Deconvolution of Atomic Photoabsorption Spectra: a Match between Theory and Experiment

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We present in this paper an extension of a recently proposed deconvolution procedure to compare directly the theoretical and experimental spectrum of a doubly excited ultra-narrow and nearly symmetric resonance in atomic *photoabsorption*. Our discussion is based on a set of analytical relations in terms of the variations of i) the ratio between the resonance width Γ and the experimental energy resolution Ω in the limit when $\Gamma/\Omega \ll 1$ and ii) the column density nl of the media in a photoabsorption experiment.

I. INTRODUCTION

In an attempt to estimate the width of a narrow isolated doubly excited resonance from measured spectra in the absence of an ultrahigh-energy resolution, Fang and Chang [1] have recently proposed a deconvolution procedure which enables a direct extrapolation to infinite energy resolution using a set of explicit analytical relations in terms of the ratio R of the resonant width Γ and the experimental energy resolution Ω in the limit of $R = \Gamma/\Omega \ll 1$. This procedure applies well for a *photoionization* experiment when the photoion and/or the photoelectron are measured directly. Unlike the photoionization, the resonant spectra in a *photoabsorption* experiment is determined by detecting the light attenuation through a medium. It is known that the measured cross section is significantly affected by the column density nl of the medium and the experimental monochromator (or slit) function $\mathcal{F}$.[2]

The photoabsorption cross-section $\sigma^{Pa}(E)$ at a photon energy E is determined experimentally using the Beer-Lambert law,

$$I(E) = I_o(E)\, e^{-nl\sigma^{Pa}(E)}. \tag{1}$$

where I_o is the intensity of the incident light, I is the attenuated intensity of the transmitted light, and nl is the column density. At a photon energy E, I_o and I can be expressed in terms of the slit function $\mathcal{F}$ centered at E and characterized by an energy resolution Ω, i.e.,

$$I_o(E) = \int i_o\, \mathcal{F}(E' - E;\Omega)\, dE' \tag{2}$$

and

$$I(E) = \int i_o\, \mathcal{F}(E' - E;\Omega)\, e^{-nl\,\sigma(E)} dE', \tag{3}$$

where σ is the cross section at an infinite energy resolution (i.e., at $\Omega = 0$). From Eqs. (1-3), the measured resonance structure in a photoabsorption experiment is represented by a convoluted spectrum in the form of

$$\sigma^{Pa}(E) = -\frac{1}{nl}\ln\Big(\int \mathcal{F}(E' - E;\Omega)\, e^{-nl\,\sigma(E')} dE'\Big). \tag{4}$$

As expected, when $nl \to 0$, the cross section takes the same form of the photoionization given by Eq. (3) of Ref. 1, i.e., $\sigma^{Pa} \to \sigma^{Pi}$, where

$$\sigma^{Pi}(E) = \int \sigma(E')\, \mathcal{F}(E' - E;\Omega)\, dE'. \tag{5}$$

The slit function $\mathcal{F}$ may be approximated at the center by a Gaussian distribution $\mathcal{G}$ and modified at its tail by a Lorentzian distribution $\mathcal{L}$. It can be expressed by a weighted combination of $\mathcal{G}$ and $\mathcal{L}$,[1,3] i.e.,

$$\mathcal{F}(E;\Omega, w_g, w_\ell) = w_g\, \mathcal{G}(E;\Omega) + w_\ell\, \mathcal{L}(E;\Omega), \tag{6}$$

where the sum of w_g and w_ℓ equals one. ($\mathcal{G}$ and $\mathcal{L}$ are given explicitly by Eq. (4) of Ref. 1.) There is no well established general procedure to determine the weighting factors w_g and w_ℓ experimentally in the absence of ultrahigh energy resolution. Based on the analytical relations discussed in the next section, we shall propose a procedure leading to the determination of w_g and w_ℓ.

