

On the line shape of the total rovibronic absorption in laser-dressed diatomic molecules

Gábor J. Halász(1), Tamás Szidarovszky(2,3), and Ágnes Vibók(4,5)

(1) Department of Information Technology, University of Debrecen, P.O. Box 400, H-4002 Debrecen, Hungary

(2) Institute of Chemistry, Eötvös Loránd University, P.O. Box 32, H-1117 Budapest, Hungary

(3) MTA-ELTE Complex Chemical Systems Research Group,
Pármány Péter Sétány 1/A, H-1117 Budapest, Hungary

(4) Department of Theoretical Physics, University of Debrecen, PO Box 400, H-4002 Debrecen, Hungary *and*

(5) ELI-ALPS, ELI-HU Non-Profit Ltd, H-6720 Szeged, Dugonics tér 13, Hungary*

Recently, the rovibronic absorption and emission spectra of diatomic molecules dressed by medium-intensity laser fields have been discussed. By computing the total absorption probability as a function of dressing wavelength an asymmetric line shape has been obtained strongly resembling to the well-known Fano line shape. Applying two-state analytical and three-state numerical models the shape of the total absorption probability function is explained. Further confirmation of the model based results is provided by high resolution accurate numerical computations using large number of basis functions.

I. INTRODUCTION

Asymmetric spectral line shapes first emerged in atomic physics, when two quantum mechanically coupled transition paths from a given ground state to an isolated discrete excited state and to a characterless continuum of states interfere with each other. The eigenstates and/or transitions associated with the asymmetric line shape are neither purely discrete nor purely continuous, but show a mixed character and are referred to as autoionising resonances. They were discovered experimentally by Beutler [1], and later Fano generalized the theory by deriving analytic formula for the asymmetric line shape [2], hence the name is “Fano line shape”. Subsequent to Fano’s work, the asymmetric Fano profile has been observed in a wide variety of phenomena. It emerges e.g. in the field of molecular [3–13], nuclear [14, 15] and solid state [16–18] physics, however, the mechanism is quite different for each example. In addition, the Fano resonances are also key elements in the optics of plasmonic nanostructures [19–24] and metamaterials [25].

Recently, we have investigated the light-dressed rovibronic spectrum of the Na_2 molecule [26, 27]. The dressing process was described within the Floquet framework [28, 29] and assuming that the dressing field was turned on adiabatically [30, 31], i.e., its envelope varies much slower than the rovibronic timescales characterizing the molecule. We have computed the field-dressed rovibronic absorption spectra of this system in which we were able to identify the direct signatures of the light-induced conical intersection (LICI) as well, which originate from the strong rovibronic coupling in the field-dressed adiabatic electronic states and the nonadiabatic coupling induced by the LICI [26].

In these works [26, 27], less attention has been paid to the dressing-field wavelength dependence of the field dressed absorption probability, however, this quantity shows quite an interesting shape. In spite of the lack of a continuum channel in the model, an asymmetric line shape can be visualized in the quantity of total absorption probability versus dressing wavelength (see Fig. 2), which resembles to the well known “Fano-like profile” [1, 2].

The goal of the present work is to understand and explain the origin of the asymmetric line shape of the total absorption probability function of light-dressed molecules by unveiling the physical mechanism behind the adiabatic light dressing process of molecules. Although at first sight it shows some similarities with the Fano line shape, the present phenomenon is definitely something different because *i)* there is no continuum channel present in the model and *ii)* there are separate numerical simulations for each dressing-field wavelength, and in this sense the total absorption probability can not be seen as a standard spectrum.

II. FIELD-DRESSED STATES AND TRANSITION AMPLITUDES

The two step process and the numerical method were discussed in detail previously in [26]. Here, only the dressing Hamiltonian and some relevant details on the numerical calculations are briefly summarized. Using the dipole approximation and considering only the ground $V_1(R) = X^1 \sum_g^+$ and the first excited $V_2(R) = A^1 \sum_u^+$ electronic states

*Electronic address: halasz@inf.unideb.hu, vibok@phys.unideb.hu

of Na₂ molecule, the time-dependent (TD) Hamiltonian of the system can be written in Floquet framework [28, 29] and can be obtained in a block diagonal form after neglecting the off-resonant light-matter coupling terms. The N th block of the Hamiltonian is

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

where R and (θ, φ) are the molecular vibrational and rotational coordinates, respectively, μ is the reduced mass, and $\mathbf{L}_{\theta\varphi}$ denotes the angular momentum operator of the nuclei. One of the rotational coordinates, θ , denotes the angle between the polarization direction of the laser light and the direction of the transition dipole. F_0 and ω are the amplitude and the frequency of the dressing laser field, respectively, $d(R)$ is the transition dipole matrix element in the body-fixed frame. The potential energies $V_1(R)$ and $V_2(R)$ and the transition dipole moment were taken from [32, 33]. The field-dressed eigenfunctions $|\Psi_i^{FD}(N)\rangle$ and quasi-energies $E_i^{FD}(N)$ can be obtained by determining the eigenpairs of the Hamiltonian of eq 1. The eigenfunctions $|\Psi_i^{FD}(N)\rangle$ can be expanded as the linear combination of products of field-free molecular rovibronic eigenstates (denoted by $|j\nu J\rangle$, 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 ground and first excited electronic states, respectively) and the Fourier vectors of the Floquet states, that is

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

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. Figure 1 displays the field-dressed diabatic potential energy curves of the $V_1(R)$ and $V_2(R)$ electronic states of Na₂ as well as the vibrational probability densities of the $|1\ 0\ 0\rangle|N\rangle$, $|2\ 2\ 1\rangle|N-1\rangle$ and $|2\ 9\ 1\rangle|N\rangle$ states.

