

Direct Signatures of Light-Induced Conical Intersections on the Field-Dressed Spectrum of Na₂

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, P.O. Box 32, H-1117 Budapest, Hungary

[‡]MTA-ELTE Complex Chemical Systems Research Group, Pázmány Péter sétány 1/A, H-1117 Budapest, Hungary

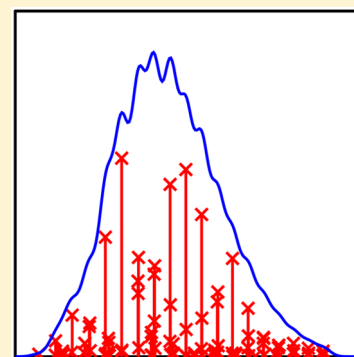
[§]Department of Information Technology, University of Debrecen, P.O. Box 400, H-4002 Debrecen, Hungary

^{||}Theoretische Chemie, Physikalisch-Chemisches Institut, Universität Heidelberg, D-69120 Heidelberg, Germany

[†]Department of Theoretical Physics, University of Debrecen, P.O. Box 400, H-4002 Debrecen, Hungary

[#]ELI-ALPS, ELI-HU Non-Profit Ltd., Dugonics tér 13, H-6720 Szeged, Hungary

ABSTRACT: Rovibronic spectra of the field-dressed homonuclear diatomic Na₂ molecule are 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, in both 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.



Theoretical and experimental studies have revealed numerous new phenomena resulting from the interaction of matter with strong laser fields, such as high harmonic generation,^{1,2} above-threshold ionization,³ dissociation,⁴ and bond softening and hardening effects.^{5–8} 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.^{9–11} LIP provides an appropriate interpretation of the dissociation processes of small molecules exposed to high-intensity laser fields. For example, LIP predicts that at low light intensities the dissociation rate of molecules behaves linearly with intensity according to Fermi's golden rule (FGR), while at larger intensities the dissociation rate is 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 to 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

conical intersections (CIs). However, when a running laser field is present, the vibrational and the rotational degrees of freedom serve as the two dynamical variables.^{13–15} Recently, a number of studies have appeared about the nature of the LICIs. Numerous theoretical and experimental studies have confirmed that LICIs have a 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, because of 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

Received: April 10, 2018

Accepted: May 7, 2018

Published: May 7, 2018

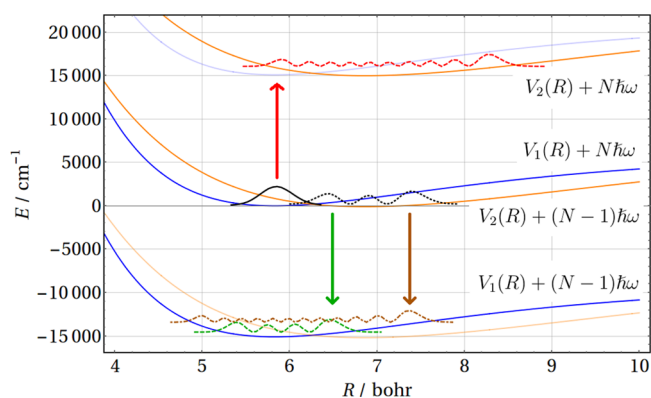


Figure 1. Field-dressed diabatic PECs of Na_2 obtained with a dressing-light wavelength of $\lambda = 657$ nm. The energy scale stands for quasienergy. Vibrational probability densities are drawn for the $|1\ 0\ 0\rangle|N\rangle$ (continuous black line on the $V_1(R) + N\hbar\omega$ PEC), $|1\ 3\ 0\rangle|N-1\rangle$ (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 $|2\ 2\ 1\rangle|N-1\rangle$.

theoretical and experimental investigations of the field-free rovibronic spectrum of diatomic molecules span for more than

a century,^{25,26} contributing significantly to our fundamental understanding of chemical and physical phenomena. Measuring or computing spectral transitions between field-dressed states is well developed for atoms²⁷ and to some extent has also been incorporated in molecular spectroscopy. For example, inducing Autler–Townes-type splittings²⁸ of rotational transitions with microwave radiation have been used to promote the assignment of rovibrational spectra²⁹ or to deduce molecular parameters, such as the transition dipole moment.^{30,31} Theoretical work considering the transitions between field-dressed rovibronic states was also done for a dressing field of specific wavelength.¹³

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.

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 time scales. 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.³² The showcase example is the Na_2 molecule.

