

## Photon absorption and scattering in Fano anti-resonances

by ABRAHAM NITZAN

Department of Chemistry, Massachusetts Institute of Technology,  
Cambridge, Massachusetts 02139

(Received 25 June 1973)

The Green's function method is utilized to obtain a modified treatment of Fano's line-shape problem which takes into account the coupling between different states in the continuous (or quasi-continuous) non-radiative manifold due to their interaction with the same radiation field states. A new expression for the absorption line-shape is obtained in the form  $\sigma_a(\epsilon) \propto [(\epsilon + qY^L)^2 + (Y^Lq^2 + 1)(1 - Y^L)]/(\epsilon^2 + 1)$ , where  $\epsilon$  is the reduced energy parameter,  $q$  is Fano's line-shape index and  $Y^L$  is the non-radiative quantum yield obtained when the non-radiative manifold is optically forbidden. As  $Y^L$  is always smaller than unity, the absorption never strictly vanishes in contrast to the result obtained in Fano's approximation. In addition, expressions are obtained for the emission line-shape and for the (energy dependent) emission quantum yield within a Fano resonance. The quantum yield so obtained is free from the singular behaviour which characterizes the same quantity obtained in Fano's approximation.

### 1. INTRODUCTION

Interference phenomena in absorption line-shapes have been a subject of intensive experimental and theoretical study since Fano in a pioneering work [1] considered the line-shapes of auto-ionizing atomic transitions. Effects of similar nature have been shown to occur in nuclear [2] and in solid state physics [3], and more recently in molecular spectroscopy [4-6].

Two of the models originally included in Fano's general analysis [1] have been particularly useful in analysing experimental results. In the first (model A, figure 1 *a*) the zero-order basis set consists of a single state and an isoenergetic continuous (or quasi-continuous) manifold, both carrying oscillator strength for optical transitions from the ground state and interacting with each other through the full hamiltonian of the system. In the second model (model B, figure 1 *b*) the zero-order basis consists of two discrete optically allowed excited levels interacting with isoenergetic optically forbidden continuum. The term 'Fano line-shape' or 'Fanian' is usually attributed to the line-shape related to model A. Both models are closely related, in particular one can always transform B into model A by diagonalizing the hamiltonian in one of the discrete states and the continuum. When both representations are available for a particular problem, it is always preferable to utilize that in which the coupling matrix elements and the density of states are weak functions of the energy (or the state index) in the continuum.†

†Many of the studies of interference effects in molecular spectroscopy suffer from choosing to work with the wrong representation in this sense. For a discussion of this point, see reference [6 b].

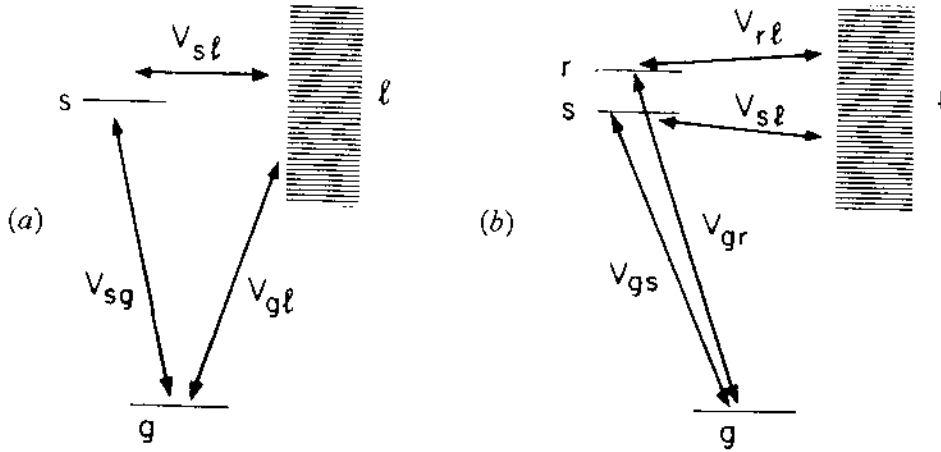


Figure 1. Conventional models for analysing interference phenomena in absorption and scattering line-shapes. (1a) A single discrete state  $|s\rangle$  interacts with a dense manifold of states  $\{|l\rangle\}$ , both carrying oscillator strength for optical transition from the ground state  $|g\rangle$ . (1b) Two discrete, closely seated, optically allowed states  $|s\rangle$  and  $|r\rangle$  interact with an optically forbidden dense manifold  $\{|l\rangle\}$ .

It is not generally realized that Fano's method involves an approximation. This method is based on obtaining the set of excited eigenstates  $\{\psi_j\}$  of the system's hamiltonian and assuming that the line-shape is proportional to the quantity  $|\langle\psi_g|\mu|\psi_j\rangle|^2\rho_j$ , where  $\psi_g$  is the ground state,  $\mu$  is the operator for optical transition and  $\rho_j$  is the density of states  $\{\psi_j\}$ .<sup>†</sup> This assumption neglects high-order interactions between closely seated  $\psi_j$  states which result from their coupling to the same radiation field states. To see how this assumption affects the calculated line-shape, it is sufficient to note that in the case of a simple resonance (one discrete, optically allowed excited state coupled to a non-radiative, optically forbidden, uniformly spaced continuum, with an energy independent coupling coefficient), Fano's method predicts a Lorentzian line-shape with a width which corresponds to the non-radiative lifetime of the discrete state, while the correct width should be the sum of the radiative width ( $\Gamma_R$ ) and the non-radiative width ( $\Gamma_{NR}$ ) of this state. When  $\Gamma_{NR} \gg \Gamma_R$ , Fano's method yields the correct result for this case to a high degree of accuracy, but this does not guarantee its success for other cases. In particular, it has been shown [7] that when Fano's approximation is used in calculating (energy dependent) quantum yields for resonance fluorescence, it leads to unphysical divergencies of these quantum yields near the points of total destructive interference (Fano's dip) for both models A and B. Mathematically, this results from the fact that in this approximation the scattering cross section does not in general vanish at the point of zero absorption cross section [7]. This suggests that also the absorption cross section remains non-zero at the bottom of the interference dip. This feature was demonstrated by Nitzan and Jortner for model B [7], but they were unable to carry on their method for model A without invoking Fano's approximation. It is the aim of this paper to solve Fano's problem (model A) without invoking this approximation and thus obtain expressions for the line-shape and quantum yield which are free from zeros and divergencies. This is done at the cost of assuming constant coupling matrix elements in an early stage of the calculation. This is not a serious flaw relative to other theoretical treatments of Fano's problem [1-7], as the same assumption

<sup>†</sup>Throughout this paper we use the state index representation and not Fano's energy representation (in which the line-shape would have been written as  $|\langle\psi_g|\mu|\psi_E\rangle|^2$ ).

is involved in a somewhat later stage in every other method. The same approach has been recently used in studying the problem of interference in the consecutive decay of a molecular resonance [8–10].

## 2. MODEL AND NOTATIONS

Our model is described in figure 2. The hamiltonian for this model system is

$$H = H_0 + H_v + H_{\text{int}}, \quad (1)$$

where

$$H_0 = H_M + H_R \quad (2)$$

is the 'unperturbed' part which consists of the hamiltonian of the free system (the molecule say)  $H_M$ , and the hamiltonian of the free radiation field  $H_R$ .  $H_v$  is some residual interaction in the system (so that  $H_M + H_v$  is the full hamiltonian of the free system) and  $H_{\text{int}}$  is the interaction between the system and the radiation field which is responsible for the optical transition. The basis set is chosen to consist of eigenstates of  $H_0$ . It is assumed that the optical region considered is spanned to a good approximation by the following eigenstates of  $H_0$ :  $\{|m\rangle\} \equiv \{|g; \mathbf{k}, \mathbf{e}\rangle\}$  are one photon states seated on the system's ground state  $|g\rangle$  ( $\mathbf{k}$  and  $\mathbf{e}$  denote the wave vector of the photon and its polarization state respectively);

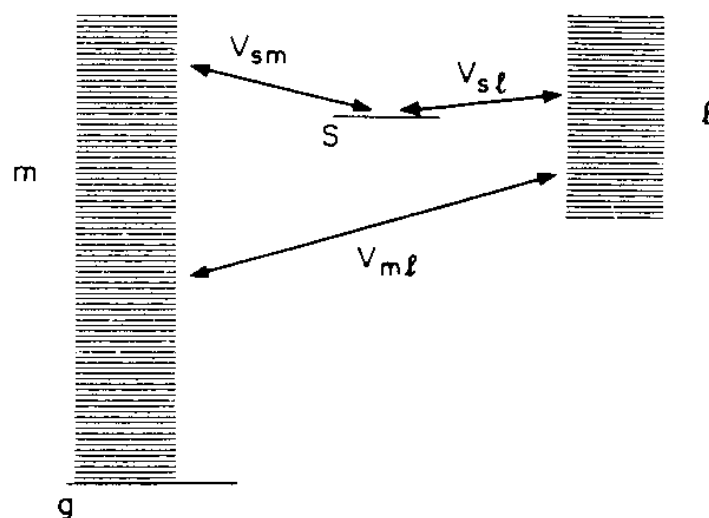


Figure 2. The model used in the present work. This is an extension of the model displayed in figure 1(a), where the radiative continuum  $\{|m\rangle\}$ , consisting of one-photon states seated on the molecular ground state, is taken into account.

