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, $\underset{\sim}{n}$, to introduce the influence of the propagation medium. The real part of $\underset{\sim}{n}-1$, 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,

$$\underset{\sim}{n}(\omega)-1 = [n(\omega)-1] + i[\frac{N\lambda}{4\pi} \sigma(\omega)] , \qquad (1)$$

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]

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

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

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

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

(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 dispersion relation.[2] Fano and his colleagues[3] have used the equivalent parameterization

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

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 :

$$b = h - d \quad , \tag{6}$$

$$a = \pm 2\sqrt{h\,d} \quad . \tag{7}$$

(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 wave-length) 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

$$\Gamma = \hbar\Delta\omega_1 \left[\frac{2\sqrt{hd}}{h + d} \right] . \tag{8}$$

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

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

where the function F ,

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

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

$$\text{``}\Gamma\text{''} = \frac{\Gamma}{(2\pi\hbar c / \lambda_o^2)}$$

(11)

such that the dimensionless variable ϵ is

$$\epsilon = \frac{\lambda_o - \lambda}{(\text{``}\Gamma\text{''}/2)} \left(\frac{\lambda}{\lambda_o}\right) \cong \frac{\lambda_o - \lambda}{(\text{``}\Gamma\text{''}/2)} \quad .$$

(12)

This "width" may be determined from the relations

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

Using the procedures just described, one can obtain pro-
visional 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 $\underset{\sim}{D} = e \sum_i \underset{\sim}{r}_i$. The mixing of quasi-bound configurations with continuum configurations is expressed by matrix elements of an inter-electron coulomb potential ν .

   Matrix elements are taken in the angular-momentum representa-
tion, in which the atom is specified by total angular momentum
J and additional quantum numbers i, k, n or β. I shall use[5] 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 ϵp.
Profile parameters then involve: a) radiative transitions between
the initial state $|iJ_i>$ and a resonance state $|kJ_k>$, governed by
the amplitude

$$< kJ_k \parallel \underset{\sim}{D} \parallel iJ_i > \quad ;$$

b) photoionization to the continuum βJ_β , governed by

$$< \beta J_\beta \parallel \underset{\sim}{D} \parallel iJ_i > \quad ;$$

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

$$< \beta J_\beta \parallel \mathcal{N} \parallel kJ_k > \quad .$$

The double bar notation designates the reduced matrix elements
of Racah[6]; 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, $a_o = 5.29167 \times 10^{-9}$ cm , while cross-section parameters a, b, and C are given in units of $(a_o)^2 = 2.80018 \times 10^{-17}$ cm^3 . For resonance half-widths in atomic units, Eq. (9) reads

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

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

$$\Gamma = \frac{455.6}{\lambda_o^2} \text{``}\Gamma\text{''} \quad ,$$

while the decay rate (in sec^{-1}) is

$$\Gamma/\hbar = \frac{2\pi c}{\lambda_o^2} \text{``}\Gamma\text{''} = \frac{1.884 \times 10^{27}}{\lambda_o^2} \times \text{``}\Gamma\text{''} \quad .$$

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:

$$\Gamma = \frac{32\pi^3}{3} \sum_{n} (\lambda_{kn})^{-3} \frac{|< kJ_k \parallel \underset{\sim}{D} \parallel nJ_n >|^2}{(2J_k + 1)}$$

$$+ \frac{32\pi^3}{3} \int_{\beta} (\lambda_{k\beta})^{-3} \frac{|< kJ_k \parallel \underset{\sim}{D} \parallel \beta J_\beta >|^2}{(2J_k + 1)} \qquad (13)$$

$$+ 2\pi \int_{\beta} \delta (E_k - E_\beta) \; \delta (J_\beta, J_k) \frac{|< kJ_k \parallel \nu \parallel \beta J_\beta >|^2}{(2J_k + 1)} \; .$$