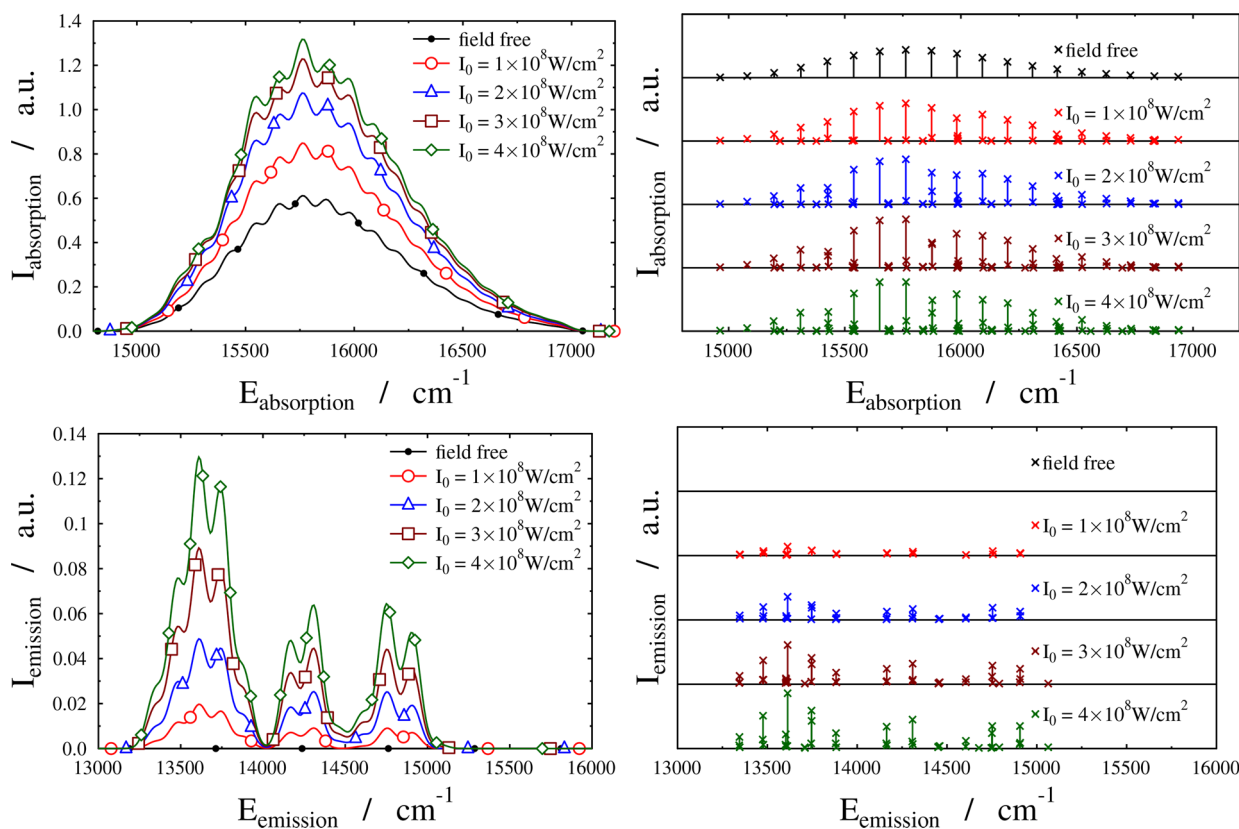


Figure 2. One-photon spectra of the field-dressed Na_2 as a function of dressing-field ($\lambda = 657$ nm) intensity, computed using eq 3. The spectra only show transitions from the field-dressed state, which becomes the rovibrational ground state $|1\ 0\ 0\rangle$ for $F_0 \rightarrow 0$. The upper 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} .

