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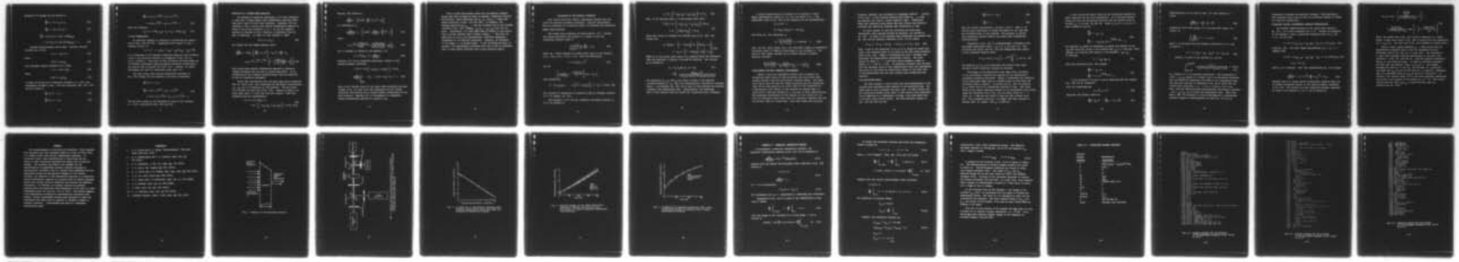

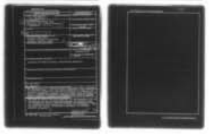

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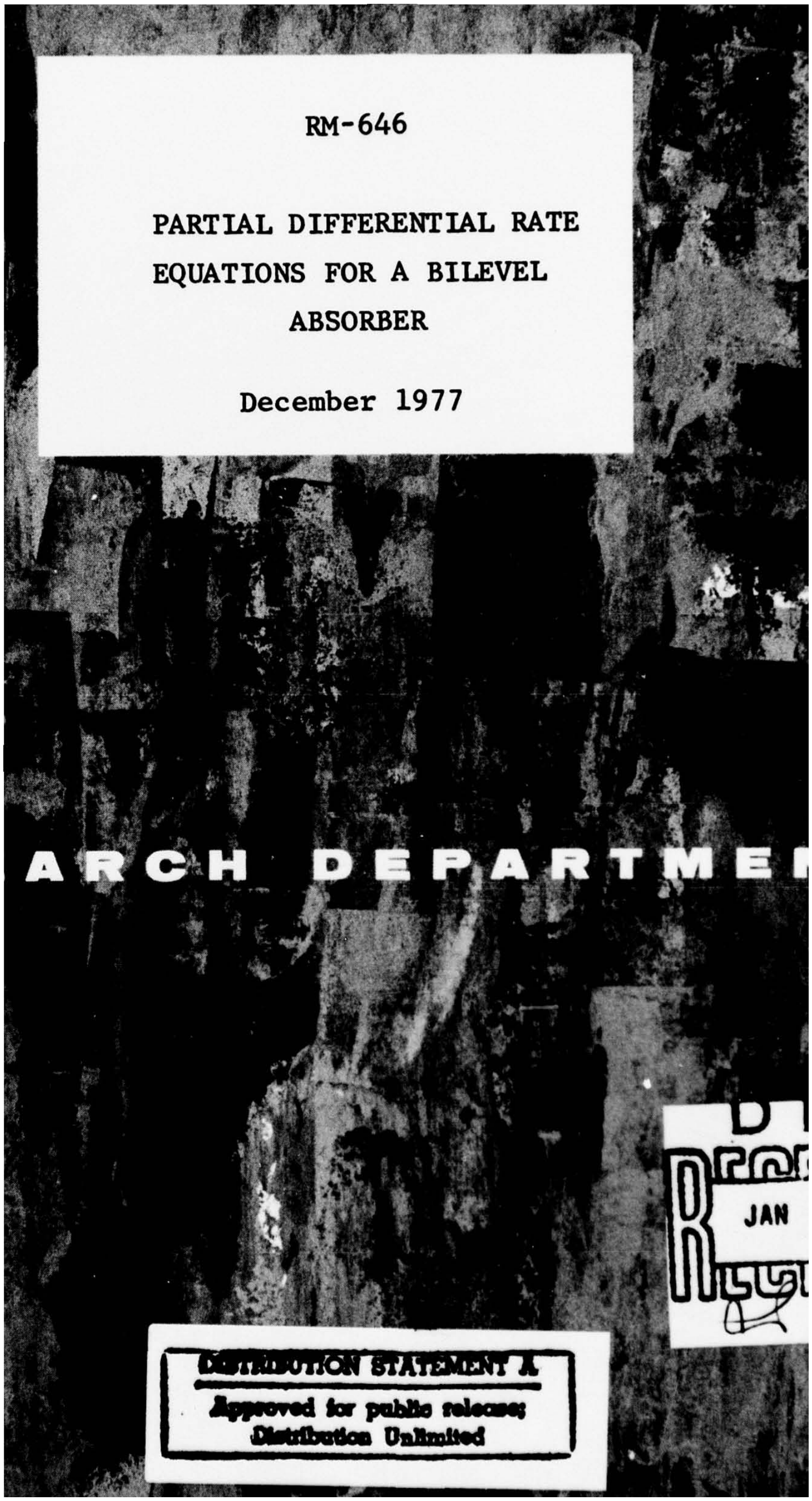