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

$$f_{ik} = \frac{2}{3} (E_i - E_k) \; \frac{|< iJ_i \parallel \underset{\sim}{D} \parallel kJ_k >|^2}{(2J_i + 1)} \; , \tag{14}$$

the profile parameter b may be written:

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

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:

$$a = \frac{8\pi}{3\Gamma} \cdot \frac{1}{\lambda} \int_\beta \delta(E_k - E_\beta) \; \delta(J_k, J_\beta) < \frac{iJ_i \parallel \underset{\sim}{D} \parallel kJ_k}{\sqrt{2J_i + 1}}> < \frac{iJ_i \parallel \underset{\sim}{D} \parallel \beta J_\beta}{\sqrt{2J_i + 1}}>^* \times \tag{16}$$

$$\times \; \frac{< kJ_k \parallel \nu \parallel \beta J_\beta >}{\sqrt{2J_k + 1}} \; .$$

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 intro-

ducing the parameter $p \equiv b/a$ and writing Eqs. (2) and (3) as

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

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

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

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

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

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 2005Å, 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]

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

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

$$q = 2.3$$

$$\lambda_o = 2005.4 \, Å$$

$$"\Gamma" = 1.8 Å$$

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

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 scale[9], I have used the data of Marr[10], multiplied by a factor of 0.753 as suggested by Marr and Heppinstall[11], 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.

ACKNOWLEDGEMENTS

REFERENCES

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. $\underline{12}$, 547 (19 6); cf. R.W. Ditchburn, Light, (Interscience Publishers, New York, 1963) 2nd ed., p. 772.

3. U. Fano, Phys. Rev. $\underline{124}$, 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. $\underline{137}$, 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. $\underline{62}$, 438 (1942).

7. W.R.S. Garton, W.H. Parkinson, and E.M. Reeves, Can. J. Phys. $\underline{44}$, 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 $\Gamma/\hbar$.

