

ANALYSIS OF ABSORPTION PROFILES
OF AUTOIONIZING LINES*

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Abstract

This paper states the scattering-theory parameterization of absorption cross-sections and refractivity for autoionizing spectral lines, and discusses empirical determination of profile parameters, as well as their physical significance.

I. INTRODUCTION

The microscopic description of the propagation of radiation employs a complex index of refraction, \underline{n} , to introduce the influence of the propagation medium. The real part of $\underline{n}-1$, the refractivity $n-1$, accounts for the phase shift of the wave, while the imaginary part accounts for the diminution of the beam intensity due to various scattering processes. That is, for radiation of angular frequency ω ,

$$\underline{n}(\omega)-1 = [n(\omega)-1] + i\left[\frac{N\lambda}{4\pi} \sigma(\omega)\right], \quad (1)$$

where $\sigma(\omega)$ is the atomic absorption coefficient (the attenuation cross-section), N is the density of absorbing atoms, and $\lambda = 2\pi c/\omega$ is the wavelength in vacuum.

The abrupt variation of $\sigma(\omega)$ with frequency, near a resonance frequency ω_0 , defines the natural profile of a spectral line. It is the task of microscopic quantum-mechanical descriptions of radiation interactions to connect the line profile (and the refractivity) with atomic characteristics such as wavefunctions or atomic matrix-elements. For autoionizing lines -- transitions to an energy level lying above the first ionization limit -- scattering theory provides the following profile parameterization:¹

$$\sigma(\epsilon) = \frac{a\epsilon+b}{\epsilon^2+1} + C(\epsilon) \quad , \quad (2)$$

$$n(\epsilon)-1 = \left(\frac{N\lambda}{4\pi} \right) \left[\frac{a-b\epsilon}{\epsilon^2+1} \right] + D(\epsilon) \quad , \quad (3)$$

where ϵ is the energy displacement from the resonance energy E_0 ,
expressed in units of the resonance half-width Γ :

$$\epsilon = \frac{E-E_0}{\Gamma/2} = \frac{\omega-\omega_0}{(\Gamma/2\hbar)} = \frac{\lambda_0-\lambda}{(\lambda\lambda_0\Gamma/4\pi\hbar c)} \cong \frac{\lambda_0-\lambda}{(\lambda_0^2\Gamma/4\pi\hbar c)} \quad . \quad (4)$$

(The approximation sign indicates the replacement of $\lambda_0\lambda$ by λ_0^2).
That is, a particular profile is characterized by the constants
 E_0 , Γ , a , and b , and by the slowly varying backgrounds $C(\epsilon)$ and
 $D(\epsilon)$. The obvious connection between the absorption profile $\sigma(\omega)$
and the refractivity, manifest from the parameterization of Eqs.
(2) and (3), is simply an expression of the Kronig-Kramers dis-
persion relation.² Fano and his colleagues³ have used the equi-
valent parameterization

$$\sigma(\epsilon) = \sigma_b + \sigma_a \frac{(\epsilon+q)^2}{\epsilon^2+1} \quad , \quad (5)$$

where q is a constant and σ_b and σ_a are slowly varying functions of ϵ .

In the present note, I wish to point out, first, the simplicity with which profile parameters may be determined and, second, the physical significance of the parameters.⁴

II. PARAMETER DETERMINATION

Given an experimental curve of σ versus ω (or σ versus λ), one first draws an interpolated background through the resonance profile, as indicated by the dotted line in Fig. 1. The resulting curve is the function $C(\omega)$ (or, in the Fano parameterization, the function $\sigma_a + \sigma_b$).

Next, one measures the maximum excursions of the curve $\sigma(\omega)$ from the background $C(\omega)$. On Fig. 1, these positive quantities are labelled h (for peak height) and d (for peak depth). (In the Fano parameterization, the minimum value of σ is σ_b .) From h and d , one then computes the parameters a and b :

$$b = h - d \quad , \quad (6)$$

$$a = \pm 2\sqrt{hd} \quad . \quad (7)$$

(The Fano parameter q is $\pm\sqrt{h/d}$.) The sign of a (and q) is positive if the minimum of σ occurs on the low-energy (long wavelength) side of the profile.

The resonance frequency ω_0 may next be determined graphically by drawing a curve parallel to the background curve $C(\omega)$, a distance $h-d$ above $C(\omega)$, as shown by the dashed line in Fig. 1. (If $d > h$, this curve lies below $C(\omega)$.) The intercept of this curve with $\sigma(\omega)$ occurs at $\omega = \omega_0$. (Actually, two intercepts occur unless $a = 0$; the $\omega = \omega_0$ intercept lies between the frequencies of maximum and minimum σ .)