Grumman Research Department Memorandum RM-646

PARTIAL DIFFERENTIAL RATE EQUATIONS FOR A BILEVEL ABSORBER*

by

B. J. Pernick

System Sciences

December 1977

*Portions of this memorandum have been accepted for publication in Applied Optics

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ABSTRACT

The interaction of a directed beam of radiation with an absorber is described using a two level model; transmitted light intensities and level populations are treated as functions of temporal and spatial independent variables; and the general rate equations are given as partial differential equations. Additionally, combinations of material constants are identified as scale parameters and used to express the rate equations in nondimensional form as a hyperbolic partial differential equation in cononical form. One integration yields a time-independent relationship between two transmitted beam intensities at different wavelengths. Also described are several calibration experiments to evaluate material parameters.

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INTRODUCTION

This memorandum describes our work in investigating the performance of an optically excited absorption system. A general two level model is used to describe the process of photo-induced transitions in an absorbing material. One particular application of interest concerns the use of photochromic and liquid crystal-photoconductor devices as unconventional photographic media for optical data processing applications -- e.g., input data recording and adaptive spatial matched filters. Since these devices do not require image development after exposure, they are attractive alternates to film recording in those applications where speed of recording is a factor. In addition, a variety of photochomics find use in opthalmic components, graphic arts, and displays (Ref. 1); thus the results of this investigation are also of value in these areas.

In general the rate equations descriptive of the two level model have a broad scope and are useful as well in such other areas as laser beam propagation, optical cross-section measurements (Ref. 2), photochemistry (Ref. 3), atomic and molecular beam spectrocopy (Ref. 4), dye laser excitation (Ref. 5), and laser isotope enrichment (Ref. 6). In the first two cases interest is primarily focused on characteristics of the attenuated light beam, for the latter examples energy level population dynamics are of concern.

This memorandum focuses on a two level model representing a photo-absorption process and considers spatial as well as temporal dependencies. The inclusion of an independent spatial variable is necessary to account for the fact that all absorbing atoms or molecules do not experience the same light level. Light has already been absorbed in passage through the material. Furthermore, since the absorption interaction is a nonlinear process, one cannot simply scale over the different spatial or time intervals nor scale from low to high power excitation levels as would be the case for a linear system. Thus, both the energy level populations and transmitted beam irradiance are functions of sample thickness as well as time, and the material will not exhibit simple exponential absorption properties. For example, the transmitted beam will initially be strongly attenuated due to a relatively large ground state population (for a ground state transition). Subsequently the transmitted beam irradiance could then increase due to changes in the energy level populations, simulating a self-induced transparency effect.

The interaction with two light beams at different wavelengths is also a topic of interest since the spectral absorpiton of the material influencing the response at one wavelength can affect the absorption properties at the other wavelength. This feature provides a basic reason for using such material in the above mentioned optical processing applications. As a result, data recording can be accomplished within an insignificant development time. With such purpose in mind, the following model analysis could lend itself towards optimization in the choice of materials and also suggests a favorable means to tailor or synthesize new material parameters for these applications (Ref. 7).

In brief, this work deals with a set of fundamental rate equations that encompasses several special cases previously studied by other investigators. A number of material constant groupings are found in the restructure of the rate equations in terms of nondimensional variables. In effect, a smaller number of basic (material constants) factors are used to describe the behavior of the absorber-radiation interaction and to greatly simplify the analysis. When two light beams of different wavelengths interact with the absorber, a time-independent relationship has been found between the beam intensities after passage through the material. This property suggests that measurements of light intensity at one wavelength can be used as a probe to infer the light intensity level at the other wavelength. In addition, several methods are demonstrated that provide estimates for a number of these material constants from calibration experiments. A photochromic material is used as a convenient "two-level" absorber to illustrate the calibration procedures. No attempt is made here to integrate numerically the restructed general rate equations for particular situations.

