Fano interference and cross-section fluctuations in molecular photodissociation

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We derive an expression for the total photodissociation cross section of a molecule incorporating both indirect processes that proceed through excited resonances, and direct processes. We show that this cross section exhibits generalized Beutler-Fano line shapes in the limit of isolated resonances. Assuming that the closed system can be modeled by random matrix theory, we derive the statistical properties of the photodissociation cross section and find that they are significantly affected by the direct processes. We identify a unique signature of the direct processes in the cross-section distribution in the limit of isolated resonances.

Spectral correlations of closed quantum systems, whose associated classical dynamics are chaotic, are known to be nearly universal and can be modeled by the Gaussian invariant ensembles of random matrix theory 1 2 3. When such systems become open through their coupling to continuum channels, their bound states acquire decay widths and become resonances, but they are still expected to exhibit universal statistics 4. Examples are the conductance fluctuations in quantum dots 5 and the statistics of the indirect molecular photodissociation cross section 6 7. If the coupling is weak, the corresponding resonances are isolated and are often characterized by a Lorentzian line shape (in quantum dots it is necessary to assume temperatures that are much smaller than the decay width). The statistics of the resonance widths are determined by the corresponding statistics of the bound states and energies $E_n$ of the closed system. For a classically chaotic system, these statistics can be derived from random matrix theory. In recent years, such a random matrix approach has been successfully used to model the statistics of resonances 4 and cross-section fluctuations in the photodissociation of classically chaotic molecules 8 9 10 11 12 13. A semiclassical treatment was discussed in Refs. 14 and 15.

However, as first observed by Beutler 16 and later interpreted by Fano 17, the line shape of an individual resonance may differ substantially from a Lorentzian: interference between the indirect decay via the quasi-bound state and direct (fast) decay to the continuum gives rise to a so-called Beutler-Fano line shape. For real bound-state wave functions, the line shape (versus energy $E$) is proportional to $(q_n + \varepsilon_n)^2/(1 + \varepsilon_n^2)$ where $\varepsilon_n = 2(E - E_n)/\Gamma_n$. Here, $q_n$ is the Fano parameter characterizing the line shape, and $\Gamma_n$ is the width of the $n$-th resonance. Beutler-Fano profiles have been observed in molecular photodissociation 18, autoionization 19, conductance through quantum wells 20 and quantum dots 21, STM spectroscopy of surface states 22, semiconductor superlattices 23, and Aharonov-Bohm rings 24.

The Fano parameter $q_n$ fluctuates from one resonance to another. Distributions of the Fano parameter have been calculated for transmission through a quantum dot 25 and for the photodissociation of molecules 26 in the one-channel case (assuming that the corresponding closed system is classically chaotic).

Here we derive an expression for the total photodissociation cross section for any number of open channels in the presence of direct decay processes (see Figs. 1 and 2). We show that in the limit of isolated resonances their line shapes have the form of generalized Beutler-Fano profiles $(|q_n + \varepsilon_n|^2)/(1 + \varepsilon_n^2)$ with a complex Fano parameter $q_n$.

Given that direct photodissociation processes affect the line shapes so dramatically, it is interesting to find out how they affect the statistics of the photodissociation cross-section when the closed system is classically chaotic. We derive a closed expression for the cross-section autocorrelation function (in energy) and find that it is universal provided that the excitation process
and the continuum coupling are spatially well-separated. System-specific information enters only in the values of the direct and indirect channel couplings. We also calculate the cross-section distribution, and find that the direct decay gives rise to a characteristic maximum in the distribution (see Fig. 2) in the regime of isolated resonances. This is in contrast to the monotonically decreasing behavior of the distribution in the same regime, in the absence of direct coupling. In summary, we show that cross-section fluctuations are significantly affected by the presence of direct decay channels, but remain universal. Our results also apply to atomic autoionization.

