Fano profiles in two-photon photoassociation spectra

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⁵ In this article we derive the lineshapes observed in two-photon photoassociation spectrocopy of molecules using an effective Hamiltonian adapted from previous work in atomic physics. The lineshape is decomposed in terms of sums and products of Breit-Wigner and Fano profiles which we associate to physical absorption and emission processes ¹⁰ and to quantum interferences between transition amplitudes. We emphasize the specific features linked to the dissociation width of the photoassociated molecules in the electronic ground state which do not exist in the atomic case.

1 Introduction

- ¹⁵ Fano profiles are universal lineshapes which are observed in atomic and molecular physics (réf). They usually appear when several paths, leading to the same final state lying in a continuum, interfere, one of them passing through an intermediate discrete state. The experimental study of such profiles provides information on the energy and lifetime of these discrete states.
- ²⁰ Fano profiles have been shown to appear in the lineshapes of the so-called dark resonances which can be observed in coherent population trapping experiments involving three-level atomic systems with two ground state sublevels g_1 and g_2 and one excited sublevel e (réf). One laser with frequency ω_1 excites the transition $g_1 \rightarrow e$ and another one with frequency ω_2 excites the transition $g_2 \rightarrow e$. If , ω_2 ²⁵ being fixed, one scans ω_1 , one observes in the variations with ω_1 of the fluorescence rate R_F emitted from e several resonances the following three features which are
 - shown on the inset of Fig. 1:
 - (1) a broad resonance when ω_1 coincides with the frequency ω_{eg_1} of the $g_1 \rightarrow e$ transition with a width on the order of the natural width γ_e of the excited state e
 - (2) a very narrow dark resonance $(R_F \text{ vanishes})$ when the resonance Raman condition between the unperturbed states g_1 and g_2 is fulfilled :

$$\hbar(\omega_1 - \omega_2) = E_{g_1} - E_{g_2}$$

(3) a narrow peak associated with resonant Raman processes between perturbed (light shifted) states.

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The widths of the narrow dip and of the narrow peak are on the order of the width of g_1 and g_2 and therefore much smaller than γ_e . A Fano profile is observed in the vicinity of the dark resonance and interpreted as due to the interference between the two paths shown in Fig. 1 (réf):

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- The atom absorbs a photon ω_1 from g_1 , reaches the state *e* from which it emits a fluorescence photon. Because of the large value of γ_e compared to

the widths of g_1 and g_2 , the state e can be considered as a continuum.

• The atom absorbs a photon ω_1 from g_1 , reaches the state e, emits then a photon ω_2 in a stimulated way, reaches the state g_2 , reabsorbs a photon ω_2 , which allows it to reach again the state e from which if finally emits the fluorescence photon.

The first path goes directly to the continuum e. The second path passes through the discrete intermediate state g_2 . Their interference gives rise to a Fano profile.



Figure 1: Processes leading to spontaneous emission of an ω photon for a an atom with a Λ level scheme coupled to two lasers ω_1 and ω_2 : (a) absorption of a ¹⁵ ω_1 photon, followed by spontaneous emission (b) stimulated Raman process bringing the atom from g_1 to g_2 (absorption of ω_1 followed by stimulated absorption of ω_2) followed by a spontaneous Raman process bringing the atom from g_2 to g_1 . The inset shows the fluorescence rate as a function of the detuning of the laser ω_1 from the $g_1 \rightarrow e$ transition. (c) The broad resonance (1), the narrow 20 dip (2) and the narrow peak (3) observed in the fluorescence rate R_F are detailed in the text.

The general shape of a Fano resonance $f_q(\epsilon)$ is written as a function of a reduced energy ϵ and a parameter q as (réf):

$$f_q(\epsilon) = \frac{(\epsilon + q)^2}{1 + \epsilon^2} \tag{4}$$

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The parameter q represents the ratio between the probabilities of resonant scattering (associated in Fig.1 with the indirect path (b) involving the state $|g_2\rangle$) and background scattering (associated in Fig.1 with the direct path (a) in Fig. 1). In the case where there is no background scattering, the parameter q is infinite, and the ³⁰ usual Breit-Wigner lineshape is recovered. The figure Fig. 2 illustrates the shape of a Fano resonance $f_q(\epsilon)$ for q = 0, q = 2, and $q = +\infty$.

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Figure 2: Shape of a Fano resonance $f_q(\epsilon)$ as a function of a reduced energy ϵ for different q parameters.

