

Light-Induced Conical Intersections: Topological Phase, Wave Packet Dynamics, and Molecular Alignment

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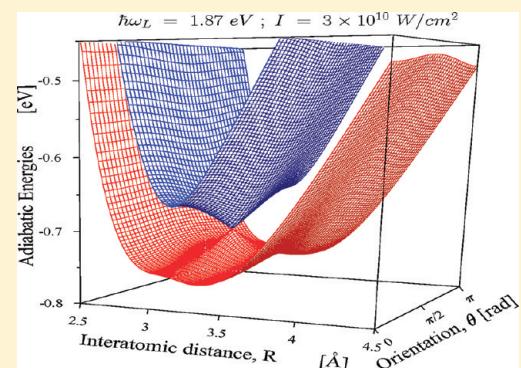
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ABSTRACT: In previous publications (*J. Phys. B: At., Mol. Opt. Phys.* **2008**, *41*, 221001; *J. Phys. B: At., Mol. Opt. Phys.* **2011**, *44*, 045603) a novel and physically interesting phenomenon was found in the field of light–matter interactions. It was shown theoretically that exposing a molecule to a laser field can give rise to the appearance of so-called light-induced conical intersections (LICIs). The existence of such LICIs may change significantly the field free physical properties of a molecular system. In this article we review the LICIs in diatomics and provide a new insight to the LICI phenomenon. The sodium dimer is chosen as an explicit sample system. We calculated the Berry phase for a contour that surrounds the point of LICI and found it to be π , which is the same value as for the case of a “natural” CI in triatomic or larger molecules. We also present results to stress the impact of LICIs on molecular wave packet dynamics and molecular alignment in different electronic states.



I. INTRODUCTION

Conical intersections (CIs) are known to play an important role in nonadiabatic processes.^{1–5} In this situation the electronic states are coupled by the nuclear motion and the energy exchange between the rapidly moving electrons and slowly moving nuclei becomes significant. At these CIs the Born–Oppenheimer adiabatic approximation⁶ breaks down due to the strong non-adiabatic couplings, which becomes infinite.¹ The molecule can switch extremely efficiently between two different energy surfaces at such CIs, which can provide a “funnel” for radiationless deactivation which may occur on a time scale faster than a single molecular vibration. Typical phenomena like dissociation, radiationless relaxation of excited states, proton transfer, or isomerization processes of polyatomic molecules are associated with the appearance of CIs. Such crossing points can appear already between low lying electronic states of triatomic molecules. For truly large polyatomic molecules, CIs are ubiquitous. There are a number of publications, review articles, and books which are associated with conical intersections,^{1–5} concerning both the electronic structure and also the nuclear dynamical subjects.

As a consequence of the well-known “noncrossing rule”, CIs—under “natural” (field-free) conditions—cannot be formed between different electronic states in diatomics. These molecules have only one degree of freedom which is generally not enough to establish a branching space and therefore at most an avoided crossing result. However, in standing or in running laser electric

field, CIs can be created even in diatomic systems. In these situations the laser light induces the CIs which couple either the center of the mass motion with the internal rovibrational degrees of freedom (in case of standing laser field) or the vibrational motion with the emerged rotational degree of freedom (in the case of a running laser field). The effect of these light-induced CIs (LICIs) on the different physical properties of the diatomic molecules has been demonstrated in several papers.^{7–12} In the very first Letter⁷ it was shown that the standing laser field (optical lattice) is able to form a periodic array of CIs and these LICIs can significantly reduce the magnitude of the trapping effect of cold diatomic molecules in the lowest electronic eigen state. The forthcoming papers have focused on the case of running laser waves. Among others it was demonstrated^{8,10–12} that there is a very strong impact of these LICIs on the molecular spectra, wave packet dynamics, and molecular alignment of the molecules in the laser field. In these articles as also in the present work, the sodium dimer was used as a sample system.

Although numerous attempts have been made to describe the dynamics of atoms and molecules in intense laser fields, there are

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many phenomena left to explore and to understand. In fact, even for diatomic molecules which are the simplest ones, the rotational degree of freedom has not been taken properly into account together with the vibrational motion, i.e., the LICIs often has been neglected (see, e.g., refs 13–15 and citations therein). The reasoning might have been that the rotational time scales are much longer than the vibrational ones (which turns out to be incorrect in the presence of LICIs). Nevertheless, several works emphasize the importance of the rotations in the presence of an intense laser field.^{16–19}

The LICIs constitute a novel and physically interesting new laser–matter phenomenon. The presence of these LICIs in diatomics may completely change their original, i.e., field free, physical properties. In other words, using either standing or running laser waves or laser pulses, it is possible to generate significant nonadiabatic effects in molecular systems.^{7–12} Application of external fields thus opens up a new direction in the area of quantum dynamics and also of control of molecular processes. The positions of the LICIs are determined by the laser frequency and the strengths of their nonadiabatic couplings by the intensity of the laser.

The light-induced nonadiabatic effects have the ability to couple different electronic states of molecules in a controllable way. Depending on the field intensity, the nonadiabatic coupling may become the largest possible (as it is well-known from the Hellman–Feynman theorem) at close vicinity of the CIs. At the CIs the nonadiabatic couplings become singular and provide the source for numerous phenomena including those of topological origin as the interesting Longuet–Higgins or Berry phase,^{20–22} the open-path phase, and the quantization feature of the non-adiabatic coupling terms. In this paper, we revisit the validity of the topological line integral approximation²³ for the case of LICIs by comparing the value of the topological or Berry phase calculated with and without the presence of an intense laser field. The full agreement of these two results clearly shows that there is no difference between the “natural” and “light-induced” CIs concerning their topological effects.