A molecule can dissociate into several channels $c$ by absorbing a photon. In the dipole approximation, the total photodissociation cross section at energy $E$ is given by

$$
\sigma(E) = \sigma_0(E) \sum_{c=1}^{\Lambda} |\langle \Phi_c^{-1}(E) | \hat{\mu} | g \rangle|^2 ,
$$

(1)

where $\hat{\mu} = \hat{\mu} \cdot \mathbf{e}$ is the component of the dipole moment $\hat{\mu}$ of the molecule along the polarization $\mathbf{e}$ of the absorbed light and $\sigma_0(E) \propto (E - E_q)$. Here $|g\rangle$ is the ground state with energy $E_q$, and $|\Phi_c^{-1}(E)\rangle$ ($c = 1, \ldots, \Lambda$) is a dissociation solution at energy $E$ defined by an outgoing wave in channel $c$ and incoming waves in all other channels. We consider a model in which the Hilbert space is divided into two parts: an internal “interacting” region, and an external “channel” region (cf. Fig. 2). The internal region is described by the Hamiltonian $H_0$ represented by an $N \times N$ matrix $H_0$ with eigenstates $|n\rangle$ ($n = 1, \ldots, N$). The external region is spanned by the $\Lambda$ open dissociation channels $|c\rangle$. The two regions are coupled by an operator $\hat{W}$ that can be represented by an $N \times \Lambda$ matrix $W$ with matrix elements $\langle c | W | n \rangle = \gamma_{nc}$. In general, the dipole operator $\hat{\mu}$ can couple the ground state to both the internal states $|n\rangle$ and the external channels $|c\rangle$. We define $|\alpha\rangle = \hat{\mu} |g\rangle$, and introduce two vectors $\alpha^n$ and $\alpha^{ch}$. The first has $N$ components $\alpha^n_m \equiv \langle n | \alpha \rangle$, describing the dipole coupling to the internal states, and the second has $\Lambda$ components $\alpha^{ch}_c \equiv \langle c | \alpha \rangle$, describing the dipole coupling to the continuum channels.

We first show that, in the regime of isolated resonances and for $\alpha^{ch} \neq 0$, the cross section describes a sum over Beutler-Fano resonances. We write

$$
\sum_{c=1}^{\Lambda} |\langle \Phi^{-1}_c(E) | \Phi^{-1}_c(E) \rangle| = -\pi^{-1} \text{Im} \hat{G} (E + i 0) \text{ and separate the channel and internal components of the Green function } \hat{G} (E + i 0) \text{. We obtain}
$$

(2)

$$
\sigma(E) / \sigma_0(E) = -\pi^{-1} \text{Im} \left[ \langle \alpha | \hat{G}_{ch} | \alpha \rangle \right] + \langle \alpha | (1 + \hat{G}_{ch} \hat{W}^\dagger) \frac{1}{E - H_0 - \hat{W} \hat{G}_{ch} \hat{W}^\dagger (1 + \hat{W} \hat{G}_{ch}) |\alpha\rangle \right] ,
$$

(3)

where $\hat{G}_{ch}$ is the channel Green function. Assuming unstructured decay continua, Eq. (2) simplifies to

$$
\sigma(E) / \sigma_0(E) = ||\alpha^{ch}||^2
$$

(4)

$$
-\frac{1}{\pi} \text{Im} \left[ (\alpha^{in} + i \pi \hat{W} \alpha^{ch})^\dagger \frac{1}{E - H_{\text{eff}}} (\alpha^{in} - i \pi \hat{W} \alpha^{ch}) \right] .
$$

Here $H_{\text{eff}} = H_0 - i \pi \hat{W} \hat{W}^\dagger$ is an effective (non-Hermitian) $N \times N$ Hamiltonian in the internal space. In the absence of direct photodissociation, $\alpha^{ch} = 0$, and Eq. (4) reduces to the result of Refs. 7 and 6.