$|s\rangle \equiv |s, \text{vac}\rangle$  is an excited state of the system which is optically accessible from the ground state (vac denote the zero photon state of the radiation field);  $\{|l\rangle\} \equiv \{|l; \text{vac}\rangle\}$  is an excited continuous or quasi-continuous manifold of eigenstates of  $H_M$  again with the vacuum state of  $H_R$ . The pertinent coupling matrix elements are

$$\langle s|H_{\text{int}}|m\rangle \equiv V_{sm}; \quad \langle l|H_{\text{int}}|m\rangle \equiv V_{lm}; \quad \langle s|H_v|l\rangle \equiv V_{sl}. \quad (3)$$

The remaining non-diagonal matrix elements of  $H$  vanish. This results from

the assumption that  $H_{\text{int}}$  is a one-photon operator and from prediagonalizing  $H$  within the manifold  $\{|l\rangle\}$ . Thus,

$$\left. \begin{aligned} \langle s|H|s\rangle &= \langle s|H_M + H_v|s\rangle \equiv E_s, \\ \langle l|H|l'\rangle &= \langle l|H_M + H_v|l'\rangle \equiv E_l\delta_{ll'}, \\ \langle m|H|m'\rangle &= \langle m|H_R|m'\rangle \equiv E_m\delta_{mm'} \quad (\text{the ground state of } H_0 \text{ defines the} \\ &\quad \text{origin for the energy variable),} \\ \langle s|H_v|m\rangle &= \langle l|H_v|m\rangle = \langle s|H_{\text{int}}|l\rangle = \langle m|H_{\text{int}}|m'\rangle = 0. \end{aligned} \right\} \quad (4)$$

In what follows we shall apply the Green's function method to calculate the absorption and scattering line-shapes and the scattering (fluorescence) quantum yields for this model. We shall repeatedly invoke the assumption of constant coupling matrix elements, namely  $V_{sm}$ ,  $V_{sl}$  and  $V_{lm}$  are assumed to be independent of indices  $l$  and  $m$  (but remain, of course, different from each other). Similar assumption is invoked for the densities of states  $\rho_l$  and  $\rho_m$  in the  $l$  and  $m$  manifolds: these are also taken to be constants over the manifolds. Indeed, in many cases we do not expect the coupling coefficient and the density of states to change appreciably within the resonance width. In cases where the transition moments  $V_{sm}$  and  $V_{lm}$  are vectors in the systems frame of reference [5], it is further assumed (as is commonly the case) that these vectors are parallel (or anti-parallel) to each other. They are thus taken as scalars throughout this work. Finally we shall assume that trivial level shifts may be neglected (see equation (13) below). It should be noted that the last two assumptions are made for the sake of simple presentation only, and may be easily relaxed at the cost of more cumbersome expressions in the following treatment.

### 3. THE ABSORPTION LINE-SHAPE

We shall utilize the Green's function method which was described in earlier works [7, 10-12]. The absorption cross section is given by [7]

$$\sigma_a(E) = -\frac{2Q}{\hbar c} \text{Im} \{ \langle m | (H_v + H_{\text{int}}) G (H_v + H_{\text{int}}) | m \rangle \}, \quad (5)$$

where  $c$  is the velocity of light and  $Q$  is the normalization volume of the system, and where

$$G = (E - H + i\eta)^{-1}; \quad \eta \rightarrow 0^+. \quad (6)$$

Our problem is to calculate the matrix element

$$L = \langle m | (H_v + H_{\text{int}}) G (H_v + H_{\text{int}}) | m \rangle. \quad (7)$$

Expanding in our basis set and setting

$$x = G_{ss}; \quad y = \sum_l G_{ls}; \quad u = \sum_l G_{sl}; \quad w = \sum_l \sum_{l'} G_{ll'}, \quad (8)$$

equation (7) takes the form

$$L = |V_{ms}|^2 x + V_{ms} V_{lm} u + V_{ml} V_{sm} y + |V_{lm}|^2 w, \quad (9)$$

where the coupling matrix elements were taken to be independent of the state indices  $m$  and  $l$ . It is convenient to make the additional definitions:

$$z = \sum_m G_{ms}; \quad v = \sum_m G_{sm}; \quad t = \sum_{ml} G_{ml}. \quad (10)$$

We now utilize the identities

$$\begin{aligned} G &= G_0 + G_0(H_{\text{int}} + H_v)G; \quad G_0 = (E - H_0 + i\eta)^{-1} \\ &= G_0 + G(H_{\text{int}} + H_v)G_0 \end{aligned} \quad (11)$$

to obtain a set of algebraic equations for the matrix elements of  $G$ :

$$G_{ss} = x = \frac{1}{E - E_s + i\eta} (1 + V_{sl}y + V_{sm}z), \quad (12a)$$

$$G_{ls} = \frac{1}{E - E_l + i\eta} (V_{ls}x + V_{lm}z), \quad (12b)$$

$$G_{ms} = \frac{1}{E - E_m + i\eta} (V_{ms}x + V_{ml}y), \quad (12c)$$

$$G_{sl} = \frac{1}{E - E_l + i\eta} (V_{sl}x + V_{ml}v), \quad (12d)$$

$$G_{sm} = \frac{1}{E - E_m + i\eta} (V_{sm}x + V_{lm}u), \quad (12e)$$

$$G_{ll'} = \frac{1}{E - E_l + i\eta} (\delta_{ll'} + V_{ls}G_{sl'} + V_{lm}\sum_m G_{ml'}), \quad (12f)$$

$$G_{ml'} = \frac{1}{E - E_m + i\eta} (V_{ms}G_{sl'} + V_{ml}\sum_l G_{ll'}). \quad (12g)$$

To obtain a closed set of algebraic equations in the variables  $x, y, z, u, v, w, t$  we sum equations (12b) and (12d) over  $l$ , equations (12c) and (12e) over  $m$ , equation (12f) over both  $l$  and  $l'$  and equation (12g) over both  $m$  and  $l'$ . For the sake of simplicity, we neglect level shifts in the resulting equations, namely we take

$$\lim_{\eta \rightarrow 0^+} \sum_l \frac{1}{E - E_l + i\eta} = -i\pi\rho_l; \quad \lim_{\eta \rightarrow 0^+} \sum_m \frac{1}{E - E_m + i\eta} = -i\pi\rho_m \quad (13)$$

(here  $\rho_l$  and  $\rho_m$  are densities of states in the  $l$  and  $m$  manifolds, respectively) and neglect the real part of these expressions. For nearly constant coupling elements and density states this approximation is valid.