The dynamics through CIs are inherently nonadiabatic and quantum mechanical, involving strong mixing of several electronic states by nuclear displacements. As a consequence, the dynamics of the system is highly affected by CIs.

We perform calculations both in the presence and in the absence of the LICIs. In the first case it was necessary to implement a two-dimensional wave packet propagation procedure including the nuclear rotation, while in the second situation a one-dimensional “rigid rotor” approximation is used, completely neglecting the LICIs. The results obtained undoubtedly reflect the impact of the LICIs for the case of molecular alignment too.

This paper is structured as follows. First, in section II, our working Hamiltonian is described. In section III we explain and clarify the Berry phase obtained due to the LICIs and discuss the numerical results of the wave packet calculations related to the two lowest states of the sodium dimer. Next, we provide calculations for the molecular alignment by moderate laser fields, for different electronic states. Our concluding remarks follow in section IV.

II. THE HAMILTONIAN

As described in refs 7–12, we solve the time-dependent Schrödinger equation for the nuclear motion of sodium dimer

including the nuclear rotation. Two electronic eigenstates X (ground, $X^1\Sigma_g^+$) and A (excited, $A^1\Sigma_u^+$) are included in the Hamiltonian which are coupled by a running laser wave of wavelength λ . The corresponding Born–Oppenheimer potentials were taken from ref 24. Our working Hamiltonian is defined by the molecular vibrational and rotational kinetic energies and by the potential energy. The latter contains the field free V_X and V_A potentials of the electronic states X and A, respectively, and the laser–molecule interaction. This interaction is given in the dipole approximation as the scalar product of the transition dipole moment d and the electric field vector $\vec{\varepsilon}$

$$\vec{d} \cdot \vec{\varepsilon} = \varepsilon_0 d(R) \cos \theta \cos(\omega_L t) \quad (1)$$

In (1) ε_0 is the maximum laser field amplitude, ($I_0 = (\varepsilon_0^2)$) is the laser intensity, $d(R)$ is the transition dipole moment for which only the z component ($\langle \psi_1^e | \Sigma_j z_j | \psi_2^e \rangle$) is nonvanishing due to symmetry, and ω_L is the laser frequency which couples the two electronic states and amounts to about 667 nm.

We represent the Hamiltonian in the Floquet picture. Therefore, the original Hamiltonian is transformed into an equivalent static problem by using the leading term in the Fourier series expansion of the solution of the time-dependent Schrödinger equation. The time-independent field-dressed form reads

$$\hat{H} = \begin{pmatrix} -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{L_{\theta\phi}^2}{2\mu R^2} & 0 \\ 0 & -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{L_{\theta\phi}^2}{2\mu R^2} \end{pmatrix} + \begin{pmatrix} V_X & (\varepsilon_0/2)d(R) \cos \theta \\ (\varepsilon_0/2)d(R) \cos \theta & V_A - \hbar\omega_L \end{pmatrix} \quad (2)$$

In this dressed state representation the interaction between the molecule and the electromagnetic field is obtained by shifting the energy of the excited potential curve by $\hbar\omega_L$. This picture is considered to be very illustrative and often used to explain various phenomena in the area of strong field physics whenever only net one-photon is absorbed by the molecule.

III. RESULTS AND DISCUSSION

In this section we discuss the conditions to be fulfilled for obtaining a LICI in the sodium dimer. As mentioned in the introduction, our aim is to demonstrate the impact of the LICIs on different physical properties of the Na_2 molecule. Three types of results are presented: (1) the topological or Berry phase, (2) the time-dependent wave packet propagation, and (3) the molecular alignment.

A. Conical Intersection and Nonadiabatic Coupling. Let us start with the diabatic Hamiltonian in eq 2. After transforming this Hamiltonian to the adiabatic picture by diagonalizing the 2×2 potential matrix given in eq 2, we obtain the adiabatic potential energy surfaces $V_{ad}^{lower}(R, \theta)$ and $V_{ad}^{upper}(R, \theta)$. These two Born–Oppenheimer potential energy surfaces can cross each other, forming a real conical intersection, only if the two conditions $\cos \theta = 0$ ($\theta = \pi/2$) and $V_X(R) = V_A(R) - \hbar\omega_L$ are simultaneously fulfilled (see Figures 1 and 2).

The characteristic features of the LICIs can be changed by varying the frequency and intensity of the light field. Increasing the frequency, for example, moves the LICI to a lower internuclear distance and to a smaller energetic position. The steepness of the

