Direct signatures of light-induced conical intersections on the field-dressed spectrum of \( \text{Na}_2 \)

Tamás Szidarovszky,∗,† Gábor J. Halász,‡ Attila G. Császár,¶ Lorenz S. Cederbaum,§ and Ágnes Vibók∗,∥

†Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös Loránd University and MTA-ELTE Complex Chemical Systems Research Group, H-1117 Budapest, Pázmány Péter sétány 1/A, Hungary
‡Department of Information Technology, University of Debrecen, PO Box 400, H-4002 Debrecen, Hungary
¶Laboratory of Molecular Structure and Dynamics, Institute of Chemistry, Eötvös University and MTA-ELTE Complex Chemical Systems Research Group, H-1117 Budapest, Pázmány Péter sétány 1/A, Hungary
§Theoretische Chemie, Physikalisch-Chemisches Institut, Universitt Heidelberg, D-69120, Heidelberg, Germany
∥Department of Theoretical Physics, University of Debrecen, PO Box 400, H-4002 Debrecen, Hungary and ELI-ALPS, ELI-HU Non-Profit Ltd., Dugonics tér 13, H-6720 Szeged, Hungary

E-mail: tamas821@caesar.elte.hu vibok@phys.unideb.hu
Abstract

Rovibronic spectra of the field-dressed homonuclear diatomic Na$_2$ molecule is investigated to identify direct signatures of the light-induced conical intersection (LICI) on the spectrum. The theoretical framework formulated allows the computation of the (1) field-dressed rovibronic states induced by a medium intensity continuous-wave laser light and the (2) transition amplitudes between these field-dressed states with respect to an additional weak probe pulse. The field-dressed spectrum features absorption peaks resembling the field-free spectrum as well as stimulated emission peaks corresponding to transitions not visible in the field-free case. By investigating the dependence of the field-dressed spectra on the dressing-field wavelength, both in full- and reduced dimensional simulations, direct signatures of the LICI can be identified. These signatures include (1) the appearance of new peaks and the splitting of peaks for both absorption and stimulated emission, and (2) the manifestation of an intensity borrowing effect in the field-dressed spectrum.

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Introduction

Theoretical and experimental studies have revealed numerous new phenomena resulting from the interaction of matter with strong laser fields, such as high harmonic generation,\(^1\) above threshold ionization,\(^3\) dissociation,\(^4\) and bond softening and hardening effects.\(^5\) The last two of these phenomena can be explained by adopting the dressed-state or light-induced potential (LIP) picture, which involves a nuclear degree of freedom (most commonly the molecular vibration) in addition to the electronic degrees of freedom in the case of molecules.\(^6\) LIP provides an appropriate interpretation of the dissociation processes of small molecules exposed to high-intensity laser field. For example, LIP predicts that at low light intensities the dissociation rate of molecules behaves linearly with intensity according to the Fermi’s golden rule (FGR), while at larger intensities the dissociation rate is rather strongly nonlinear.\(^9\)

Including a second nuclear degree of freedom in the Hamiltonian of the light-matter interaction results in the “light-induced conical intersection” (LICI) picture. LICI was first discussed for diatomics under the presence of a standing external electric field.\(^12\) In this situation the translational motion of the molecule can strongly couple with the electronic degrees of freedom, while the vibrational motion provides the second dynamical variable, forming a branching space in diatomics and leading to a periodic array of light induced CIs. However, when a running laser field is present, the vibrational and the rotational degrees of freedom serve as the two dynamical variables.\(^13\)\(^14\) Recently, a number of studies appeared about the nature of the LICIs. Numerous theoretical and experimental studies have confirmed that LICIs have noticeable impact on different dynamical properties (like molecular alignment, photodissociation probability, etc...).\(^14\)\(^19\) Furthermore, a strong effect in the angular distribution of the photofragments has been revealed that serves as a direct signature of the LICI.\(^18\) The first experimental observation of LICIs in diatomic molecules was made by Bucksbaum et al.\(^20\) Besides the diatomic studies, a few results are available for polyatomics as well.\(^21\)\(^24\) In this case, due to the presence of several vibrational degrees
of freedom, LICI can form without rotation, which opens up the door for manipulating and controlling nonadiabatic effects by light.