Performing the summations described above and neglecting level shifts, we get from equation (12)

$$x = \frac{1}{E - E_s + i\eta} (1 + V_{sl}y + V_{sm}z), \quad (14a)$$

$$y = i\pi\rho_l V_{ls}x - i\pi\rho_l V_{lm}z, \quad (14b)$$

$$z = -i\pi\rho_m V_{ms}x - i\pi\rho_m V_{ml}y, \quad (14c)$$

$$u = -i\pi\rho_l V_{sl}x - i\pi\rho_l V_{ml}v, \quad (14d)$$

$$v = -i\pi\rho_m V_{sm}x - i\pi\rho_m V_{lm}u, \quad (14e)$$

$$w = -i\pi\rho_l - i\pi\rho_l V_{ls}u - i\pi\rho_l V_{lm}t, \quad (14f)$$

$$t = -i\pi\rho_m V_{ms}u - i\pi\rho_m V_{ml}w. \quad (14g)$$

This is a closed set of linear homogeneous algebraic equations which yields after some algebraic manipulations

$$x = G_{ss} = (E - \tilde{E}_s + (i/2)\Gamma_s)^{-1}, \quad (15 a)$$

$$y = \sum_l G_{ls} = - \frac{\pi^2 \rho_l \rho_m V_{lm} V_{ms} + i\pi V_{ls} \rho_l}{1 + N} G_{ss}, \quad (15 b)$$

$$u = \sum_l G_{sl} = - \frac{\pi^2 \rho_l \rho_m V_{sm} V_{ml} + i\pi \rho_l V_{sl}}{1 + N} G_{ss}, \quad (15 c)$$

$$w = \sum_{l'} \sum_l G_{ll'} = - \frac{(\pi^2 \rho_l \rho_m V_{lm} V_{ms} + i\pi \rho_l V_{ls})u + i\pi \rho_l}{1 + N}, \quad (15 d)$$

$$z = \sum_m G_{ms} = - \frac{\pi^2 \rho_m \rho_l V_{ml} V_{ls} + i\pi V_{ms} \rho_m}{1 + N} G_{ss}, \quad (15 e)$$

$$v = \sum_m G_{sm} = - \frac{\pi^2 \rho_m \rho_l V_{sl} V_{lm} + i\pi \rho_m V_{sm}}{1 + N} G_{ss}, \quad (15 f)$$

$$t = \sum_{ml} \sum_m G_{ml} = - \frac{\pi^2 \rho_m \rho_l V_{ml} + (\pi^2 \rho_m \rho_l V_{ml} V_{ls} + i\pi \rho_m V_{ms})u}{1 + N}, \quad (15 g)$$

where

$$N = \pi^2 \rho_l \rho_m |V_{lm}|^2, \quad (16)$$

$$\tilde{E}_s = E_s - D_s, \quad (17 a)$$

$$D_s = \frac{\pi^2 \rho_l \rho_m (V_{lm} V_{ms} V_{sl} + V_{ml} V_{ls} V_{sm})}{1 + N}, \quad (17 b)$$

$$\Gamma_s = \frac{\Gamma_s^L + \Gamma_s^M}{1 + N}, \quad (18 a)$$

$$\Gamma_s^L = 2\pi |V_{sl}|^2 \rho_l, \quad (18 b)$$

$$\Gamma_s^M = 2\pi |V_{sm}|^2 \rho_m. \quad (18 c)$$

It will prove convenient to define the additional parameters

$$\Gamma_l^M = 2\pi |V_{lm}|^2 \rho_m, \quad (19 a)$$

$$\Gamma_m^L = 2\pi |V_{lm}|^2 \rho_l. \quad (19 b)$$

Note that the parameters  $\Gamma_i^K$  ( $i = s, l, m$ ;  $K = L, M$ ) have a simple physical interpretation as the width of a single state  $i$  interacting with a single continuum  $K$ .

The rest of the calculation is now straightforward. We insert equations (15 a-d) for  $x, y, u$  and  $w$  into equation (9) and find after a few algebraic steps

$$L = -(i/2) \frac{\Gamma_m^L}{N+1} + G_{ss} A, \quad (20)$$

where

$$A = \frac{\frac{1}{4} \Gamma_s^L \Gamma_m^L}{(N+1)^2} (q-i) (q^* - i) \quad (21)$$

and where  $q$  is Fano's line-shape index given by

$$q = \frac{V_{ms}}{\pi \rho_l V_{ml} V_{ls}}. \quad (22)$$

In what follows we assume that all the coupling matrix elements are real.† Using Fano's notation we also define the dimensionless energy variable

$$\epsilon = \frac{E - \tilde{E}_s}{\Gamma_s/2} \quad (23)$$

which differs, however, from the energy variable in Fano's case as  $\tilde{E}_s$  and  $\Gamma_s$  are given now by equations (17a) and (18a), respectively. In terms of  $\epsilon$ , equation (23), expression (15a) for  $G_{ss}$  takes the form

$$G_{ss} = \frac{2}{\Gamma_s} \frac{\epsilon - i}{\epsilon^2 + 1}. \quad (24)$$

Utilizing now equations (21) and (24), equation (20) takes the form

$$L = \left(\frac{1}{2}\right) \frac{\Gamma_m^L}{N+1} \left[ -i + \frac{\Gamma_s^L}{\Gamma_s(N+1)} \frac{\epsilon - i}{\epsilon^2 + 1} (q - i)^2 \right]. \quad (25)$$

A further simplification is obtained by noting (from the definition (18a) of  $\Gamma_s$ ) that

$$\frac{\Gamma_s^L}{(N+1)\Gamma_s} = \frac{\Gamma_s^L}{\Gamma_s^L + \Gamma_s^M} \equiv Y^L = 1 - Y^M, \quad (26a)$$

where  $Y^L$  has the simple physical meaning of the quantum yield of the decay of the initially prepared state  $s$  into the non-radiative channel  $\{|l\rangle\}$  provided that the channels  $\{|l\rangle\}$  and  $\{|m\rangle\}$  were non-interacting. (Similarly  $Y^M$  is the radiative quantum yield under the same conditions.)

It should be noted that the parameters  $Y^L$ ,  $q$  and  $N$  are not all independent. It is easily verified that

$$Y^L = \frac{1}{q^2 N + 1}. \quad (26b)$$

Inserting now equation (26a) into equation (25) and separating real and imaginary parts we obtain

$$L = \left(\frac{1}{2}\right) \frac{\Gamma_m^L}{N+1} \frac{1}{\epsilon^2 + 1} \{Y^L(\epsilon q^2 - \epsilon - 2q) - i[(\epsilon + Y^L q)^2 + (Y^L q^2 + 1)(1 - Y^L)]\}. \quad (27)$$