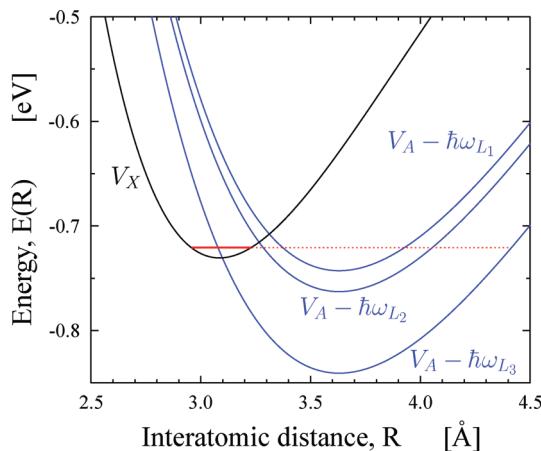


Figure 1. Electronic ground state potential energy curve V_X associated with the $X^1\Sigma_g^+$ electronic state of Na_2 and the potential energy curve $V_A - \hbar\omega_L$ dressed by laser light applying three different photon energies ($\hbar\omega_{L_1} = 1.87 \text{ eV}$, $\hbar\omega_{L_2} = 1.89 \text{ eV}$, and $\hbar\omega_{L_3} = 1.968 \text{ eV}$) where V_A is the respective curve of the $A^1\Sigma_u^+$ electronic state. The positions of the light-induced conical intersections (LICIs) are obtained where the conditions ($\cos \theta = 0$, ($\theta = \pi/2$) and $V_X(R) = V_A(R) - \hbar\omega_L$) are simultaneously fulfilled ($R_{\text{CI}_1} = 3.31 \text{ \AA}$, $R_{\text{CI}_2} = 3.27 \text{ \AA}$, and $R_{\text{CI}_3} = 3.10 \text{ \AA}$).

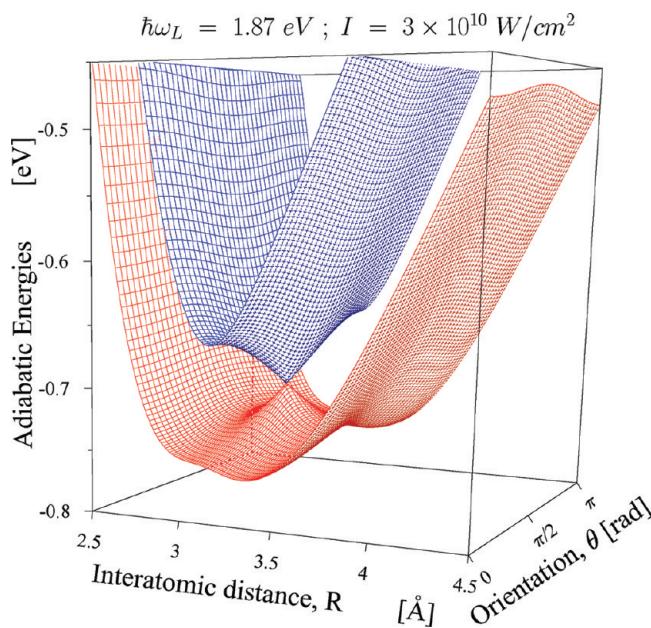


Figure 2. Light-induced conical intersection (LICI) between the $V_{ad}^{\text{lower}}(R, \theta)$ and $V_{ad}^{\text{upper}}(R, \theta)$ adiabatic potential energy surfaces in the sodium dimer. The applied field intensity and photon energy are $I = 3.0 \times 10^{10} \text{ W/cm}^2$ and $\hbar\omega_L = 1.87 \text{ eV}$.

surfaces at the LICI, on the other hand, is related to the strength of the nonadiabatic coupling and can be controlled by the laser intensity.

As a result of the diabatic-to-adiabatic transformation of the Hamiltonian, the laser–matter couplings are eliminated from the potential energy matrix but at the same time they appear as momentum couplings in the kinetic energy part of the adiabatic Hamiltonian. It is known from earlier works^{1,5,7} that these nonadiabatic couplings can be obtained as the derivatives of the transformation angle Φ of the adiabatic-to-diabatic transformation

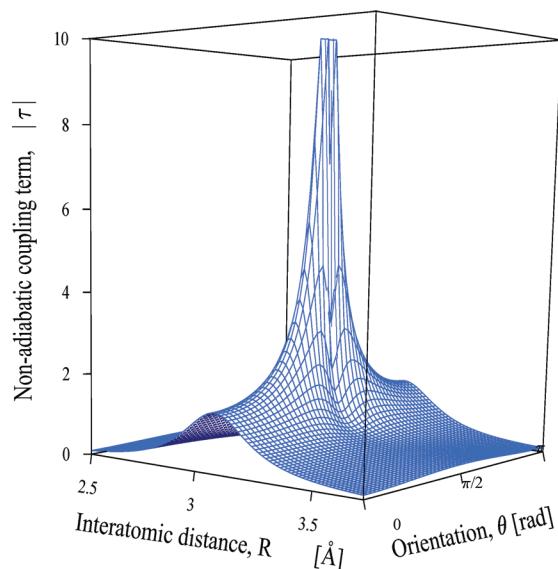


Figure 3. The absolute value of the nonadiabatic coupling term ($|\tau_{12}| = (\tau_{12R}^2 + \tau_{12\theta}^2)^{1/2}$) for Na_2 . The applied field intensity and photon energy are $I = 3.0 \times 10^{10} \text{ W/cm}^2$ and $\hbar\omega_L = 1.968 \text{ eV}$.

matrix with respect to the corresponding nuclear coordinate ($\tau_{12R} = \partial\Phi/\partial R$ and $\tau_{12\theta} = \partial\Phi/\partial\theta$). In Figure 3 the absolute value of the nonadiabatic coupling in the close vicinity of the LICI is shown which is calculated according to

$$|\tau_{12}| = \sqrt{\tau_{12R}^2 + \tau_{12\theta}^2} \quad (3)$$

It is observed that this value can be extremely large and infinite at the LICI as is the case of natural CIs of polyatomic molecules.^{7,8} Therefore, one can conclude that practically no difference exists between the nonadiabatic effects that are inherently present in polyatomics or introduced by the LICIs.

