Strong impact of light-induced conical intersections on the spectrum of diatomic molecules

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Abstract

We show that dressing of diatomic molecules by running laser waves gives rise to conical intersections (CIs). Due to the presence of such CIs, the rovibronic molecular motions are strongly coupled. A pronounced impact of the CI on the spectrum of the Na₂ molecule is demonstrated via numerical calculation for weak and moderate laser intensity, and an experiment is suggested on this basis. The position of the light-induced CI and the strength of its non-adiabatic couplings can be chosen by changing the frequency and intensity of the used running laser wave. This offers new possibilities of controlling the photo-induced rovibronic molecular dynamics.

(Some figures in this article are in colour only in the electronic version)

The spectrum of diatomics in weak laser fields is usually interpreted in terms of the Franck–Condon (FC) principle (see e.g. [1]). If the laser light becomes more intense, the common approach is to take into consideration the two relevant electronic potential energy curves (PECs) coupled by the laser, and to account for rotational transitions via the selection rule ΔJ = ±1 (see e.g. [2–4] and citations therein). For even stronger laser intensities, molecular rotations must be accounted for, as carried out e.g. in [5].

For standing laser waves, we have shown [6] that laser light induces conical intersections (CIs) which couple the centre of mass motion with the internal rovibronic degrees of freedom. As we shall discuss in this work, laser-induced CIs are formed even for running laser waves. It is well known [7] that for the formation of a CI, one needs at least two nuclear degrees of freedom whose changes affect the electronic wavefunction. These are not available for a free diatomic molecule. However, as we shall demonstrate below, the rotation becomes the missing degree of freedom to allow for the formation of CIs for diatomics in the presence of a laser field. Since Na₂ is a favourite and well-studied molecule of laser physics [8, 9], we choose it as our example. The situation is best illustrated in figure 1. The top panel shows the PECs of the X¹Σ⁺ and A¹Σ⁺ electronic states of Na₂. The vertical arrow labelled by ℏωL indicates the transition between these two electronic states by a weak laser field in accordance with FC theory. Figure 1(b) depicts the adiabatic potentials obtained by dressing the two aforementioned PECs by the laser following the standard approach of [2–4] referred to above. In figure 1(c), we plot the laser-induced CI resulting from our approach as discussed below.

The presence of CIs is well known in polyatomics to exert an enormous impact on the molecular dynamics [7, 10]. We will show here for the first time that this is also the case for the CI induced by running laser waves in diatomics.

Let us briefly describe now the underlying theoretical background. Using the same formalism and assumptions as in [6], one can derive the following Hamiltonian for rovibronic molecular motions:

\[
H = \left( -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{L_{\phi}^2}{2\mu R^2} \right) \otimes \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \begin{pmatrix} V_X(R) & (E_0/2) d(R) \cos \theta \\ (E_0/2) d(R) \cos \theta & V_A(R) - \hbar \omega_L \end{pmatrix}. \tag{1}
\]
coordinates, respectively; *L* the diatomic; and have used here a rather strong laser intensity of 10\(^{14}\) \text{W cm}^{-2}. CI induced by a running laser wave. For visualization reasons, we have used here a rather strong laser intensity of 10\(^{14}\) \text{W cm}^{-2}. Here, the centre of mass motion has been physically adequate for the case of running waves. Subscripts \(X\) and \(A\) refer to the two electronic states coupled by the laser (whose frequency is \(\omega_L\) and amplitude is \(\tilde{E}_0\)). To be specific, we assume that these two electronic states possess \(\Sigma\)-type symmetry, such that the molecule–light coupling term is proportional to \(d(R)\ \cos \theta\), where \(d(R)\) is the corresponding dipole transition matrix element in the body fixed frame. As discussed in detail in our previous work [6], the potential matrix of the Hamiltonian (1) gives rise to a CI whenever the conditions \(V_X(R) = V_A(R) - \hbar \omega_L\) and \(\theta = \pi/2\) are met. This situation is shown explicitly in figure 1(c).