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 $\sigma_a(\omega) + \sigma_b(\omega)$.
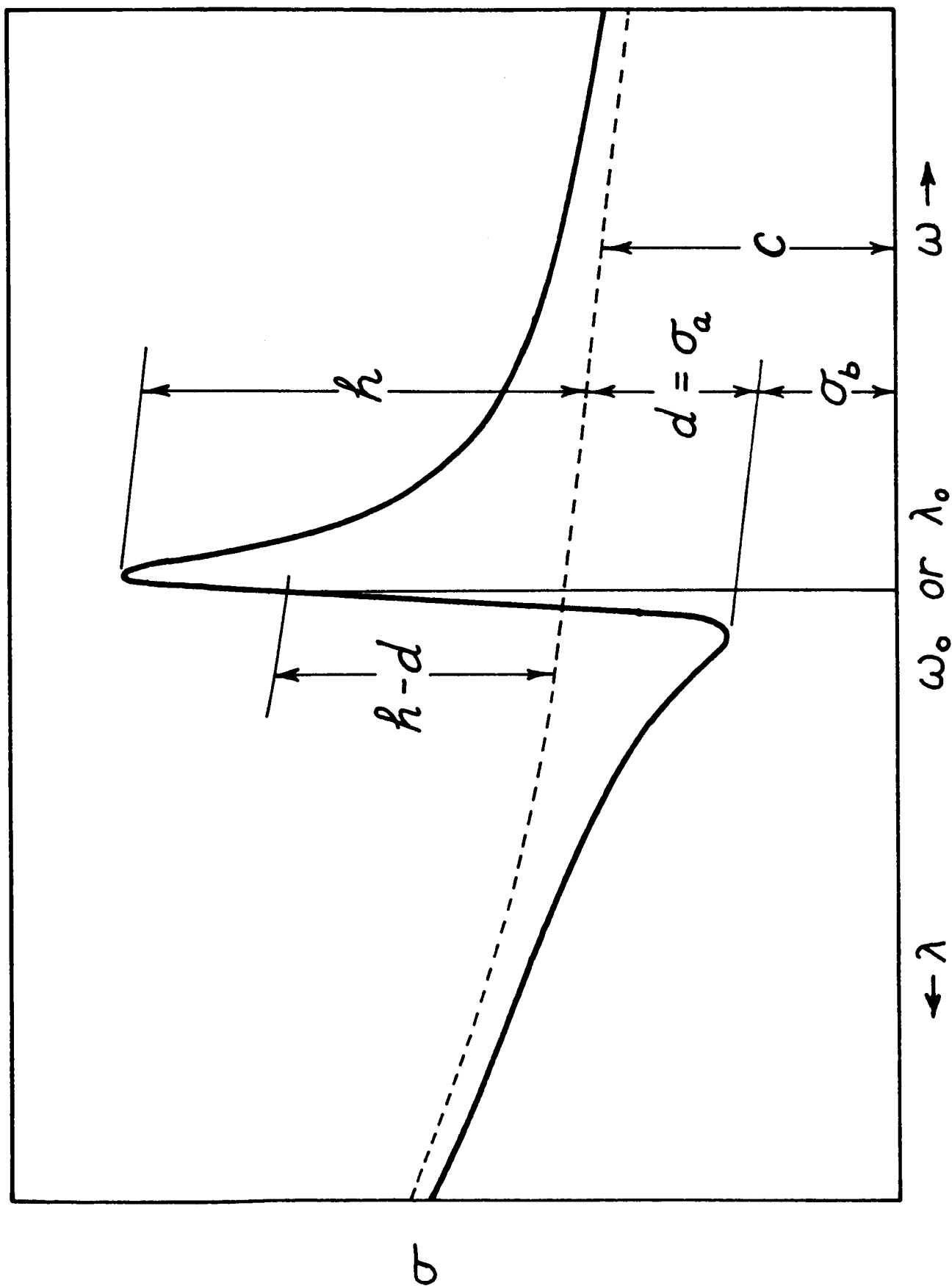
FIG. 2. Graphical definition of Δw_1 and $\Delta w_{\frac{1}{2}}$ used for