B. Topological or Berry Phase. The topological phase is a subject of importance and interest in many areas of chemistry and physics. It is also known as the “Berry phase” because of the fundamental work of Berry.²² Almost half century ago Herzberg and Longuet–Higgins pointed out²⁰ that the Born–Oppenheimer real electronic wave function undergoes a sign change when the nuclear coordinates are transported in a closed path around a CI of two electronic potential energy surfaces. Later on Mead and Truhlar showed²⁶ that the resulting multivaluedness of the electronic wave function can be eliminated by multiplying it by a phase factor, but only at the cost of introducing a vector-potential-like term into the Hamiltonian of the nuclear Schrödinger equation. This vector potential not only is a mathematical curiosity but has experimental evidence that has already been observed, for example, in the spectra of the Cu_3 ²⁷ and Na_3 ²⁸ molecules. Consequently, one has to choose between a vanishing vector potential and the single-valuedness of the electronic wave function; it is not obvious that both are fulfilled simultaneously. To continue, we conclude that the appearance of the topological or Berry phase in a molecular system can be considered as a clear fingerprint of the CI independently of whether it is a natural or a laser-induced one.

Next we focus on the calculation of the value of the topological phase using the line integral method. Applying this technique for the nonadiabatic coupling vector²³ along a closed contour in nuclear configuration space provides a computable quantity,

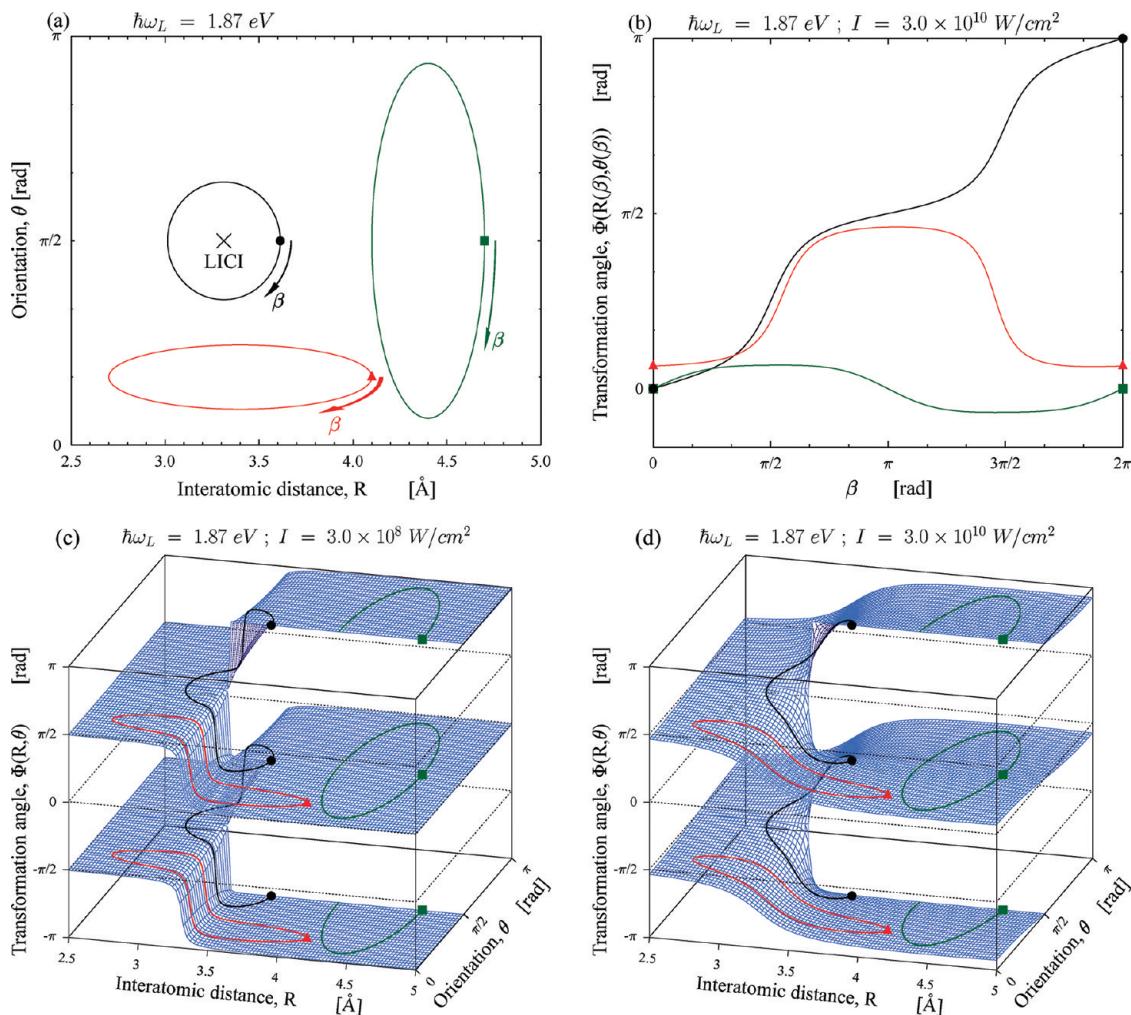


Figure 4. (a) Geometrical arrangement of the contours used in the topological phase calculations. Three different paths are presented but only one of them surrounds the LICI. (b) Transformation angles as a function of the position along the path for the three different geometrical arrangements. Only the curve marked by a solid black circle is calculated along a contour surrounding the CI. (c, d) Three dimensional plots of the transformation angle as multivalued functions of R and θ for two different intensities of the laser field: (c) $I = 3.0 \times 10^8 \text{ W/cm}^2$ and (d) $I = 3.0 \times 10^{10} \text{ W/cm}^2$.