The resonance half-width Γ may be obtained from a measurement of the frequency displacement $\Delta\omega_1$ between profile maximum and profile minimum (see Fig. 2), by using the formula

$$\Gamma = \pi\Delta\omega_1 \left[\frac{2\sqrt{hd}}{h+d} \right]. \quad (8)$$

Alternatively, Γ may be obtained from a measurement of the width $\Delta\omega_{\frac{1}{2}}$ of the profile peak at half-maximum height by using the formula

$$\Gamma = \pi\Delta\omega_{\frac{1}{2}} F(r), \quad \text{with} \quad r \equiv a/b, \quad (9)$$

where the function F ,

$$F(r) = \frac{\sqrt{1+r^2} + 1}{3\sqrt{1+r^2} - 1} , \quad (10)$$

is plotted in Fig. 3. Knowing $r = a/b$, one can read the value of $\Gamma / \hbar \Delta \omega_{\frac{1}{2}}$ from Fig. 3.

The preceding remarks also apply to the analysis of profiles plotted on a wavelength scale. One then employs quantities λ_0 , $\Delta \lambda_{\frac{1}{2}}$ and $\Delta \lambda_1$ in place of ω_0 , $\Delta \omega_{\frac{1}{2}}$ and $\Delta \omega_1$. Analysis simplifies with the introduction of a quantity " Γ ", a profile "width" expressed in ångstroms,

$$" \Gamma " = \frac{\Gamma}{(2\pi \hbar c / \lambda_0^2)} \quad (11)$$

such that the dimensionless variable ϵ is

$$\epsilon = \frac{\lambda_0 - \lambda}{(" \Gamma " / 2)} \left(\frac{\lambda}{\lambda_0} \right) \cong \frac{\lambda_0 - \lambda}{(" \Gamma " / 2)} . \quad (12)$$

This "width" may be determined from the relations

$$" \Gamma " = \Delta \lambda_1 \left[\frac{2 \sqrt{\hbar d}}{\hbar + d} \right] = \Delta \lambda_{\frac{1}{2}} F(r) .$$

Using the procedures just described, one can obtain provisional values for the profile parameters. Because of the errors introduced in estimating the background level and resonance width, slight parameter adjustments will usually be required in order to secure an optimum fit of the observational data.

III. PARAMETER INTERPRETATION

Two interactions contribute to the profile parameters of autoionizing lines.^{1,3} The interaction of the atom with the radiation field is expressed by matrix elements of the atomic dipole moment $\underline{D} = e \sum_i \underline{r}_i$. The mixing of quasi-bound configurations with continuum configurations is expressed by matrix elements of an inter-electron coulomb potential v .

Matrix elements are taken in the angular-momentum representation, in which the atom is specified by total angular momentum J and additional quantum numbers i, k, n or β . I shall use⁵ $i, k,$ and n for a discrete quasi-bound configuration, such as the $2s\ 2p$ of helium, and β for a continuum configuration, such as $1s\ \epsilon p$. Profile parameters then involve: a) radiative transitions between the initial state $|iJ_i\rangle$ and a resonance state $|kJ_k\rangle$, governed by the amplitude

$$\langle kJ_k \parallel \underline{D} \parallel iJ_i \rangle ;$$

b) photoionization to the continuum βJ_β , governed by

$$\langle \beta J_\beta \parallel \underline{D} \parallel iJ_i \rangle ;$$

and c) the mixing of bound and continuum configurations, governed by the autoionization amplitude

$$\langle \beta J_\beta \parallel \mathcal{N} \parallel kJ_k \rangle .$$

The double bar notation designates the reduced matrix elements of Racah⁶; the operator \mathcal{N} , being a scalar, has no matrix elements between states with different J .

To simplify the following formulas, I shall use units such that $e = m = \hbar = 1$. Wavelengths are then expressed in Bohr radii, $a_0 = 5.29167 \times 10^{-9}$ cm, while cross-section parameters a , b , and c are given in units of $(a_0)^2 = 2.80018 \times 10^{-17}$ cm². For resonance half-widths in atomic units, Eq. (9) reads

$$\Gamma = \Delta E_{\frac{1}{2}} \times \frac{F(r)}{13.605},$$

where $\Delta E_{\frac{1}{2}}$ is expressed in eV. If one uses the wavelength "width", and expresses wavelengths in angstroms, then the width (in atomic units) is

$$\Gamma = \frac{455.6}{\lambda_0^2} \text{ "r" },$$

while the decay rate (in sec⁻¹) is

$$\Gamma/\hbar = \frac{2\pi c}{\lambda_0^2} \text{ "r" } = \frac{1.884 \times 10^{27}}{\lambda_0^2} \times \text{ "r" }$$

The symbol α denotes

Sommerfeld's fine structure constant, $\alpha = 7.29720 \times 10^{-3}$, $\alpha^{-1} = 1.370388 \times 10^2$.