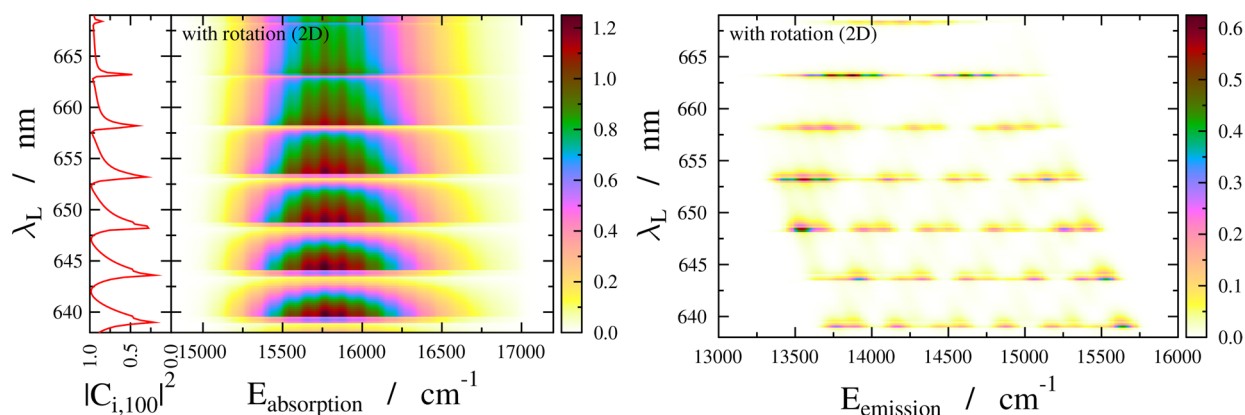


Figure 3. One-photon spectra of the field-dressed Na_2 as a function of dressing-field wavelength at a dressing-field intensity of $I_0 = 10^8 \text{ W cm}^{-2}$, computed using eq 3 and convolving the spectra at each fixed dressing-field wavelength with a Gaussian function having $\sigma = 50 \text{ cm}^{-1}$. The left panel shows absorption, whereas 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 $I_0 \rightarrow 0 \text{ W cm}^{-2}$, which was used to obtain the spectra.

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 Na_2 , the time-dependent (TD) Hamiltonian of the system can be represented in the Floquet picture³³ 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

$$\hat{H}(N) = \begin{bmatrix} -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial R^2} + \frac{\mathbf{L}_{\theta\varphi}^2}{2\mu R^2} & \\ & \otimes \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \end{bmatrix} + \begin{bmatrix} V_1(R) + N\hbar\omega & (F_0/2)d(R) \cos(\theta) \\ (F_0/2)d(R) \cos(\theta) & V_2(R) + (N-1)\hbar\omega \end{bmatrix} \quad (1)$$

where R and (θ, φ) are the molecular vibrational and rotational coordinates, respectively, μ denotes the reduced mass of the diatomic, $\mathbf{L}_{\theta\varphi}$ is the rotational angular momentum operator of the nuclei, F_0 and ω 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 θ 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 2π .) We use the potential energy curves (PECs) and the transition dipole function of refs 34 and 35, respectively.

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 $\theta = \pi/2$.¹⁸

One can obtain all field-dressed (FD) eigenstates $|\Psi_i^{\text{FD}}(N)\rangle$ and quasi-energies $E_i^{\text{FD}}(N)$ 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 Na_2 , that is, 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, ν 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. Because only bound electronic states are considered on our basis, our model is incapable of describing processes involving ionization. Nonetheless, such processes are expected to be negligible for the dressing-field parameters considered in this work.

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, that is

$$|\Psi_i^{\text{FD}}(N)\rangle = \sum_{J,\nu} C_{i,1\nu J} |1\nu J\rangle |N\rangle + \sum_{J,\nu} C_{i,2\nu J} |2\nu J\rangle |N-1\rangle \quad (2)$$

where $|N\rangle$ is the N th Fourier vector of the Floquet state and $C_{i,j\nu J}$ are the expansion coefficients obtained by diagonalizing the Hamiltonian of eq 1 after representing it 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 $\langle t|N\rangle = e^{iN\omega t}$.

Given the Hamiltonian and the field-dressed states, we now turn to the computation of the spectrum of field-dressed molecules, that is, we turn to the computation of transition amplitudes between field-dressed states, as induced by a weak probe pulse. Because 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,³⁶ we use first-order TD perturbation theory to compute the transition amplitudes induced by the probe pulse. Then, the amplitudes are proportional to $\langle \Psi_i^{\text{FD}} | \hat{\mathbf{d}} \hat{\mathbf{e}} | \Psi_j^{\text{FD}} \rangle = \langle \Psi_i^{\text{FD}} | \hat{\mathbf{d}} \cos(\theta) | \Psi_j^{\text{FD}} \rangle$, where $\hat{\mathbf{e}}$ 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 $E_j^{\text{FD}} = E_i^{\text{FD}} \pm \hbar\omega_p$, where ω_p is the angular frequency of the weak probe pulse. The matrix element of the operator $\hat{\mathbf{d}} \cos(\theta)$ between two field-dressed states of eq 2 gives