To obtain the field-dressed rovibronic spectrum one has to compute the transition amplitudes between field-dressed states $|\Psi_i^{FD}(N)\rangle$ and $|\Psi_j^{FD}(N')\rangle$ within the framework of first-order time-dependent perturbation theory. These are as follows

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

where \hat{d} is the electric dipole moment operator.

The first term represents the field-dressed absorption and the corresponding intensity of transitions can be obtained as

$$I_{i,j} \propto \left| \sum_{J,\nu,J',\nu'} c_{i,1\nu J}^* c_{j,2\nu' J'} \langle 1\nu J | \hat{d} \cos \theta | 2\nu' J' \rangle \right|^2. \quad (4)$$

In what follows, we compute absorption spectra obtained from a single $|\Psi_i^{FD}(N)\rangle$ field-dressed state, which we assume to be populated adiabatically from the field-free ground state, $|1\ 0\ 0\rangle$, by switching on the dressing field slowly. Our working formula is eq 4 and the stick spectra are convolved with a Gaussian function with standard deviation of $\sigma = 50\text{cm}^{-1}$. We performed numerical simulation for several different dressing wavelengths and intensities, the results are displayed on the right side of Fig. 2. Striking at first sight, that in the spectrum horizontal streaks appear suggesting that the intensity of the spectrum depends on the wavelength of the dressing field. This trend looks characteristic and independent from the dressing field intensity but towards higher intensities additional pronounced patterns emerge.

To understand and quantify the above mentioned phenomenon further investigations are needed and therefore, we compute the total absorption probability $I_{\text{tot}} = \sum_j I_{i,j}$ as well. Assuming that the $c_{i,k\nu J}$ expansion coefficients in eq 4 are real, we can obtain the following formula for the total absorption probability as function of dressing field wavelength

$$I_{\text{tot}} = \sum_{J, \nu, J', \nu'} \left[(c_{i,1\nu J}^2 T(1\nu J | 2\nu' J')^2 + 2 \sum_{J_1, \nu_1} c_{i,1\nu J} c_{i,1\nu_1 J_1} T(1\nu J | 2\nu' J') T(1\nu_1 J_1 | 2\nu' J') \right]. \quad (5)$$

Here $(J_1 \neq J \text{ or } \nu_1 \neq \nu)$ and $T(1\nu J | 2\nu' J')$, $T(1\nu_1 J_1 | 2\nu' J')$ are the expressions of the corresponding transition dipole matrix elements. The computed total absorption probabilities are shown on the left side of Fig. 2 for three different dressing field intensities. It is eye catching that their asymmetric line shape resembles that of a Fano resonance. In order to explain this finding on Fig. 2, a two-state analytical and a three-state numerical model are introduced and examined.

III. RESULTS AND DISCUSSIONS

In this section a two-state analytical and three-state numerical model will be discussed so as to understand the structure and shape of the total absorption probability function. For supporting the results given by these models, an accurate N-state numerical calculations will also be provided.

A. Two-state analytical model

The model to be discussed here is a 2×2 diabatic potential matrix of the following type:

$$\mathbf{V} = \begin{bmatrix} V_X & W \\ W & V_A - \hbar\omega_L \end{bmatrix}. \quad (6)$$

Here V_X and V_A are the potential energies which are coupled by a laser pulse of frequency ω_L and W is the light-matter coupling term. This matrix can easily be diagonalized to obtain the adiabatic eigenstates and eigenenergies by using the two-dimensional orthogonal matrix $\mathbf{U} = \begin{bmatrix} \cos \varphi & \sin \varphi \\ -\sin \varphi & \cos \varphi \end{bmatrix}$. Here $\varphi = \frac{1}{2} \arctan \frac{2W}{V_A - V_X - \hbar\omega_L}$ is the mixing angle which is identical, up to an additive constant, to the ADT (adiabatic-to-diabatic transformation) angle. The corresponding dressed eigenstates and eigenenergies are as follows:

$$\psi_l = (\cos \varphi, -\sin \varphi) \begin{pmatrix} \psi_X | 1 \rangle \\ \psi_A | 0 \rangle \end{pmatrix}; \quad \psi_u = (\sin \varphi, \cos \varphi) \begin{pmatrix} \psi_X | 1 \rangle \\ \psi_A | 0 \rangle \end{pmatrix} \quad (7)$$

and

$$V_{\pm} = \frac{V_A + V_X + \hbar\omega_L}{2} \pm \sqrt{\frac{(V_A - V_X - \hbar\omega_L)^2}{4} + W^2}. \quad (8)$$