determining Γ . For profiles as a function of λ , read $\Delta\lambda_1$ and $\Delta\lambda_{\frac{1}{2}}$ in place of Δw_1 and $\Delta w_{\frac{1}{2}}$.
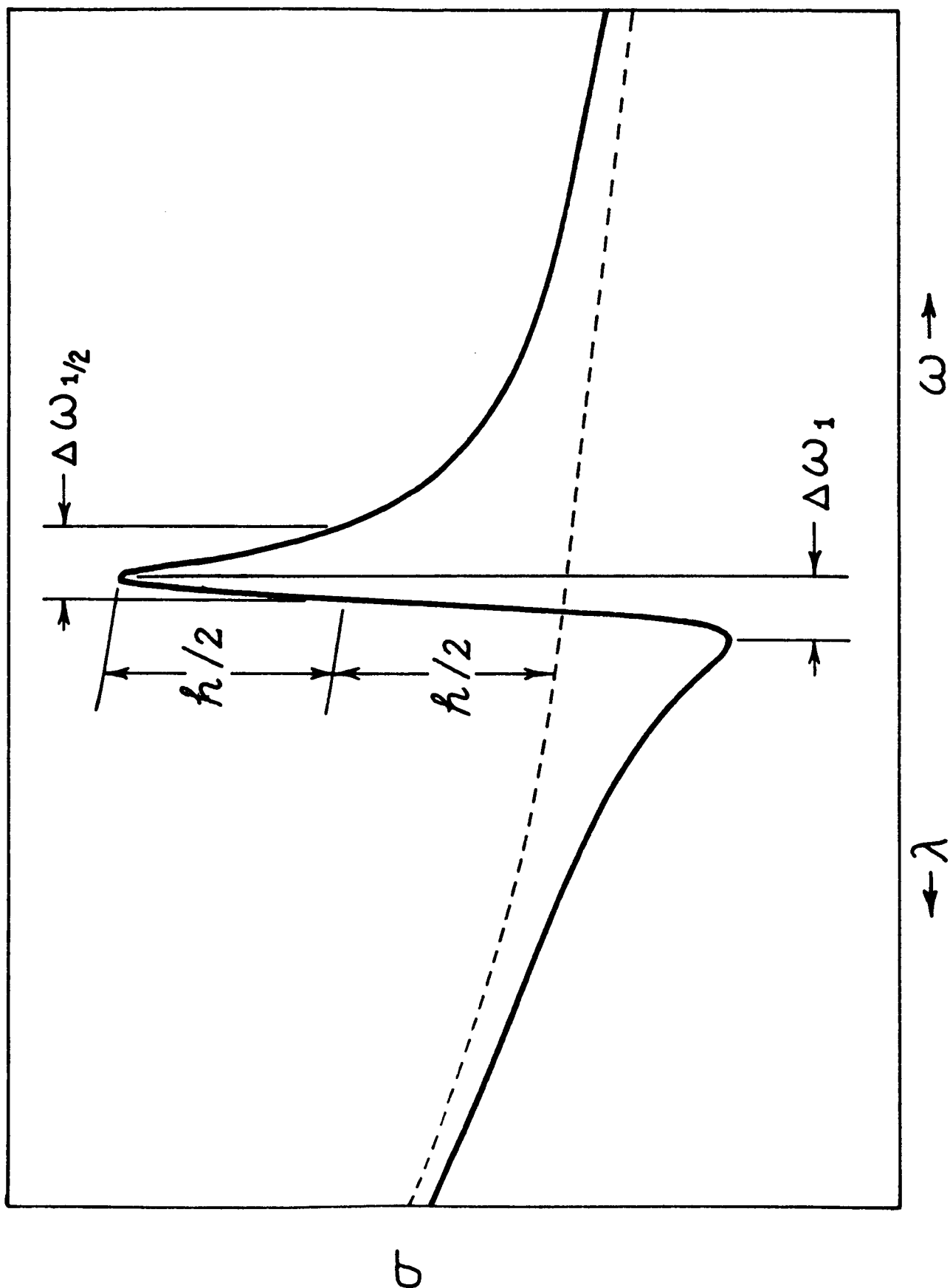
$\Delta\omega_{1/2}$