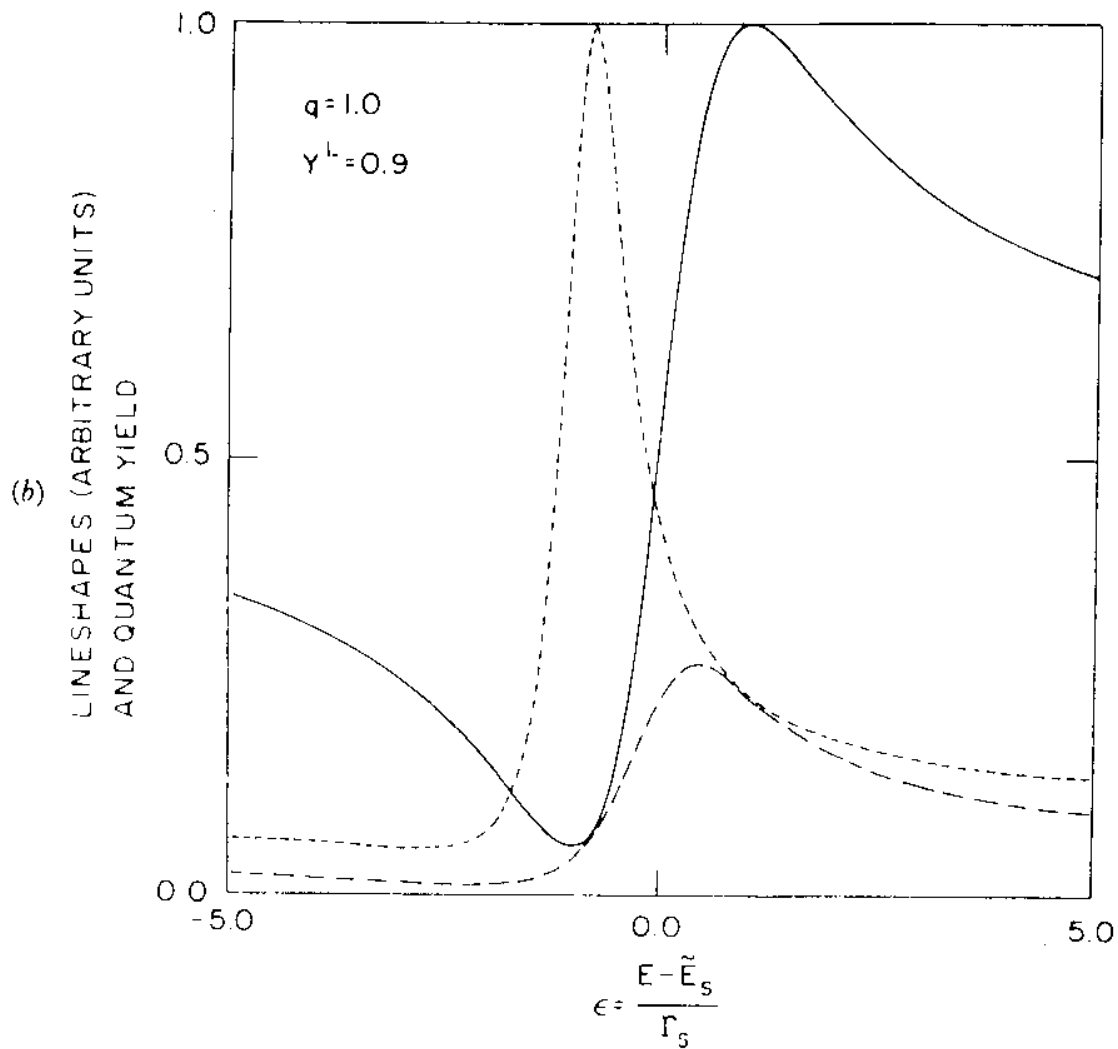
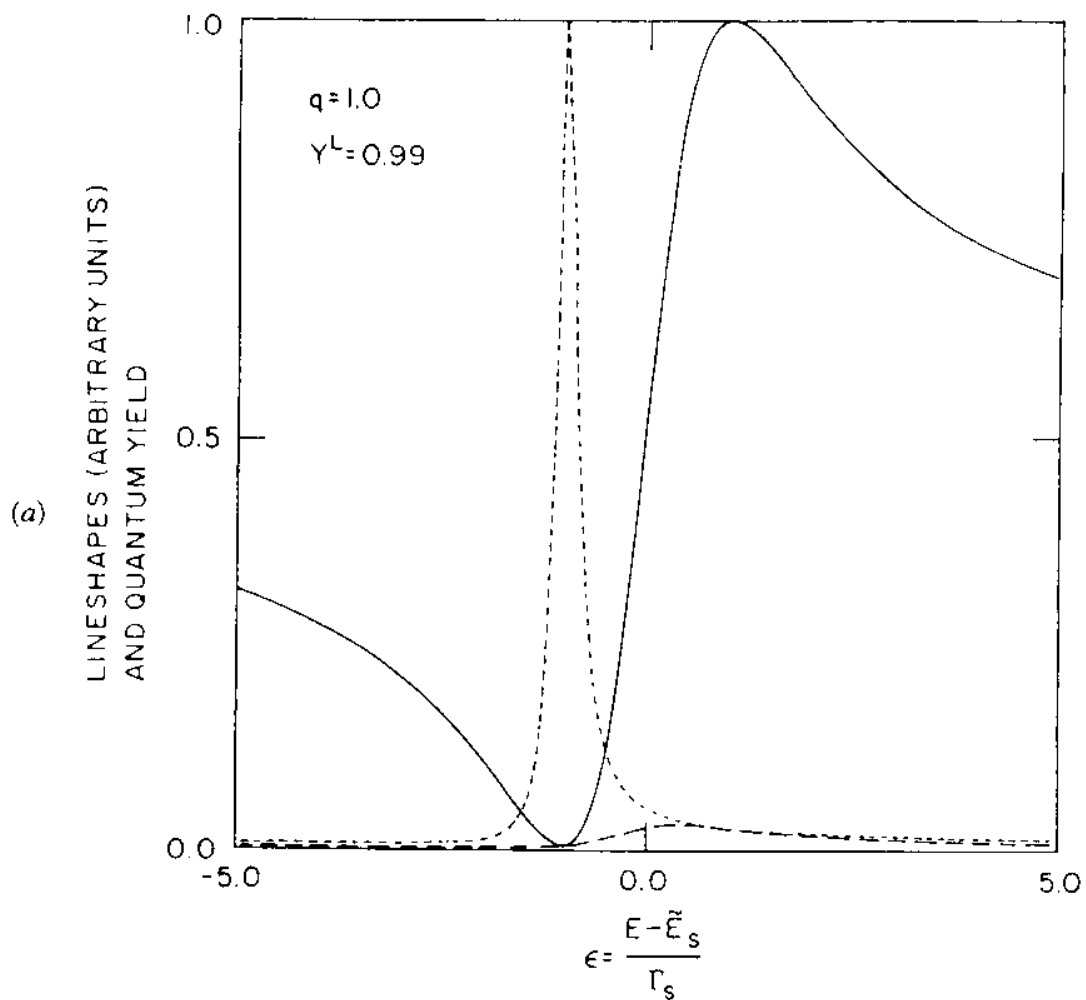
Substituting this result for the matrix element  $L$  into equation (5) we arrive at the final result for the absorption cross section:

$$\sigma_a(\epsilon) = \frac{Q}{\hbar c} \frac{\Gamma_m^L}{N+1} \frac{(\epsilon + q Y^L)^2 + (Y^L q^2 + 1)(1 - Y^L)}{\epsilon^2 + 1}. \quad (28)$$

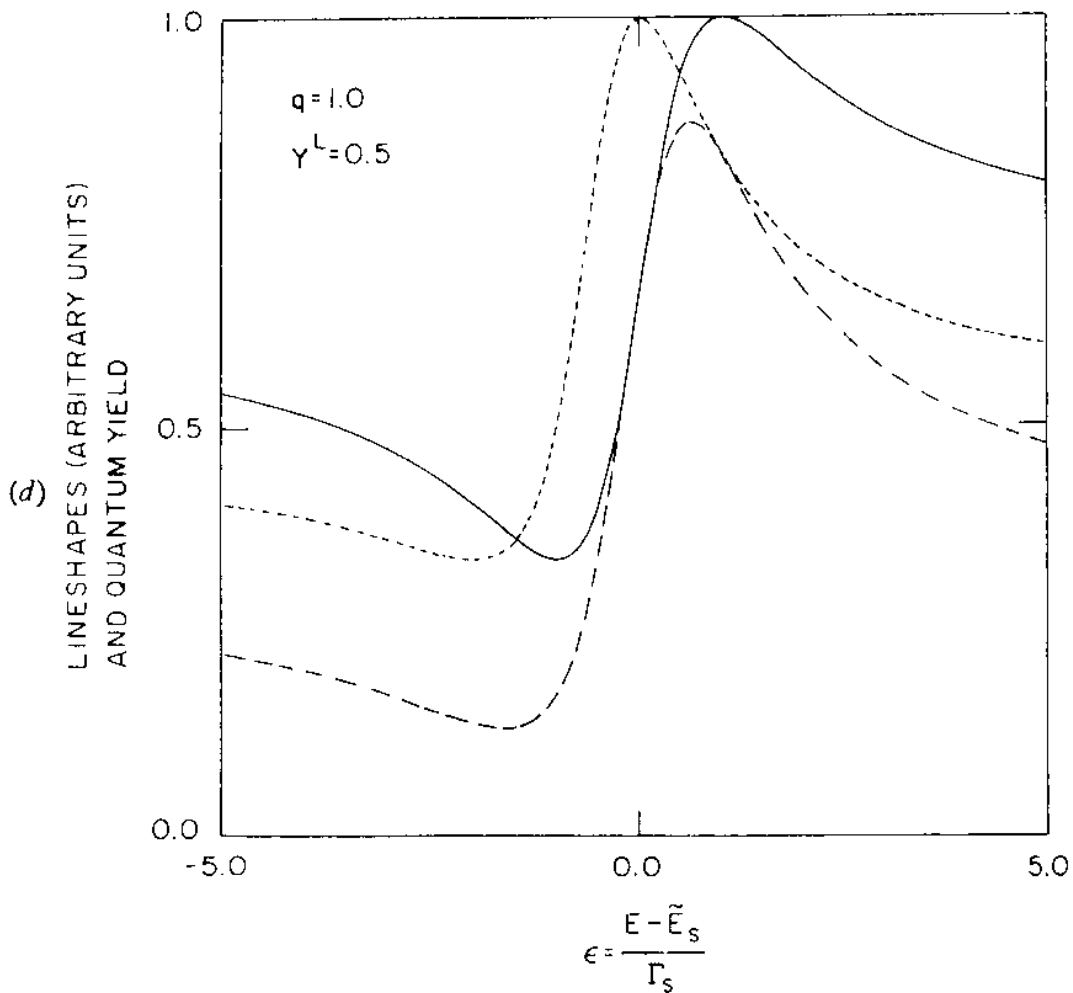
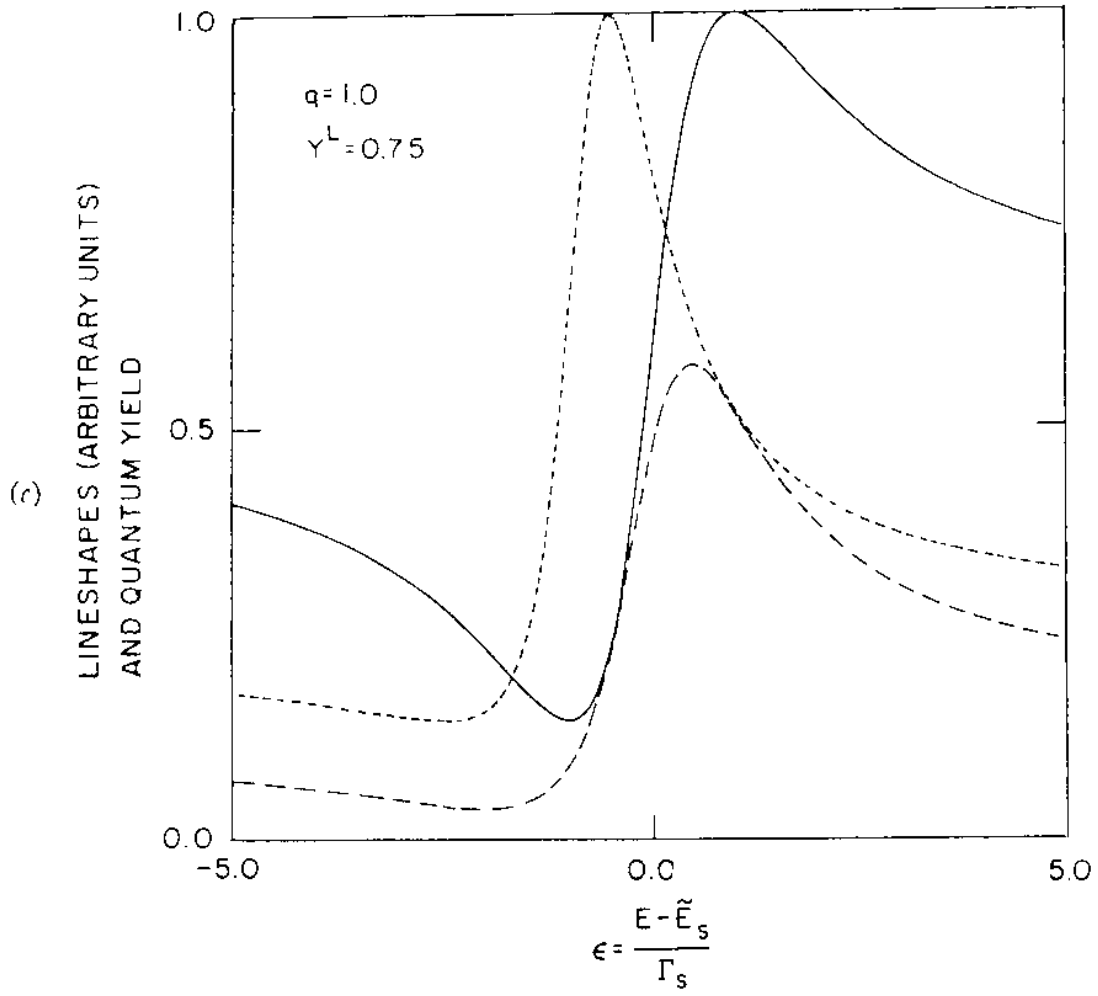
A few examples of the line-shape predicted by equation (28) for different values of the parameters  $q$  and  $Y^L$  are displayed in figure 3. The following points are now in order.