$$\begin{aligned}
 & \langle \Psi_i^{\text{FD}}(N) | \hat{d} \cos(\theta) | \Psi_j^{\text{FD}}(N') \rangle \\
 &= \left(\sum_{J,v} C_{i,1v}^* \langle 1vJ | \langle N | + \sum_{J,v} C_{i,2v}^* \langle 2vJ | \langle N-1 | \right) \\
 & \quad \hat{d} \cos(\theta) \left(\sum_{J',v'} C_{j,1v'} \langle 1v'J' | \langle N' \rangle + \sum_{J',v'} C_{j,2v'} \langle 2v'J' | \langle N'-1 \rangle \right) \\
 &= \sum_{J,v,J',v'} C_{i,1v}^* C_{j,2v'} \langle 1vJ | \hat{d} \cos(\theta) | 2v'J' \rangle \langle N | \langle N'-1 \rangle \\
 & \quad + \sum_{J,v,J',v'} C_{i,2v}^* C_{j,1v'} \langle 2vJ | \hat{d} \cos(\theta) | 1v'J' \rangle \langle N-1 | \langle N' \rangle \\
 &= \sum_{J,v,J',v'} C_{i,1v}^* C_{j,2v'} \langle 1vJ | \hat{d} \cos(\theta) | 2v'J' \rangle \delta_{N,N'-1} \\
 & \quad + \sum_{J,v,J',v'} C_{i,2v}^* C_{j,1v'} \langle 2vJ | \hat{d} \cos(\theta) | 1v'J' \rangle \delta_{N,N'+1} \quad (3)
 \end{aligned}$$

In eq 3 we exploited the fact that Na₂ 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(second) term represents transitions with transition frequencies ν_{ij}^{\pm} (ν_{ij}^{\mp}), where $\nu_{ij}^{\pm} = (hc)^{-1} |E_j^{\text{FD}}(N) \pm \hbar\omega - E_i^{\text{FD}}(N')|$. The first(second) electronic state contributes through the i th field-dressed state, and the second (first) electronic state contributes through the j th field-dressed state in the transitions with frequencies ν_{ij}^{\pm} (ν_{ij}^{\mp}).

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 contrary, for all dressing-field wavelengths considered in this study, the second term in the last line of eq 3 represents stimulated emission from the $|\Psi_i^{\text{FD}}(N)\rangle$ state, as induced by the probe pulse.

Henceforth we discuss the field-dressed states and related spectra of the Na₂ molecule. Figure 1 demonstrates the field-dressed diabatic PECs of the X¹Σ_g⁺ and A¹Σ_u⁺ electronic states of Na₂, 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.

In what follows, we consider spectra obtained from a single $|\Psi_i^{\text{FD}}(N)\rangle$ 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 the transition amplitudes, as computed by eq 3, or their convolution with a Gaussian function with a standard deviation of $\sigma = 50\text{ cm}^{-1}$.

Figure 2 shows field-dressed spectra of Na₂ obtained with a dressing-light wavelength of $\lambda = 657\text{ nm}$, 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 Na₂ with all peaks above $15\ 000\text{ cm}^{-1}$, resulting from transitions between the $|1\ 0\ 0\rangle$ ground state and the $|2\ v\ 1\rangle$ rovibronic states. Because of the significantly different equilibrium distances of the X¹Σ_g⁺ and A¹Σ_u⁺ PECs (see Figure 1), the $|1\ 0\ 0\rangle$ ground state has considerable Franck-Condon (FC) overlaps with many vibrational states of A¹Σ_u⁺, leading to a dozen or so absorption peaks even in the field-free case. This group of peaks located above $15\ 000$

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 X¹Σ_g⁺ and highly excited rovibrational states on A¹Σ_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 $13\ 000$ and $15\ 500\text{ cm}^{-1}$. The