The spectral intensities between the different light-dressed states can be obtained as a straightforward application of eq 5. These are: $I_{l,u} \propto \alpha^2 \cdot \cos^4 \varphi = \alpha^2 \cdot \left(\frac{2W^2}{4W^2 + \Delta^2 - \Delta \sqrt{4W^2 + \Delta^2}} \right)^2$; $I_{u,l} \propto \alpha^2 \cdot \sin^4 \varphi = \alpha^2 \cdot \left(\frac{2W^2}{4W^2 + \Delta^2 + \Delta \sqrt{4W^2 + \Delta^2}} \right)^2$ and $I_{u,u} = I_{l,l} \propto \alpha^2 \cdot \cos^2 \varphi \sin^2 \varphi = \alpha^2 \cdot \frac{W^2}{4W^2 + \Delta^2} = \alpha^2 \cdot \frac{1}{4 + (\frac{\Delta}{W})^2}$, where $\alpha = \langle \psi_X | \hat{d} \cos \theta | \psi_A \rangle$ and $\Delta = V_A - V_X - \hbar\omega_L$. Let us define I_1 which is equal to $I_{l,u}$ if $V_A \geq V_X + \hbar\omega_L$ or $I_{u,l}$ otherwise, and $I_2 = I_{u,u} = I_{l,l}$. Then the total absorption can be obtained as:

$$I_{\text{tot}} = I_1 + I_2 \propto \alpha^2 \cdot \begin{cases} \cos^2(\varphi) & \text{if } V_A \geq V_X + \hbar\omega_L \\ \sin^2(\varphi) & \text{otherwise} \end{cases} = \alpha^2 \cdot \frac{2W^2}{4W^2 + \Delta^2 - |\Delta| \sqrt{4W^2 + \Delta^2}}. \quad (9)$$

A two-state model and the different spectral intensities are presented in Fig. 3. On the upper panel, the light dressing process is visualized for different values of the tuning function $\Delta(\omega_L)$. We show how the corresponding adiabatic dressed energies ($V_l = V_-$, $V_u = V_+$) are located to each other and with respect to the field-free V_X , V_A energies for the different values of the tuning function $\Delta(\omega_L) \lesseqgtr 0$. Note, that in the field-free case, the diabatic ground state is

located at the bottom. As a result of dressing, the order of diabatic states can change (see in middle panel of Fig. 3 at $\Delta = 0$). Accordingly, the field-free ground state will no longer be at the bottom, and therefore, the order of the corresponding adiabatic state from which the spectrum is computed also changes. It can be seen that in case of $\Delta(\omega_L) < 0$ and $\Delta(\omega_L) > 0$, the corresponding ψ_u, V_u and ψ_l, V_l states, respectively, are located closer to the field-free ground states, therefore the dressed spectrum is measured from the ψ_u state if $\Delta(\omega_L) < 0$ and from the ψ_l state if $\Delta(\omega_L) > 0$. However, this is not unequivocal in the case of $\Delta(\omega_L) = 0$, when the $\psi_X |1\rangle$ and $\psi_A |0\rangle$ diabatic states are degenerate. In this situation the adiabatic approximation can not be applicable anymore. The corresponding adiabatic energies and spectra for different situations are shown in the middle and lower panel of Fig. 3, respectively. The black dotted line shows (in middle panel) the adiabatic states from which the total absorption I_{tot} is measured (in lower panel). It can be seen that there is a discontinuity at $\Delta(\omega_L) = 0$ of the derivative of the total absorption intensities, moreover the $I_{u,u}$ and $I_{l,l}$ functions possess Lorentzian shape.

Note, that there is only a significant mixing between the diabatic states as long as the value of Δ is comparable to or less than the value of the W coupling strength. This requirement is more easily fulfilled in the three state model discussed in the next section.

B. Three-state numerical model

The relevant 3×3 diabatic V matrix is given in the form

$$V = \begin{bmatrix} V_{X_0} & 0 & W \\ 0 & V_{X_2} & \beta W \\ W & \beta W & V_A - \hbar\omega_L \end{bmatrix}. \quad (10)$$

Here V_{X_0} , V_{X_2} and V_A are the potential energies which are coupled by a laser pulse of frequency ω_L . W is the light-matter coupling term and the value of the β parameter is $\langle \psi_{X_2} | \hat{d} \cos \theta | \psi_A \rangle / \langle \psi_{X_0} | \hat{d} \cos \theta | \psi_A \rangle$. The corresponding dressed eigenstates are as follows:

$$\begin{aligned} \psi_l &= (c_{l,X_0}, c_{l,X_2}, c_{l,A}) \begin{pmatrix} \psi_{X_0} |1\rangle \\ \psi_{X_2} |1\rangle \\ \psi_A |0\rangle \end{pmatrix}, \\ \psi_m &= (c_{m,X_0}, c_{m,X_2}, c_{m,A}) \begin{pmatrix} \psi_{X_0} |1\rangle \\ \psi_{X_2} |1\rangle \\ \psi_A |0\rangle \end{pmatrix}, \\ \psi_u &= (c_{u,X_0}, c_{u,X_2}, c_{u,A}) \begin{pmatrix} \psi_{X_0} |1\rangle \\ \psi_{X_2} |1\rangle \\ \psi_A |0\rangle \end{pmatrix}. \end{aligned} \quad (11)$$