which makes it possible to investigate the topological features of the molecular systems. It has been proved²³ that the line integral value of the nonadiabatic coupling vector along a closed contour Γ in the configuration space is equal

$$\alpha = \oint_{\Gamma} \vec{\tau}_{12}(s) \cdot d\vec{s} = \pi \begin{cases} 2n + 1, \Gamma \text{ encircles odd number of CIs} \\ 2n, \Gamma \text{ encircles even number of CIs} \end{cases} \quad (n = 0, \pm 1, \pm 2, \dots)$$
(4)

Here α is the topological or Berry phase. Nevertheless, it is important to emphasize that eq 4 is valid only for a limited region in the configuration space. For larger regions one has to take more than two adiabatic states (group of states) into account but the main conclusion will remain the same. However, this kind of extension will not be detailed in this communication.

Recalling eq 4, the Berry phase α_{12} is given for a closed path Γ as follows

$$\alpha_{12} = \Phi(s_0)_{\text{end of the path}} - \Phi(s_0)_{\text{beginning of the path}} \quad (5)$$

Thus, at first one has to calculate the diabatic–adiabatic transformation angle $\Phi(R, \theta)$ as a function of interatomic distance R and orientation θ and then α_{12} can be obtained from the difference of Φ at the beginning and at the end of the path. The obtained results are summarized in Figure 4. In the first block (Figure 4a) we display three different contours where only one of them surrounds LICI. To proceed, one can calculate the value of the topological phase along these closed paths. It can clearly be seen in Figure 4b that α_{12} differs from zero only in that situation where the closed contour surrounds the LICI. This situation is illustrated by the path with a black circle. In this case the phase takes on the value $\alpha_{12} = \pi$. If a contour in a given plane does not encircle the LICI, the value $\alpha_{12} = 0$ is found. Examples are displayed for this case by the closed paths shown by squares and triangles. To illustrate this finding from a different aspect, three-dimensional pictures are displayed for the transformation angle in Figure 4c and Figure 4d choosing $\hbar\omega_L = 1.870 \text{ eV}$ photon energy with two different intensities, $I = 3.0 \times 10^8 \text{ W/cm}^2$ (Figure 4c) and $I = 3.0 \times 10^{10} \text{ W/cm}^2$ (Figure 4d). The overall views of these figures are quite similar, only the shape of the steps differs as a

