the ground electronic PEC, and the well established approach as described by Seideman [9] is most adequate. See for example Fig. 2a and d for a weak laser field, $I_0 = 3 \cdot 10^8$ W/cm^2, and Fig. 3d for a moderate laser field, $I_0 = 3 \cdot 10^{10}$ W/cm^2.

(2) When the initial wavepacket does have a significantly large amplitude at the LICI point $R = R_0$ (i.e., the off-resonance condition described above in (1) does not hold), the LICI effect on the alignment of the diatom by a weak laser field is highly pronounced. The results for $\langle\cos^2\theta\rangle$ as a function of time, obtained within the framework of the rigid rotor approximation, are very different from the exact ones (see for example Figs. 2b and c for weak laser fields and Fig. 3b for moderate laser fields).

(3) When the initial wavepacket does possess a significantly large amplitude at the LICI point $R = R_0$, the LICI effect on the population of the electronically excited PEC is much larger than one might expect on the basis of the calculations within the framework of the rigid rotor approximation. This holds in particular when the laser intensities are low. See for example Fig. 4a where the population of the first excited electronic state is three times larger than the population calculated employing the rigid rotor approximation. We also point to the different types of oscillations exhibited by the populations shown in Fig. 4, reflecting the different underlying physics.

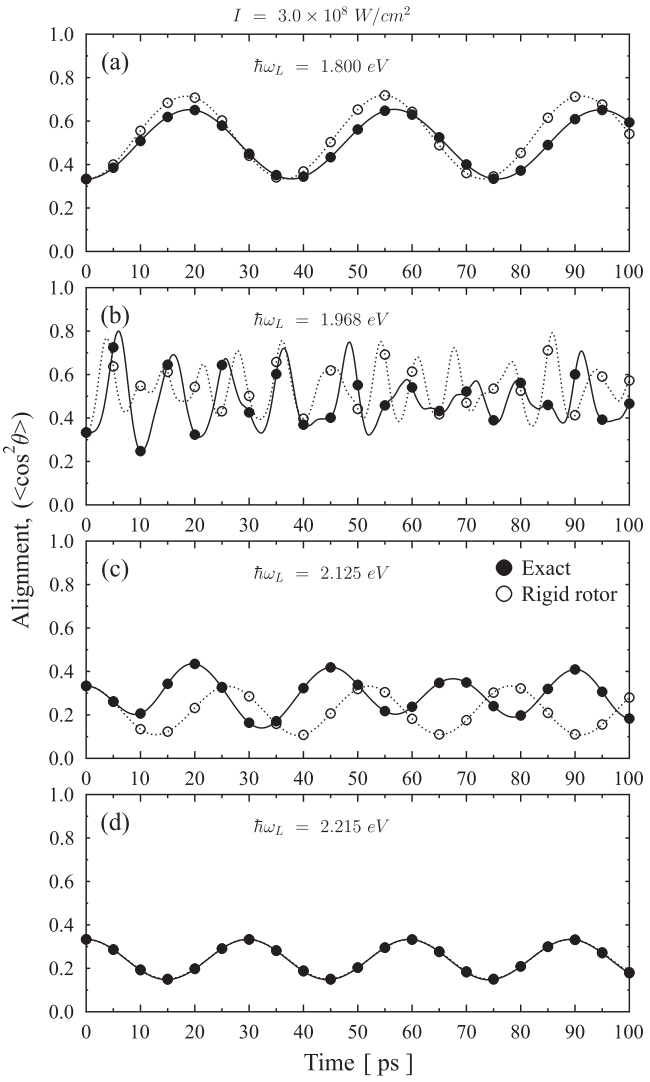

Fig. 2. The degree of alignment as defined in Eq. (12) as a function of time for a weak laser field of intensity $I_0 = 3{\cdot}10^8\,W/cm^2$. The effect of the LICI on the alignment for different laser frequencies is most pronounced for the photon energy 1.968 eV where the initial wavepacket (i.e., the ground vibrational and rotational field free state on the ground electronic potential energy curve) has its maximal amplitude at $R = R_0$ where the LICI is located (see Fig. 1).