In this numerical model ψ_{X_0} , ψ_{X_2} and ψ_A are the diabatic wavefunctions that may correspond to the $|1\ 0\ 0\rangle$, $|1\ 0\ 2\rangle$ and $|2\ 6\ 1\rangle$ states of the Na_2 molecule, respectively. β measures the ratio of the dipole matrix elements obtained with different diabatic wavefunctions which can be approximated by similar ratio of the corresponding spherical functions $\beta \approx \frac{\langle Y_1^0 | \cos \theta | Y_2^0 \rangle}{\langle Y_1^0 | \cos \theta | Y_0^0 \rangle} = 2/\sqrt{5} \approx 0.9$. In this three-state model, the adiabatic eigenstates (ψ_l, ψ_m, ψ_u) and eigenenergies (V_l, V_m, V_u) are calculated numerically. The arrangement of the adiabatic eigenenergies are displayed on the upper panel of Fig. 4. Similarly to the two-state model, the spectrum is measured again from that adiabatic state which corresponds to the field-free ground state. But after the dressing process, the field-free ground state will no longer be at the bottom, the corresponding adiabatic state from which the spectrum is measured also changes. This is shown in the second panel of Fig. 4 in which the black dotted lines denote the energy of the corresponding adiabatic initial states. The total absorption spectrum is visualized in the third panel of Fig. 4. If $\Delta < 0$ the total absorption probability is calculated from the middle adiabatic state, while in case of $\Delta > 0$, from the lower adiabatic one. Similarly to the two-state model, at $\Delta = 0$ the corresponding diabatic states are degenerated, therefore the adiabatic approximation can not be applied. It is clearly noticeable that the function of total absorption jumps at $\Delta = 0$. The lower panel of Fig. 4 displays the coefficients of the diabatic wavefunctions. Applying eq. 5 for the three-state model, it can easily be seen that the shape of the total absorption function is determined by the value of the c_{m,x_0} and c_{m,x_2} coefficients when $\Delta < 0$, while by the value of the c_{m,x_0} and c_{m,x_2} coefficients, when $\Delta > 0$. At $\Delta < 0$ the value of c_{m,x_0} is positive, while the value of c_{m,x_2} is negative, but both continuously decrease as $\Delta \rightarrow 0$. Therefore, the square of their sum is monotonically decreasing. In case of $\Delta > 0$, the value of both coefficients are positive, the square of

their sum increases for a while, reaches a maximum, and then begins to decrease. As a result, we obtained, at least in some sense, a similar shape to the Fano profile, which originates from a basically different process.

In Fig. 5 total absorption probabilities for several different coupling strengths are displayed. It is striking that the shapes of the curves at $\Delta < 0$ interval, regardless of the value of the coupling strengths, are similar and always monotonically decrease. However, on the right side at $\Delta > 0$, the trend is different. Here, moving from the small coupling values to the larger ones, the symmetrically shaped curves turn slowly to asymmetric ones. The increasing coupling strength mixes the c_{m,x_0} and c_{m,x_2} coefficients more and more, resulting, at some point of $\Delta > 0$, significantly larger and larger values for the square of their sum. If this amount reaches its maximum, a peak is formed, then the curves slowly decrease, forming shapes that resemble Fano resonances. To demonstrate the similarity with the Fano profile, in Fig. 5 at $\Delta > 0$, the Fano fitted curves are also displayed. Apart from the largest coupling strength, an almost perfect fit has been achieved.

C. N-state numerical results

In realistic molecular systems it can be necessary to consider a large number of field-free eigenstates involved in the dressing process. To investigate such an example, we turn our attention back to the light-dressed Na_2 molecule, for which all the computational details can be found in [26]. In Fig. 6 we show total absorption probabilities as a function of the dressing-light wavelength near the wavelength region, where the dressing field is resonant with the $|241\rangle \leftarrow |100\rangle$ transition. The continuous line in Fig. 6 represents the total absorption from the light-dressed state, which is connected to the $|100\rangle$ field-free ground state by the adiabatic theorem. The adiabatic one-to-one correspondence between $|100\rangle$ and a specific light dressed state is unequivocal for off-resonant dressing-light wavelengths, in Fig. 6 the correlating light-dressed states are the 56th and the 45th states, for blue- and red shifted wavelengths, respectively. Near resonance, however, the many closely lying $|10J\rangle$ and $|24J\rangle$ states become strongly mixed and the adiabatic theorem becomes less meaningful. This is clearly indicated by the several jumps in the continuous curve of Fig. 6. Nonetheless, Fig. 6 demonstrates that even when a large number of field-free states are involved, by scanning through resonance the character of the adiabatic light-dressed state changes, leading to the Fano-like line shape in the total absorption, as predicted by the three-state model.

IV. CONCLUSIONS

Recently, a theoretical approach for simulating rovibronic absorption and emission spectra of diatomic molecules dressed by medium-intensity laser fields has been developed [26, 27]. The showcase example was the homonuclear sodium dimer molecule, which is a suitable for demonstrating and understanding various aspects of light-dressed spectroscopy. By computing the total absorption probability as a function of dressing-field wavelength an asymmetric line shape has been found strongly resembling to the well-known Fano profile. The present work is devoted to provide a profound explanation for this behavior of the total absorption function by applying two-state analytical and three-state numerical model.