The resonance half-width is the sum of transition probabilities to lower lying bound states and the transition probability for autoionization:

$$\Gamma = \frac{32\pi^3}{3} \sum_n (\lambda_{kn})^{-3} \frac{|\langle kJ_k \parallel \underline{D} \parallel nJ_n \rangle|^2}{(2J_k + 1)} + \frac{32\pi^3}{3} \int_{\beta} (\lambda_{k\beta})^{-3} \frac{|\langle kJ_k \parallel \underline{D} \parallel \beta J_{\beta} \rangle|^2}{(2J_k + 1)} + 2\pi \int_{\beta} \delta(E_k - E_{\beta}) \delta(J_{\beta}, J_k) \frac{|\langle kJ_k \parallel \underline{D} \parallel \beta J_{\beta} \rangle|^2}{(2J_k + 1)} \quad (13)$$

The symbol \int stands for summation on discrete quantum numbers and integration over continuous labels, such as energy.

The first two sums go over all levels whose energy is less than the energy E_k of the excited level. The third sum goes over all continuum configurations whose energy E_{β} is equal to E_k (δ is the

Dirac or Kronecker delta).

With the introduction of the oscillator strength f_{ik} , given in atomic units by

$$f_{ik} = \frac{2}{3} (E_i - E_k) \frac{|\langle iJ_i \| D \| kJ_k \rangle|^2}{(2J_i + 1)}, \quad (14)$$

the profile parameter b may be written:

$$b = \frac{1}{\Gamma} \left\{ 4\pi\alpha f_{ik} - \frac{2\pi^2}{3} \cdot \frac{1}{\lambda} \int_{\beta} \delta(E_{\beta} - E_k) \delta(J_{\beta}, J_k) \frac{\langle kJ_k \| \nu \| \beta J_{\beta} \rangle \langle \beta J_{\beta} \| D \| iJ_i \rangle}{\sqrt{2J_k + 1} \sqrt{2J_i + 1}} \right\}^2 \quad (15)$$

That is, b is $\frac{4\pi}{137}$ the oscillator strength, less an amount arising from dilution by the continuum, expressed in units of the resonance width.

The parameter a may be written:

$$a = \frac{8\pi}{3\Gamma} \cdot \frac{1}{\lambda} \int_{\beta} \delta(E_k - E_{\beta}) \delta(J_k, J_{\beta}) \frac{\langle iJ_i \| D \| kJ_k \rangle \langle iJ_i \| D \| \beta J_{\beta} \rangle^*}{\sqrt{2J_i + 1} \sqrt{2J_i + 1}} \times \frac{\langle kJ_k \| \nu \| \beta J_{\beta} \rangle}{\sqrt{2J_k + 1}} \quad (16)$$

When there is no continuum having an energy equal to the resonance

energy, or when selection rules prevent mixing of the continuum configuration with the excited configuration, then a is zero.

IV. PROFILE DISPLAY

When $|a| > |b|$, profiles are most readily plotted by introducing the parameter $p \equiv b/a$ and writing Eqs. (2) and (3) as

$$\sigma = a \left[\frac{\epsilon + p}{\epsilon^2 + 1} \right] + C, \quad (17)$$

$$(n-1) = \left(\frac{N\lambda}{4\pi} \right) a \left[\frac{p - \epsilon}{\epsilon^2 + 1} \right] + D. \quad (18)$$

When $|a| < |b|$, the parameter $r \equiv a/b$ can be used:

$$\sigma = b \left[\frac{1 + r\epsilon}{\epsilon^2 + 1} \right] + C, \quad (19)$$

$$n-1 = \left(\frac{N\lambda}{4\pi} \right) b \left[\frac{r - \epsilon}{\epsilon^2 + 1} \right] + D. \quad (20)$$

The implication of the Kronig-Kramers relation is evident in these expressions; a determination of the ratio a/b from absorption data permits one to predict refractivity immediately. Fig. 4

exhibits this connection graphically.

As an example, consider the autoionizing line of thallium near 2005 Å, studied in absorption by Garton, Parkinson, and Reeves.⁷ Analysis of the profile, following the steps of Section III, yields the following profile parameters:⁸

$$a = 20.0 \times 10^{18} \text{ cm}^2$$

$$b = 18.9 \times 10^{18} \text{ cm}^2$$

$$q = 2.3$$

$$\lambda_0 = 2005.4 \text{ Å}$$

$$" \Gamma " = 1.8 \text{ Å}$$

$$\Gamma/\hbar = 8.6 \times 10^{12} \text{ sec}^{-1}$$

The background C can be taken as a linear function of wavelength. This absorption profile is shown in Fig. 5. It then follows that the refractivity is as shown in Fig. 6.