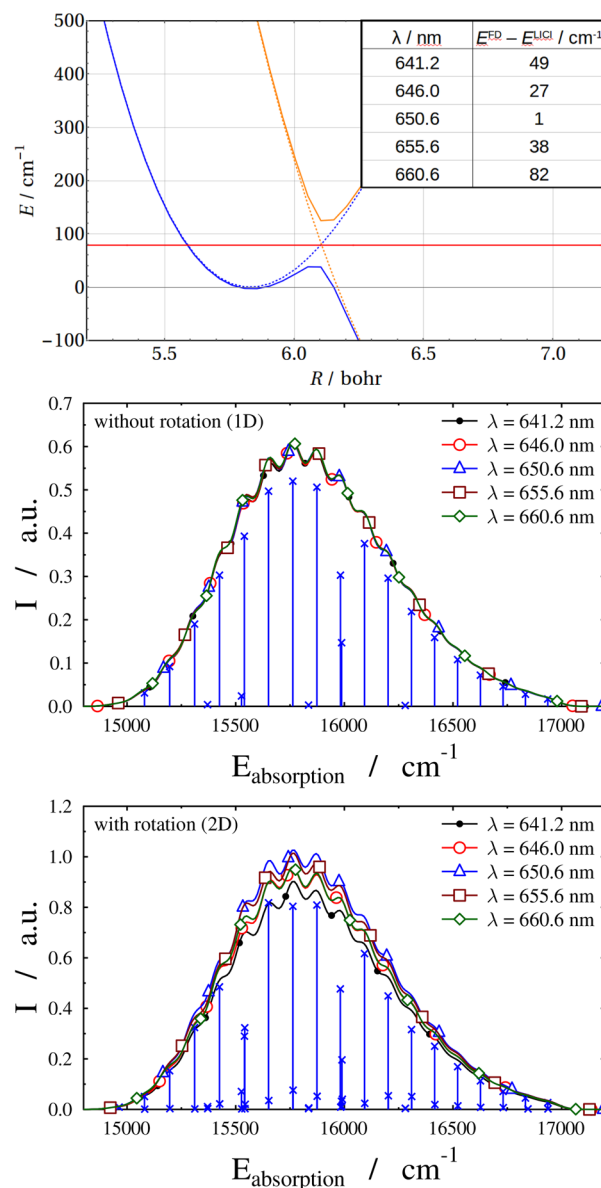


Figure 4. Absorption spectra of the field-dressed Na₂ at five nonresonant dressing-field wavelengths and a dressing-field intensity of $I = 10^8\text{ Wcm}^{-2}$, obtained within the 1D (middle panel) and 2D (lowest panel) models; see the text. The stick spectra in the middle and lowest panels represent 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 energy difference between the LICI and the quasienergy of the field-dressed state correlating to $|1\ 0\ 0\rangle$ at $F_0 \rightarrow 0$.