In general, the resolvent in Eq. (3) can be written as

$$
(E - H_{\text{eff}})^{-1} = \sum_{n,c} |R_n\rangle \langle L_n| (E - E_n - 1), \text{ where } |R_n\rangle \text{ and } |L_n\rangle \text{ are bi-orthonormal right and left eigenvectors of } H_{\text{eff}} \text{ with complex eigenvalues } E_n. \text{ However, in the regime of isolated resonances we can apply the Breit-Wigner approximation } |R_n| \approx |L_n| \approx |n\rangle \text{ and } \text{Im } E_n = -\Gamma_n / 2 \approx -\pi \sum_c |\gamma_{nc}|^2 \text{. The cross-section } \sigma(E) \text{ can then be written as a sum over resonances. In the presence of direct photodissociation, the contribution from each of these resonances has a generalized Beutler-Fano line shape } |q_n + e_n|^2 / (1 + e_n^2) \text{ with a complex parameter } q_n \text{ whose real part and modulus are given by}
$$

$$
\text{Re } q_n = \text{ Re } \left[ \frac{\alpha^{in}_{n} \sum_{c=1}^{\Lambda} \alpha^{ch}_c \gamma_{nc}}{\pi \sum_{c=1}^{\Lambda} |\alpha^{ch}_c|^2 \sum_{c=1}^{\Lambda} |\gamma_{nc}|^2} \right] ,
$$

$$
|q_n|^2 = 1 + \frac{|\alpha^{in}_{n}|^2 - \pi^2}{\pi^2 \sum_{c=1}^{\Lambda} |\alpha^{ch}_c|^2 \sum_{c=1}^{\Lambda} |\gamma_{nc}|^2} .
$$

(5)

In general, $\text{Im } q_n \neq 0$, and there is no energy for which the cross section vanishes. However, for $\beta = 1$ and $\Lambda = 1$, Eq. (5) simplifies to Fano’s expression $\text{Re } q_n = \alpha^{in}_{n} / (\pi \alpha^{ch}_c \gamma_{nc})$ and $\text{Im } q_n = 0 \text{ (assuming that all matrix elements are real)}$.

In the following we calculate the statistical properties of the photodissociation cross section assuming that the dynamics in the closed interaction region are fully chaotic. The matrix $H_0$ is taken to be a $N \times N$ random matrix from the Gaussian Orthogonal Ensemble (GOE) or from the Gaussian Unitary Ensemble (GUE), with distribution $P(H_0) dH_0 \propto$
\[ \exp[-(\beta N/4)\text{Tr} H_0^2] dH_0. \] Here \( \beta = 1 \) in the GOE and \( \beta = 2 \) in the GUE. In the limit of large \( N \), the average eigenvalue distribution (normalized to 1) is \( \nu(E) = (2\pi)^{-1}\sqrt{4-E^2} \) for \( |E| < 2 \) (and zero otherwise), and the corresponding mean eigenvalue spacing is \( \Delta(E) = 1/[N\nu(E)] \). In the same limit (i.e., for large \( N \)), \( \alpha_n^\text{in} \) and \( \gamma_n^\text{ac} \) (\( c = 1, \ldots, \Lambda \)) are independently distributed Gaussian random variables, and for each \( n \) \[ P(\alpha_n^\text{in}, \gamma_n) \propto \exp \left[ -\beta/2 (\alpha_n^\text{in}, \gamma_n) M^{-1} (\alpha_n^\text{in}, \gamma_n) \right]. \] (5)

Here \( \gamma_n^\text{in} = (\gamma_n^\text{in}, \ldots, \gamma_n^\text{in}\Lambda) \) and

\[ M = N^{-1} V^\dagger V \quad \text{with} \quad V = (\alpha^\text{in}, W) \] (6)

is an \((\Lambda + 1) \times (\Lambda + 1)\) matrix. In the following we assume the channel vectors (columns of \( W \)) to be mutually orthogonal. This can always be achieved by a suitable orthogonal (unitary) transformation in channel space.