Two-photon photoassociation processes involve three-state systems analogous to the ⁵ previous one (Fig. 3) (réf): the state g_1 is in the molecular case a colliding state $|E, g_1\rangle$ of a pair of atoms in a given electronically ground molecular potential $|g_1\rangle$ with a scattering energy E; a laser ω_1 drives the transition from this state $|E, g_1\rangle$ to a vibrational state $|v_e, e\rangle$ in an electronically excited molecular potential $|e\rangle$; another laser ω_2 drives the transition from this state $|v_e, e\rangle$ to another vibrational state $|v_2, g_2\rangle$ in an electronically ground state molecular potential $|g_2\rangle$. Dark resonances have been observed in these configurations (réf). They can be calculated using the modified quantum defect theory (MQDT) (réf). But this approach does not suggest clearly the existence of Fano processes. We try in this paper to extend to this molecular problem the approach described in (Lounis, et al., 1992) to get some 15 physical insight into the physical mechanisms. We show that it is possible to express the experimental signal used to detect the two-photon photo-association process in

- terms of sums and products of Breit-Wigner and Fano profiles. This decomposition leads to physical interpretations in terms of quantum interferences analogous to the one given in (réf) for the atomic case. Such analytical expressions are in addition 20 very useful for fitting the experimental signals and for extracting from these fits
- information on the energy of g_2 and of the relaxation processes (dissociation, ionization, collision) affecting this state.



Figure 3: Level scheme for two-photon photoassociation lineshapes showing Fano profiles. A molecular state $|v_e, e\rangle$ of vibrational number v_e in an electronically excited potential is coupled by a photon ω_1 to a scattering state $|E, g_1\rangle$ in a $|g_1\rangle$ s channel and by a photon ω_2 to a molecular state of vibrational number v_2 in a $|g_2\rangle$ channel.

There are important differences between the molecular and the atomic cases which should be emphasized:

- The two colliding atoms can interact directly and undergo an elastic collision without involving the coupling with the lasers.
- The three-level scheme in the molecular case is not closed: radiative decay of a molecule from the electronically excited state will not in general lead to the two other states (scattering and bound) with which it is coupled by the lasers.
- The colliding state g_1 is not a discrete state. It belongs to a continuum and has an energy dispersion. This should broaden the dark resonance. But, the experiments we have in mind are done with ultracold atoms and this broadening is in general negligible.
- In the atomic case, the state g_2 is a ground state and cannot decay. More precisely, the sum of the populations of the three levels is conserved. This is why R_F goes to zero at the center of the dark resonance. In the molecular case, the state g_2 can decay because of dissociation processes and we will see that R_F does not go to zero. This is why Breit-Wigner profiles appear in addition to Fano profiles.
- ²⁵ We give in section 2 a brief outline of the calculation of the scattering of atoms in the context of photoassociation, generalizing the calculation developed for the atomic case. The interested reader can find more details in the reference (Portier, 2007) avalaible online. We identify the paths whose interference contributes to a Fano resonance. A physical interpretation of the photoassociation lineshapes is be ³⁰ then given in section 3.

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2 Calculation of the scattering matrix

In this section, we first express the Hamiltonian which describes photoassociation as a function of the relevant parameters. We then seperate the effect of the interaction of the lasers from the effect of the interaction between the atoms. This allows us to ⁵ express the scattering matrix for the photoassociation problem as a function of the wavefunctions which are solutions of the problem of scattering of two atoms in absence of light, and which are supposed to be known. We then gives the interpretation of the different factors in the scattering amplitude.

2.1 Presentation of the problem

Photoassociation is described here as light assisted scattering between atoms. We use a basis of light dressed collisional channel which is a product of a basis for collision channels and a basis for the light radiation (Simoni, et al., 2002). A collision channel is characterized by the electronic state of the two atoms, and their relative rotational state (Mies, 1980). In this problem we consider three collision 15 channels noted g₁, g₂ and e, the first two of which correspond to an electronic ground state (g₁ and g₂ can coincide), and the third one correspond to an electronically excited state. We consider also two laser modes characterized by their polarizations and their frequencies ω₁ and ω₂, and their numbers of photons N₁ and N₂. The laser fields 1 and 2 couple the dressed channel |e, N₁ - 1, N₂⟩ to the dressed 20 channel |g₁, N₁, N₂⟩ and |g₂, N₁ - 1, N₂ + 1⟩ respectively.

The initial state of the experiment is $|E, g_1, N_1, N_2\rangle$, where *E* denotes the scattering energy of the two colliding atoms. We will calculate here the scattering matrix element $S_{g_1g_1}$ and the quantity $1 - |S_{g_1g_1}|^2$ which will be interpreted as the probability per collision event that relaxation occurs, and which is proportional to ²⁵ the photoassociation rate. This relaxation may correspond to spontaneous emission from a $|e, N_1 - 1, N_2\rangle$ state or relaxation of a $|g_2, N_1 - 1, N_2 + 1\rangle$ molecule due to dissociation or atom-molecule collision. In the basis $\{|g_1, N_1, N_2\rangle, |e, N_1 - 1, N_2\rangle, |g_2, N_1 - 1, N_2 + 1\rangle\}$, the Hamiltonian describing light assisted collision is written H = K + V, where K is the radial kinetic energy and V describes the effects ³⁰ of interacting potentials and light couplings:

$$K = -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} \tag{5}$$

$$V = \begin{pmatrix} V_{g_1}(r) & V_{rad1}(r) & 0 \\ V_{rad1}(r) & V_e(r) - i\frac{\gamma_e(r)}{2} - \Delta_1 & V_{rad2}(r) \\ 0 & V_{rad2}(r) & V_{g_2(r)} - i\frac{\gamma_{g_2}(r)}{2} - \Delta_1 + \Delta_2 \end{pmatrix}$$
(6)