In order to place the relative measurements of reference (7) on an absolute scale⁹, I have used the data of Marr¹⁰, multiplied by a factor of 0.753 as suggested by Marr and Heppinstall¹¹, to normalize the reference (7) data in the wavelength region below 1980 Å. The profile of fig. 5, when extrapolated into the region 1970 - 1900 Å, agrees with the Marr-Heppinstall data.

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REFERENCES

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1. B.W. Shore, Harvard College Observatory, Shock Tube Spectroscopy Laboratory, Scientific Report #13, June, 1966. To be published in Revs. Mod. Phys., April, 1967.
2. R. de L. Kronig, J. Opt. Soc. Am. 12, 547 (1966); cf. R.W. Ditchburn, Light, (Interscience Publishers, New York, 1963) 2nd ed., p. 772.
3. U. Fano, Phys. Rev. 124, 1866 (1961); F. Prats and U. Fano, Atomic Collision Processes, edited by M.R.C. McDowell (North-Holland Publishing Co., Amsterdam, 1964) p. 600; U. Fano and J.W. Cooper, Phys. Rev. 137, A1364 (1965).
4. Both tasks were briefly discussed in reference 1.
5. In reference 1, the present labels iJ_i , kJ_k , nJ_n , and βJ_β , were abbreviated to I, K, N, and c.
6. G. Racah, Phys. Rev. 62, 438 (1942).
7. W.R.S. Garton, W.H. Parkinson, and E.M. Reeves, Can. J. Phys. 44, 1745 (1966).

8. The quantity referred to as Γ in reference (7) is the conventional Γ divided by $2\pi\hbar$. Multiply the Γ of reference (7) by 2π to obtain the conventional decay rate Γ/\hbar .
9. The ordinate scale of FIG. 4 in reference (7) is incorrectly labelled. The values shown are "arbitrary units".
10. G.V. Marr, Proc. Phys. Soc. (London) A. 224, 83 (1954).
11. G.V. Marr, and R. Heppinstall, Proc. Phys. Soc. 87, 293 (1966).

FIG. 1. Illustration of graphical determination of quantities h , d and ω_0 or λ_0 , and Fano parameters $\sigma_a(\omega) + \sigma_b(\omega)$.