2. Theoretical background

Let us first describe how the propagation of an initial wavepacket with a time-dependent hamiltonian in the Floquet picture has been carried out. The time dependent Schrödinger equation which we wish to solve is

$$\hat{H}(t)\Psi(t) = i\hbar\partial_t\Psi(t); \tag{2}$$

where $H(t) = H(t+T)$ stands for the time dependent Hamiltonian for a diatomic molecule in a cw laser field with the frequency $\omega_L = 2\pi/T$. In our studied case,

$$\hat{H}(t) = \hat{H}_A(R,\theta)\left|\Psi_A^{elec}\right\rangle\left\langle\Psi_A^{elec}\right| + \hat{H}_X(R,\theta)\left|\Psi_X^{elec}\right\rangle\left\langle\Psi_X^{elec}\right| + \mathcal{E}_0\cos\theta d(R)\cos(\omega_L t)\left[\left|\Psi_A^{elec}\right\rangle\left\langle\Psi_X^{elec}\right| + \left|\Psi_X^{elec}\right\rangle\left\langle\Psi_A^{elec}\right|\right] \tag{3}$$

where $\hat{H}_X$ and $\hat{H}_A$ are the field free nuclear Hamiltonians for the ground and excited electronic states, respectively, R is the internuclear distance, and θ is the angle between the molecular axis and the polarization direction. The field-free Hamiltonians $\hat{H}_X$ and $\hat{H}_A$ are explicitly given by

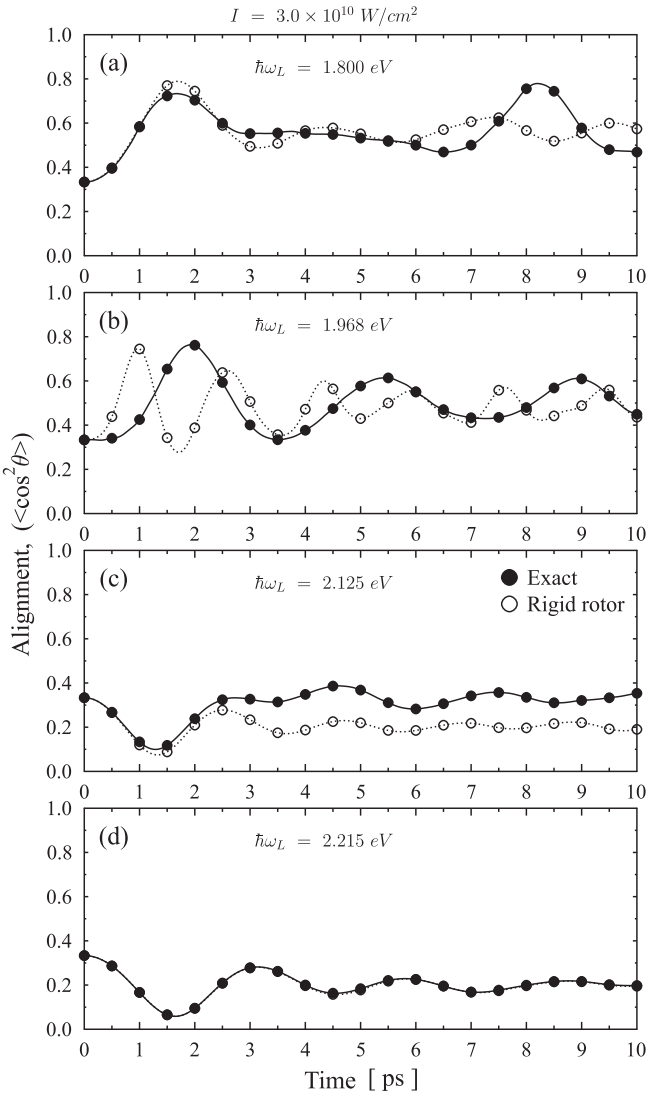

Fig. 3. The degree of alignment as defined in Eq. (12) as a function of time for a for a moderate laser field intensity $I_0 = 3{\cdot}10^{10} W/cm^2$. The effect of the LICI on the alignment for different laser frequencies is most pronounced for the photon energy 1.968 eV where the initial wavepacket (i.e., the ground vibrational and rotational field free state on the ground electronic potential energy curve) has its maximal amplitude at $R = R_0$ where the LICI is located (see Fig. 1).

$$\widehat{H}_{X/A} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{\widehat{L}^2(\theta,\phi)}{2\mu R^2} + V_{X/A}(R).$$

Note that the eigenvalues and eigenfunctions of $\widehat{H}_X$ and $\widehat{H}_A$ can be assigned three good quantum numbers ($X/A, v, j$). That is,

$$\widehat{H}_{X/A}\chi^{X/A}_{jv}(R)Y_{v,j}(\theta,\phi) = E^{X/A}_{jv}\chi^{X/A}_{jv}(R)Y_{v,j}(\theta,\phi) \tag{4}$$

where $Y_{j,\ m}(\theta,\phi) \sim P_j(\cos\theta)e^{im\phi}$ are the spherical harmonic functions. Without loss of generality we can take $m = 0$. The label X/A is associated with the electronic state (ground or excited one), j corresponds to the free rotational motion of the diatom, and v specifies the vibrational state of the diatomic molecule. Of course, due to an interaction with the laser, all degrees of freedom (electronic, rotational and vibrational motions) are coupled and the assignment in the three good quantum number is lost.