The density effect in photoabsorption can be easily illus-

trated by the variation of the convoluted spectra of an isolated resonance with changing nl and Ω. For simplicity, we will limit our discussion using a Fano-type of resonance described by an asymmetry parameter q and the smoothly varying background cross section σ_b, i.e.,[4]

$$\sigma(E) = \sigma_b \frac{(q+\epsilon)^2}{1+\epsilon^2}, \tag{7}$$

where the reduced energy $\epsilon = (E - E_r)/(\frac{1}{2}\Gamma)$ is defined in terms of the energy E_r and the width Γ of the resonance. The cross section σ is expected to reach its peak value $\sigma_{max} = \sigma_b(1+q^2)$ and a zero at energies

$$E_{max} = E_r + \frac{1}{2}(\Gamma/q) \quad \text{and} \quad E_{min} = E_r - \frac{1}{2}(\Gamma q), \tag{8}$$

respectively. Fig. 1 presents a number of selected convoluted *photoionization* spectra using Eq. (5) with R ranging from 1/10 to 1/25 and a slit function $\mathcal{F}$ represented either by a Gaussian distribution $\mathcal{G}$ or a Lorentzian distribution $\mathcal{L}$. These spectra correspond to a fictitious resonance derived from Eq. (7) with $E_r = 2.110$ Ry, $\sigma_b = 1.0$ Mb, $q^2 = 2500$, and $\Gamma = 10^{-6}$ Ry. As expected, for a given ratio R, the peak cross section σ_{max} corresponding to the spectrum convoluted

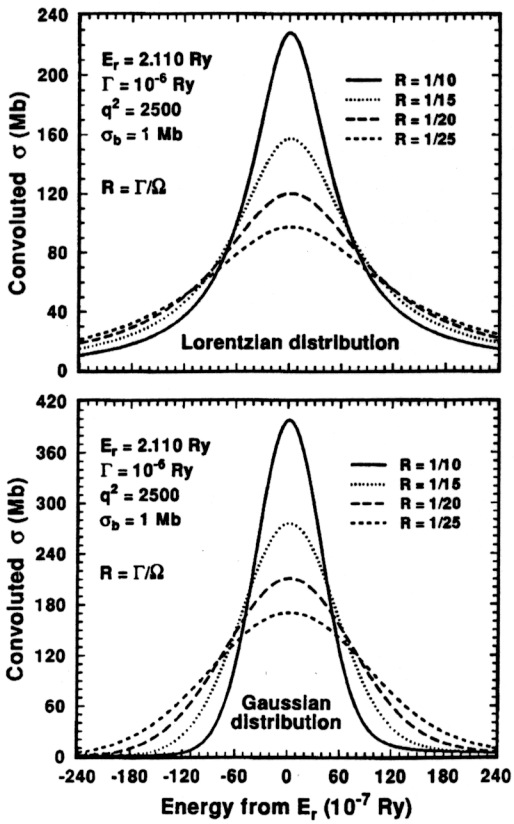

Fig. 1. Convoluted *photoionization* spectra using Eq. (5) with R ranging from 1/10 to 1/25.

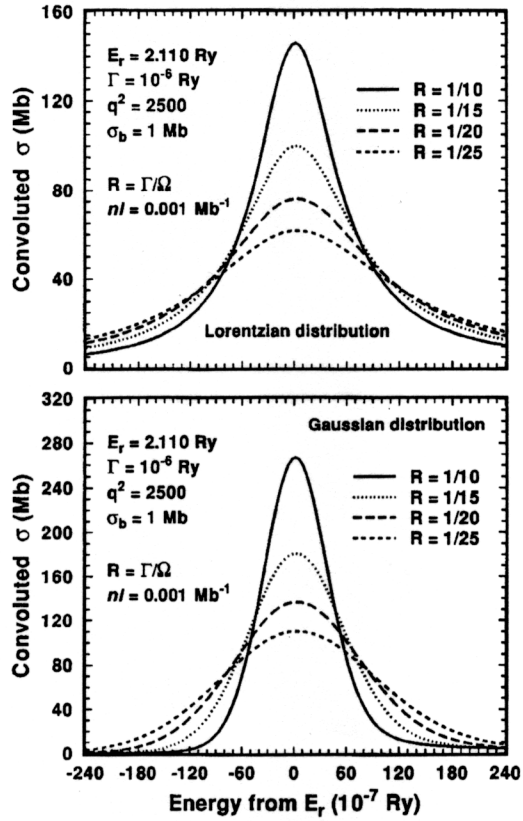

Fig. 2. Convoluted *photoabsorption* spectra using Eq. (4) with R ranging from 1/10 to 1/25 and a column density $nl = 0.001$ Mb^{-1}.