$\Delta\omega_1$

$h/2$

$h/2$

$\omega \rightarrow$

$\rightarrow \lambda$

b

FIG. 3.   The function F(r) used with eqn. 9 to estimate Γ .

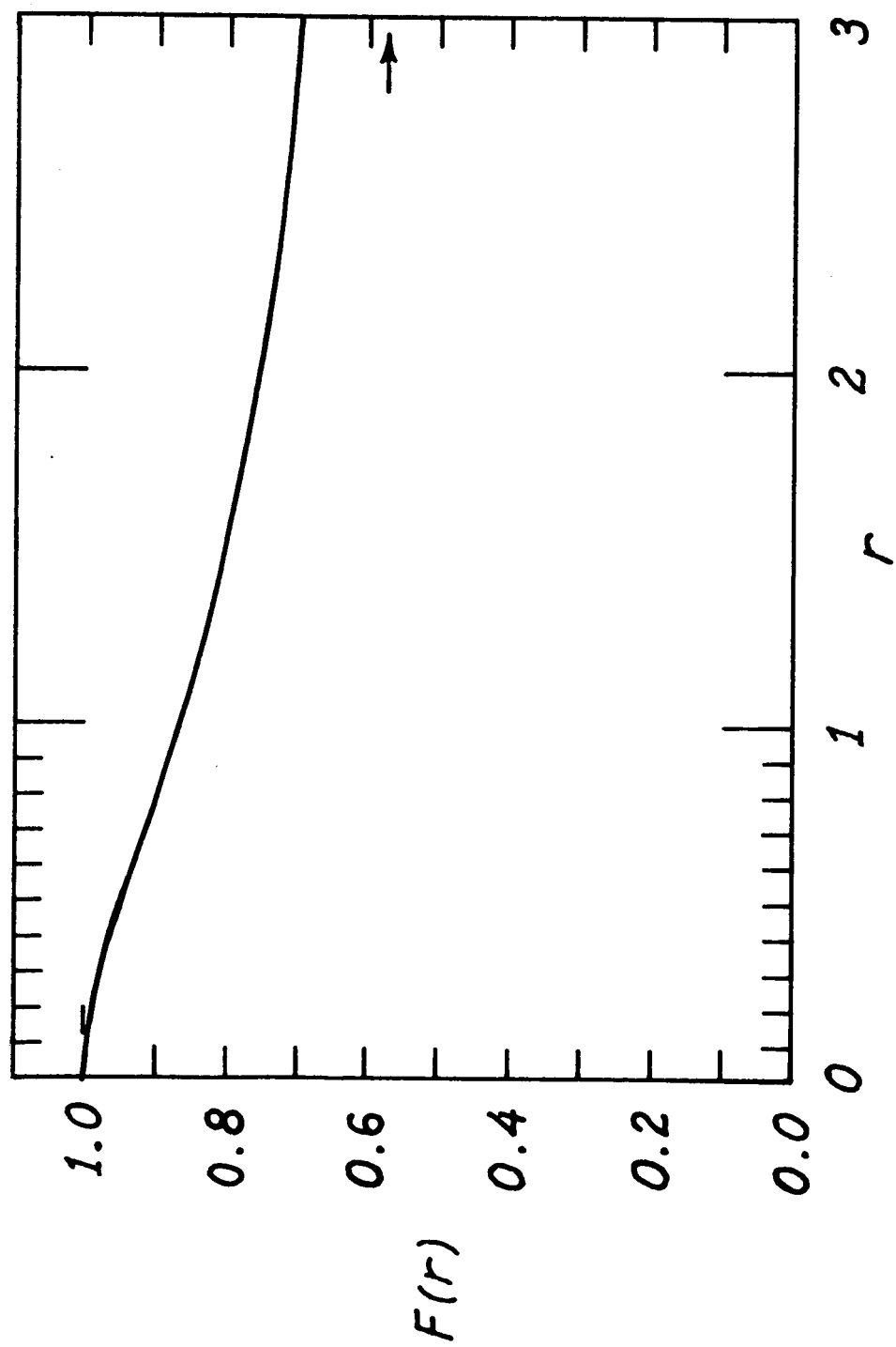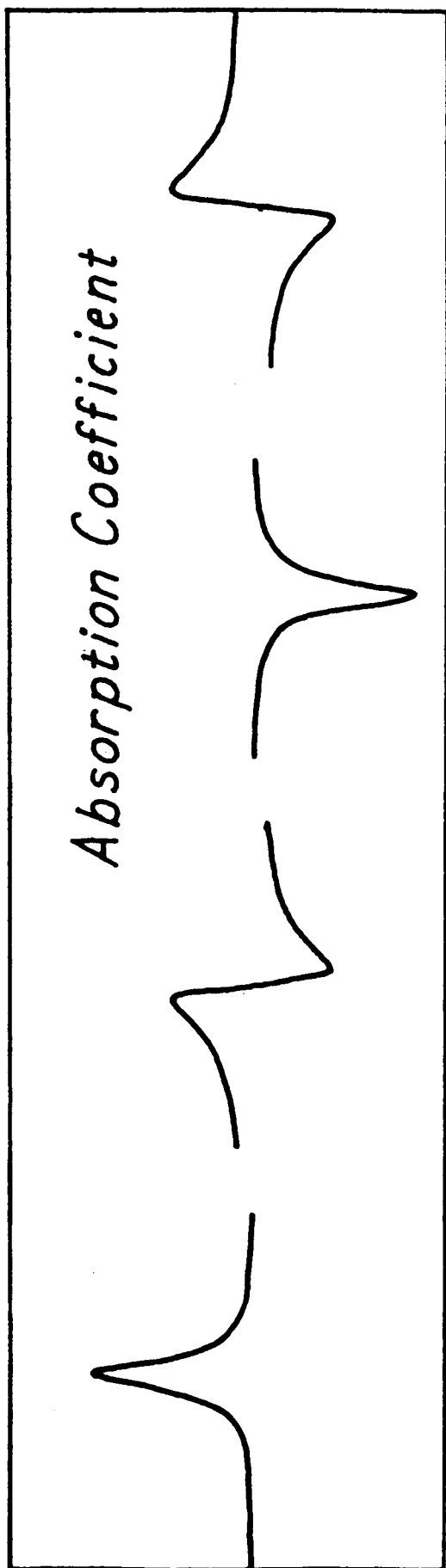The arrow indicates asymptotic value.