Previous studies mainly concentrated on the dynamics of diatomic systems under the influence of strong electric fields. In the present work, we focus on the description of the field-dressed static rovibronic spectrum of diatomics. The theoretical and experimental investigations of the field-free rovibronic spectrum of diatomic molecules have been studied extensively for more than a century, significantly contributing to our fundamental understanding of chemical and physical phenomena. Measuring or computing spectral transitions between field-dressed states is well developed for atoms, and to some extent has also been incorporated to molecular spectroscopy. For example, inducing Autler–Townes-type splittings of rotational transitions with microwave radiation have been used to promote the assignation of rovibrational spectra or to deduce molecular parameters, such as the transition dipole moment. Theoretical work considering the transitions between field-dressed rovibronic states was also done for a dressing field of specific wavelength.

The purpose of the present work is to investigate the frequency- and intensity dependence of the field-dressed rovibronic spectrum of the homonuclear diatomic molecule Na$_2$ and to identify the direct signatures of LICIs on the spectrum.

**Theoretical approach**

In this study we are providing a framework to simulate the weak-field absorption and stimulated emission spectrum of field-dressed homonuclear diatomic molecules. First, we determine the field-dressed states, which we assume are formed from the field-free eigenstates of the system through the interaction with an external laser field of medium intensity, turned on adiabatically with respect to the characteristic molecular timescales. Second, we compute the dipole transition amplitudes between the field-dressed states with respect to a weak second pulse, using first order time-dependent perturbation theory. The showcase example
is the Na₂ molecule.

The field-dressed Floquet Hamiltonian of Na₂

Using the dipole approximation and considering only the ground \( V_1(R) = X^1\Sigma_g^+ \) and the first excited \( V_2(R) = A^1\Sigma_u^+ \) electronic states of Na₂, the time-dependent (TD) Hamiltonian of the system can be represented in the Floquet picture and can be written in a block diagonal form after neglecting the off-resonant light-matter coupling terms. The \( N \)th block of the Hamiltonian reads

\[
\hat{H}(N) = \left[ -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{L_{\theta\varphi}^2}{2\mu R^2} \right] \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + \begin{bmatrix} V_1(R) + N\hbar\omega & (F_0/2)d(R)\cos(\theta) \\ (F_0/2)d(R)\cos(\theta) & V_2(R) + (N-1)\hbar\omega \end{bmatrix}, \tag{1}
\]

where, \( R \) and \( (\theta, \varphi) \) are the molecular vibrational and rotational coordinates, respectively, \( \mu \) denotes the reduced mass of the diatomic, and \( L_{\theta\varphi} \) is the rotational angular momentum operator of the nuclei. \( F_0 \) and \( \omega \) are the amplitude and the frequency of the dressing electric field, respectively. \( d(R) \) is the dipole transition matrix element in the body-fixed frame and \( \theta \) also describes the angle between the polarization direction of the linearly polarized electric field and the direction of the transition dipole (\( \hbar \) is Planck’s constant divided by \( 2\pi \)).

After diagonalizing the diabatic potential matrix of Eq. (1), the resulting adiabatic or light-induced surfaces form a conical intersection for geometry parameters determined by the following conditions: \( V_1(R) = V_2(R) - \hbar\omega \) and \( \theta = \pi/2 \).

One can obtain all field-dressed (FD) eigenstates \( |\Psi_i^{FD}(N)\rangle \) and quasi-energies \( E_i^{FD}(N) \) by determining the eigenpairs of the Hamiltonian of Eq. (1) and applying an energy shift of \( k\hbar\omega \) to the quasienergies as necessary, where \( k \) is an integer.

We diagonalize the Hamiltonian of Eq. (1) after constructing its matrix representation using the basis of field-free rovibrational states. The field-free eigenstates of Na₂, \( i.e., \) the basis functions used to expand the field-dressed states, can be characterized by three quantum numbers and are represented as \( |j\nu J\rangle \), where the molecule is in the \( j \)th electronic, \( \nu \)th
vibrational, and $J$th rotational state, and $j = 1$ and $j = 2$ stand for the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ electronic states, respectively.