using Gaussian distribution is substantially higher than the one using Lorentzian distribution. The density effect in *photoabsorption* measurement is unambiguous demonstrated by the substantial reduction in peak cross sections shown in Fig. 2 when the same spectrum is convoluted using Eq. (4) with a column density $nl = 0.001\ Mb^{-1}$.

II. PEAK CROSS SECTIONS

For an ultra-narrow and nearly symmetric resonance, the peak cross section σ_{max} is very well approximated by the cross section at $E = E_r$, i.e., $\sigma_{max} \approx \sigma(E_r)$, since, from Eq. (8), the energy corresponding to the peak cross section, i.e., E_{max}, equals approximately the resonant energy E_r as the difference $E_{max} - E_r$ is substantially smaller than the resonance width, i.e., as $q^2 \gg 1$ and $\frac{\Gamma}{q} \ll \Gamma$.

In a photoionization experiment,

$$\sigma_{max}^{Pi} \cong \int \sigma(E')\ \mathcal{F}(E' - E_r; \Omega)\ dE'. \tag{9}$$

Although Eq. (5) is not in general integrable for an arbi-

trary energy E, Eq. (9) can be integrated analytically. For a Lorentzian distribution,

$$\sigma^{L}_{max} = \sigma_b\ (1 + q^2 R)/(1 + R) \tag{10}$$

and for a Gaussian distribution,

$$\sigma^{G}_{max} = \sigma_b\ (1 + \pi^{1/2}(q^2 - 1))Re^{R^2} F_c(R), \tag{11}$$

where $F_c(x) = 1 - (2/\sqrt{\pi})\ \int_0^x e^{-y^2}\, dy$ is the *complementary error function*. For a nearly symmetric ultra-narrow resonance, such as the fictitious resonance shown in Figs. 1 and 2, our calculation shows that the approximate σ_{max} at $E = E_r$, derived from Eqs. (10) and (11), are within 0.05% of the exact peak cross sections determined from the numerically calculated spectra using Eq. (5). In a photoabsorption experiment, the peak cross section σ_{max} can also be approximated similarly from Eq. (4) as

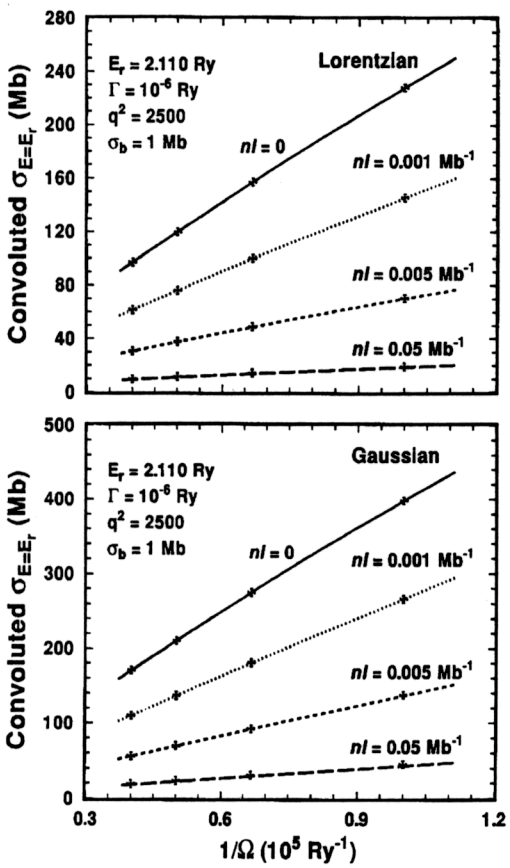

Fig. 3. Comparison between σ_{max} (nearly straight lines) obtained from Eq. (12) and the exact peak cross sections at $R = \frac{1}{25}, \frac{1}{20}, \frac{1}{15}$ and $\frac{1}{10}$ for a number of column densities nl derived directly from the numerically calculated convoluted spectra using Eqs. (4) and (5) for photoabsorption and photoionization (i.e., when $nl = 0$), respectively.