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.

Absorption Coefficient

Refractivity

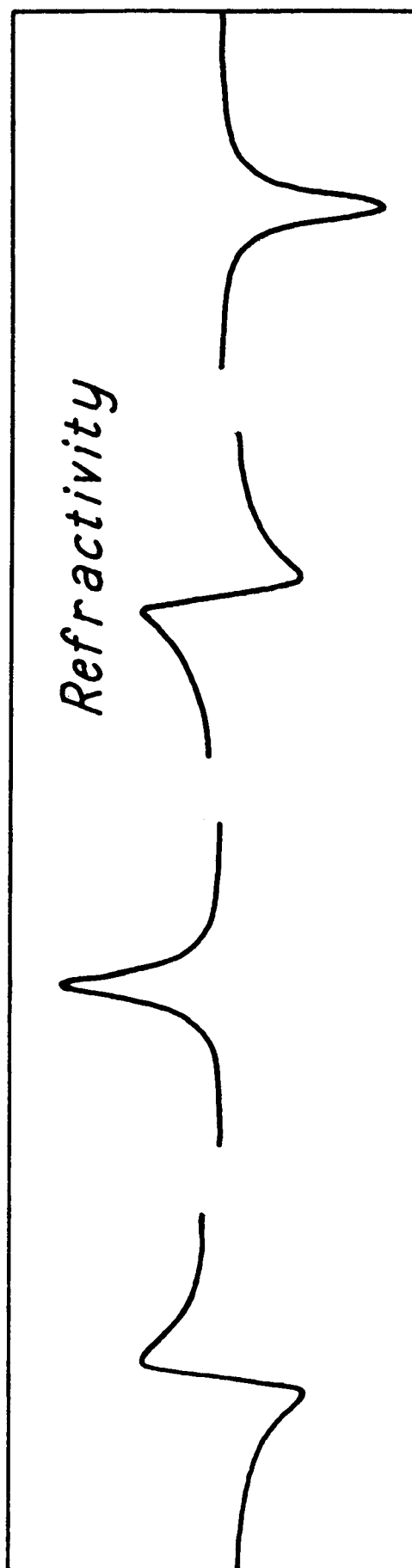$\lambda \rightarrow$

a   b   c   d

FIG. 5.　Absorption cross-section for autoionizing
line of neutral thallium near 2005 Å.　The
data of Garton, Parkinson and Reeves[7], ob-