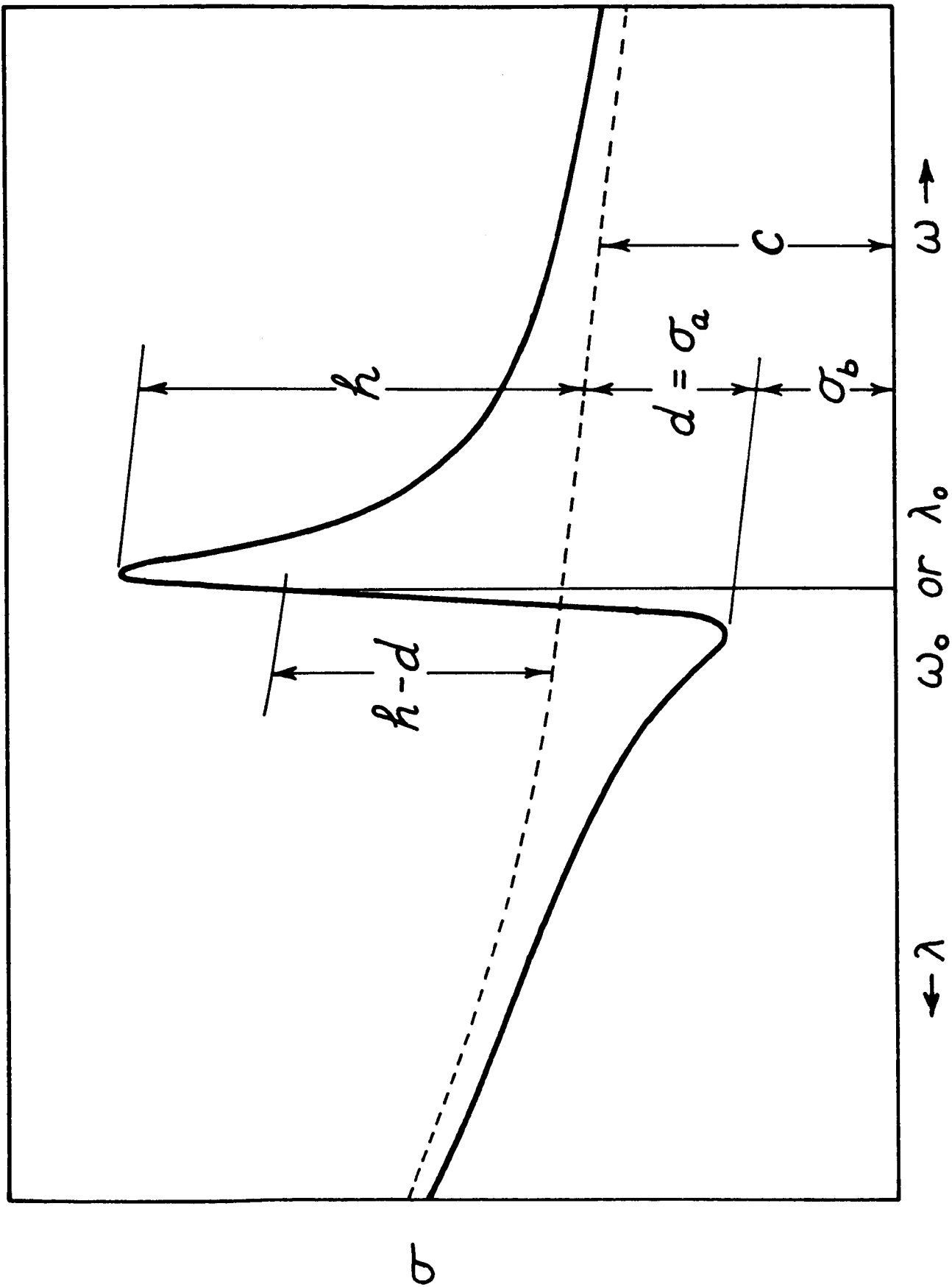


FIG. 2. Graphical definition of $\Delta\omega_1$ and $\Delta\omega_{\frac{1}{2}}$ used for determining Γ . For profiles as a function of λ , read $\Delta\lambda_1$ and $\Delta\lambda_{\frac{1}{2}}$ in place of $\Delta\omega_1$ and $\Delta\omega_{\frac{1}{2}}$.