In our case the initial state is taken to be the ground vibrational and rotational eigenstate of $\widehat{H}_X$, $\chi^X_{v=0}(R)P_0(\cos\theta)$, and therefore,

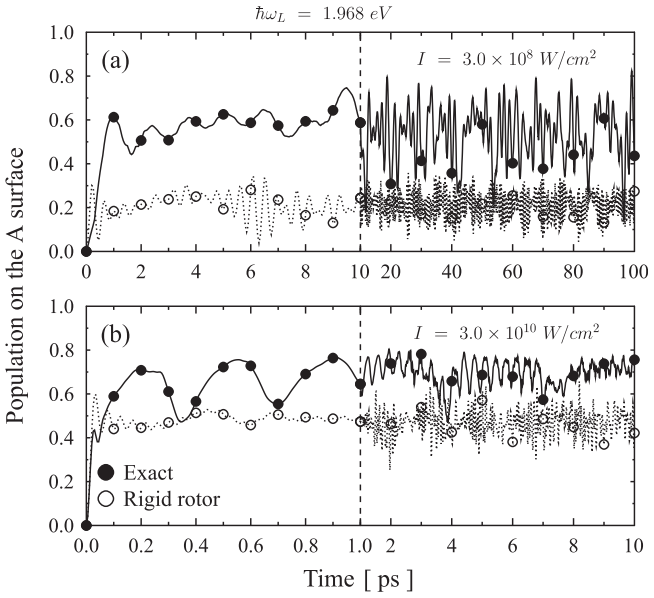

Fig. 4. The population of the propagated wavepacket on the electronically excited PEC (see Eq. (15)) as a function of time for a weak and a moderate laser field intensity. The laser frequency is chosen such that the initial wavepacket is maximal at the LICI point (see Fig. 1). The results clearly show that the exact population on the excited PEC is larger than the population calculated within the framework of the rigid-rotor approximation.

$$|\Psi(t=0)\rangle = \chi^X_{v=0}(R)P_0(\cos\theta)|\Psi^{elec}_X\rangle. \tag{5}$$

Using the Shirley approach [10] (see also the (t,t') method in Ref. [11]) we can expand the solution of Eq. (2) using the quasi-energy (Floquet) solutions which we denote here by $|\Psi^{QE}_\alpha(t)\rangle$ (we will explain what they are later). Following Shirley the solution of Eq. (2) is given by,

$$|\Psi(t)\rangle = \sum_\alpha C_\alpha|\Psi^{QE}_\alpha(t)\rangle \tag{6}$$

where

$$\Psi^{QE}_\alpha(R,\theta,t) = e^{-iE^{QE}_\alpha t/\hbar} \left[\phi^X_\alpha(R,\theta,t)|\Psi^{elec}_X\rangle + \phi^A_\alpha(R,\theta,t)|\Psi^{elec}_A\rangle\right] \tag{7}$$

$$\phi^X_\alpha(R,\theta,t) = \sum_{n=-\infty}^{\infty} e^{i\omega_L nt}\varphi^X_{n,\alpha}(R,\theta)$$

$$\phi^A_\alpha(R,\theta,t) = \sum_{n=-\infty}^{\infty} e^{i\omega_L nt}\varphi^A_{n,\alpha}(R,\theta)$$

and

$$C_\alpha = \langle\Psi^{QE}_\alpha(t=0)|\Psi(t=0)\rangle = \langle\phi^X_\alpha(R,\theta,t=0)|\chi^X_{v=0}(R)P_0(\cos\theta)\rangle. \tag{8}$$

Correspondingly, E^{QE}_α and the n-th Fourier components of the quasi-energy (Floquet) solution $\varphi^{X/A}_{n,\alpha}(R,\theta)|\Psi^{elec}_{X/A}\rangle$ are the eigenvalues and eigenstates of the time-independent Floquet matrix, $\mathcal{H}_F$, whose (n,n') matrix element is defined as (see for example, Refs. [12] and [13])

$$[\widehat{\mathcal{H}}_F]_{n,n'} = \frac{1}{T}\int_0^T e^{-i\omega_L nt}\left[-ih\frac{\partial}{\partial t} + \widehat{H}(t)\right]e^{+i\omega_L n't}dt \tag{9}$$