Here, \(R\) and \((\theta, \varphi)\) are the molecular vibrational and rotational coordinates, respectively; \(\mu\) stands for the reduced mass of the diatomic; and \(L_{\varphi}\) represents the angular momentum operator of the nuclei. The centre of mass motion has been eliminated via the usual adiabatic separation approach which is physically adequate for the case of running waves. Subscripts \(X\) and \(A\) refer to the two electronic states coupled by the laser (whose frequency is \(\omega_L\) and amplitude is \(\tilde{E}_0\)). To be specific, we assume that these two electronic states possess \(\Sigma\)-type symmetry, such that the molecule–light coupling term is proportional to \(d(R)\ \cos \theta\), where \(d(R)\) is the corresponding dipole transition matrix element in the body fixed frame. As discussed in detail in our previous work [6], the potential matrix of the Hamiltonian (1) gives rise to a CI whenever the conditions \(V_X(R) = V_A(R) - \hbar \omega_L\) and \(\theta = \pi/2\) are met. This situation is shown explicitly in figure 1(c).

The conventional Hamiltonian \(\hat{H}\), widely used for diatomics in laser fields (see e.g. [2–4]), is obtained from (1) by replacing \(\cos \theta\) by its optical transition matrix element:

\[
\langle 0 | \cos \theta | 1 \rangle = \int_0^\pi P_\theta(\cos \theta) \cos \theta P_1(\cos \theta) \sin \theta \, d\theta. \quad (2)
\]

Here, \(|i\rangle = P_\theta(\cos \theta)\) are the Legendre polynomials.

To illustrate the impact of the light-induced CI on observable quantities, we discuss the Na\(_2\) molecule, considered above in figure 1. The PECs and the transition dipole functions pertaining to the \(X^1\Sigma^+_g\) and \(A^1\Sigma^+_u\) electronic states are taken from [12] and the laser wavelength is \(\lambda = 663\text{ nm}\).

The solution of the eigenvalue problem of Hamiltonian (1) provides the quasi-energy eigenvalue spectrum. These quasi-energy eigenvalues and eigenfunctions are calculated numerically by representing \(\hat{H}\) as a matrix in the basis set of the free molecular rovibronic states. An energy truncation criterion is used to reduce the number of basis functions to a manageable size. Numerical convergence with respect to this energy cutoff has been checked and achieved. We shall thus hereafter refer to the obtained numerical results as ‘exact’.

In the case of weak laser intensities, one expects that the second-order perturbation theory (PT2) in \(\tilde{E}_0\) will be adequate for the energy levels. Indeed, if we use the common approach (which we call in the following the ‘no CI’ case), we find this expectation to be fulfilled. The situation changes dramatically when full account of the CI is taken. This is apparent in figure 2, where the deviations of the PT2 results from the exact ones are shown. The breakdown of PT2 in the vicinity and above the energetic location of the CI is clearly demonstrated.

In figure 2, all the lowest energy levels of Hamiltonian (1) have been considered. To make contact with a possible experiment, we study below the absorption spectrum of Na\(_2\) where the levels are weighted by their intensities. We discuss three types of spectra: the FC spectrum obtained by employing the standard FC principle, the ‘no CI’ spectrum determined by the standard approach, and the ‘exact’ spectrum following from (1). The Golden rule expression for the ‘exact’ spectral intensity is given by \(\wp(E)|^2\), where

\[
\wp(E) = \langle \Psi_0^g(R, \theta) | d(R) \cos \theta | \Psi_E^g(R, \theta) \rangle + \langle \Psi_0^u(R, \theta) | d(R) \cos \theta | \Psi_E^u(R, \theta) \rangle. \quad (3)
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\(\hbar\omega_L\) stands for the reduced mass of the diatomic; and \(\mu\) the reduced mass of the diatomic; and have used here a rather strong laser intensity of 10\(^{14}\) \text{W cm}^{-2}. CI induced by a running laser wave. For visualization reasons, we have used here a rather strong laser intensity of 10\(^{14}\) \text{W cm}^{-2}. Here, the centre of mass motion has been physically adequate for the case of running waves. Subscripts \(X\) and \(A\) refer to the two electronic states coupled by the laser (whose frequency is \(\omega_L\) and amplitude is \(\tilde{E}_0\)). To be specific, we assume that these two electronic states possess \(\Sigma\)-type symmetry, such that the molecule–light coupling term is proportional to \(d(R)\ \cos \theta\), where \(d(R)\) is the corresponding dipole transition matrix element in the body fixed frame. As discussed in detail in our previous work [6], the potential matrix of the Hamiltonian (1) gives rise to a CI whenever the conditions \(V_X(R) = V_A(R) - \hbar \omega_L\) and \(\theta = \pi/2\) are met. This situation is shown explicitly in figure 1(c).