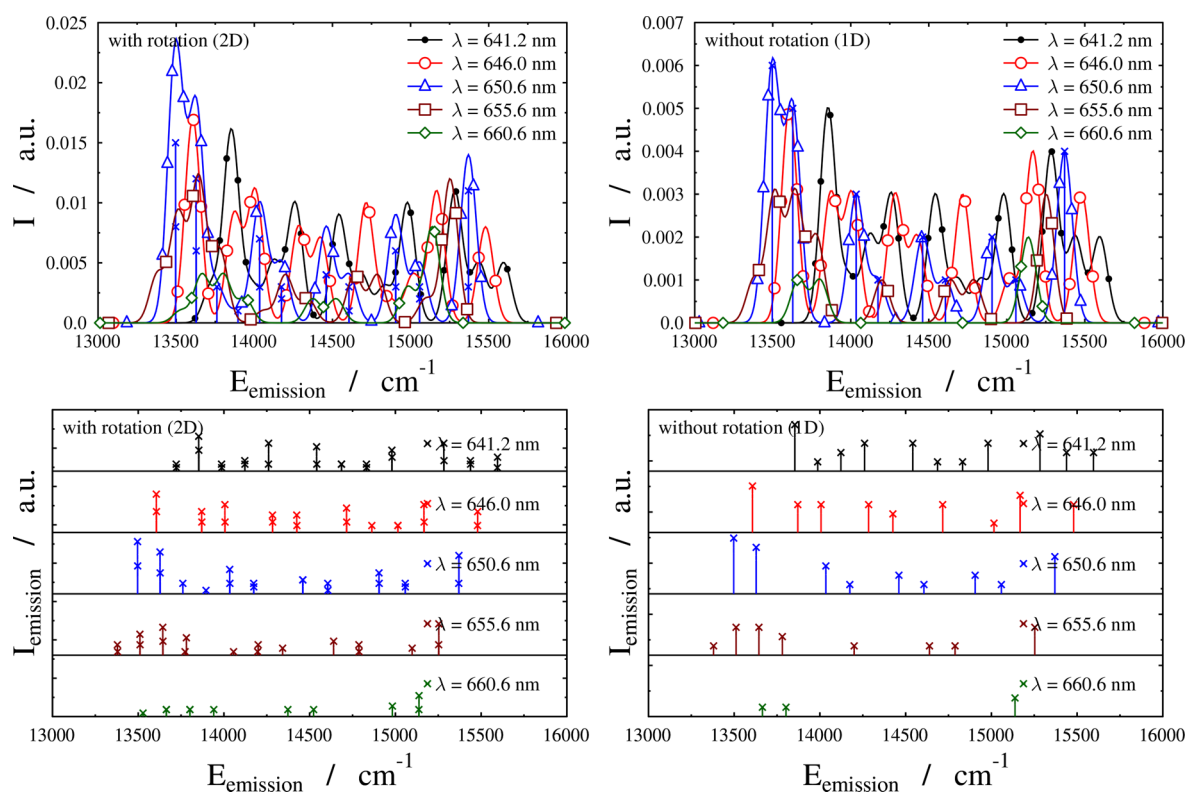


Figure 5. Stimulated emission spectra of the field-dressed Na_2 at five nonresonant dressing-field wavelengths and a dressing-field intensity of $I = 10^8 \text{ W cm}^{-2}$, obtained within the 2D (two panels on the left-hand side) or 1D model (two panels on the right-hand side); see the text.

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; that is, they are stimulated emission peaks. On the basis of Figure 1, one can conclude that the stimulated emission peaks between $13\,000$ and $15\,500 \text{ cm}^{-1}$ in Figure 2 primarily originate from transitions between the low-lying $|2\ 2\ J\rangle|N-1\rangle$ rovibrational states and the vibrationally highly excited $|1\ 1\ \nu\ J \pm 1\rangle|N-1\rangle$ rovibrational states, where J is odd. The three distinct groups of stimulated emission peaks seen in Figure 2 are a clear indication of the FC overlaps between $|2\ 2\ J\rangle$ and the vibrationally excited states of $|1\ 1\ \nu\ J \pm 1\rangle$ type.

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 $|1\ 0\ 0\rangle \leftrightarrow |2\ \nu\ 1\rangle$ type. Thus, as expected, the most significant mixing of field-free states in the dressed state correlating to $|1\ 0\ 0\rangle$ at $F_0 \rightarrow 0$ occurs 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, 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.

We aim to identify features in the field-dressed spectra that 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 θ -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 nonresonant 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, whereas the spectra labeled 1D were computed by restricting the set of 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 and thus the disappearance of the LICI.¹⁸ Therefore, all spectra obtained in the 1D model inherently lack any signatures originating from a LICI.

Figure 4 shows that the 2D spectra exhibit significantly more absorption peaks than their 1D counterparts. This is expected because in the 2D case field-free states with $J > 1$ rotational quantum number are populated and mixed into the field-dressed states, which together with the $\Delta J = \pm 1$ selection rule for one-photon processes leads 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 θ -dependent adiabatic PECs or the nonadiabatic couplings near the LICI. Figure 4 also shows 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 Figure 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 LICl. In the 1D case, variations of the peak intensities in the vicinity of the diabatic PEC crossing (there is no LICl 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 nonadiabatic couplings is known to cause the breakdown of the Franck–Condon principle²⁶ and lead to irregular variations in peak intensities, often referred to as intensity borrowing.^{36,37} This leads to the conclusion that the significant intensity variation of the peaks in the 2D spectra near a LICl originates from strong nonadiabatic effects induced by the LICl.

In summary, this study determined 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 number of dressing-field parameters, and the $T = 0$ K field-dressed spectra were simulated assuming an adiabatic turn-on of the dressing field; that is, the transitions computed correspond to an initial dressed state, which correlates to the rovibronic ground state of Na_2 in the field-free limit. 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 LICl 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, that is, 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 LICl. These signatures of the LICl originate from the strong rovibronic coupling in the field-dressed adiabatic electronic states and the nonadiabatic coupling induced by the LICl.

AUTHOR INFORMATION

Corresponding Authors

*T.Sz.: E-mail: tamas821@caesar.elte.hu.

*Á.V.: E-mail: vibok@phys.unideb.hu.

ORCID

Tamás Szidarovszky: 0000-0003-0878-5212

Attila G. Császár: 0000-0001-5640-191X

Ágnes Vibók: 0000-0001-6821-9525

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the EU-funded Hungarian grant EFOP-3.6.2-16-2017-00005. We acknowledge financial support by the Deutsche Forschungsgemeinschaft (Project ID CE10/50-3). We are grateful to NKFIH for support (grant nos. PD124623 and K119658).