To summarize the findings we may say the following. (i) First of all, our main conclusion is that the adiabatic dressing approximation is not applicable at $\Delta = 0$ due to degeneracy of the diabatic states at this point. The adiabatic path from which the spectrum is computed changes at $\Delta = 0$ and a jump may appear in the total absorption probability. (ii) Due to the densely spaced rotational states, the significantly increasing interference terms (mixed product of diabatic basis coefficients) lead to a peak in the interval of $\Delta > 0$, which reaches a maximum then slowly goes down with further increasing the value of Δ . (iii) The above effect is significantly enhanced by increasing the coupling strength which leads to a more efficient mixing of the coefficients providing the formation of even higher peaks. The higher the coupling strength, the more prominent the effect. (iv) The total absorption probability can be an asymmetric, but not continuous function. Despite its similarity to the well known Fano line shape, it is inherently different from that one.

For supporting the results of the model studies, high-resolution accurate numerical calculations with large number of diabatic basis functions were provided.

Acknowledgements

This research was supported by the EU-funded Hungarian grant EFOP-3.6.2-16-2017-00005. The authors are grateful to NKFIH for support (Grant K128396 and FK134291). The work in Budapest was also supported by the János Bolyai Research Scholarship of the Hungarian Academy of Sciences and by the ELTE Institutional Excellence

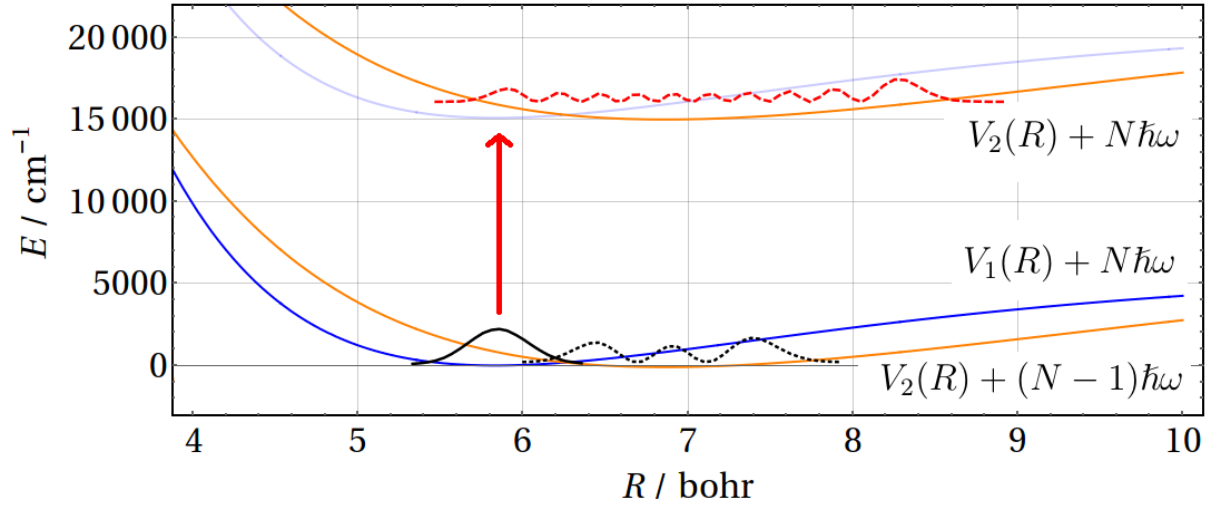


Figure 1: Field-dressed diabatic potential energy curves (PECs) of Na_2 obtained with a dressing-light wavelength of $\lambda = 657$ nm. The energy scale stands for quasienergy. Vibrational probability densities are drawn for the $|1\ 0\ 0\rangle|N\rangle$ (continuous black line on the $V_1(R) + N\hbar\omega$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

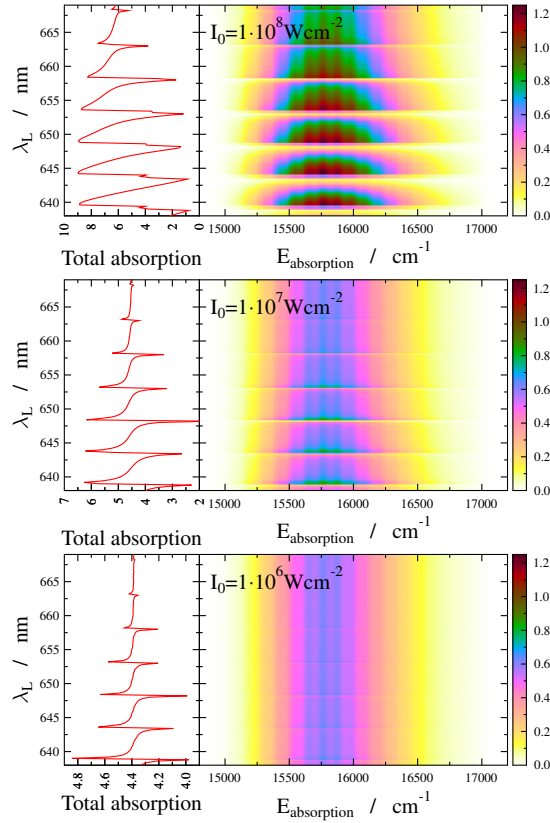


Figure 2: One-photon absorption spectra of the field-dressed Na_2 as a function of dressing-field wavelength for three different dressing-field intensities. Left panels display the total absorption probabilities as a function of dressing-field wavelength.

Program (TKP2020-IKA-05) financed by the Hungarian Ministry of Human Capacities. The authors thank Lorenz S. Cederbaum for fruitful discussions.