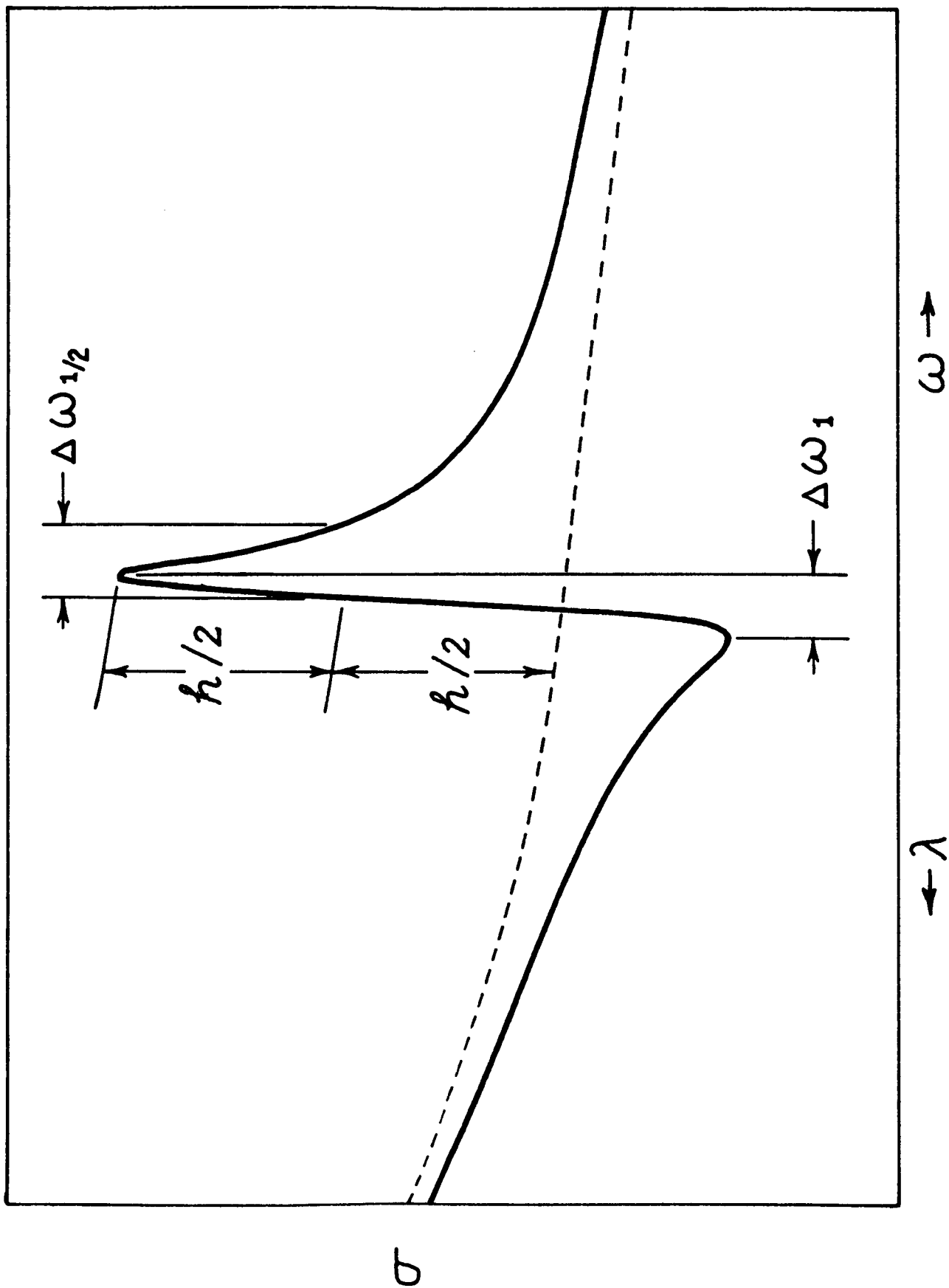


FIG. 3. The function $F(r)$ used with eqn. 9 to estimate Γ .
The arrow indicates asymptotic value.

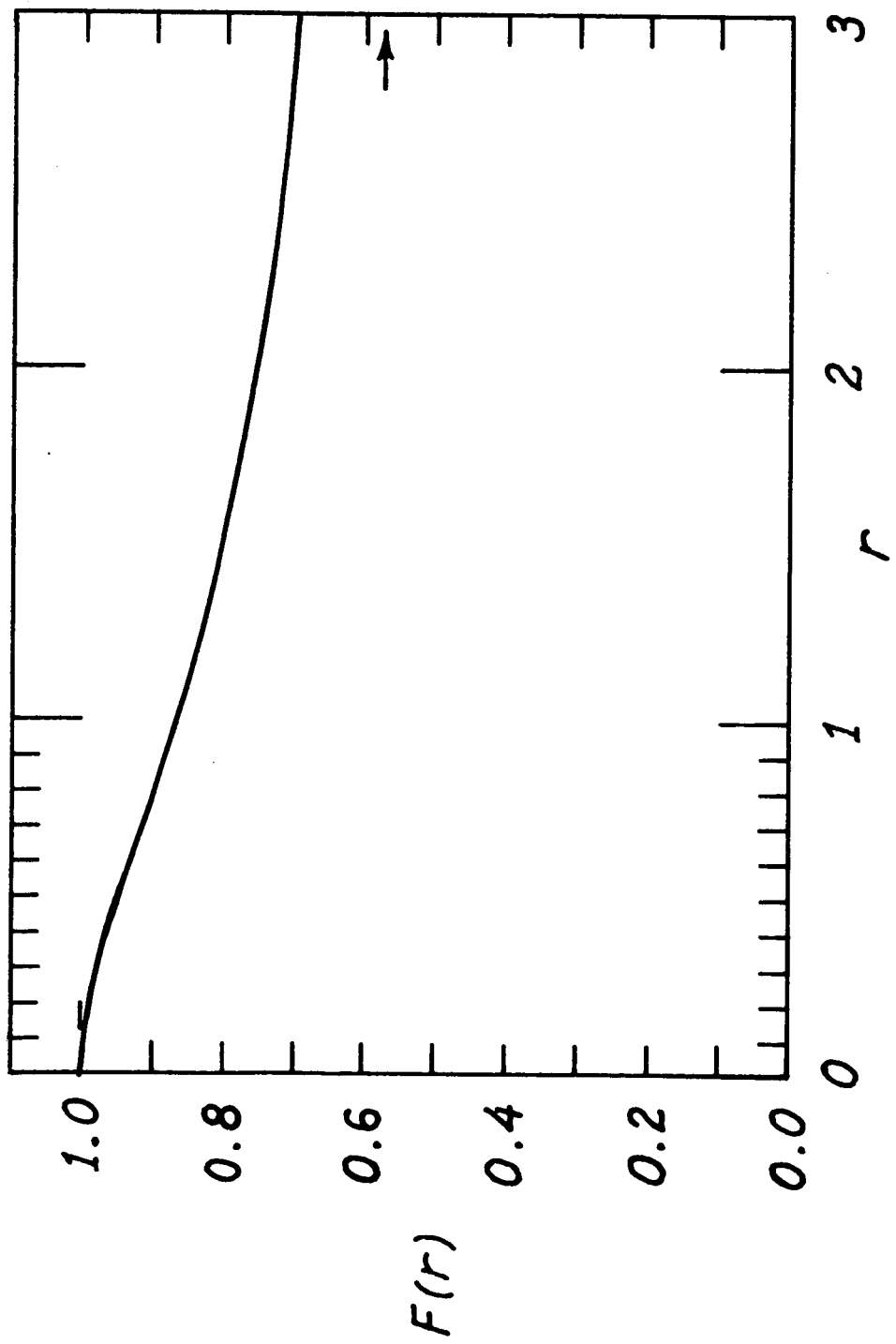
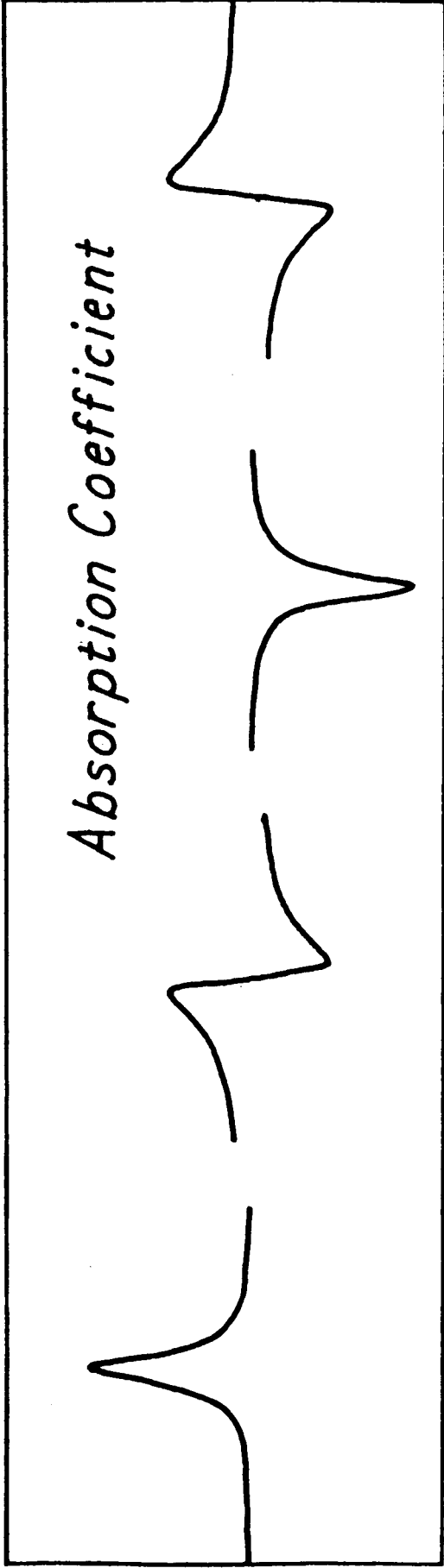