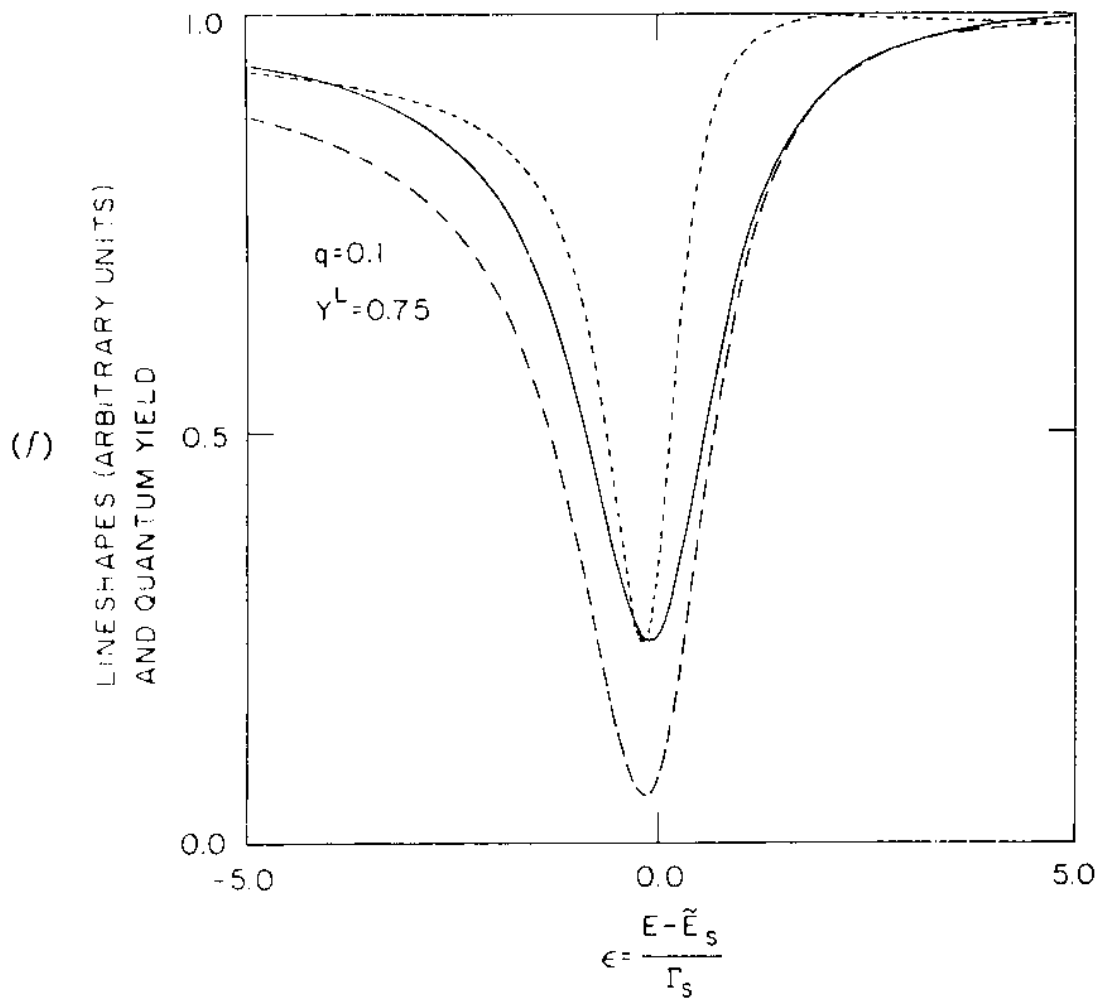
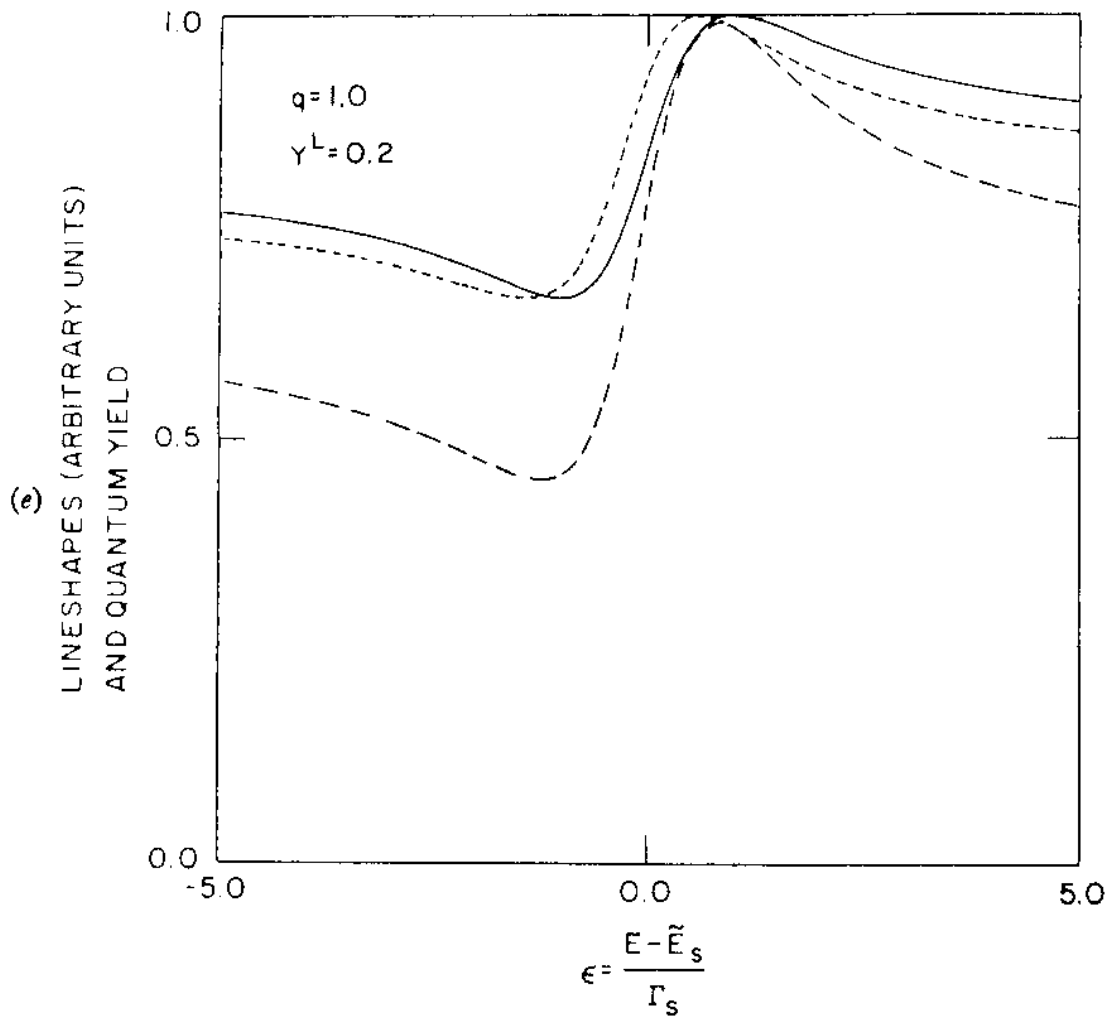
(a) Equation (28) is an expression for the energy dependence of the total absorption cross section of our model system. This is a two-parameter expression: the absorption line-shape is determined by the values of the 'quantum