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\wp(E) = \langle \Psi_0^g(R, \theta) | d(R) \cos \theta | \Psi_E^g(R, \theta) \rangle + \langle \Psi_0^u(R, \theta) | d(R) \cos \theta | \Psi_E^u(R, \theta) \rangle. \quad (3)
\]
Here, \( \tilde{\Psi}_o(R, \theta) = (\Psi^X_0(R, \theta), \Psi^A_0(R, \theta))^T \) stands for that particular eigenstate of Hamiltonian (1) which reduces to the ground state of the free diatomic molecule in the limit of \( \varepsilon_0 \to 0 \). Similarly, \( \Psi_E(R, \theta) = (\Psi^X_E(R, \theta), \Psi^A_E(R, \theta))^T \) represents any other eigenstate of Hamiltonian (1), with quasi-energy \( E \). The physical picture behind the just-defined spectral intensity is as follows. First, a sample of free diatomic molecules (cold enough to be predominantly in their ground states) is dressed by an adiabatically switched on CW laser pulse with the central frequency \( \omega_L \). This leads, via an adiabatic passage, to the dressed molecular state \( \tilde{\Psi}_o(R, \theta) \) described above. Subsequently, the system is probed by another laser which facilitates the dipole transitions from \( \tilde{\Psi}_o(R, \theta) \) to \( \Psi_E(R, \theta) \) according to the standard Golden rule theory as described by equation (3). The FC spectrum is obtained from (3) by identifying the initial state \( \tilde{\Psi}_o(R, \theta) \) with the ground state of a free diatomic molecule, and by choosing the final states \( \Psi_E(R, \theta) \) to be the eigenstates of the \( A^1\Sigma_g^+ \) state in the absence of the laser. It is known [1] that the FC spectrum becomes precise in the weak-field limit of \( \varepsilon_0 \to 0 \). For the ‘no CI’ case, the spectrum is obtained from (3) by substituting for \( \tilde{\Psi}_o(R, \theta) \) and \( \Psi_E(R, \theta) \) the corresponding eigenstates of the modified approximative Hamiltonian \( \tilde{H} \) which was defined above using equation (2).

The computed spectra are depicted in figure 3 for a weak laser intensity of \( 3 \times 10^8 \text{ W cm}^{-2} \). Figure 3(a) gives an overview of the calculated transition intensities. For most lines, the FC approximation describes the spectrum qualitatively well. Nevertheless, clear deviations from the ‘no CI’ spectrum are seen for most lines, with the intensity of the FC lines being higher (in particular for lines with energies of about 18 000 and 28 000 cm\(^{-1} \) above the ground state). Moreover, many FC lines are seen to split into two in the ‘no CI’ spectrum. Interestingly, even at this weak laser field one can see the obvious differences between the ‘no CI’ and the ‘exact’ spectra. The richness of the ‘exact’ spectrum becomes apparent on an expanded energy scale. In figure 3(b), we show the vicinity of the FC line between 15 400 and 16 200 cm\(^{-1} \). While there is only a single FC line (characterized by the electronic state \( A \), and \( \nu = 6, J = 1 \)), we observe two lines in the ‘no CI’ spectrum. The second weaker line is mainly the vibrational level (\( \nu = 4, J = 0 \)) of the lower electronic state \( X \) and has acquired its intensity by borrowing it from the more intense line (\( \nu = 6, J = 1 \)) of the \( A \) electronic state. This borrowing of intensity is a well-known non-adiabatic effect [10]. Interestingly, the CI gives rise to further substantial splittings. Each of the ‘no CI’ peaks splits into essentially three lines. For the weak laser intensity at hand, the splitting is mostly due to rotations. The assignment of the exact levels in figure 3(b) refers to the leading configuration in the expansion of the corresponding eigenstates in terms of the free molecular states. In reality, several (or even many) configurations contribute. For example, the state associated with the most intense borrowing line in the spectrum (labelled by \( X, \nu = 4, J = 4 \)) has a weight on the excited \( A \) electronic state of 20%. The averaged rotational quantum number \( J_X \) on the \( X \) electronic state equals \( J_X \pm \Delta J_X = 1.8 \pm 1.8 \), where \( \Delta J_X \) is the standard deviation. Analogously, on the \( A \) electronic state, \( J_A \pm \Delta J_A = 0.4 \pm 1.2 \).