FIG. 4. Comparison of absorption cross-section σ with corresponding refractivity for a) ordinary lines b), c) and d), autoionizing lines. (Curve c shows a "window" resonance). For simplicity, all resonances are shown here with identical widths.



a b $\lambda \rightarrow$ c d

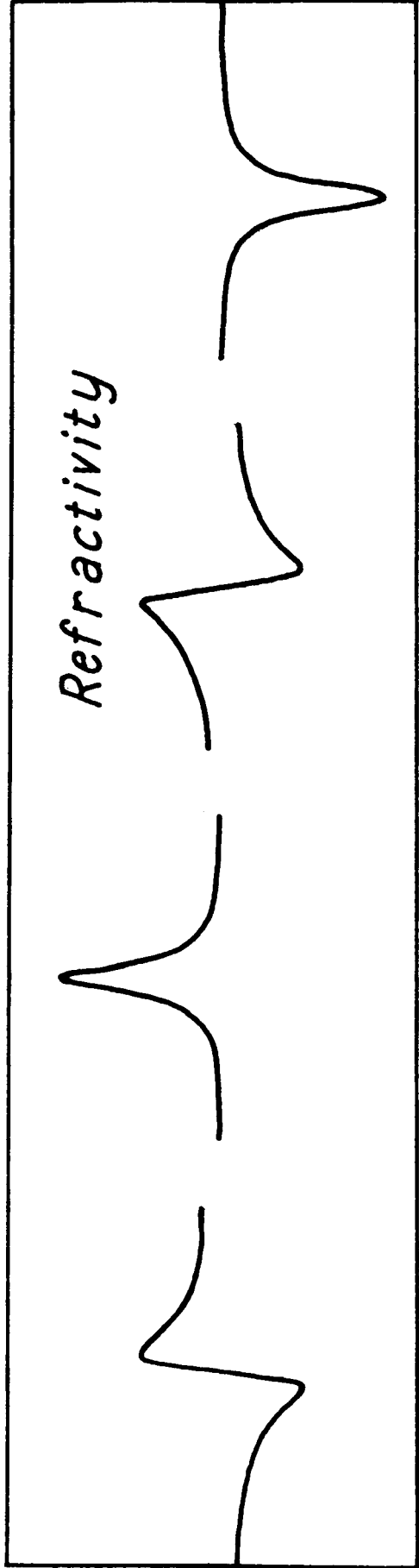


FIG. 5. Absorption cross-section for autoionizing line of neutral thallium near 2005 Å. The data of Garton, Parkinson and Reeves⁷, obtained with an analog recorder, is indistinguishable from the heavy line. The dots show data of Marr¹⁰, corrected by Marr and Heppinstall¹¹, used for normalization below 1980 Å.