†The definition of  $V_{ml}$  and  $V_{ms}$  implies that these quantities are real. A complex  $V_{ls}$  may, however, be encountered if, for example,  $H_v$  is a spin-orbit coupling operator. This possibility is disregarded here as in all the previous works on this problem.









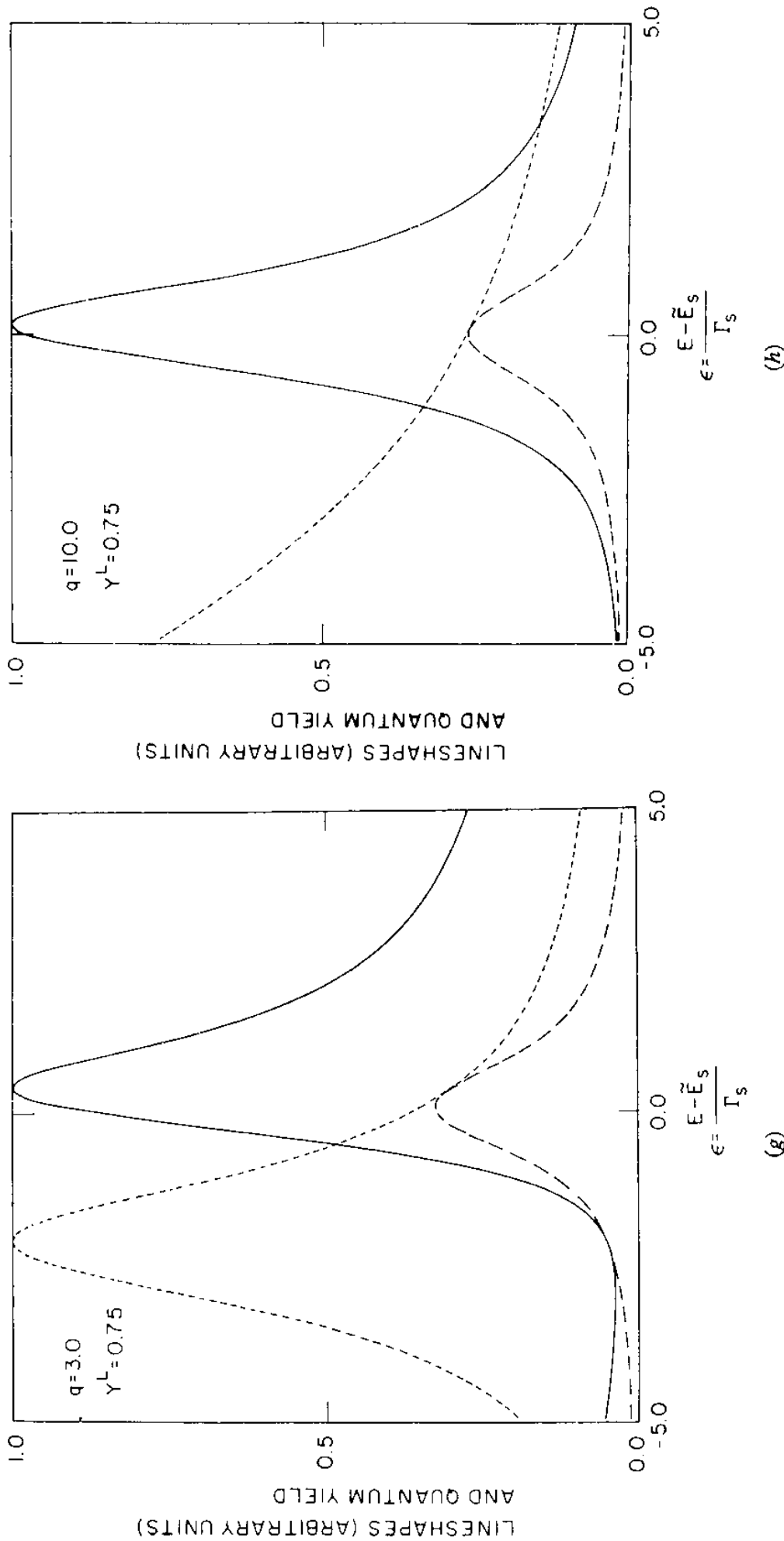


Figure 3. Results of numerical calculation for the absorption cross section (equation 28), the resonance scattering cross section (equation 39) and the scattering quantum yield (equation 40), for different parameters  $q$  and  $Y_L$ . —: absorption cross section, - - - -: scattering cross section, - · - · -: quantum yield. Absorption and scattering line-shapes are normalized by the maximum absorption cross section in the considered spectral region. (a)  $q = 1.0$ ,  $Y_L = 0.99$ ; (b)  $q = 1.0$ ,  $Y_L = 0.90$ ; (c)  $q = 1.0$ ,  $Y_L = 0.75$ ; (d)  $q = 1.0$ ,  $Y_L = 0.50$ ; (e)  $q = 1.0$ ,  $Y_L = 0.20$ ; (f)  $q = 0.1$ ,  $Y_L = 0.75$ ; (g)  $q = 3.0$ ,  $Y_L = 0.75$ ; (h)  $q = 10.0$ ,  $Y_L = 0.75$ .

yield'  $Y^L$  and of the 'line-shape index'  $q$  given by equations (26a) and (22) respectively. Note that Fano's original result

$$\sigma_a(\epsilon) = \frac{Q}{\hbar c} \Gamma_m^L \frac{(\epsilon + q)^2}{\epsilon^2 + 1} \quad (29)$$

is a one-parameter result: the line-shape index  $q$  fully determines the form of the predicted absorption profile.

(b) Our result, equation (28), is reduced to Fano's expression, equation (29), on setting  $Y^L = 1$  and  $N = 0$  (the second follows from the first by equation (26b) if  $q \neq 0$ ). Actually  $Y^L$  is smaller than 1 unless  $q = 0$ . It may be concluded that Fano's expression provides a good approximation to equation (28) when  $1 - Y^L \ll 1$  and  $q \gtrsim 1$  (the second condition is necessary for  $N = (1/Y^L - 1)/q^2$  to be much smaller than 1). Fano's result is of course useful for any  $q$ , as long as only the relative absorption is concerned and the coefficient  $(1 + N)^{-1}$  in equation (28) may be disregarded.