Using the notation termed "Floquet-state nomenclature" in Ref. 33, the field-dressed states can be expressed as the linear combination of products of field-free molecular rovibronic states and the Fourier vectors of the Floquet states, i.e.,

$$|\Psi_{FD}^i(N)\rangle = \sum_{J,v} C_{i,1vJ} |1vJ\rangle |N\rangle + \sum_{J,v} C_{i,2vJ} |2vJ\rangle |N - 1\rangle$$

where $|N\rangle$ is the $N$th Fourier vector of the Floquet state, and $C_{i,jvJ}$ are the expansion coefficients obtained by diagonalizing the Hamiltonian of Eq. (1) in the basis of the field-free rovibrational states. As detailed in Ref. 33, the time-dependence of the periodic Floquet state is determined by the time-dependence of its Fourier vectors $\langle t|N\rangle = e^{iN\omega t}$.

**Transitions between field-dressed states**

Given the Hamiltonian and the field-dressed states, we now turn to the computation of the spectrum of field-dressed molecules, i.e., we turn to the computation of transition amplitudes between field-dressed states as induced by a weak probe pulse. Since we assume the probe pulse to be weak, transitions induced by it should be dominated by one-photon processes. Therefore, following the standard approach of theoretical molecular spectroscopy, we use first-order TD perturbation theory to compute the transition amplitudes induced by the probe pulse. Then, the amplitudes are proportional to $\langle \Psi_{i FD}^j | \hat{d} \hat{e} | \Psi_{i FD}^i \rangle = \langle \Psi_{i FD}^j | d \cos(\theta) | \Psi_{i FD}^i \rangle$, where $\hat{e}$ is a unit vector defining the polarization direction of the probe pulse, which we assume to be identical to that of the dressing pulse. The conservation of energy requires that $E_{FD}^j = E_{FD}^i \pm \hbar \omega_p$, where $\omega_p$ is the angular frequency of the weak probe pulse. The
matrix element of the operator $\hat{d}\cos(\theta)$ between two field-dressed states of Eq. (2) gives

$$
\langle \Psi_{FD}^i(N) | \hat{d}\cos(\theta) | \Psi_{FD}^j(N') \rangle = 
\left( \sum_{J,v,J'} C^*_i,1vJ \langle 1vJ | N \rangle + \sum_{J,v,J'} C^*_i,2vJ \langle 2vJ | (N-1) \rangle \right) \hat{d}\cos(\theta) \left( \sum_{J',v'J''} C_j,1v'J' \langle 1v'J' | N' \rangle + \sum_{J',v'J''} C_j,2v'J' \langle 2v'J' | (N'-1) \rangle \right) = 
\sum_{J,v,J',v'} C^*_i,1vJ C_j,2vJ' (1vJ|\hat{d}\cos(\theta)|2v'J')(N|N'-1) + \sum_{J,v,J',v'} C^*_i,2vJ C_j,1vJ' (2vJ|\hat{d}\cos(\theta)|1v'J')(N-1|N') = 
\sum_{J,v,J',v'} C^*_i,1vJ C_j,2vJ' (1vJ|\hat{d}\cos(\theta)|2v'J')\delta_{N,N'-1} + \sum_{J,v,J',v'} C^*_i,2vJ C_j,1vJ' (2vJ|\hat{d}\cos(\theta)|1v'J')\delta_{N,N'+1}.
$$

In Eq. (3) we exploited the fact that Na$_2$ has no permanent dipole, and that the $|N\rangle$ Fourier vectors are orthogonal with respect to the scalar product defined in the time-domain of the extended Hilbert space of Floquet theory.33

In the last line of Eq. (3), the first term represents transitions with transition frequencies $\nu_{ij} = (hc)^{-1}|E_{FD}^j(N) + h\omega - E_{FD}^i(N)|$, to which the first electronic state contributes through the $i$th field-dressed state and the second electronic state contributes through the $j$th field-dressed state.