tained with an analog recorder, is indis-
tinguishable from the heavy line.　The dots
show data of Marr[10], corrected by Marr and
Heppinstall[11], used for normalization below
1980 Å.
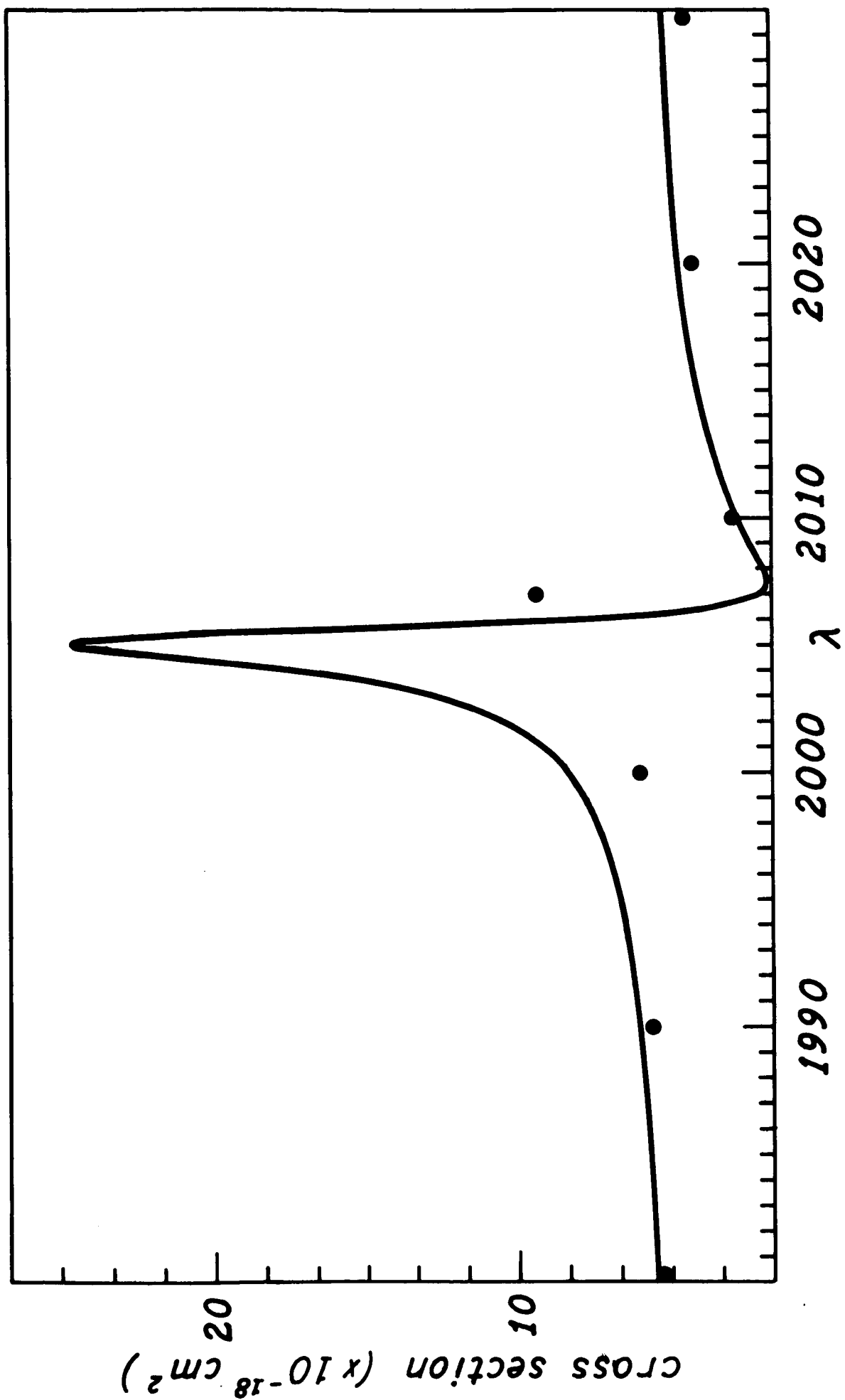
cross section (x 10^{-18} cm^2)

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

refractivity (x 10⁻⁸) vs λ