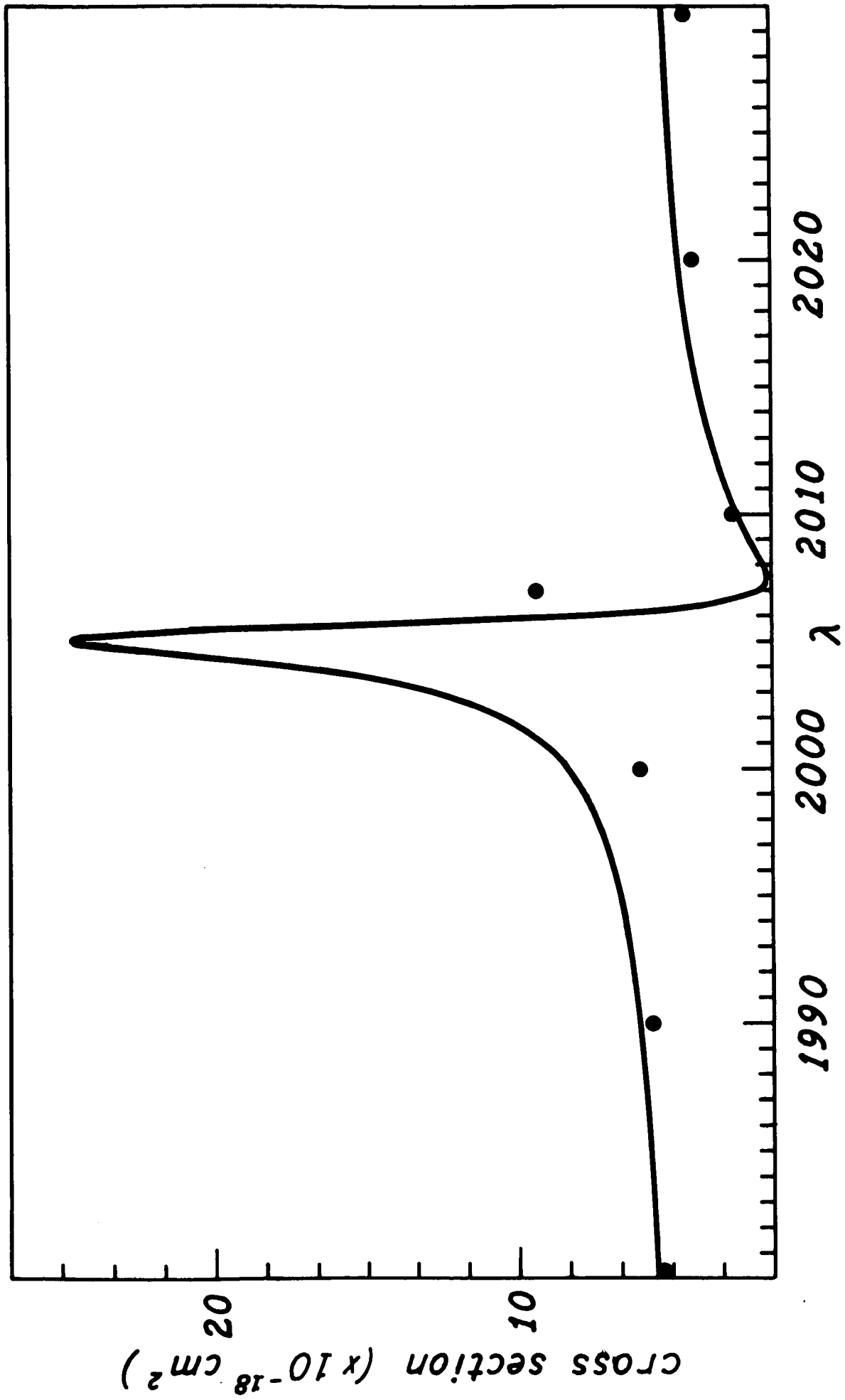


FIG. 6. Refractivity of neutral thallium near 2005 Å predicted from absorption profile of FIG. 5. Ordinate scale refers to a density of 10^{16} absorbers per cm^3 .