REFERENCES

- (1) Krause, J. L.; Schafer, K. J.; Kulander, K. C. High-Order Harmonic Generation from Atoms and Ions in the High Intensity Regime. *Phys. Rev. Lett.* **1992**, *68*, 3535–3538.
- (2) Lewenstein, M.; Balcou, P.; Ivanov, M. Y.; L'Huillier, A.; Corkum, P. B. Theory of High-Harmonic Generation by Low-Frequency Laser Fields. *Phys. Rev. A: At., Mol., Opt. Phys.* **1994**, *49*, 2117–2132.
- (3) Schafer, K. J.; Yang, B.; DiMauro, L. F.; Kulander, K. C. Above Threshold Ionization Beyond the High Harmonic Cutoff. *Phys. Rev. Lett.* **1993**, *70*, 1599–1602.
- (4) Bandrauk, A. D.; Sink, M. L. Laser Induced Preassociation in the Presence of Natural Predissociation. *Chem. Phys. Lett.* **1978**, *57*, 569–572.
- (5) Aubanel, E. E.; Gauthier, J.-M.; Bandrauk, A. D. Molecular Stabilization and Angular Distribution in Photodissociation of H_2^+ in Intense Laser Fields. *Phys. Rev. A: At., Mol., Opt. Phys.* **1993**, *48*, 2145–2152.
- (6) Bandrauk, A. D.; Aubanel, E. E.; Gauthier, J. M. *Molecules in Laser Fields*; Marcel Dekker, 1994; Vol. 1.
- (7) Bucksbaum, P. H.; Zavriyev, A.; Muller, H. G.; Schumacher, D. W. Softening of the H_2^+ Molecular Bond in Intense Laser Fields. *Phys. Rev. Lett.* **1990**, *64*, 1883–1886.
- (8) Zavriyev, A.; Bucksbaum, P. H.; Muller, H. G.; Schumacher, D. W. Ionization and Dissociation of H_2 in Intense Laser Fields at 1.064 micron, 532 nm, and 355 nm. *Phys. Rev. A: At., Mol., Opt. Phys.* **1990**, *42*, 5500–5513.
- (9) Wunderlich, C.; Kobler, E.; Figger, H.; Hänsch, T. W. Light-Induced Molecular Potentials. *Phys. Rev. Lett.* **1997**, *78*, 2333–2336.
- (10) Sändig, K.; Figger, H.; Hänsch, T. W. Dissociation Dynamics of H_2^+ in Intense Laser Fields: Investigation of Photofragments from Single Vibrational Levels. *Phys. Rev. Lett.* **2000**, *85*, 4876–4879.
- (11) Chang, B. Y.; Sola, I. R.; Shin, S. Molecular Events in the Light of Strong Fields: A Light-Induced Potential Scenario. *Int. J. Quantum Chem.* **2016**, *116*, 608–621.
- (12) Moiseyev, N.; Šindelka, M.; Cederbaum, L. S. Laser-Induced Conical Intersections in Molecular Optical Lattices. *J. Phys. B: At., Mol. Opt. Phys.* **2008**, *41*, 221001.
- (13) Šindelka, M.; Moiseyev, N.; Cederbaum, L. S. Strong Impact of Light-Induced Conical Intersections on the Spectrum of Diatomic Molecules. *J. Phys. B: At., Mol. Opt. Phys.* **2011**, *44*, 045603.
- (14) Halász, G. J.; Vibók, Á.; Šindelka, M.; Moiseyev, N.; Cederbaum, L. S. Conical Intersections Induced by Light: Berry Phase and Wavepacket Dynamics. *J. Phys. B: At., Mol. Opt. Phys.* **2011**, *44*, 175102.
- (15) Halász, G. J.; Šindelka, M.; Moiseyev, N.; Cederbaum, L. S.; Vibók, Á. Light-Induced Conical Intersections: Topological Phase, Wave Packet Dynamics, and Molecular Alignment. *J. Phys. Chem. A* **2012**, *116*, 2636–2643.
- (16) Halász, G. J.; Csehi, A.; Vibók, Á.; Cederbaum, L. S. Influence of Light-Induced Conical Intersection on the Photodissociation Dynamics of D_2^+ Starting from Individual Vibrational Levels. *J. Phys. Chem. A* **2014**, *118*, 11908–11915.
- (17) Csehi, A.; Halász, G. J.; Cederbaum, L. S.; Vibók, Á. Towards Controlling the Dissociation Probability by Light-Induced Conical Intersections. *Faraday Discuss.* **2016**, *194*, 479–493.
- (18) Halász, G. J.; Vibók, Á.; Cederbaum, L. S. Direct Signature of Light-Induced Conical Intersections in Diatomics. *J. Phys. Chem. Lett.* **2015**, *6*, 348–354.
- (19) Shu, C. C.; Yuan, K. J.; Dong, D.; Petersen, I. R.; Bandrauk, A. D. Identifying Strong-Field Effects in Indirect Photofragmentation. *J. Phys. Chem. Lett.* **2017**, *8*, 1–6.
- (20) Natan, A.; Ware, M. R.; Prabhudesai, V. S.; Lev, U.; Bruner, B. D.; Heber, O.; Bucksbaum, P. H. Observation of Quantum Interferences via Light-Induced Conical Intersections in Diatomic Molecules. *Phys. Rev. Lett.* **2016**, *116*, 143004.
- (21) Kim, J.; Tao, H.; White, J. L.; Petrović, V. S.; Martinez, T. J.; Bucksbaum, P. H. Control of 1,3-Cyclohexadiene Photoisomerization