The potentials V_{g_1} , V_{g_2} and V_e describe the radial interaction between the colliding atoms in the g_1 , g_2 and e states. The origin of the energy scale is such that $V_{g_1}(\infty) = V_{g_2}(\infty) = V_e(\infty) = 0$. The quantities $\Delta_1 = \omega_1 - \omega_{eg_1}^{at}$ and $\Delta_2 = \omega_2 - \omega_{eg_2}^{at}$ are the detunings of the lasers 1 and 2 from the atomic frequencies between the asymptotic states e and g_1 at $\omega_{eg_1}^{at}$, and e and g_2 (see Fig. 2) at $\omega_{eg_2}^{at}$. The couplings V_{rad1} and V_{rad2} are the matrix elements of the electric-dipole interaction, and depend on the dipole of the molecule which varies with the interatomic distance r. The widths $\gamma_e(r)$ and $\gamma_{g_2}(r)$ account for the decay processes which limit the lifetime of the atoms in the e state and in the g_2 state. These widths depend on the interatomic distance owing to the interaction between the atoms. $\gamma_e(r)$ tends for large interatomic distance to a constant proportional to an atomic radiative width, and is modulated for shorter interatomic distance due to the electrostatic interaction between the atoms. Depending on the considered atoms, the width $\gamma_{g_2}(r)$ can be s associated for example to autoionization, or spin relaxation, and takes non vanishing values for small interatomic distance where the two atoms interact.

As the Hamiltonian H is not hermitian owing to the decay widths $\gamma_e(r)$ and $\gamma_{g_2}(r)$, the probability current is not conserved during to the collision: if the atoms collide initially in the g_1 channel, there is a non zero probability that they undergo photoassociation in molecule in the e or g_2 potential, followed by a decay to another state different from g_1, g_2 or e. As a consequence, the scattering matrix is non unitary. In order to estimate the photoassociation rate K_{PA} , we will calculate the loss of unitarity of the scattering matrix, which is proportional to the photoassociation rate:

$$K_{PA} \propto 1 - |S_{g_1g_1}|^2$$
 (7)

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2.2 Introduction of the elastic scattering unperturbed by the laser light

The coupling V is seperated as $V = V_A + V_B$. V_A describes in an uncoupled way the interaction between atoms in the $|g_1, N_1, N_2\rangle$ state in the one hand, and the ²⁰ interaction between the atoms in the $|g_1, N_1 - 1, N_2 + 1\rangle$ and $|e, N_1 - 1, N_2\rangle$ states perturbed by the second laser on the other hand. The coupling V_B describes the interaction with the laser ω_1 .

$$V_{A} = \begin{pmatrix} V_{g_{1}}(r) & 0 & 0 \\ 0 & V_{e}(r) - i\frac{\gamma_{e}(r)}{2} - \Delta_{1} & V_{rad2}(r) \\ 0 & V_{rad2}(r) & V_{g_{2}(r)} - i\frac{\gamma_{g_{2}}(r)}{2} - \Delta_{1} + \Delta_{2} \end{pmatrix}$$
(8)
$$V_{B} = \begin{pmatrix} 0 & V_{rad1}(r) & 0 \\ V_{rad1}(r) & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$
(9)

²⁵ We note $H_0 = K + V_A$, and Q and P the projectors onto the subspace spanned by the states $|e, N_1 - 1, N_2\rangle$ and $|g_2, N_1 - 1, N_2 + 1\rangle$ on the one hand, and $|g_1, N_1, N_2\rangle$ on the other hand:

$$P = |g_1, N_1, N_2\rangle \langle g_1, N_1, N_2|$$
(10)

$$Q = |e, N_1 - 1, N_2\rangle \langle e, N_1 - 1, N_2| + |g_2, N_1 - 1, N_2 + 1\rangle \langle g_2, N_1 - 1, N_2 + 1|$$
(11)

³⁰ Notice that PH_0P describes an elastic collision of an atom pair in the g_1 state, whose properties are supposed to be known. We note $S_{g_1g_1}^{(0)} = e^{i\eta_{g_1}}$ the scattering matrix element which describes this elastic collision, and which is expressed as a function

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of a phase shift η_{g_1} .

We calculate the scattering matrix element $S_{g_1g_1}$ which caracterizes the collision perturbed by the lasers as a function of $S_{g_1g_1}^{(0)}$. The two-potential scattering formula gives a relation between the transfer matrices elements, where the transfer matrix is 5 defined as a function of a scattering matrix as $S = 1 - 2\pi i T$ (Joachain, 1983):

$$T_{g_1g_1} = T_{g_1g_1}^{(0)} + \langle \phi_{g_1}^{E^-}, g_1, N_1, N_1 | V_B | \psi_{g_1}^{E^+}, g_1, N_1, N_2 \rangle$$
(12)

where $\phi_{g_1}^{E^-}$ (¹) and $\psi_0^{E^+}$ are the radials part of the scattering wavefunctions decribing a stationary state of the Hamiltonian PH_0P with ingoing boundary condition, and a stationary state of the Hamiltonian *PHP* with outgoing boundary condition respectively.