-
- [1] H. Beutler *Zeit. Phys.* 1934, **91**, 132.
 - [2] U. Fano *Phys. Rev.* 1961, **124**, 1866.
 - [3] A. D. Bandrauk, J. P. Laplante, *J. Phys. Chem.* 1976, **65**, 2602.
 - [4] A. D. Bandrauk, M. L. Sink, *Chem. Phys. Lett.* 1978, **57**, 569.
 - [5] S. Miret-Artés, O. Atabek, A. D. Bandrauk, *Phys. Rev. A* 1992, **45**, 8056.
 - [6] E. F. van Dishoeck, M. C. van Hemert, A. C. Allison, A. Dalgarno, *J. Chem. Phys.* 1984, **81**, 5709.
 - [7] B. Yan, C. H. Greene, *Phys. Rev. A* 2017, **95**, 032706.
 - [8] C. H. Greene, P. Giannakeas, J. Pérez-Ríos, *Rev. Mod. Phys.* 2017, **89**, 035006.
 - [9] L. Argenti, *et al Phys. Rev. A* 2013, **87**, 053405.
 - [10] C. Ott, *et al Science* 2013, **340**, 716.
 - [11] L. Medišauskas, *et al New J. Phys.* 2015, **17** 053011.
 - [12] A. Blech, *et al Nat. Com.* 2020, **11**, 999.
 - [13] P. Paliwal, A. Blech, C. P. Koch, E. Narevicius, 2021, preprint arXiv:2105.05959
 - [14] S. E. A. Orrigo, *et al Phys. Lett. B* 2006, **633**, 469.
 - [15] S. E. A. Orrigo, H. Lenske, *Phys. Lett. B* 2009, **677**, 214.
 - [16] O. Újsághy, J. Kroha, L. Szunyogh, A. Zawadowski, *Phys. Rev. Lett.* 2000, **85**, 2557.
 - [17] J. D. Lee, J. Inoue, M. Hase, *Phys. Rev. Lett.* 2006, **97**, 157405.
 - [18] P. Fan, Z. Yu, S. Fan, M. L. Brongersma, *Nat. Mater.* 2014, **13**, 471.
 - [19] H. Varguet, *et al J. Phys. B* 2019, **52**, 055404.
 - [20] B. Gurlek, V. Sandoghdar, D. Martín-Cano, *ACS Photonics* 2018, **5**, 456.
 - [21] S. Franke, *et al Phys. Rev. Lett.* 2019, **122**, 213901.
 - [22] S. Glutsch, *Phys. Rev. B* 2002, **66**, 075310.
 - [23] E. V. Denning, J. Iles-Smith, J. Mork, *Phys. Rev. B* 2019, **100**, 214306.
 - [24] I. Medina, F. J. García-Vidal, A. I. Fernández-Domínguez, J. Feist, *Phys. Rev. Lett.* 2021, **126**, 093601.
 - [25] B. Luk'yanchuk, *et al Nat. Mater.* 2010, **9**, 707.
 - [26] T. Szidarovszky, G. J. Halász, A. Császár, L. S. Cederbaum, Á. Vibók, *J. Phys. Chem. Lett.* 2018, **9**, 2739.
 - [27] T. Szidarovszky, G. J. Halász, A. Császár, Á. Vibók, *Phys. Rev. A* 2019, **100**, 033414.
 - [28] J. H. Shirley, *Phys. Rev.* 1965, **138**, B979.
 - [29] S. I. Chu, *J. Chem. Phys.* 1981, **75**, 2215.
 - [30] J. C. Lefebvre, T. T. Nguyen-Dang, F. Dion, M. M. J. Vrakking, V. N. Serov, O. Atabek, *Phys. Rev. A* 2013, **88**, 053416.
 - [31] G. Bing, I. Franco, *Phys. Rev. A* 2018, **98**, 063412.
 - [32] S. Magnier, *et al J. Chem. Phys.* 1993, **98**, 7113.
 - [33] W. T. Zemke, *et al J. Mol. Spectrosc.* 1981, **85**, 150.