Using Light-Induced Conical Intersections. *J. Phys. Chem. A* **2012**, *116*, 2758–2763.

(22) Demekhin, P. V.; Cederbaum, L. S. Light-Induced Conical Intersections in Polyatomic Molecules: General Theory, Strategies of Exploitation, and Application. *J. Chem. Phys.* **2013**, *139*, 154314.

(23) Corrales, M. E.; González-Vázquez, J.; Balerdi, G.; Solá, I. R.; de Nalda, R.; Bañares, L. Control of Ultrafast Molecular Photodissociation by Laser-Field-Induced Potentials. *Nat. Chem.* **2014**, *6*, 785–790.

(24) Kim, J.; Tao, H.; Martinez, T. J.; Bucksbaum, P. Ab Initio Multiple Spawning on Laser-Dressed States: a Study of 1,3-Cyclohexadiene Photoisomerization via Light-Induced Conical Intersections. *J. Phys. B: At., Mol. Opt. Phys.* **2015**, *48*, 164003.

(25) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold, 1945; Chapter 3.

(26) Quack, M.; Merkt, F. *Handbook of High-Resolution Spectroscopy*; Wiley, 2011.

(27) Cohen-Tannoudji, C.; Dupont-Roc, J.; Grynberg, G. *Atom-Photon Interactions: Basic Processes and Applications*; Wiley-VCH Verlag GmbH and Co. KGaA, 2004.

(28) Autler, S. H.; Townes, C. H. Stark Effect in Rapidly Varying Fields. *Phys. Rev.* **1955**, *100*, 703.

(29) Lee, C. Y.; Pate, B. H. Dressed States of Molecules and Microwave-Infrared Double-Resonance Spectroscopic Techniques Employing an Electric Quadrupole Focusing Field. *J. Chem. Phys.* **1997**, *107*, 10430–10439.

(30) Sanli, A.; Pan, X.; Magnier, S.; Huennekens, J.; Lyyra, A. M.; Ahmed, E. H. Measurement of the Na_2 $5^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$ and $6^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$ Transition Dipole Moments Using Optical-Optical Double Resonance and Autler–Townes Spectroscopy. *J. Chem. Phys.* **2017**, *147*, 204301.

(31) Ahmed, E. H.; Huennekens, J.; Kirova, T.; Qi, J.; Lyyra, A. M. The Autler–Townes Effect in Molecules: Observations, Theory, and Applications. *Adv. At., Mol., Opt. Phys.* **2012**, *61*, 467–514.

(32) Landau, L. D.; Lifshitz, E. M. *Quantum Mechanics*, 3rd ed.; Pergamon, 1977.

(33) Chu, S.-I.; Telnov, D. A. Beyond the Floquet Theorem: Generalized Floquet Formalisms and Quasienergy Methods for Atomic and Molecular Multiphoton Processes in Intense Laser Fields. *Phys. Rep.* **2004**, *390*, 1–131.

(34) Magnier, S.; Millié, P.; Dulieu, O.; Masnou-Seeuws, F. Potential Curves for the Ground and Excited States of the Na_2 Molecule up to the $(3s+5p)$ Dissociation Limit: Results of Two Different Effective Potential Calculations. *J. Chem. Phys.* **1993**, *98*, 7113–7125.

(35) Zemke, W. T.; Verma, K. K.; Vu, T.; Stwalley, W. C. An Investigation of Radiative Transition Probabilities for the $A^1\Sigma_u^+ - X^1\Sigma_g^+$ Bands of Na_2 . *J. Mol. Spectrosc.* **1981**, *85*, 150–176.

(36) Bunker, P. R.; Jensen, P. *Molecular Symmetry and Spectroscopy*; NRC Research Press, 1998.

(37) Köppel, H.; Domcke, W.; Cederbaum, L. S. Multimode Molecular Dynamics Beyond the Born-Oppenheimer Approximation. *Adv. Chem. Phys.* **1984**, *57*, 59–246.