¹⁰ The matrix element in the right hand of the equation (12) can be expressed using only only solution $\phi_{g_1}^{E\pm}$ for the scattering decribed by the PH_0P Hamiltonian which are supposed to be known, and the resolvent operator $G^+(E) = \lim_{\epsilon \to 0^+} (E - H + i\epsilon)^{-1}$:

$$T_{g_1g_1} = T_{g_1g_1}^{(0)} + \left\langle \phi_{g_1}^{E^-}, g_1, N_1, N_1 | PV_B QG^+(E) QV_B P | \phi_{g_1}^{E^+}, g_1, N_1, N_2 \right\rangle$$
(13)

¹⁵ Using (13), the definition of the *T* matrix as a function of the *S* matrix, and the the expression of $S_{g_1g_1}^{(0)}$ as a function of the phase η_{g_1} , we get:

$$S_{g_1g_1} = S_{g_1g_1}^{(0)} - \left\langle \phi_{g_1}^{E^-}, g_1, N_1, N_1 | PV_B QG^+(E) QV_B P | \phi_{g_1}^{E^+}, g_1, N_1, N_2 \right\rangle$$
(14)

Expanding $QG^+(E)Q$ as a power series of V_B and using projection operator techniques to make a partial resummation of this perturbation series (see for example (réf)), one can write (14) as

$$S_{g_1g_1} = S_{g_1g_1}^{(0)} - 2\pi i \langle \phi_{g_1}^{E^-}, g_1, N_1, N_1 \left| PV_B \frac{Q}{E - H_{\text{eff}}} V_B P \right| \phi_{g_1}^{E^+}, g_1, N_1, N_2 \rangle \quad (15)$$

20 Where Heff is an effective Hamiltonian defined by:

$$H_{\rm eff} = QH_0Q + QV_BPG_0^+(E)PV_0Q \tag{16}$$

with $G_0^+(E) = \lim_{\epsilon \to 0^+} (E - H_0 + i\epsilon)^{-1}$. The effective Hamiltonian H_{eff} describes the reduced evolution in the subspace (11). Note that it is calculated to he second order in V_B , but $S_{g_1g_1}$ in (15) contains all orderd in V_B since H_{eff} appears in the denominator.

25 we get

We assume that the frequency of the lasers and the level scheme are such that the only transitions that may be excited involve a bound state in the e potential with a

¹ The scattering wavefunctions $\phi_{g_1}^{E\pm}$ are written as a function of a wavefunction $f_{g_1}^E(r)$ as:

$$\phi_{g_1}^{E\pm}(r) = \sqrt{\frac{2\mu}{\pi\hbar^2 k}} e^{\pm i\eta_{g_1}} f_{g_1}^E(r)$$

with $f_{g_1}^E(r \to \infty) = sin\left(kr - \frac{l_{g_1}\pi}{2} + \eta_{g_1}\right)$

where $k = \sqrt{2\mu E/\hbar^2}$ is the wavevector, l_{g_1} is the angular momentum for the rotation of the atoms associated with g_1 , and η_{g_1} the phase shift of the wave function.

vibrational quantum number b_e and a binding energy $E_e^{b_e}$ described by a wavefunction $\phi_e^{b_e}$, and a bound state in the g_2 potential with a vibrational quantum number b_2 and a binding energy $E_{g_2}^{b_2}$ described by a wavefunction $\phi_{g_2}^{b_2}$. The projector Q given by (11) can then be approximated by \tilde{Q} :

$$Q \approx \widetilde{Q} = |e, N_1 - 1, N_2\rangle \langle e, N_1 - 1, N_2| \otimes |\phi_e^{b_e}\rangle \langle \phi_e^{b_e}| + |g_2, N_1 - 1, N_2 + 1\rangle \langle g_2, N_1 - 1, N_2 + 1| \otimes |\phi_{g_2}^{b_{g_2}}\rangle \langle \phi_{g_2}^{b_{g_2}}|$$
(17)

We thus have by using (17) and (15) the following expression:

$$S_{g_{1}g_{1}} = S_{g_{1}g_{1}}^{(0)} - 2\pi i \langle \phi_{g_{1}}^{E-} | V_{\text{rad1}} | \phi_{e}^{b_{e}} \rangle \\ \langle \phi_{e}^{b_{e}}, e, N_{1} - 1, N_{2} | (E - H_{\text{eff}})^{-1} | \phi_{e}^{b_{e}}, e, N_{1} - 1, N_{2} \rangle \\ \langle \phi_{e}^{b_{e}} | V_{\text{rad1}} | \phi_{g_{1}}^{E+} \rangle$$
(18)

¹⁰ We have expressed the scattering matrix $S_{g_1g_1}$ as a function of characteristics of the elastic scattering unperturbed by light (the scattering matrix $S_{g_1g_1}^{(0)}$, and the wavefunctions $\phi_{g_1}^{E\pm}$) on the one hand, and as a function of an operator $H_{\rm eff}$ which contains all the physics associated with the laser interaction on the other hand.