$$\sigma^{pa}_{max} \cong -\frac{1}{nl} \ln\left(\int \mathcal{F}(E' - E_r; \Omega) e^{-nl\sigma(E')} dE'\right). \tag{12}$$

Fig. 3 shows that the approximate peak cross sections σ_{max}, represented by the nearly straight lines obtained from Eq. (12) are in close agreement with the exact peak cross sections at $R = \frac{1}{25}, \frac{1}{20}, \frac{1}{15}$ and $\frac{1}{10}$ for a number of column densities nl derived directly from the numerically calculated convoluted spectra using Eqs. (4) and (5) for photoabsorption and photoionization (i.e., when $nl = 0$), respectively.

In general, Eq. (12) can not be integrated analytically due to the exponential term $e^{-nl\sigma}$. However, when $e^{-nl\sigma}$ is expanded into an infinite series, each individual term becomes integrable and σ_{max} can be expressed in terms of a polynomial in R, i.e.,

$$\sigma_{max} \rightarrow \sigma^{Pa}(E = E_r) = q^2 \sigma_b\ X(R, nl), \tag{13}$$

where

$$X(R, nl) = \sum_{i=1} (-1)^{i+1}\ \xi_i(\rho)\ R^i \tag{14}$$

and ρ is a parameter given by

$$\rho = nlq^2\sigma_b. \tag{15}$$

For a Lorentzian distribution, the first few expansion coefficients are

$$\xi_1 = 1 - \frac{1}{4}\rho + \frac{1}{16}\rho^2 - \frac{5}{384}\rho^3 + \frac{7}{3072}\rho^4 - \cdots \tag{16}$$

$$\xi_2 = 1 - \frac{1}{2}\rho + \frac{1}{4}\rho^2 - \frac{3}{32}\rho^3 + \frac{11}{384}\rho^4 - \cdots \tag{17}$$

$$\xi_3 = 1 - \frac{3}{4}\rho + \frac{9}{16}\rho^2 - \frac{119}{384}\rho^3 + \frac{141}{1024}\rho^4 - \cdots \tag{18}$$

$$\xi_4 = 1 - \rho + \rho^2 - \frac{35}{48}\rho^3 + \frac{41}{96}\rho^4 - \cdots \tag{19}$$

$$\xi_5 = 1 - \frac{5}{4}\rho + \frac{25}{16}\rho^2 - \frac{545}{384}\rho^3 + \frac{3175}{3072}\rho^4 - \cdots, \tag{20}$$

and for a Gaussian distribution

$$\xi_1 = \sqrt{\pi}(1 - \frac{1}{4}\rho + \frac{1}{16}\rho^2 - \frac{5}{384}\rho^3 + \frac{7}{3072}\rho^4 - \cdots) \tag{21}$$

$$\xi_2 = 2 - \pi(\frac{1}{2}\rho - \frac{1}{4}\rho^2 + \frac{3}{32}\rho^3 - \frac{11}{384}\rho^4 + \cdots) \tag{22}$$

$$\xi_3 = \sqrt{\pi}(1 - \frac{7}{4}\rho + (\frac{23}{48} + \frac{\pi}{3})\rho^2 - (\frac{47}{384} + \frac{\pi}{4})\rho^3 + (\frac{79}{3072} + \frac{\pi}{8})\rho^4 - \cdots) \quad (23)$$

$$\xi_4 = \frac{4}{3}(1 - \rho) - \pi(\rho - 2\rho^2 + (\frac{47}{48} + \frac{\pi}{4})\rho^3 - (\frac{35}{96} + \frac{\pi}{4})\rho^4 + \cdots) \quad (24)$$

$$\xi_5 = \sqrt{\pi}(\frac{1}{2} - \frac{71}{24}\rho + (\frac{307}{96} + \pi)\rho^2 - (\frac{673}{768} + \frac{9\pi}{4})\rho^3 + (\frac{20329}{92160} + \frac{37\pi}{24} + \frac{\pi^2}{5})\rho^4 - \cdots). \quad (25)$$