**Average cross section.** In the center of the band \( (E = 0) \), the average cross section is \( \langle \sigma \rangle = \sigma_0 \left[ (|\alpha_n^\text{in}|^2/\pi + \sum_{c=1}^{\Lambda} |\alpha_c^\text{ch}|^2/(1+\lambda_c)) \right] = \sigma_\text{ind} + \sum_c \sigma_c^\text{dir} \), where \( \sigma_\text{ind} \) and \( \sigma_c^\text{dir} \) are the average cross sections in the limiting cases of purely indirect and purely direct dissociation, respectively. Here \( \lambda_1, \ldots, \lambda_\Lambda \) are the \( \Lambda \) dimensionless eigenvalues of the matrix \( \pi^2 \nu W^\dagger W \). It is often convenient to characterize the strength of the coupling to the continuum by transmission coefficients \( T_c = 4\lambda_c/(1+\lambda_c)^2 \).

**Cross-section autocorrelation function.** We define a dimensionless cross section autocorrelation function \[ S(E, \omega) = \sigma_\text{ind}^{-2} \left[ \langle \sigma(E-\omega/2)\sigma(E+\omega/2) \rangle - \langle \sigma \rangle^2 \right]. \] (7)

In the Breit-Wigner approximation, this correlation is most conveniently calculated in the time domain \([7, 31]\). Defining \( C(E, t) = \int_{-\infty}^{\infty} d\omega e^{i\omega t} S(E, \omega) \), and using (5) we find

\[ C(E, t) = \frac{1}{4\pi^2} \left[ A_\beta(t) - B_\beta(t)b_2,\beta(t) \right] \] (8)

where \( b_2,\beta(t) \) is the two-level form factor \([1]\), and \( A_\beta(t), B_\beta(t) \) are functions that depend in general on the matrix \( M \) in Eq. (6) and the dipole coupling coefficients to the continuum \( \alpha_c^\text{ch} \).

The expression for \( A_\beta(t) \) and \( B_\beta(t) \) simplify when the dipole “channel” is orthogonal to all channel vectors, i.e., \( W^\dagger \alpha^\text{in} = 0 \). This is the case when the excitation process and the continuum coupling are spatially well separated. Using the so-called rescaled Breit-Wigner approximation \([7, 31]\), we find

\[ A_1(t) = \pi \sum_{c=1}^{\Lambda} (1 + 2T_c t)^{-1/2} \left[ 3 + \frac{1}{2} \sum_c \tau_c (1 + 2T_c t)^{-1} \right] \]

\[ B_2(t) = \pi \sum_{c=1}^{\Lambda} (1 + T_c t)^{-1/2} \left[ 1 - \frac{1}{4} \sum_c \tau_c (1 + T_c t)^{-1} \right] \]

for \( \beta = 1 \). A similar result is obtained for \( \beta = 2 \)

\[ A_2(t) = \pi \sum_{c=1}^{\Lambda} (1 + T_c t)^{-1} \left[ 2 + \frac{1}{4} \left( \sum_c \tau_c (1 + T_c t)^{-1} \right)^2 \right] \]

\[ B_2(t) = \pi \sum_{c=1}^{\Lambda} (1 + T_c t)^{-1} \left[ 1 - \frac{1}{4} \sum_c \tau_c (1 + T_c t)^{-1} \right] \]

The results \([9, 10]\) describe universal correlations; they depend on the coefficients \( \tau_c/T_c = \sigma_c^\text{dir}/\sigma_\text{ind} \) which measure the strength of the direct photodissociation channels, but they do not depend on the microscopic details of the system (such as the ground state or the nature of the excitation mechanism).