(c) The condition  $Y^L \sim 1$  is equivalent to

$$\Gamma_s^L \gg \Gamma_s^M \text{ or } |V_{sl}|^2 \rho_l \gg |V_{sm}|^2 \rho_m \quad (30)$$

namely the (independent) non-radiative decay of the state  $s$  should be much faster than the (independent) radiative decay of this state. The condition  $N \ll 1$  is equivalent to

$$\pi^2 \rho_m \rho_l |V_{lm}|^2 = (\frac{1}{2}) \pi \Gamma_l^M \rho_l = (\frac{1}{2}) \pi \Gamma_m^L \rho_m \ll 1, \quad (31)$$

which states that the radiative width  $\Gamma_l^M$  of the states  $\{|l\rangle\}$  should be much smaller than their average spacing (and equivalently the width  $\Gamma_m^L$  of the states  $\{|m\rangle\}$  due to their interaction with the continuum  $\{|l\rangle\}$  should be much smaller than their spacing). The first condition, (30), is what we saw necessary for Fano's theory to describe correctly a simple Lorentzian resonance. The second condition (31) has been encountered in the study of interference effects in consecutive decay, as a condition for lack of interference due to coupling between two continuous manifolds [8-10].

(d) As  $Y^L$  never exactly equals unity, it is evident from equation (28) that  $\sigma_a(\epsilon)$  is non-zero even at its minimum value. There is thus no danger of unphysical divergence of the quantum yield for resonance fluorescence as occurs in the approximate treatment [7].

(e) Sharf has recently shown [5] that when the transition moments  $V_{ms}$  and  $V_{ml}$  are not parallel to each other (as may be the case for molecular transitions), Fano's approach has to be modified and the resulting expression for the absorption line-shape does not vanish at its minimum point. The result (28) shows that also in the more commonly encountered case of collinear transition moments there is never total cancellation of the absorption cross section.

(f) As a consistency check on the result (27) we note that in the limit  $q \rightarrow \infty$  and  $N \rightarrow 0$  (which corresponds to the case of one discrete state coupled to two non-interacting continua,  $\sigma_a(\epsilon)$  takes the form

$$\sigma_a(\epsilon) \xrightarrow[q \rightarrow \infty]{N \rightarrow 0} \frac{Q}{\hbar c} \Gamma_m^L Y^L \frac{q^2}{\epsilon^2 + 1} = \frac{Q}{\hbar c} |V_{ms}|^2 \frac{\Gamma_s}{(E - E_s)^2 + (\Gamma_s/2)^2} \quad (32)$$

which is the expected result for this limit.

We now turn to the calculation of the photon scattering cross section and the quantum yield.

## 4. RESONANCE FLUORESCENCE AND QUANTUM YIELD

In this section we calculate the probability of transition between two states of the radiative manifold. This probability is related to the non-diagonal matrix element  $\langle m|H_{\text{int}} + H_v)G(H_{\text{int}} + H_v)|m'\rangle = \langle m|H_{\text{int}}GH_{\text{int}}|m'\rangle$  of the  $T$  operator which is defined by  $T = (H_{\text{int}} + H_v) + (H_{\text{int}} + H_v)G(H_{\text{int}} + H_v)$ . As in our model the coupling matrix elements are independent of the particular state  $m$ , this reduces again to the problem of calculating  $L$ , equation (7), and we can directly use the result given by equations (20)–(22). The full expression for the total scattering cross section is given by [7]

$$\sigma_{\text{R}}(\epsilon) = \frac{2}{\pi} \left[ \frac{Qk_f}{\hbar^2 c} \right]^2 |L|^2, \quad (33)$$

where, as before,  $Q$  is the normalization volume of the system,  $c$  is the velocity of light and where  $k_f$  is the absolute magnitude of the wave vector of the scattered light. Equation (33) gives the cross section for the process  $|g; \mathbf{k}, \mathbf{e}\rangle \rightarrow |g; \mathbf{k}_f, \mathbf{e}_f\rangle$  as a function of the incident photon energy  $E = \hbar\omega$ .

To calculate  $|L|^2$  it is convenient to recast equation (27) in the form

$$L = \frac{1}{2} \frac{\Gamma_m^L}{N+1} \frac{Y^L(q^2 - 1) + 1 - i(\epsilon + 2Y^Lq)}{\epsilon + i}, \quad (34)$$

from which we get

$$|L|^2 = \frac{1}{4} \left( \frac{\Gamma_m^L}{N+1} \right)^2 \frac{(Y^Lq^2 - Y^L + 1)^2 + (\epsilon + 2Y^Lq)^2}{\epsilon^2 + 1}. \quad (35)$$

Inserting this expression into equation (33) the result of the total scattering cross section is obtained in the form

$$\sigma_{\text{R}}(\epsilon) = \frac{1}{2\pi} \left( \frac{Qk_f}{\hbar^2 c} \right)^2 \left( \frac{\Gamma_m^L}{N+1} \right)^2 \frac{(Y^Lq^2 - Y^L + 1)^2 + (\epsilon + 2Y^Lq)^2}{\epsilon^2 + 1}. \quad (36)$$

The quantum yield for this scattering process is (from equations (36) and (28))

$$Y_{\text{R}}(\epsilon) = \frac{\sigma_{\text{R}}(\epsilon)}{\sigma_{\alpha}(\epsilon)} = \frac{Qk_f^2}{2\pi\hbar^3c} \frac{\Gamma_m^L}{N+1} \frac{(Y^Lq^2 - Y^L + 1)^2 + (\epsilon + 2Y^Lq)^2}{(\epsilon + qY^L)^2 + (Y^Lq^2 + 1)(1 - Y^L)}. \quad (37)$$

These results may be simplified by using the well-known expression for the density of states in the radiation field

$$\rho_m = \frac{Qk_f^2}{\pi^2\hbar^3c} \quad (38)$$

together with the definition (equation (16)) of the number  $N$ , to obtain the final forms:

$$\sigma_{\text{R}}(\epsilon) = \frac{Q}{\hbar c} \frac{\Gamma_m^L N}{(N+1)^2} \frac{(Y^Lq^2 - Y^L + 1)^2 + (\epsilon + 2Y^Lq)^2}{\epsilon^2 + 1}, \quad (39)$$

$$Y_{\text{R}}(\epsilon) = \frac{N}{N+1} \frac{(Y^Lq^2 - Y^L + 1)^2 + (\epsilon + 2Y^Lq)^2}{(\epsilon + qY^L)^2 + (Y^Lq^2 + 1)(1 - Y^L)}. \quad (40)$$

These equations together with equation (26b) are our final results for the scattering cross section and for the total quantum yield for resonance fluorescence as a function of the incident light energy within a Fano line-shape. Numerical calculations based on these results are displayed in figure 3. The following remarks should be made at this point.

(a) Nitzan and Jortner [7] have recently distinguished between quantum yield measured in a long-time experiment using a highly resolved photon beam, and that measured in a short-time experiment after a broad-band pulse excitation at the interesting spectral region. It is evident that the result (40) is the 'long-time' quantum yield which depends on the incident light energy. The long-time and the short-time yields become identical in the case of a simple resonance, as is demonstrated by equation (46) below.

(b) The quantum yield given by equation (40) is a well-behaved function of  $\epsilon$  which never exceeds unity and does not exhibit the singular behaviour which characterizes the result obtained in Fano's approximation [7]. This last approximate result is essentially that which is obtained from equation (40) by replacing  $Y^L$  by unity. This leads to

$$Y_R(\epsilon) \propto \frac{q^4 + (\epsilon + 2q)^2}{(\epsilon + q)^2} \quad (41)$$

which diverge when  $\epsilon \rightarrow -q$ , namely at the bottom of Fano's dip.