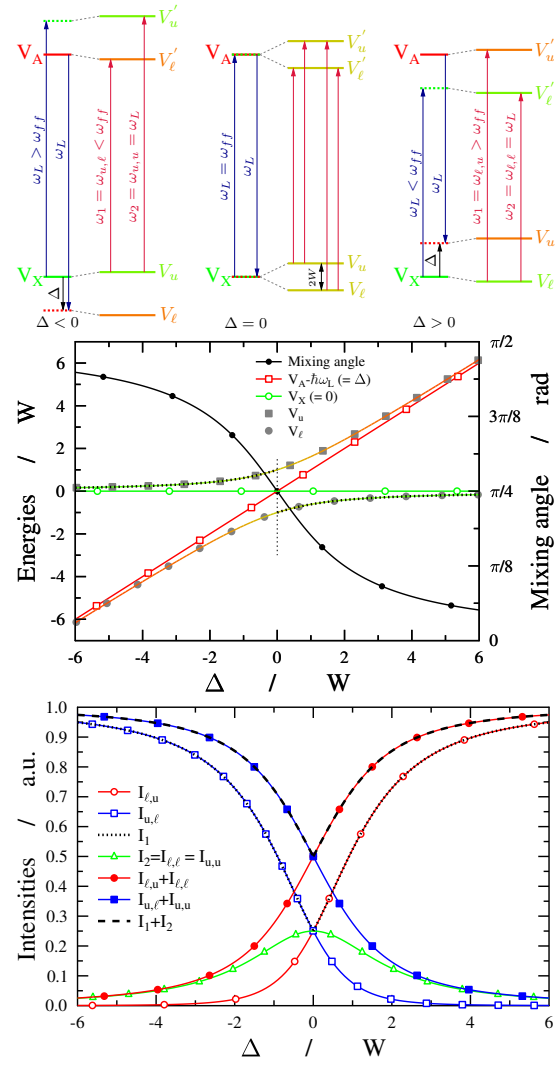


Figure 3: The two-state analytical model. Upper panel: The energetic arrangement of the corresponding diatomic and adiabatic states. Middle panel: The two diatomic (green and red) and two adiabatic (colored) energy curves. The dotted black curve shows the path from which the total absorption probability is measured. The black curve denotes the mixing angle. Lower panel: The total absorption probability and the different components of it.

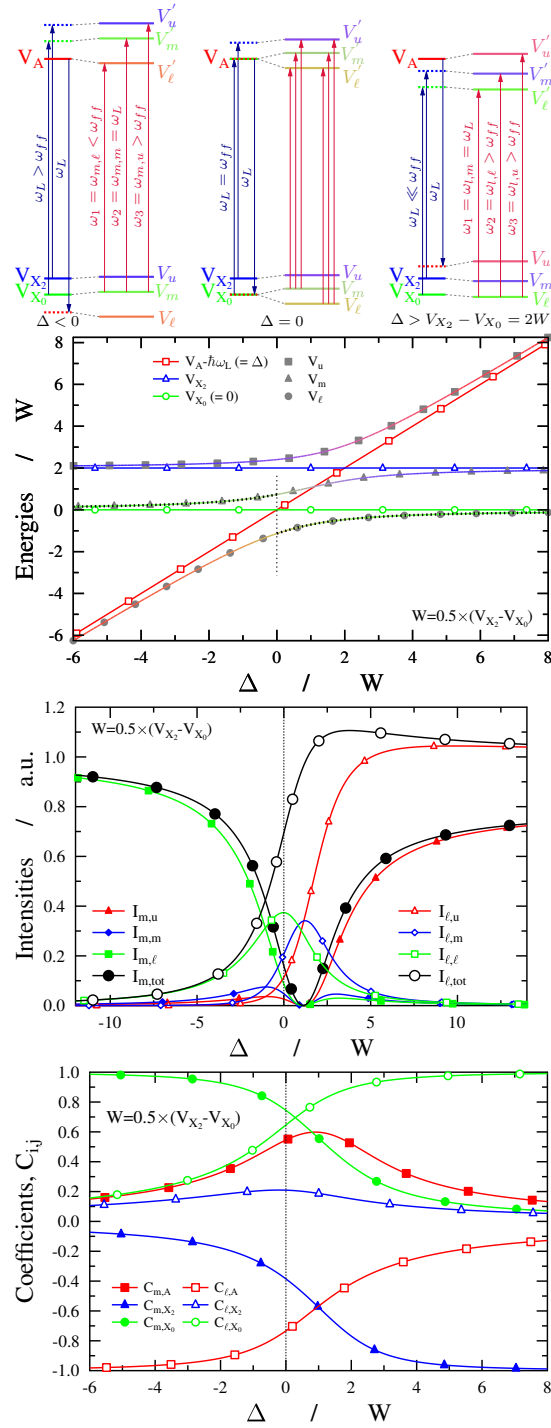


Figure 4: The three-state numerical model. Upper panel: The energetic arrangement of the corresponding diabatic and adiabatic states. Second panel: The three diabatic (green, blue and red) and three adiabatic (colored) energy curves. The dotted black curve shows the path from which the total absorption probability is measured. Third panel: The total absorption probability and the different components of it. Lower panel: The coefficients of the corresponding diabatic basis functions from which the ψ_l and ψ_m adiabatic wavefunctions build up.