Two special cases of \([9, 10]\) are of interest. First, in the limit of \( \tau_c = 0 \), the results of Ref.\([5]\) are recovered, valid in the absence of direct coupling to the continuum. Second, consider the case of \( \Lambda \) equivalent open channels \( T_c = T, \sigma_c^\text{dir} = \sigma_\text{dir} \). In the limit \( \Lambda \to \infty, T \to 0 \) with \( \Delta T \equiv \kappa \) constant, the expressions in Eq. (6) simplify to

\[ A_\beta(t) = A_\beta e^{-\kappa |t|}, \quad B_\beta(t) = B \theta e^{-\kappa |t|/2} \] (11)

with \( A_1 = 3 + \theta/2 + 3\theta^2, A_2 = 2(1+\theta/16), B = (1-\theta/4), \) and \( \theta = \Lambda T = \kappa \sigma_\text{dir}/\sigma_\text{ind} \). We obtain

\[ S(E, \omega) = \frac{1}{4\pi^2} \left[ A_\beta f(\omega) - B^2 \int \frac{d\omega'}{\pi} f(\omega - \omega') Y_{2,\beta}(\omega') \right], \]

where \( Y_{2,\beta}(\omega) \) is the two-level cluster function \([1]\), and \( f(\omega) = (\kappa/2)/(\omega^2 + \kappa^2/4) \). Fig. 3 shows Eq. (12) (solid lines) together with results from random matrix simulations (symbols). For \( \beta = 1 \) and in the presence of direct decay, the correlation function is close to a Lorentzian.

**Cross-section distribution.** The distribution \( P(\sigma/\sigma_\text{ind}) \) is calculated from its Fourier transform \( F_\beta(s) = \)
\[
\langle e^{-i s \sigma/\sigma_{\text{ind}}} \rangle \text{ within the Breit-Wigner approximation. We have calculated } F_\beta(s) \text{ for } \Lambda \text{ equivalent open channels in the limit of } \Lambda \rightarrow \infty \text{ with } \Lambda T = \kappa \text{ kept constant. In this case, } \Gamma_n \simeq \Gamma = 2\Lambda N, \text{ and using } (5) \text{ we obtain}
\]
\[
F_\beta(s) = e^{i \pi s/(2\Gamma N)} \left( \frac{\det[(E - H_0)^2 + \Gamma^2/4]}{\det[(E - H_0)^2 + \Gamma_s^2/4]} \right)^{1/2}
\]
(13)

with \[
\Gamma_s^2 = \left( \Gamma + 4\pi i s/(N\beta) \right) \left( \Gamma - 2\pi i s \theta/(N\beta) \right).
\]
Eq. (13) can be evaluated using the results of Ref. 32. For \( \beta = 2 \)
\[
F_2(s) = e^{i \pi s/2N} e^{-\pi \Gamma_s/\Delta} \times \left[ \cosh \left( \frac{\pi \Gamma_s}{\Delta} \right) + \frac{1}{2} \sinh \left( \frac{\pi \Gamma_s}{\Delta} \right) \left( \frac{\Gamma + \Gamma_s}{\Gamma} \right) \right].
\]
(14)

For \( \beta = 1 \) the corresponding result can be expressed in terms of a four-fold integral \[32\]. Fig. 4 shows the inverse Fourier transform of \( F_\beta(s) \) (solid lines) in comparison with random matrix simulations (symbols). In the presence of direct coupling, the cross-section distribution exhibits a maximum (see Fig. 4b). In the limit of isolated resonances, this maximum is a clear signature of the direct processes.

In conclusion, we have shown that a direct coupling to the continuum leads to generalized Fano resonances in the total photodissociation cross section, and used random matrix theory to derive the signatures of these direct processes in the cross-section statistics.

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FIG. 4: Cross section distributions. (a) The cross section vs. energy \( E \) in the absence of direct coupling (\( \theta = 0 \)) and for one random matrix realization of \( H_0 \). Here \( \beta = 1, N = 64, \Lambda = 10, \) and \( x_c = 5 \times 10^{-2} \) for all \( c \). (b) Same as in (a) but in the presence of direct processes (\( \theta = 0.125 \)). (c) Cross-section distributions at \( E = 0 \) for \( \theta = 0 \) (squares) and \( \theta = 0.125 \) (circles). (d) as in (c) but for \( \beta = 2 \). The solid lines in (c) and (d) are the inverse Fourier transform of \( F_\beta(s) \).

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