2.3 Expression of the effective Hamiltonian

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¹⁵ In order to calculate the matrix element $\langle \phi_e^{b_e}, e, N_1 - 1, N_2 | (E - H_{\text{eff}})^{-1} | \phi_e^{b_e}, e, N_1 - 1, N_2 \rangle$ which appears in (18), we write $E - H_{\text{eff}}$ in the basis spanned by $| \phi_e^{b_e}, e, N_1 - 1, N_2 \rangle$ and $| \phi_{g_2}^{b_{g_2}}, g_2, N_1 - 1, N_2 + 1 \rangle$ using the definition (16) :

$$E - H_{\text{eff}} = \begin{pmatrix} E + \Delta_1 - E_e^{b_e} - \delta_e^{b_e} + i\frac{\gamma_1 + \Gamma}{2} & -\Omega \\ -\Omega & E + \Delta_1 - \Delta_2 - E_{g_2}^{b_2} + i\frac{\gamma_2}{2} \end{pmatrix}$$
(19)

The quantities appearing in (19) are the following:

- the widths $\gamma_1 = \langle \phi_e^{b_e} | \gamma_e(r) | \phi_e^{b_e} \rangle$ and $\gamma_2 = \langle \phi_{g_2}^{b_2} | \gamma_{g_2}(r) | \phi_{g_2}^{b_2} \rangle$ of the bound states in the *e* and g_2 potentials respectively,
 - the Rabi frequency $\Omega = \langle \phi_e^{b_e} | V_{rad2}(r) | \phi_{g_2}^{b_2} \rangle$ for the coupling induced by the second laser between the two bound states.
 - the light induced shift $\delta_e^{b_e}$ and broadening Γ of the excited bound state (²)
 - ² According to the definition of H_{eff} (16), the light induced shift $\delta_e^{b_e}$ and broadening Γ are given by $\delta_e^{v_e} - i\frac{\Gamma}{2} = \langle \phi_e^{b_e}, e, N_1 - 1, N_2 | QV_B P G_0^+(E) P V_B Q | \phi_e^{b_e}, e, N_1 - 1, N_2 \rangle$

Using the decomposition of the identity operator \mathbb{I} on the eigenstates of $PH_0P = K + V_{g_1}$ which are noted $\phi_{g_1}^{n_{g_1}}$ (bound state of vibrational number $|n_{g_1}\rangle$ and $\phi_{g_1}^{E'+}$ (scattering state of energy E'), we obtain the explicit expression for the light induced shift and broadening within this model:

$$\delta_{e}^{v_{e}} = \sum_{v_{g_{1}}} \frac{\left| \langle \phi_{e}^{v_{e}} | V_{rad1} | \phi_{g_{1}}^{v_{g_{1}}} \rangle \right|^{2}}{E - E_{g_{1}}^{v_{g_{1}}}} + vp \int dE' \frac{\left| \langle \phi_{e}^{v_{e}} | V_{rad1} | \phi_{g_{1}}^{E'+} \rangle \right|^{2}}{E - E'}$$

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due to its coupling with the laser ω_1 .

Introducing new detunings (see Fig. 3) Δ'_1 et Δ'_2

$$\begin{aligned}
\Delta_1' &= E + \Delta_1 - E_e^{\nu_e} - \delta_e^{\nu_e} \\
\Delta_2' &= \Delta_2 + E_{g_2}^{\nu_2} - E_e^{\nu_e} - \delta_e^{\nu_e}
\end{aligned}$$
(20)

We rewrite (19)

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$$E - H_{\rm eff} = \begin{pmatrix} \Delta'_1 + i\frac{\gamma_1 + \Gamma}{2} & -\Omega \\ -\Omega & \Delta'_1 - \Delta'_2 + i\frac{\gamma_2}{2} \end{pmatrix}$$
(21)

$$\begin{array}{c} \gamma_{1} + \Gamma \\ & & \\ & & \\ & \Delta_{2}^{\prime} \sqrt{\frac{1}{1-1}} \sqrt{\Delta_{1}^{\prime}} \\ & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & &$$

Figure 4: Equivalent level scheme (left: molecular states, right: states including the photon quantum numbers) for the two-photon photoassociation scheme depicted in Fig. 3.