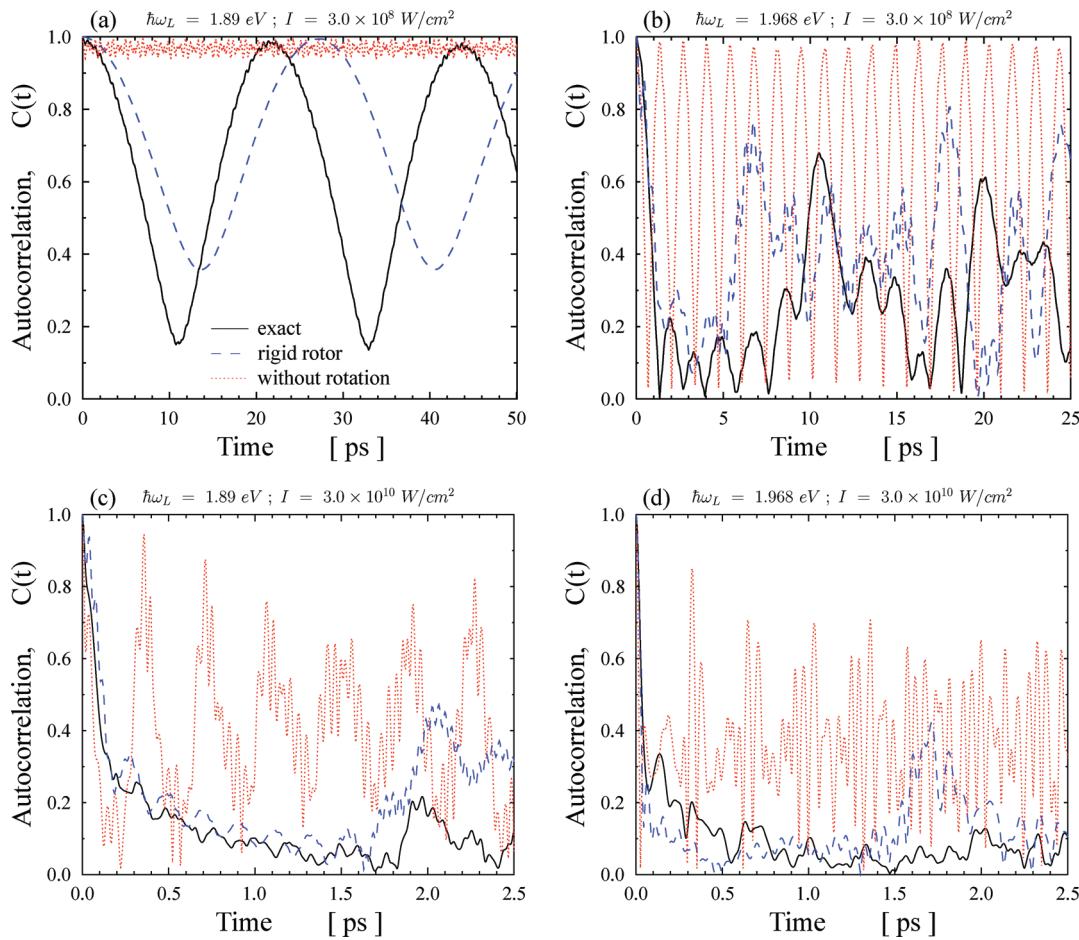


Figure 5. Autocorrelation function is as a function of time for both the one- and the two-dimensional situations. In the one-dimensional calculations the rotational or the vibrational motions have been frozen, while in the two-dimensional one the laser-induced conical intersection (LICI) is taken into account. The applied laser field intensity and photon energy are $I = 3.0 \times 10^8 \text{ W/cm}^2$ (a, b) and $I = 3.0 \times 10^{10} \text{ W/cm}^2$ (c, d); $\hbar\omega_L = 1.89 \text{ eV}$ (a, c) and $\hbar\omega_L = 1.968 \text{ eV}$ (b, d). The curves displayed as dotted, dashed, and solid lines refer to the “without rotation”, “rigid rotor”, and “exact” cases, respectively.

consequence of the two different intensities. However, the difference between the starting and the ending values of the transformation angle for closed contours is not affected by modifying the intensity.

Finally, we can conclude that the value of the topological phase is independent of whether it is due to a LICI or a “natural CI”, it only depends on whether the close contour providing the path for the integration in eq 4 encircles a CI (LICI) or not.

C. Wave Packet Dynamics. In this section we illustrate the impact of the LICI on the time-dependent wave packet propagation. We expect that the effect of LICI is in general similar to that found for conical intersections occurring naturally in polyatomic molecules. In the latter case the CIs introduce strong nonadiabatic couplings mixing the electronic states via the vibrational motions while in the present situation the LICI produces an intense nonadiabatic coupling via mixing the rotational and vibrational motions on both electronic surfaces.

We solved the time-dependent Schrödinger equation using the Hamiltonian in eq 2. The details of our solution are given in previous publications.^{8,11,12} However, for the sake of clarity we summarize here by the main steps of the wave packet calculations.

The evolution of the wave function is calculated by using the time propagator technique

$$|\psi(R, \theta, t)\rangle = \exp\left(-\frac{i}{\hbar}\hat{H}t\right)|\psi(R, \theta, 0)\rangle \quad (6)$$

Expressing the above Hamiltonian in matrix representation in the basis set of the free molecular electronic and rovibrational states ($(|\varphi_{v,j}^X(R, \theta)\rangle; 0)^T$ and $(0; |\varphi_{v,j}^A(R, \theta)\rangle)^T$), its eigenvalues (E_j) and eigen functions (ϕ_j) can be calculated numerically. The initial wave function can be written as the linear combination of these eigen functions: $|\psi(R, \theta, t=0)\rangle = \sum_j c_j \phi_j$. Applying this form for the initial wave function we can rewrite eq 6

$$|\psi(R, \theta, t > 0)\rangle = \sum_j \exp\left(-\frac{i}{\hbar}E_j t\right) c_j \phi_j \quad (7)$$

In the numerical calculations the initial wave function is chosen as the electronic and rovibrational ground state solution of the field free Hamiltonian: $|\psi(R, \theta, t=0)\rangle \geq (|\varphi_{v=0, j=0}^X(R, \theta)\rangle; 0)^T$.

To make the meaning of the wave packet propagation clear in the present situation, we are studying the dynamics of a molecular system which is first in a field free space and then suddenly exposed to the running laser wave.