(c) The result (40) for the quantum yield is fully determined by the two parameters  $Y^L$  and  $q$  ( $N$  is given in terms of these parameters by equation (26 b)). Simpler expressions are obtained for various limits. In particular consider the following cases:

(c1)  $N \rightarrow \infty$  and  $q \rightarrow 0$ :

$$Y_R(\epsilon) = \frac{\epsilon^2 + (1 - Y^L)^2}{\epsilon^2 + (1 - Y^L)}; \quad (42)$$

(c2)  $N \rightarrow \infty$  and  $Y^L \rightarrow 0$ :

$$Y_R(\epsilon) = 1; \quad (43)$$

(c3)  $q \rightarrow \infty$  and  $Y^L \rightarrow 0$  such that  $N = 1/(Y^L q^2)$  remains finite:

$$Y_R(\epsilon) = \frac{N}{N+1} \frac{\epsilon^2 + (1/N + 1)^2}{\epsilon^2 + (1/N + 1)}. \quad (44)$$

In case (c1) there is a strong coupling between the states  $\{|l\rangle\}$  and the radiative continuum. All the energy which is absorbed directly to the  $\{|l\rangle\}$  manifold is emitted back and  $Y_R(\epsilon) < 1$  only in the vicinity of the discrete state  $|s\rangle$  ( $\epsilon \sim 0$ ). In both cases (c2) and (c3) the state  $|s\rangle$  is uncoupled to the non-radiative manifold  $\{|l\rangle\}$  and decays to the radiative channel only. In case (c2) there is a strong coupling between the manifold  $\{|l\rangle\}$  and the radiative continuum and consequently the emission yield is 1 everywhere. In case (c3) the  $\{|l\rangle\} - \{|m\rangle\}$  coupling strength is finite (and is measured by the value of  $N$ ).  $Y_R(\epsilon)$  takes a maximum value of unity near the totally emitting state  $s$  (when  $\epsilon = 0$ ) but far enough from this energy  $\epsilon^2 \gg (1/N + 1)^2$ , we have  $Y_R(\epsilon) \sim N/(N + 1)$  for this case, as part of the radiation energy absorbed in the continuum  $\{|l\rangle\}$  is not emitted back.  $Y_R(\epsilon)$  approaches unity when the coupling between the states  $\{|l\rangle\}$  and the radiative channel  $\{|m\rangle\}$  becomes larger, namely when  $N$  increases.

(d) The case of one discrete state interacting with two uncoupled continua corresponds to the limit  $N \rightarrow 0$  and  $q \rightarrow \infty$ . In this case we have

$$Y_R(\epsilon) = N \frac{(Y^L)^2 q^4}{(Y^L)^2 q^2 + Y^L q^2 (1 - Y^L)} = Y^L N q^2 \quad (45)$$

or, using the definitions (16) and (22) for  $N$  and  $q$ ,

$$Y_R(\epsilon) = Y^L \frac{|V_{ms}|^2 \rho_m}{|V_{ls}|^2 \rho_l} = Y^L \frac{\Gamma_s^M}{\Gamma_s^L} = \frac{\Gamma_s^M}{\Gamma_s^M + \Gamma_s^L}, \quad (46)$$

which is the well-known result for this case. Note that in this case the quantum yield is no longer energy dependent.

(e) As is seen from the graphs (figure 3) the quantum yield  $Y_R(\epsilon)$  goes through unity near the interference dip. This may be shown in general:  $Y_R(\epsilon)$  (equation (40) with (26 b)) is unity for  $\epsilon = q(N-1)Y^L$ .

An interesting cross-check of the results obtained in this paper is provided by calculating the cross section for scattering into the non-radiative channel  $L$ ,

$$\sigma_{NR}(\epsilon) = \frac{2\pi}{\hbar} \frac{c}{Q} |\langle l|T|m\rangle|^2 \rho_l. \quad (47)$$

The method of calculating the non-diagonal matrix element  $\langle l|T|m\rangle$  is identical to that for the diagonal term  $\langle m|T|m\rangle$  and one gets for  $\sigma_{NR}(\epsilon)$ :

$$\sigma_{NR}(\epsilon) = \frac{Q}{\hbar c} \Gamma_m^L \frac{1}{(N+1)^2} \frac{[\epsilon + (1-N)Y^L q]^2}{\epsilon^2 + 1}, \quad (48)$$

while the non-radiative quantum yield is

$$Y_{NR}(\epsilon) = \frac{\sigma_{NR}(\epsilon)}{\sigma_a(\epsilon)} = \frac{1}{N+1} \frac{(\epsilon + (1-N)Y^L q)^2}{(\epsilon + qY^L)^2 + (Y^L q^2 + 1)(1 - Y^L)}. \quad (49)$$

It is now straightforward, though somewhat tedious, to ascertain that

$$Y_R(\epsilon) + Y_{NR}(\epsilon) = 1 \quad (50)$$

for any  $\epsilon$ , which provides the consistency check. Note that a zero interference dip always occurs in  $\sigma_{NR}(\epsilon)$  and  $Y_{NR}(\epsilon)$  which corresponds to the value of  $Y_R(\epsilon) = 1$  found above.

## 5. CONCLUSION

In this paper we have modified the treatment of Fano's line-shape problem by taking into account the coupling between the system and the radiation field to infinite order. It has been shown that under conditions where different states in the non-radiative dense manifold interact with each other via their interaction with the same radiation field states, this modification is necessary and Fano's result (equation (29)) for the absorption line-shape has to be replaced by the expression (28). This modified result is reduced to Fano's expression only for the case where the radiative quantum yield is negligible and when the line-shape index  $q$  is not too small. In addition we have obtained expressions for the emission (or scattering) line-shape (equation 39)) and for the 'long-time' energy-dependent quantum yield (equation (40)). The result for the quantum yield is free from the singular behaviour which characterizes the result obtained in Fano's approximation [7].

Fano's original result [1] seems to be adequate for interpretation of most of the experiments performed to date. We are unaware of any measurement of the scattering cross section or the long-time quantum yield within a Fano resonance. Also, line-shapes which were interpreted as Fano's were observed mostly in spectral regions characterized by vanishingly small emission quantum yields.

This is, as we have shown, the condition for the validity of Fano's approximation if only relative intensities are considered. In the Rydberg spectra of some large molecules, (e.g. naphthalene) absorption line-shapes of the Fano type fail to vanish at the bottom of the interference dip [6]. However, the non-radiative width involved is too large relative to the radiative width [6] to enable our theory to account for this phenomenon. It seems that background absorption provides a better interpretation of the observed line-shape.†

Careful quantum yield measurements seem to be the best way to experimentally verify the results of the present theory. The sharp maximum predicted near the bottom of Fano's dip (see, e.g., figure 3 *a*) may be unobservable because of the unavoidable presence of background absorption. However, characteristic energy dependence of the quantum yield should be observed also when interference effects are very small (e.g. figure 3 *h*). The use of modern high intensity light sources makes possible the detection of quantum yields as low as  $10^{-6}$ – $10^{-7}$ . With these techniques, the prediction of the present theory may be amenable to experimental verification.

I am indebted to Professor J. Jortner and Mr. S. Mukamel for suggesting the cross-check presented in equations (47)–(50) and for helping me in locating an error in the original computations.

This work has been supported in part by the National Science Foundation and Project Squid, Office of Naval Research.

†Florida *et al.* [6 *b*] have attempted an interpretation based on a Fano type analysis, which does not involve background absorption. However, also in their analysis, background absorption is necessary to fit theory to experiment on the low energy side of the transition.

#### REFERENCES

- [1] (a) FANO, U., 1961, *Phys. Rev.*, **124**, 1866. (b) FANO, U., and COOPER, J. W., 1965, *Phys. Rev.*, **137**, A1364; *Rev. mod. Phys.*, **40**, 441.
- [2] PRESTON, M. A., 1962, *Physics of the Nucleus* (Addison-Wesley), p. 503.
- [3] (a) PHYLIPS, J. C., 1964, *Phys. Rev. Lett.*, **12**, 447. (b) SHIBATANI, A., and TOYOZAWA, Y., 1968, *J. phys. Soc. Japan*, **25**, 335.
- [4] (a) ANGUS, J. G., CHRIST, B. J., and MORRIS, G. C., 1968, *Aust. J. Chem.*, **21**, 2153. (b) JORTNER, J., and MORRIS, G. C., 1969, *J. chem. Phys.*, **51**, 3689.
- [5] SHARF, B., 1970, *Chem. Phys. Lett.*, **5**, 459.
- [6] (a) SCHEPS, R., FLORIDA, D., and RICE, S. A., 1972, *J. chem. Phys.*, **56**, 295. (b) FLORIDA, D., SCHEPS, R., and RICE, S. A., 1972, *Chem. Phys. Lett.*, **15**, 4.
- [7] NITZAN, A., and JORTNER, J., 1972, *J. chem. Phys.*, **57**, 2870.
- [8] LEFEBVRE, R., and BESWICK, J. A., 1972, *Molec. Phys.*, **23**, 1223.
- [9] KAY, K. G., and RICE, S. A., 1972, *J. chem. Phys.*, **57**, 3041.
- [10] NITZAN, A., JORTNER, J., and BERNE, B. J., 1973, *Molec. Phys.*, **26**, 281.
- [11] FREED, K., and JORTNER, J., 1969, *J. chem. Phys.*, **50**, 2916.
- [12] NITZAN, A., and JORTNER, J., 1972, *Molec. Phys.*, **24**, 109.