where $\{(n',n)\}_{0,\ \pm1,\ \pm2,\ldots}$. For our case the Floquet matrix splits into two uncoupled matrices. One Floquet matrix has the (n,n') matrix elements

$$[\widehat{\mathcal{H}}_F]_{n',n} = \delta_{2n',2n}\left[\widehat{H}_X(R,\theta) + \hbar 2n\omega_L\right]|\Psi_X^{elec}\rangle\langle\Psi_X^{elec}| + \delta_{2n'+1,2n+1}\left[\widehat{H}_A(R,\theta) + \hbar(2n+1)\omega_L\right]|\Psi_A^{elec}\rangle\langle\Psi_A^{elec}| + \delta_{n',n\pm1}\frac{\mathcal{E}_0}{2}\cos(\theta)d(R)\left[|\Psi_A^{elec}\rangle\langle\Psi_X^{elec}| + |\Psi_X^{elec}\rangle\langle\Psi_A^{elec}|\right] \quad (10)$$

The second Floquet matrix has the (n,n') matrix elements

$$[\widehat{\mathcal{H}}_F]_{n',n} = \delta_{2n',2n}\left[\widehat{H}_A(R,\theta) + \hbar 2n\omega_L\right]|\Psi_A^{elec}\rangle\langle\Psi_A^{elec}| + \delta_{2n'+1,2n+1}\left[\widehat{H}_X(R,\theta) + \hbar(2n+1)\omega_L\right]|\Psi_X^{elec}\rangle\langle\Psi_X^{elec}| + \delta_{n',n\pm1}\frac{\mathcal{E}_0}{2}\cos(\theta)d(R)\left[|\Psi_A^{elec}\rangle\langle\Psi_X^{elec}| + |\Psi_X^{elec}\rangle\langle\Psi_A^{elec}|\right] \quad (11)$$

Since the quasi-energy spectrum of the above two Floquet matrices is exactly the same we use the first Floquet matrix given in Eq. (10). By substituting Eqs. (7) and (5) into Eq. (6) we get the desired solution of the time-dependent Schrödinger equation.

The degree of the alignment as a function of time is given by the expectation value of $\cos^2\theta$ taken with the wavepacket $|\Psi(t)\rangle$, that is,

$$\text{Alignment}(t) = \langle\Psi(t)|cos^2\theta|\Psi(t)\rangle \quad (12)$$

The population on the electronic excited potential curve

$$\text{Population}_A(t) = |\langle\Psi_A^{elec}|\Psi(t)\rangle_{elec}|^2 \quad (13)$$

is defined as usual as the weight of the total wavepacket on the excited electronic state.

Before presenting results of our numerical calculations, we note in passing that the Floquet approach we used here is applicable when the duration of the laser field is sufficiently long to support more than 10–15 optical cycles (see Fig. 7 of Ref. [17]). General formula for the applicability of the adiabatic theory for the Floquet operator is given in Ref. [18]. For the study the photo-induced dynamics when the Floquet adiabatic theory is not applicable other approaches (such as in Ref. [19]) should be used.

3. Results and discussion

For the case where the photoinduced dynamics is a one-net photon process [12] (as in our case) it is enough to take $\{n',n\} = 0,-1$ for the first symmetry Floquet matrix as defined in Eq. (10) (or $\{n',n\} = 0,+1$ for the second symmetry Floquet matrix as defined in Eq. (11)). The initial state is the field-free state which is defined above in Eq. (5). Our results presented in Figs. 1–4 were obtained by calculating the eigenvalues and eigenvectors of the Floquet matrix given in above in Eq. (10) for $n = 0$ and $n' = 0$ (i.e., one-net photon is absorbed). The time dependent solution for one-net photon absorption is given by

$$\Psi(R,\theta,t) = \sum_\alpha C_\alpha e^{-iE_\alpha^{QE}t/\hbar}. \quad (14)$$
$$\left[\varphi^X_{n=0,\alpha}(R,\theta)|\Psi_X^{elec}\rangle + e^{-i\omega_L t}\varphi^A_{n=-1,\alpha}(R,\theta)|\Psi_A^{elec}\rangle\right]$$

where

$$\begin{pmatrix} \langle\Psi_X^{elec}|\mathcal{H}_F|\Psi_X^{elec}\rangle & \langle\Psi_X^{elec}|\widehat{\mathcal{H}}_F|\Psi_A^{elec}\rangle \\ \langle\Psi_A^{elec}|\mathcal{H}_F|\Psi_X^{elec}\rangle & \langle\Psi_A^{elec}|\widehat{\mathcal{H}}_F|\Psi_A^{elec}\rangle \end{pmatrix}\begin{pmatrix} \varphi^X_{n=0,\alpha}(R,\theta) \\ \varphi^A_{n=-1,\alpha}(R,\theta) \end{pmatrix} = E_\alpha^{QE}\begin{pmatrix} \varphi^X_{n=0,\alpha}(R,\theta) \\ \varphi^A_{n=-1,\alpha}(R,\theta) \end{pmatrix}. \quad (15)$$