As will be shown, the first term in the last line of Eq. (3) leads to the usual field-free absorption spectrum in the limit of the dressing field intensity going to zero. On the other hand, the second term in the last line of Eq. (3) represents transitions with transition frequencies $\nu_{ij} = (hc)^{-1}|E_{FD}^j(N) - h\omega - E_{FD}^i(N)|$, in which the second electronic state contributes through the $i$th field-dressed state and the first electronic state contributes through the $j$th field-dressed state. For all dressing-field wavelengths considered in this study, the second term in the last line of Eq. (3) represents stimulated emission from the $|\Psi_{FD}^i(N)\rangle$ state, as induced by the probe pulse.
Results and discussion

Here we compute the field-dressed states and related spectra of the Na$_2$ molecule. Figure 1 demonstrates the field-dressed diabatic potential energy curves (PEC) of the $X^1\Sigma_g^+$ and $A^1\Sigma_u^+$ electronic states of Na$_2$ as well as the vibrational probability densities of the $|1 0 0\rangle|N\rangle$, $|1 3 0\rangle|N - 1\rangle$, $|1 11 0\rangle|N - 1\rangle$, $|2 2 1\rangle|N - 1\rangle$, and $|2 9 1\rangle|N\rangle$ states.

![Field-dressed diabatic PECs of Na$_2$](image)

Figure 1: Field-dressed diabatic PECs of Na$_2$ obtained with a dressing-light wavelength of $\lambda = 657$ nm. The energy scale stands for quasienergy. Vibrational probability densities are drawn for the $|1 0 0\rangle|N\rangle$ (continuous black line on the $V_1(R) + N\hbar\omega$ PEC), $|1 3 0\rangle|N - 1\rangle$ (green dashed line on the $V_1(R) + (N - 1)\hbar\omega$ PEC), $|1 11 0\rangle|N - 1\rangle$ (brown dashed line on the $V_1(R) + (N - 1)\hbar\omega$ PEC), $|2 2 1\rangle|N - 1\rangle$ (black dotted line on the $V_2(R) + (N - 1)\hbar\omega$ PEC), and $|2 9 1\rangle|N\rangle$ (red dashed line on the $V_2(R) + N\hbar\omega$ PEC) states. Upward- and downward pointing vertical arrows represent transitions of absorption and stimulated emission, respectively. The two product states with the largest contribution to the field-dressed state correlating to $|1 0 0\rangle$ at $F_0 \rightarrow 0$ are $|1 0 0\rangle|N\rangle$ and $|2 2 1\rangle|N - 1\rangle$.

Field-dressed spectra and their interpretation

In the following, we consider spectra obtained from a single $|\Psi^\text{FD}_1(N)\rangle$ field-dressed state, which we imagine to be populated adiabatically from the field-free ground state, $|1 0 0\rangle$, by slowly turning on the dressing field. In all spectra shown, we plot the absolute square of
transition amplitudes as computed by Eq. (3), or their convolution with a Gaussian function having $\sigma = 50 \text{ cm}^{-1}$.

Figure 2 shows field-dressed spectra of Na$_2$ obtained with a dressing-light wavelength of $\lambda = 657$ nm, which is nearly resonant with the $|1 0 0\rangle \leftrightarrow |2 2 1\rangle$ transition. In this case the two product states with the largest contribution to the field-dressed state correlating to $|1 0 0\rangle$ at $F_0 \rightarrow 0$ are $|1 0 0\rangle |N\rangle$ and $|2 2 1\rangle |N - 1\rangle$, with $|1 0 J\rangle |N\rangle$ (even $J$) and $|2 2 J \pm 1\rangle |N - 1\rangle$ states giving further contributions, whose magnitudes depend on the dressing-field intensity. Figure 2 shows that for low dressing-field intensities one basically obtains the field-free absorption spectrum of Na$_2$ with all peaks above $15000 \text{ cm}^{-1}$, resulting from transitions between the $|1 0 0\rangle$ ground state and the $|2 v 1\rangle$ rovibronic states. Due to the significantly different equilibrium distances of the X$^1\Sigma_g^+$ and A$^1\Sigma_u^+$ PECs, see Figure 1, the $|1 0 0\rangle$ ground state has considerable Frank–Condon (FC) overlaps with many vibrational states of A$^1\Sigma_u^+$, leading to a dozen or so absorption peaks even in the field-free case. This group of peaks located above $15000 \text{ cm}^{-1}$ originates from the contribution of the first term in the last line of Eq. (3). At higher dressing-field intensities the profile of this group of peaks changes, involving peaks primarily originating from transitions between the $|1 0 J\rangle |N\rangle$ low-lying rotational states of X$^1\Sigma_g^+$ and highly excited rovibrational states on A$^1\Sigma_u^+$ of the type $|2 v J \pm 1\rangle |N\rangle$, where $J$ is even.