Under a typical experimental condition, even at a fairly low column density nl, the parameter ρ may be close to or greater than unity as $q^2 \gg 1$. Consequently, the peak cross section σ_{max} can be estimated approximately from Eq. (13) only if R is very small and the number of contributing ξ_i terms is limited. More discussion will be given in section III.

III. PROPOSED PROCEDURES

A. Determination of w_ℓ and w_g in Photoionization

When $\Gamma \ll \Omega$ (or, $R \ll 1$), for a nearly symmetric resonance with $q^2 \gg 1$, the observed $\sigma_{max} = w_\ell \sigma^L_{max} + w_g \sigma^G_{max}$ can be expressed approximately according to Eqs. (10) and (11) as

$$\sigma_{max} \rightarrow (w_\ell + w_g \pi^{1/2})(q^2 \sigma_b) R, \quad (26)$$

or, σ_{max} varies linearly as functions of $1/\Omega$. As a result,

$$(w_\ell + w_g \pi^{1/2})(q^2 \Gamma \sigma_b) = S_1, \quad (27)$$

where S_1 is the slope determined experimentally by a plot of σ_{max} *vs.* $1/\Omega$ according to Eq. (12). In addition, according to Eq. (17) of Ref. 1,

$$(1.3282 w_\ell + 1.9646 w_g)(q^2 \Gamma \sigma_b) = S_2, \quad (28)$$

where S_2 is also a slope determined experimentally by a procedure detailed in Ref. 1. Eqs. (27) and (28), together with $w_\ell + w_g = 1$, offer an unambiguous procedure to determine the weighting factors w_ℓ and w_g in a photoionization experiment.

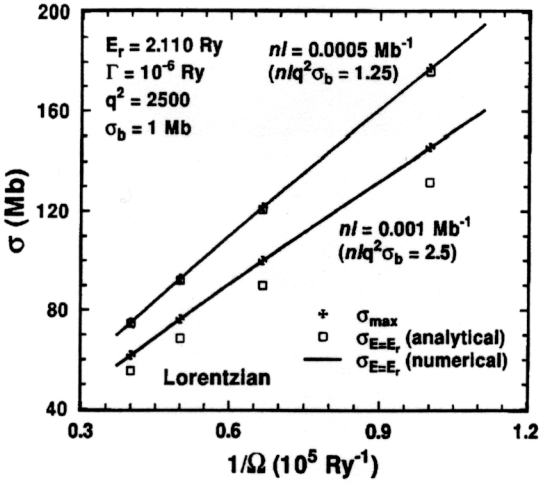

Fig. 4. Comparison of the approximate peak cross sections, $\sigma_{E=E_r}$, obtained from the *analytical* expression Eq. (13), the *numerically* calculated $\sigma_{E=E_r}$ from Eq. (12) and the exact σ_{max} from Eq. (4).

B. Determination of $q^2\sigma_b$ and Γ

Fig. 4 shows that the approximate peak cross sections, $\sigma_{E=E_r}$, obtained from the *analytical* expression Eq. (13) remain in close agreement with the *numerically* calculated $\sigma_{E=E_r}$ from Eq. (12) and the exact σ_{max} from Eq. (4) for a value of $\rho = nlq^2\sigma_b$ as large as 1.25. Clearly, as ρ increases to a value of 2.5, Eq. (13) is no longer applicable.