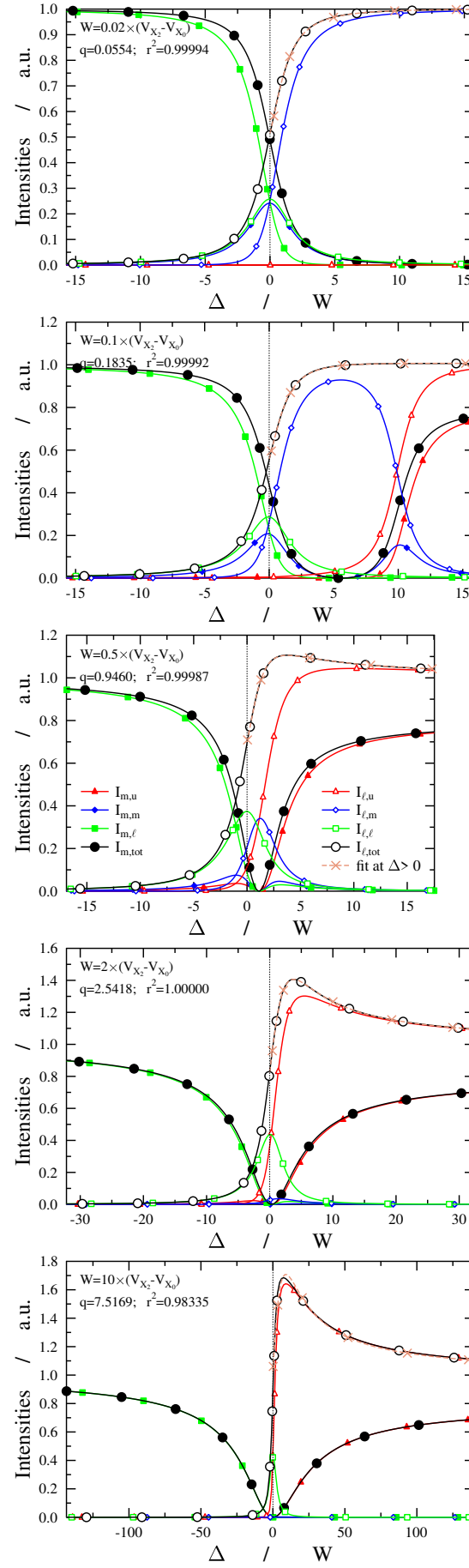


Figure 5: The three-state numerical model. The total absorption probabilities and the different components of it calculated at 5 different coupling strengths. The dashed line with cross denotes the Fano fitted curve ($I_{\text{fit}} = a + (1 - a) \frac{(q - \varepsilon)^2}{b + \varepsilon^2}$; $\varepsilon = \frac{\Delta}{W} - c$; a, b and c are parameters). The goodness of the fit is characterized by r^2 .

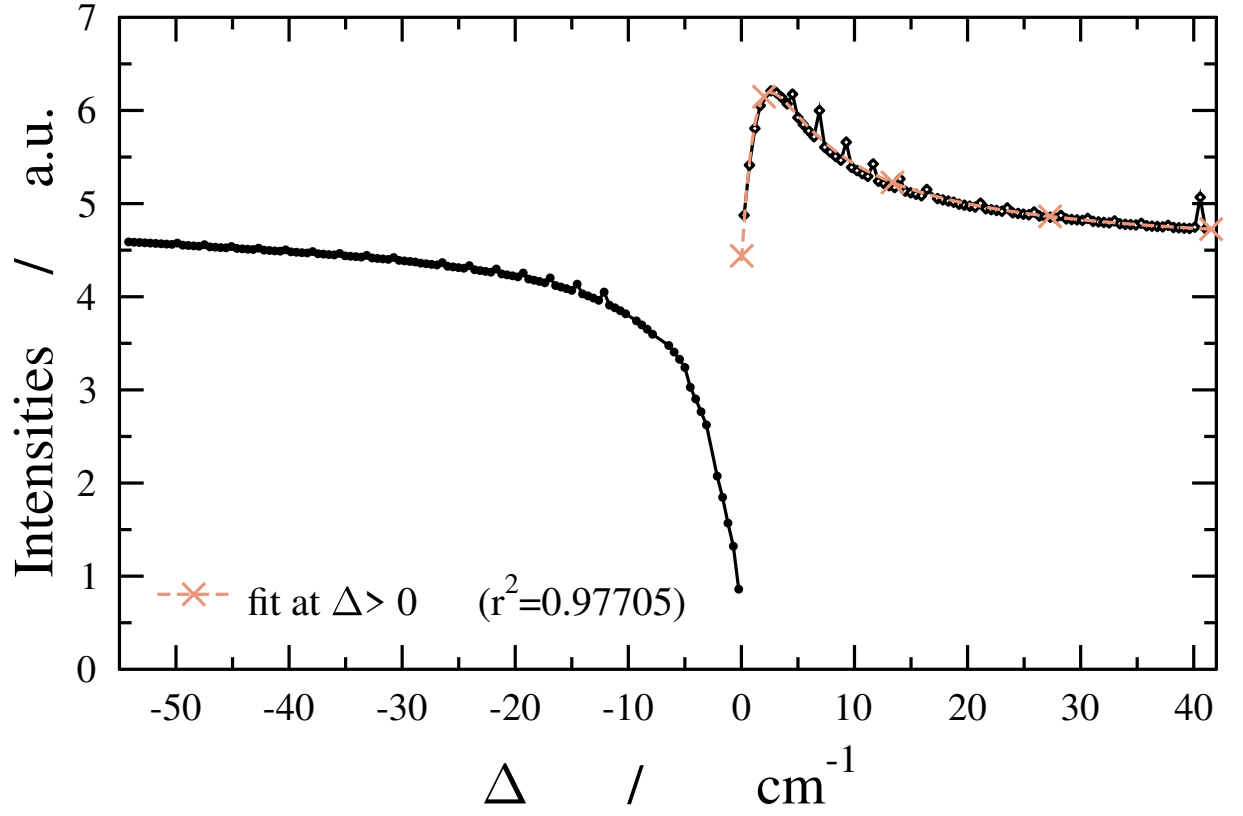


Figure 6: The total absorption probability of the Na₂ molecule. The N-state numerical results are denoted by black solid lines (there is a discontinuity at $\Delta = 0$). The dashed line with cross denotes the Fano fitted curve ($I_{\text{fit}} = a + (1-a) \frac{(q-\varepsilon)^2}{b+\varepsilon^2}$; $\varepsilon = \frac{\Delta}{W} - c$; a, b and c are parameters). The goodness of the fit is characterized by r^2 .