Figure 2 also shows that for increasing dressing-field intensities another group of transitions (composed of three subgroups) appears between $13000$ and $15500 \text{ cm}^{-1}$. The origin of these peaks is the second term in the last line of Eq. (3) and they show transitions in which the quasienergy of the final state is lower than that of the initial state, i.e., they are stimulated emission peaks. Based on Figure 1 one can conclude that the stimulated emission peaks between $13000$ and $15500 \text{ cm}^{-1}$ in Figure 2 primarily originate from transitions between the low-lying $|2 2 J\rangle |N - 1\rangle$ rovibronal states and the vibrationally highly excited $|1 v J \pm 1\rangle |N - 1\rangle$ rovibronal states, where $J$ is odd. The three distinct groups of stimulated emission peaks seen in Figure 2 is a clear indication of the FC overlaps between
\(|22J\rangle\) and the vibrationally excited states of \(|1vJ\pm1\rangle\) type.

Figure 2: One-photon spectra of the field-dressed Na\(_2\) as a function of dressing-field (\(\lambda = 657\) nm) intensity, computed using Eq. 3. The spectra only show transitions from the field-dressed state which becomes the rovibrational ground state \(|100\rangle\) for \(F_0 \rightarrow 0\). The upper two panels show absorption peaks, while the lower two panels present stimulated emission peaks. The curves shown in the left panels are obtained by convolving the right hand side spectra with a Gaussian function having \(\sigma = 50\) cm\(^{-1}\).

Signatures of LICIs in the field-dressed spectrum

By changing the dressing-field frequency from 657 nm, the field-dressed states and their corresponding spectra naturally change as well, as presented in Figure 3. From now on we focus on how the presence of a LICI can directly be observed in field-dressed spectra. In this regard, we point out that, as Figure 3 shows, the spectra feature prominent variations in the absorption peak intensities as well as significant stimulated emission, when the dressing-field wavelength is near a resonant transition of \(|100\rangle \leftrightarrow |2v1\rangle\) type. Thus, as expected, the most significant mixing of field-free states in the dressed state correlating to \(|100\rangle\) at \(F_0 \rightarrow 0\)
occur at the vicinity of resonant frequencies. This strong mixing can lead to the correlation between light-dressed states and field-free states becoming unambiguous. Therefore, in order to avoid any confusion arising from comparing spectra originating from different field-dressed states, we investigate the effects of a LICI in light-dressed spectra obtained with nonresonant dressing fields. The wavelength of these nonresonant fields were chosen to be located exactly halfway between resonant wavelengths.

Figure 3: One-photon spectra of the field-dressed Na$_2$ as a function of dressing-field wavelength at a dressing-field intensity of $I_0 = 10^8$ Wcm$^{-2}$, computed using Eq. (3) and convolving the spectra at each fixed dressing-field wavelength with a Gaussian function having $\sigma = 50$ cm$^{-1}$. The left panel shows absorption, while the right panel presents stimulated emission peaks. The left side of the left panel shows the absolute square of the coefficient of the field-free ground state for the field-dressed state correlating to $|1 0 0\rangle$ at $I_0 \rightarrow 0$ Wcm$^{-2}$, which was used to obtain the spectra.

We aim to identify features in the field-dressed spectra which resemble one of the two following characteristic features of LICIs in diatomics: (1) coupling between the vibrational and a rotational degree of freedom manifested in the $\theta$-dependent adiabatic PECs, and (2) nonadiabatic couplings between the two adiabatic field-dressed electronic states connected by the LICI.