¹⁰ 2.4 Calculation of the scattering matrix element $S_{g_1g_1}$

We note \mathcal{D} the determinant of (21). The central matrix element in (18) can be expressed as:

$$\langle \phi_e^{b_e}, e, N_1 - 1, N_2 | (E - H_{\text{eff}})^{-1} | \phi_e^{b_e}, e, N_1 - 1, N_2 \rangle = \frac{\Delta_1' - \Delta_2' + i \frac{\gamma_2}{2}}{\mathcal{D}}$$
 (22)

Using the expression of $\phi_{g_1}^{E\pm}$ given in footnote (¹) and the expression of Γ given in footnote (²) one can show that :

$$2\pi i \langle \phi_{g_1}^{E-} | \mathcal{V}_{\text{rad1}} | \phi_e^{b_e} \rangle \langle \phi_e^{b_e} | \mathcal{V}_{\text{rad1}} | \phi_{g_1}^{E+} \rangle = i \Gamma e^{2i\eta_{g_1}}$$
(23)

15 From (22), (23) and (18), we finally get the scattering matrix element:

$$S_{g_1g_1} = e^{2i\eta_{g_1}} - i\Gamma e^{2i\eta_{g_1}} \frac{\Delta'_1 - \Delta'_2 + \frac{i\gamma_2}{2}}{\mathcal{D}} = e^{2i\eta_{g_1}} \frac{\mathcal{N}}{\mathcal{D}}$$
(24)
with $\mathcal{N} = \Delta'_1(\Delta'_1 - \Delta'_2) - \Omega^2 - \frac{\gamma_2(\gamma_1 - \Gamma)}{i} + \frac{i}{2} [(\gamma_1 - \Gamma)(\Delta'_1 - \Delta'_2) + \gamma_2 \Delta'_1]$

In the following section, we identify $S_{g_1g_1}$ as a sum of amplitudes associated with distinct processes.

 $\Gamma = 2\pi \left| \left\langle \phi_e^{b_e} | V_{rad1} | \phi_{g_1}^{E+} \right\rangle \right|^2$

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2.5 Eigenvalues of the effective Hamiltonian. Physical interpretation.

If z_I and z_{II} are the eigenvalues of H_{eff} , the determinant \mathcal{D} of (21) can be written:

$$\mathcal{D} = (\Delta'_1 - z_I)(\Delta'_1 - z_{II}) \tag{25}$$

If the coupling Ω induced by the laser ω_2 is zero, z_I and z_{II} are the complex energies of the states $|v_e, e, N_1 - 1, N_2\rangle$ and $|v_2, g_2, N_1 - 1, N_2 + 1\rangle$. In the case $\Omega \neq 0$, z_I and z_{II} include a light shift and a broadenind due to the perturbation induced by the laser ω_2 . Inserting the following expression

$$\frac{\Delta_1' - \Delta_2' + i\frac{\gamma_2}{2}}{\mathcal{D}} = \frac{1}{z_I - z_{II}} \left[\frac{z_I - \Delta_2' + \frac{i\gamma_2}{2}}{\Delta_1' - z_I} - \frac{z_{II} - \Delta_2'}{\Delta_1' - z_{II}} \right]$$
(26)

into (24) shows that, considered as a function of Δ'_1 (Δ'_2 being fixed), the scattering matrix element $S_{g_1g_1}$ is a sum of three amplitudes: the first one, independent of Δ'_1 corresponds to direct scattering in the potential $|g_1\rangle$; the second one is resonant when ¹⁰ the detuning Δ'_1 coincides with the perturbed energy z_I of $|v_e, e, N_1 - 1, N_2\rangle$ (resonant excitation in a direct one photon absorption process); the third one is resonant when Δ'_1 coincides with the perturbed energy of $|v_2, g_2, N_1 - 1, N_2\rangle$ (resonant Raman process between the two perturbed ground states $|E, g_1, N_1, N_2\rangle$ and $|v_2, g_2, N_1 - 1, N_2 + 1\rangle$ by absorption of a photon ω_1 and stimulated emission of a photon ω_2).

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It clearly appears that there are two paths leading to the dissociation of $|v_1, e\rangle$, one passing directly through the "continuum" γ_1 associated with $|v_1, e\rangle$, and one passing indirectly through the state $|v_2, e\rangle$. On the contrary, there is only one direct path leading to the dissociation of $|v_2, e\rangle$.



Figure 4 : Paths leading to the decay products of the $|v_e, e\rangle$ molecule of width γ_1 . In red solid line is represented the direct path: absorption of a ω_1 photon followed by the decay of the $|v_e, e\rangle$ molecule. In blue dashed line is represented the indirect ²⁵ path: absorption of a ω_1 , stimulated emission and absorbtion of a ω_2 photon followed by the decay of the $|v_e, e\rangle$ molecule. Specific features of the lineshape are due to the width γ_2 of the $|v_2, b_2\rangle$ molecule.