Since Ω (not R) is an experimentally measured variable, we shall now work with an alternative polynomial, in stead of the polynomial $X(R, nl)$, for σ_{max}, i.e.,

$$\sigma_{max} = (q^2 \sigma_b \Gamma)\, Y(\eta, nl), \quad (29)$$

where $Y(\eta, nl)$ takes the form

$$Y(\eta, nl) = \sum_{i=1} (-\Gamma)^{i-1}\, \xi_i(\rho)\, \eta^i \quad (30)$$

and

$$\eta = 1/\Omega. \quad (31)$$

Our proposed procedure starts with a best fit of the measured σ_{max} at a number of energy resolutions to an expression

$$\sigma_{max}(\eta; nl) = \sum_{\mu=1} \alpha_\mu(nl)\, \eta^\mu. \quad (32)$$

By comparing Eq. (32) to Eq. (29), the fitted coefficients α_μ for a given nl is independent of Ω. In addition, the ratio

of two fitted values of α_μ at two different column densities equals to the ratio of two ξ_μ, i.e.,

$$\frac{\alpha_\mu(nl)}{\alpha_\mu(n'l')} = \frac{\xi_\mu(\rho)}{\xi_\mu(\rho')}. \tag{33}$$

Since σ_{max} is a slowly varying function of η, a number of experimentally determined ratios between several pairs of α_1 obtained at different column densities should be sufficient to fit adequately a value of $q^2\sigma_b$. With a best fitted $q^2\sigma_b$, the resonant width Γ can be determined readily from Eq. (13) or (29).

IV. RESULTS AND DISCUSSION

Fig. 5 presents the variation of the *simulated* photoabsorption peak cross sections σ_{max} as a function of $1/\Omega$ at several column densities. It is derived from the convoluted spectra numerically calculated from Eq. (4) for a fictitious resonance with a width $\Gamma = 5 \times 10^{-5}$ Ry, $q^2 = 400$, and $\sigma_b = 0.015\ Mb$. Following the procedure outlined in section III.B, for each nl, a parameter α_1 is first least-square fitted from Eq. (29). Second, from Eq. (30), we obtain a best fitted value of 5.42 Mb and 5.54 Mb for $q^2\sigma_b$ using the Lorentzian and Gaussian distribution, respectively. Finally, Eq. (13) leads to a width of 5.67×10^{-5} Ry (Lorentzian) and 5.48×10^{-5} Ry (Gaussian). The 10% error introduced in this application is not unexpected due to values of ρ which exceed unity for some of the column densities.

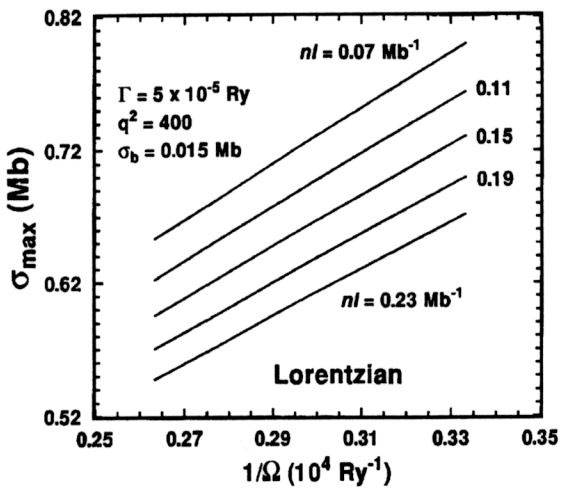

Fig. 5. Variation of *simulated* photoabsorption peak cross sections σ_{max} (from Eq. (4)) as a function of $1/\Omega$ at column densities ranging from 0.07 Mb^{-1} to 0.23 Mb^{-1}. (Only Lorentzian data are shown.)

The deconvolution procedure proposed in this paper works best when $q^2 \gg 1$. It clearly posts a difficult experimental challenge as it also requires simultaneously a small parameter $\rho = nlq^2\sigma_b$ when a small column density nl may adversely reduce the signal to noise ratio in a photoabsorption experiment. In spite of this difficulty, the procedure proposed above offers a realistic possibility to take advantage of the density effect, in an attempt to determine experimentally the width of an ultra-narrow and nearly symmetric atomic resonance which can not be measured directly otherwise.

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