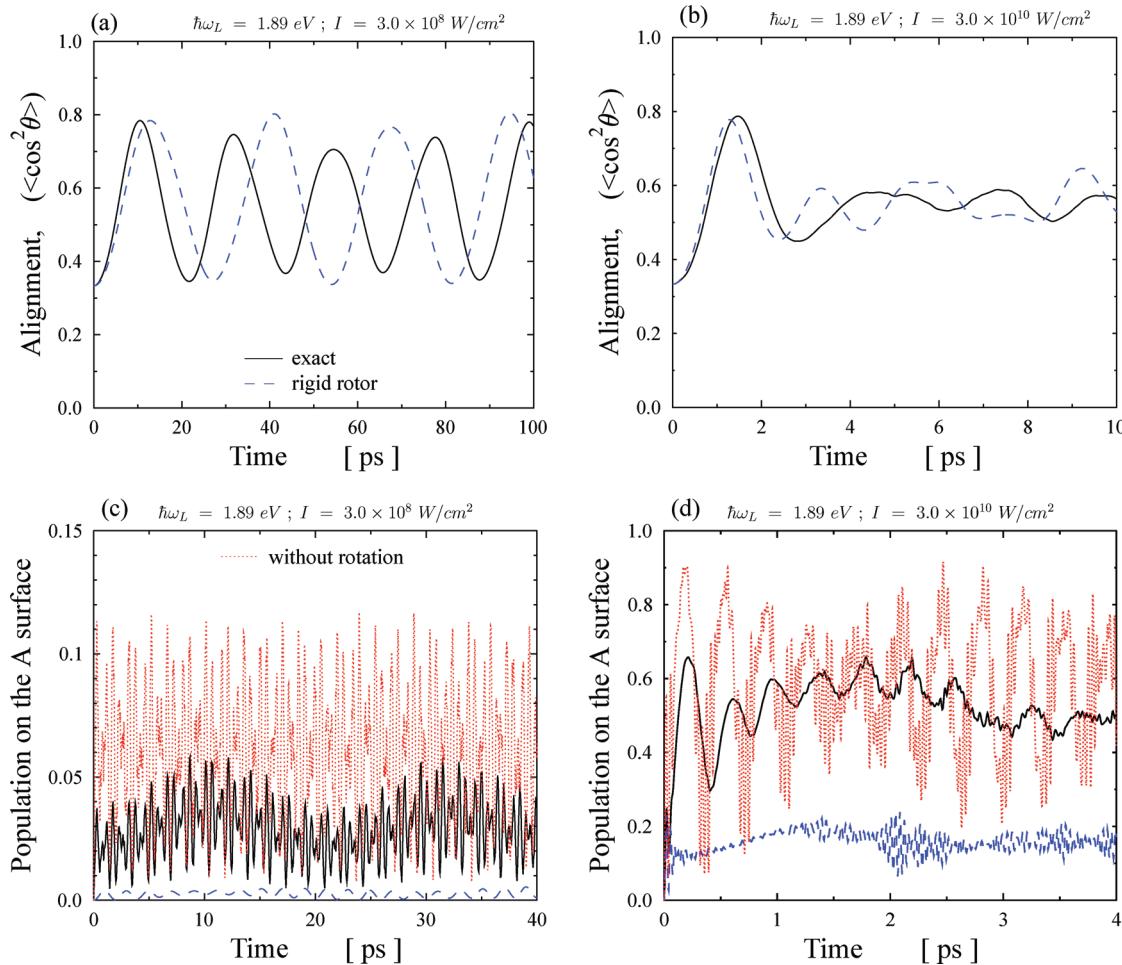


Figure 6. Molecular alignment (a, b) and population on the excited state V_A diabatic surface (c, d) as a function of time. In the two-dimensional exact calculation (solid line) the laser-induced conical intersection (LICI) is taken into account. In the one-dimensional cases the “rigid rotor” (dashed line) and “without rotation” (dotted line) model were applied. $\hbar\omega_L = 1.89$ eV photon energy and two different intensities $I = 3.0 \times 10^8 \text{ W/cm}^2$ (a, c) and $I = 3.0 \times 10^{10} \text{ W/cm}^2$ (b, d) were used.

Using the wave function obtained from eq 6, we can calculate the autocorrelation function as

$$\begin{aligned} C(t) &= |\langle \psi(R, \theta, 0) | \psi(R, \theta, t) \rangle| \\ &= \left| \int_0^\pi d\theta \sin \theta \int_0^\infty dR \psi(R, \theta, 0)^* \psi(R, \theta, t) \right| \end{aligned} \quad (8)$$

This function provides the overlap between the initial and time evolved wave packet.

In order to have a better visualization of the effect of the LICI on the wave packet dynamics, we compare the results obtained from the full two-dimensional calculations with the results obtained for a one-dimensional model. In the first case the LICI effect is taken into consideration in the numerical calculations whereas in the second case the LICI effect is excluded from the numerical calculations.

Following the procedure described in ref 11, we freeze the rotational degree of freedom. This means that the orientation of the system is fixed during the process and the molecular axis is parallel to the polarization of the laser field; i.e., we set $\cos \theta = 1$ in the Hamiltonian equation 2, to maximize the coupling between

the electronic states. This approximation implies that the molecular rotation is frozen and therefore the LICI does not exist (as it does not exist for field-free diatomic molecular potential energy curves). Another possibility to eliminate the LICI effect from our calculations is by using another one-dimensional model Hamiltonian where the molecular vibrations are frozen and only the rotations of the diatomics are taken into consideration in our calculations. For the sake of clarity, we compare the results obtained from a one-dimensional model (referred to as the “without rotation” case) and from another one-dimensional model (referred to as the “without vibration” or “rigid rotor” case) with the results obtained from the exact two-dimensional one (“exact” case). The results obtained for the autocorrelation function are displayed in Figure 5 for two different energies ($\hbar\omega_L = 1.89$ eV; $\hbar\omega_L = 1.968$ eV) and for two different intensities ($I = 3.0 \times 10^8 \text{ W/cm}^2$; $I = 3.0 \times 10^{10} \text{ W/cm}^2$). The differences between the “without rotation” and “exact” results are very significant. The first striking result in Figure 5a that the “without rotation” autocorrelation function hardly deviates from the value of 1 (the system seems to be unaffected by the laser field) while the other curve shows oscillation with large amplitude. The differences between “rigid rotor” and “exact” results are also very significant although they are less

dramatic than the differences between “without rotation” and “exact” results. The time period of the autocorrelation function obtained for the “rigid rotor” case is slightly larger than the exact value for the time periodicity. However, in the “rigid rotor” approximation the autocorrelation function oscillates between 0.35 and 1.0 whereas the exact autocorrelation function oscillates from 0.15 to 1.0. The conclusion is that the visualization of LICl effect on the dynamics depends on the approximation we use where the LICl effect is excluded from the calculations.

Although the diabatic V_A surface remains practically unoccupied in the “exact” case, the presence of the coupling to it involves a few excited rovibrational states on the X surface in addition to the ground state one. In Figure 5b the curves display oscillations about the same frequencies but while the “without rotation” model shows large constant amplitude, this feature of the other two curves is rapidly changing in time. The trend is slightly different for the case of larger intensity, see panels c and d of Figure 5. Here all types of functions oscillate in time; the “exact” function is nearly smooth showing a more or less continuous decay, while the autocorrelation function originated from the one-dimensional models is rather structured. The oscillations of the “without rotation” curve are very rapid with large amplitude.