We note that the absorption profiles depicted in figure 3 require spectroscopic resolution better than \( 50 \text{ cm}^{-1} \) which can be obtained in the lab (see, e.g., [9]). In supersonic beam experiments [8], the predicted phenomenon should be possible to observe. Figure 3 may thus serve as a proposal of a future experiment aimed at demonstrating the impact of light-induced CIs on molecular rovibrionic spectra even for rather weak fields.

Let us discuss now the situation encountered at the larger field intensity of \( 10^{11} \text{ W cm}^{-2} \). Here, all the molecular degrees of freedom are strongly coupled, and the corresponding eigenstates of Hamiltonian (1) cannot be assigned to their field-free counterparts. This complicates the use of the Golden rule formula (3), as we are unable to populate the initial state \( \tilde{\Psi}_o(R, \theta) \) via an adiabatic passage. In order to gain an insight into the nature of the obtained dressed molecular states, we instead consider the projection

\[
P(E) = \left| \langle \Psi^X_{E_0, J_0} | \phi^X_{E, J, \theta} \rangle \right|^2
\]

of each dressed state \( \tilde{\Psi}_E(R, \theta) \) on the field-free molecular ground state \( \phi^X_{E_0, J_0} \). The quantity \( P(E) \) possesses a clear physical meaning. It is the probability of populating the dressed state \( \tilde{\Psi}_E(R, \theta) \) when the
laser pulse is imposed abruptly on the sample of free diatomic molecules residing in their ground states \( \phi_{J=0,|\mu|\rho}(R) \). For the considered field intensity, pulse-shaping techniques allow the production of nearly any square laser pulse, depending on the availability of a source that can cover the required bandwidth [11].

Figure 4 shows the obtained profile of \( P(E) \). Surprisingly, it turns out that the ‘no CI’ spectrum has no resemblance whatsoever with the exact spectrum. The ‘no CI’ spectrum has become very sparse and the intensity of its lines is enormously. The high density of lines in the exact spectrum, on the other hand, is a signature of the singular non-adiabatic coupling induced by a strong CI [10]. In particular, the spectrum above the energy of about 20 000 cm\(^{-1} \) exhibits a typical irregular pattern like the spectra of CIs in polyatomics which have been shown to behave like the spectra of random matrix ensembles [13]. This irregularity reflects the complete mixing of multiple configurations in the respective eigenstates. Our numerical analysis shows that both the X and A electronic states are essentially equally populated in all the eigenstates above the CI energy. Similarly, also the field-free vibrational as well as rotational levels are enormously mixed. For example, for the lines between 40 000 and 45 000 cm\(^{-1} \), one typically finds \( J_X \pm \Delta J_X = 20 \pm 20 \) and \( J_A \pm \Delta J_A = 25 \pm 25 \), while \( \nu_X \pm \Delta \nu_X = 3 \pm 3 \) and \( \nu_A \pm \Delta \nu_A = 5 \pm 5 \). In all cases, the magnitudes of the calculated averages are roughly equal to their standard deviations.

We have shown that even diatomic molecules exhibit CIs. These are induced by running laser waves, and live in the space of the molecular rotational and vibrational degrees of freedom. We have demonstrated that these CIs have a strong impact on the molecular spectrum even for weak laser fields. For intermediate laser fields, this impact becomes dramatic and the resulting spectrum has no resemblance with those computed by standard approaches. The coupling of two electronic states via the light-induced CI is substantially and sometimes even dramatically stronger than without it, and consequently, one can apply rather weak fields to achieve strong coupling between these two states. If needed, e.g., when the field is strong and other electronic states are close by, one can easily include more electronic states in the formalism. Spectra of field-free molecules, such as that of copper trimer [14] or sodium trimer [15], have been shown to bear the signature of the Berry phase in the electronic wavefunction due to CIs [16]. The same classic consequence of the Berry phase in the electronic wavefunction is also found here for light-induced CIs. In sharp contrast to field-free polyatomic molecules where the CI is given by nature, the energetic position of the CI discussed here can be controlled by the laser frequency and the strength of its non-adiabatic coupling by the laser intensity. Finally, we stress that for polyatomics there are, of course, also laser-induced CIs. It is anticipated that their interplay with the CIs given by nature will lead to a wealth of new phenomena.

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