Figure 4 shows spectra of field-dressed Na$_2$ obtained for five non-resonant dressing-field wavelengths (641.2, 646.0, 650.6, 655.6, and 660.6 nm). At each dressing-field wavelength, two types of spectra are computed. The spectra labeled 2D were obtained as described above, while the spectra labeled 1D were computed by restricting the field-free eigenstates
in the basis to those having $J = 0$ or $1$. This restriction in the rotational quantum number leads to the inhibition of rotational motion, thus the dissappearance of the LICI. Therefore, all spectra obtained in the 1D model inherently lack any signatures originating from a LICI.
Figure 4: Absorption spectra of the field-dressed $\text{Na}_2$ at five non-resonant dressing-field wavelengths and a dressing-field intensity of $I = 10^8 \text{ Wcm}^{-2}$, obtained within the 1D (middle panel) and 2D (lowest panel) model, see text. The stick spectra in the middle and lowest panels represent the spectra obtained with the dressing-field wavelength of $\lambda = 650.6 \text{ nm}$. In the upmost panel diabatic and adiabatic PECs at $\theta = 0$ are shown along with the quasienergy of the field-dressed state correlating to $|1 0 0\rangle$ at $F_0 \rightarrow 0$ for $\lambda = 650.6 \text{ nm}$. The table inset in the upmost panel shows for different dressing-field wavelengths the difference between the energy position of the LICI and the quasienergy of the field-dressed state correlating to $|1 0 0\rangle$ at $F_0 \rightarrow 0$. 
Figure 5: Stimulated emission spectra of the field-dressed Na$_2$ at five non-resonant dressing-field wavelengths and a dressing-field intensity of $I = 10^8$ W cm$^{-2}$, obtained within the 2D (two panels on the lefthand side) or 1D model (two panels on the righthand side), see text.

Fig. 4 demonstrates that the 2D spectra exhibit significantly more absorption peaks than their 1D counterparts. This is expected, since in the 2D case field-free states with $J > 1$ rotational quantum number are populated and mixed in to the field-dressed states, which together with the $\Delta J = \pm 1$ selection rule for one-photon processes lead to the appearance of many additional transition peaks. In the adiabatic representation of field-dressed PECs, the large number of absorption peaks in the 2D spectra are identified as signatures of either the strong rovibrational coupling arising from the $\theta$-dependent adiabatic PECs or the nonadiabatic couplings near the LICI. Figure 4 also demonstrates that the peak intensities in the 2D spectra are more sensitive to the dressing-field wavelength than their 1D counterparts. This is also visible in the stimulated emission peaks, as shown in Fig. 5.

Interestingly, variations in the intensity of both the absorption and stimulated emission peaks in the 2D case seem to be most prominent when the field-dressed state correlating
to $|1 0 0\rangle$ at $F_0 \rightarrow 0$ has a quasienergy located near the energy position of the LICI. In the 1D case, variations of the peak intensities in the vicinity of the diabatic PEC crossing (there is no LICI in the 1D case) seem to be less pronounced in the stimulated emission spectra and are barely visible in the absorption spectra. In classical molecular spectroscopy, the presence of an intrinsic conical intersection and non-adiabatic couplings are known to cause the breakdown of the Frank-Condon principle and lead to irregular variations in peak intensities, often referred to as intensity borrowing. This leads to the conclusion that the significant intensity variation of the peaks in the 2D spectra near a LICI originates from strong non-adiabatic effects induced by the LICI.

**Summary and conclusions**

This study investigates direct signatures of LICIs on the spectra of molecules. The theoretical framework and the working equations have been formulated for computing one-photon transitions between field-dressed rovibronic states. The field-dressed states of our showcase molecule, Na$_2$, have been computed for a The field-dressed spectra feature absorption peaks as well as stimulated emission peaks. The absorption peaks resemble the field-free spectra, while the stimulated emission peaks correspond to transitions not visible in the field-free case. By investigating the dressing-field wavelength dependence of the field-dressed spectra for both full- and reduced-dimensional simulations, direct signatures of the LICI in the field-dressed spectrum are identified. These signatures are (1) the appearance of new peaks and the splitting of peaks for both absorption and stimulated emission, and (2) the manifestation of an intensity borrowing effect, i.e., an increase in the overall peak intensities when the quasienergy of the initial field-dressed state is in the vicinity of the energy position of the LICI. These signatures of the LICI originate from the strong rovibronic coupling in the field-dressed adiabatic electronic states and the non-adiabatic coupling induced by the LICI.
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