The two eigenvalues z_I and z_{II} can be calculated perturbatively when Ω is small

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compared to the real and imaginary parts of the difference $\Delta'_2 + \frac{i(\Gamma + \gamma_1 - \gamma_2)}{2}$ of the diagonal elements of (21). One finds:

$$z_{I} = -s\Delta'_{2} - i\left[\frac{(\Gamma + \gamma_{1})}{2} - s\frac{(\Gamma + \gamma_{1} - \gamma_{2})}{2}\right]$$
(27)

$$z_{II} = \Delta_2' + s\Delta_2' - i\left[\frac{\gamma_2}{2} - s\frac{(\Gamma + \gamma_1 - \gamma_2)}{2}\right]$$
(28)

where s is a saturation parameter (s \ll 1 in the perturbative limit), and given by Ω^2

$$s = \frac{1}{\Delta_2'^2 + \frac{(\Gamma + \gamma_1 - \gamma_2)^2}{4}}$$
(29)

5 3 Interpretation of the lineshapes

3.1 Photoassociation rate

The calculation of the photoassociation rate K_{PA} which is proportional to the loss rate per collision event gives:

$$K_{PA} \propto 1 - \left| S_{g_1 g_1} \right|^2 = \frac{\gamma_1 \Gamma}{|D|^2} \left[(\Delta_2' - \Delta_1')^2 + \frac{\gamma_2^2}{4} \right] + \frac{\Omega^2 \gamma_2 \Gamma}{|\mathcal{D}|^2}$$
(30)

In the rate (30) we identify two contributions noted $|S_{g_1e}|^2$ and $|S_{g_1g_2}|^2$:

$$\left|S_{g_{1}e}\right|^{2} \equiv \frac{\gamma_{1}\Gamma}{|D|^{2}} \left[(\Delta_{2}' - \Delta_{1}')^{2} + \frac{\gamma_{2}^{2}}{4} \right]$$
(31)

$$\left|S_{g_1g_2}\right|^2 \equiv \frac{\Omega^2 \gamma_2 \Gamma}{|\mathcal{D}|^2} \tag{32}$$

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The first contribution (31) is zero if $\gamma_1 = 0$ and is attributed to the radiative decay of the $|\phi_e^{b_e}, e, N_1 - 1, N_2\rangle$ state. The second contribution (32) is zero if the coupling Ω induced by the second laser tends to zero. It is attributed to the decay of the $|\phi_{g_2}^{b_{g_2}}, g_2, N_1 - 1, N_2 + 1\rangle$ state. By construction, we have $|S_{g_1g_2}|^2 + |S_{g_1e}|^2 + |S_{g_1g_1}|^2 = 1$ which corresponds to the fact that for a collision in the initial channel $|g_1, N_1, N_2\rangle$, the final state can be either in the $|g_1, N_1, N_2\rangle$ channel (elastic collision), or in a channel resulting from the decay of the $|e, N_1 - 1, N_2\rangle$ or $|g_2, N_1 - 1, N_2 + 1\rangle$

3.2 Loss rate associated with the decay widths γ_1

20 3.2.1 Case $\Delta'_2 \neq 0$

Using the factorization of \mathcal{D} and the expression (27) and (28) of z_I and z_{II} in the perturbative limit, we get for the loss rate $|S_{g_1e}|^2$

$$|S_{g_1e}|^2 = \frac{\gamma_1 \Gamma}{(\Delta_1' + s\Delta_2')^2 + \frac{(\gamma_1 + \Gamma - s(\Gamma + \gamma_1 - \gamma_2))^2}{4}} \times$$
(33)

$$\begin{bmatrix} \frac{(\Delta_1' - \Delta_2')^2}{(\Delta_1 - \Delta_2' - s\Delta_2')^2 + \frac{(\gamma_2 + s(\Gamma + \gamma_1 - \gamma_2))^2}{4}} \\ + \frac{\frac{\gamma_2^2}{4}}{(\Delta_1 - \Delta_2' - s\Delta_2')^2 + \frac{(\gamma_2 + s(\Gamma + \gamma_1 - \gamma_2))^2}{4}} \end{bmatrix}$$

which is noted:

$$\left|S_{g_1 e}\right|^2 = A \times (B_1 + B_2) \tag{34}$$

We interprete now the three factors A, B_1 and B_2 and illustrate their contribution in Fig. 5.



Figure 5: Decomposition of the loss rate $|S_{g_1e}|^2$ induced by photoassociation and associated with the decay of the molecule $|v_e, e\rangle$ in the case $\Delta'_2 \neq 0$.

- The factor A corresponds to the photoassociation of the $|\phi_e^{b_e}, e, N_1 1, N_2\rangle$ 1. state and is a Breit-Wigner profile for which the resonance condition is written $\Delta'_1 = -s\Delta'_2$. This is a one photon resonance condition between the state $|E, g_1\rangle$ and the state $|v_e, e\rangle$ shifted by the second photon. Taking s = 0in the factor A, this is to say $\Omega = 0$, we find the one-photon photoassociation lineshape.
- The factor B_1 can be expressed as a Fano profile (4) of parameter q defined 2. by (11) and centered on $\Delta'_1 = (1 + s)\Delta'_2$ close to the two-photon resonance with $|\phi_{g_2}^{b_2}, g_2, N_1 - 1, N_2 + 1\rangle$:

$$B_{1} = \frac{(\Delta_{1}' - \Delta_{2}')^{2}}{\left[(\Delta_{1} - \Delta_{2}' - s\Delta_{2}')^{2} + \frac{(\gamma_{2} + s(\Gamma + \gamma_{1} - \gamma_{2}))^{2}}{4}\right]} \equiv \frac{(\epsilon + q)^{2}}{\epsilon^{2} + 1}$$
(35)
With:

With:

$$\epsilon = \frac{\Delta_1' - \Delta_2' - s\Delta_2'}{\left(\gamma_2 + s(\Gamma + \gamma_1 - \gamma_2)\right)/2} \tag{36}$$

$$q = \frac{s\Delta_2'}{\left(\gamma_2 + s(\Gamma + \gamma_1 - \gamma_2)\right)/2} \tag{37}$$

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The Fano lineshapes for different q parameters are drawn on figure. In the

present case, the Fano lineshape is associated with the interference between two paths coupling the initial state $|E, g_1, N_1, N_2\rangle$ to the continuum of decay products of $|v_e, e, N_1 - 1, N_2\rangle$: the first path is direct and onvolves only the first laser. The second path is indirect and involves once the couling induced by the first laser, and twice the coupling induced by the second laser. The relevant paths are represented on Fig. 4. For $\epsilon = -q$, this is to say $\Delta'_1 = \Delta'_2$, there is a destructive interference between the two amplitudes corresponding to the two paths, and $B_1 = 0$. We notice that for small intensities of laser 2 ($s \ll 1$), the denominator of the reduced energy (36), and also the characteristic width of the resonance is γ_2 . The analysis of the loss associated with the decay of the state $|v_e, e\rangle$ provides information on the width γ_2 of the state $|v_2, g_2\rangle$ (réf).

3. Due to the factor B_2 , the inhibition of the loss rate $|S_{g_1e}|^2$ associated with the decay width γ_1 is never complete in the present case whatever the detuning Δ'_1 is. The factor B_2 is a Breit-Wigner profile for which the resonance condition is $\Delta'_2 - \Delta'_1 = -s\Delta'_2$. This is a Raman resonance condition betwen the state $|E, g_1\rangle$ and the state $|v_2, g_2\rangle$.

²⁰ **3.2.2 Case** $\Delta'_2 = 0$

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We illustrate here loss rate $|S_{g_1e}|^2$ in the case where $\Delta'_2 = 0$ but still $s \ll 1$. The factor B_1 in (35) is a specific case of a Fano lineshape with a parameter q = 0 (see equation (11) and Fig. 2). The lineshape shows even more clearly than in the $\Delta'_2 \neq 0$ ²⁵ case the inhibition of photoassociation when the Raman resonance condition between the unperturbed states $\Delta'_1 = \Delta'_2$ is fulfilled. However the inhibition is not complete due to the contamination of the energy of the electronically excited state $|v_e, e\rangle$ by the width γ_2 . The study of such lineshape is very useful to measure the energy of the $|v_2, g_2\rangle$ molecule (réf).



Figure 7: Decomposition of the loss rate $|S_{g_1e}|^2$ induced by photoassociation and associated with the decay of the molecule $|v_{e}, e\rangle$ in the case $\Delta'_2 = 0$.

35 3.3 Loss rate associated with the decay width γ_2

Using the factorization of \mathcal{D} and the expressions (27) and (28) of z_I and z_{II} in the perturbative limit ($s \ll 1$), we get for the loss rate $|S_{g_1g_2}|^2$

$$|S_{g_1,g_2}|^2$$

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$$= \frac{\Omega^{2} \gamma_{2} \Gamma}{\left[\left(\Delta_{1}' + s \Delta_{2}' \right)^{2} + \frac{\left(\gamma_{1} + \Gamma - s(\Gamma + \gamma_{1} - \gamma_{2}) \right)^{2}}{4} \right] \left[\left(\Delta_{1}' - \Delta_{2}' - s \Delta_{2}' \right)^{2} + \frac{\left(\gamma_{2} + s(\Gamma + \gamma_{1} - \gamma_{2}) \right)^{2}}{4} \right]}$$
(1)

The rate $|S_{g_1g_2}|^2$ is therefore the product of two lorentzians centered on $\Delta'_1 = -s\Delta'_2$ (resonance associated with the excitation of the state $|v_e, e, N_1 - 1, N_2\rangle$ perturbed by the second photon) and $\Delta'_1 = (1 + s)\Delta'_2$ (resonance associated with the excitation of the state $|v_2, g_2, N_1 - 1, N_2 + 1\rangle$ perturbed by the second photon).



Figure 5 : Loss rate $|S_{g_1g_2}|^2$ associated with the decay of the $|v_2, g_2\rangle$ molecule.

We emphasized in section 2.5 that there is only one path leading to the dissociation of the $|v_2, g_2\rangle$ molecule. This explains why $|S_{g_1g_2}|^2$ shows no Fano lineshape.

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Conclusion

References

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20 ‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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