The spatial components of the quasi-energy solutions were calculated using the particle in a box functions, $\{\sqrt{2/L}\sin(k\pi R/L)\}_{k=1,2,\ldots,N_b}$ which are multiplied by Legendre polynomials $\{P_j(\cos\theta)\}_{j=0,1,2,\ldots,N_J}$. In our numerical calculations we have used $N_b = 500$ and $N_J = 95$ for the X surface whereas for the A surface we have considered correspondingly 96 Legendre polynomials. The ground and the first electronic excited potential energy curves (PECs) and the dipole transition matrix element for m Na_2 where borrowed from Ref. [14]. In Figs. 2 and 3 we show correspondingly the degree of alignment as defined in Eq. (12) as a function of time for a weak and moderate laser fields. The effect of the LICI on the alignment for different laser frequencies is most pronounced when the initial wavepacket (i.e., the ground vibrational and rotational field free state on the ground electronic potential energy curve) has its maximal amplitude at $R = R_0$ where the LICI is located (see Fig. 1). Comparison between Figs. 2 and 3 shows that the alignment dynamics (over 100 ps) is rather erratic for the case of weak laser intensity $I = 3\cdot10^8$ W/cm^2, but becomes more regular for the higher intensity of $I = 3\cdot10^{10}$ W/cm^2. Our interpretation of this behavior is as follows. An erratic profile of $\langle\cos^2\theta\rangle$ in the low intensity case demonstrates that many rovibronic energy levels of the system are coupled by light due to presence of LICI. On the other hand, imposition of higher intensity light of $I = 3\cdot10^{10}$ W/cm^2 implies a non-perturbative shift of the dressed quasi-energy levels and their repulsion. This means in turn that the resulting dynamics is driven by a smaller number of Floquet levels than in the weak field regime, and is thereby less erratic. In Fig. 4 we show the population of the propagated wavepacket on the electronically excited PEC (see Eq. (13)) as a function of time for a weak and a moderate laser field intensity. The laser frequency is chosen such that the initial wavepacket is maximal at the LICI point (see Fig. 1). The results clearly show that the exact population on the excited PEC is larger than the population calculated within the framework of the rigid-rotor approximation. While the population of the excited PEC is somewhat increased in the moderate frequency case compared to the low frequency case, the observed increase is less than 10%. We expect the mentioned increase to be substantially larger provided that one carries out a more realistic wavepacket calculation allowing for multiphoton processes. We insist, however, that the basic qualitative features of light induced dynamics relevant to the LICI phenomenon are rather well described by our single photon treatment.

4. Concluding remarks

In the present paper we have studied an impact of the LICI on molecular alignment. According to our model calculations, the most pronounced effect of LICI on the alignment factor $\langle\cos^2\theta\rangle$ takes place in the low intensity regime and is demonstrated by an erratic dependence of $\langle\cos^2\theta\rangle$ upon time as plotted in Fig. 2. For the sake of clarity, let us emphasize in this context that a crucial condition for observing LICI effects is to prepare an initial state having a significant amplitude in the region where the LICI is located. As we recall, location of the LICI point is controllable by changing the laser frequency. In the case of low laser frequencies one does not generate LICI, and therefore one may adequately describe molecular alignment using the conventional rigid rotor calculations.

The impact of the LICI on the population of the propagated wavepacket on the excited electronic potential energy can be measured (one can measure e.g. the photon emission or by the subsequent ionization by a probe laser of a suitable frequency which too small for ionizing the ground electronic state). In the case the field-free molecules are not cold enough to initially be in their ground rotational state as was considered in our calculations, one can easily include the effect of the temperature on the populations by starting with initially excited rotational and if needed also vibrational states and subsequently weight the results by the common Boltzman factors.

The effects of the LICI on the degree of the alignment of the propagated wavepacket can be measured by applying a second

strong laser pulse which emits high harmonics [15,16] and acts as a probe laser. The harmonic generation spectra (HGS) is most pronounced when the molecules are aligned along the polarization direction. Therefore, the measurement of the HGS as function of the time delay between the two laser pulses (the weak laser pulse which populates the excited electronic state and the strong one which produces the harmonics) will provide a measurable quantity of the impact of LICIs on the alignment of diatomic molecules.

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