One can conclude from the above discussion that the effect of the molecular rotation on the dynamical properties of the diatomics is quite remarkable, and thus it is strongly recommended to take it into account in realistic numerical simulations.

D. Molecular Alignment for the Ground and Excited Electronic States. Molecular alignment or orientation can play an important role in any experiment or application using gas molecules. The behavior of a molecule is strongly dependent on its alignment. For example, in a strong laser field, the probability of ionization depends on its alignment relative to the polarization direction of the laser field. The ionization is an important element of many strong-field processes, for instance, it provides the first step in generating high-harmonics; therefore the alignment dependence of ionization will also play a role in the total efficiency of harmonic generation.²⁹

In ref 12 we examined the impact of the LICl for the degree of molecular alignment (a suitable measure of the molecular alignment is the expectation value of $\cos^2 \theta$) and for the population on the excited potential energy surface V_A in moderate intensity ($I = 3.0 \times 10^8 \text{ W/cm}^2$ and $I = 3.0 \times 10^{10} \text{ W/cm}^2$) laser fields using our wave packet approximation. Our working formulas are as follows

- (i) The degree of the alignment as a function of time

$$\langle \cos^2 \theta \rangle = \langle \psi(R, \theta, t) | \cos^2 \theta | \psi(R, \theta, t) \rangle \quad (9)$$

Here θ is again the angle between the light polarization direction and the internuclear axis. The average value of the $\cos^2 \theta$ function is calculated with using the total $\psi(R, \theta, t)$ wave function.

- (ii) The population on the excited potential energy surface V_A

$$P_A(t) = \langle \psi_{\text{dia}}^A(R, \theta, t) | \psi_{\text{dia}}^A(R, \theta, t) \rangle \quad (10)$$

Here ψ_{dia}^A is the wave packet on the excited diabatic energy surface.

In order to add some more insight into the impact of the LICl on the alignment of diatomic molecules by lasers as before, we compared the results obtained from the two-dimensional model Hamiltonian where the LICl effect is included to the results obtained from the one-dimensional model where the LICl effect

is excluded. In the one-dimensional model Hamiltonian we freeze the vibrational degree of freedom obtaining the “rigid rotor” approximation, which is often and successfully used in theoretical descriptions of molecular alignment. This model represents a one-dimensional treatment; therefore no LICl can be formed. In the following we compare the results obtained by this approximation (referred to as the no LICl “rigid rotor” case) with the two-dimensional full calculations (“exact” case).

In panels a and b of Figure 6 the alignment functions are presented both for the “rigid rotor” and “exact” cases for the energy $\hbar\omega_L = 1.968 \text{ eV}$ and for two different intensities $I = 3.0 \times 10^8 \text{ W/cm}^2$ and $I = 3.0 \times 10^{10} \text{ W/cm}^2$. Different time scales are used in the two pictures. Since the processes are much faster in the case of higher intensity, thus the time scale has been zoomed for this situation. As for the case of lower intensity the processes are much slower, the period of time of the oscillations is greater, and the difference is significant between the “exact” and “rigid rotor” curves. In ref 12, we showed that for very specific values of the laser frequencies the LICl induces erratic behavior of the alignment parameter $\langle \cos^2 \theta \rangle$. Panels c and d of Figure 6 show the populations of the aligned molecules on the excited electronic surface. As one can see, the results obtained from the one-dimensional approximations and those from the two-dimensional exact calculations are very different irrespective of the values of the applied intensities. Again the “without rotation” case displays rapid oscillations with large amplitude. On the other hand the “rigid rotor” approximation tends to underestimate the population on the excited state surface. See for example Figure 6d where the population of the aligned molecules at the first excited electronic state is very significant and it is about three times larger than the population which is obtained when the LICl is excluded from the calculations by using the “rigid rotor” approximation. *This is probably the most important message of this paper to the experimentalist and encourage them to measure the population of the aligned molecules in their first excited electronic state and compare it with the results obtained from “standard rigid rotor” calculations.* Note however, that for laser frequencies which are sufficiently small such that the amplitude of the initial wave packet at region where the LICl is located is almost equal to zero, the “standard rigid rotor” calculations provide an excellent description of the alignment of the diatomics by the laser field.^{30,31}

IV. CONCLUSIONS

CIs between electronic states have important implications for nonadiabatic processes when the nuclear dynamics takes place on more than one Born–Oppenheimer potential energy surface. In this case the electronic states are coupled by the nuclear motion and the energy exchange between the electrons and nuclei becomes significant. Recently, it was pointed out that CIs not only exist inherently in the molecules but also can be induced by running or standing laser fields.^{7,8} In this situation the laser light couples the different electronic states. These LICls constitute a novel and physically interesting new laser–matter phenomenon. Applying laser waves or laser pulses, it is possible to generate significant nonadiabatic effects in molecular systems which opens up a new direction in the area of quantum dynamics and also in molecular quantum control processes. The positions of the LICls are determined by the laser frequency and the strengths of their nonadiabatic couplings by the intensity of the laser. The presence of the LICls in molecular systems may completely change their original, i.e., field-free, physical properties.

In this paper we clarify the different types of effects of LICl on the molecular dynamics. In the concluding remarks we wish to focus on the LICl effect on the population of the aligned molecules in their first excited electronic state since we believe that this is the most straightforward and significant measurable quantity.

We hope that our present work will stimulate experimental investigations.

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