TWO LEVEL RATE EQUATIONS

Two unidirectional beams of excitation and of probing radiation are at normal incidence to the boundary face of the absorber material, as shown in Figure 1. It is assumed that the probe beam is much weaker than the excitation beam. For generality, the wavelengths of the excitation and probing beams, λ_1 and λ_2, respectively, are considered to be different. (Both beams need not be of different wavelengths; for example, the polarization state of the weaker probe beam could be different from the polarization state of the excitation beam, assuming that the absorber material is polarization insensitive.) It is also assumed that light scattered out of either beam is not significant for homogeneous materials and can be neglected. Thus, only the absorption properties in the direction of propagation are of concern. For the one-dimensional geometry considered here, both beams are of uniform intensity in any plane normal to the direction of propagation along the x-axis, but vary with distance x and time t.

Let $I_1 = I_1 (x,t)$ represent the excitation light intensity and $I_2 = I_2 (x,t)$ the probe light intensity. If $N_L (x,t)$ denotes the number of absorber molecules in the lower energy level per unit volume, and $N_U (x,t)$ the number density of absorber molecules in the upper energy level, then the total number density is

$$N_o = N_L + N_U = \text{const.} \qquad (1)$$

The rate of decrease of excitation light intensity in the direction of propagation is given by

$$\frac{\partial I_1}{\partial x} = - (\sigma_{L1} N_L + \sigma_{U1} N_U + \alpha) I_1 \qquad (2)$$

where σ_{L1}, σ_{U1} are the absorption cross-sections at wavelength λ_1 for the lower and upper levels, respectively, and α represents the absorption rate due to a host material interaction, if any.* Similarly the rate of decrease of probe light intensity is given by

$$\frac{\partial I_2}{\partial x} = - (\sigma_{L2} N_L + \sigma_{U2} N_U + \beta) I_2 \qquad (3)$$

where the absorption constants have similar meaning to those for Eq. (2).

Changes in the number densities N_L and N_U are given by the population rate equations as

$$\frac{\partial N_U}{\partial t} = \sigma_{L1} \phi_{L1} N_L I_1 - \sigma_{U1} \phi_{U1} N_U I_1$$

$$+ \sigma_{L2} \phi_{L2} N_L I_2 - \sigma_{U2} \phi_{U2} N_U I_2 - N_U/\tau \qquad (4a)$$

and

$$\frac{\partial N_U}{\partial t} = - \frac{\partial N_L}{\partial t} \qquad (4b)$$

The quantities ϕ_{L1}, ϕ_{U1}, ϕ_{L2}, ϕ_{U2} are the quantum efficiencies for each particular absorption reaction and τ is the "life time" or decay time constant for the upper energy state. As a realistic and practical situation we shall assume that both excitation and probe beams are uniform across the plane of incidence and constant in time. Consequently, the initial and boundary conditions are

---

* The units for I_1 and I_2 are photons/sec-cm^2. The factor hν is used to convert to units of ergs/sec-cm^2 or watts/cm^2, when h is Planck's constant and ν is the frequency of light.

$$
\begin{aligned}
I_1\ (0,t) &= A_1 \\
I_2\ (0,t) &= A_2 \\
N_U\ (x,0) &= N_{Uo} \\
N_L\ (x,0) &= N_{Lo}
\end{aligned}
\qquad (5)
$$

In the event that the material is initially unexcited then $N_{Uo} = 0$ and $N_{Lo} = N_o$.

Other investigators have worked with less general two level models. Variations from their results are due to specific assumptions made concerning the importance of selected terms in the governing equations. It is worth while to note briefly these differences from the more general rate equations stated above. In dealing with a photochromic material Baldwin (Ref.8) treats changes in the upper energy level number density due only to absorption transitions from the lower to the upper level and spontaneous decay down from the upper level. This is equivalent to setting $\sigma_{U1}\ \Phi_{U1} = \sigma_{L2}\ \Phi_{L2} = \sigma_{U2}\ \Phi_{U2} = 0$ in Eq. (4). In addition, he also takes $\alpha = 0$ in Eq. (2) and $\sigma_{L2} = \beta = 0$ in Eq. (3). The photochromic rate equations studied by Mohn (Ref. 9) are equivalent to setting $\sigma_{L2}\ \Phi_{L2} = 0$ in Eq. (4) and $\sigma_{L2} = \beta = 0$ in Eq. (3). Tomlinson (Ref. 10) deals with a model set of equations equivalent to setting $1/\tau = 0$ and does not include the influence of a probe irradiation; i.e., terms containing I_2 and Eq. (3) are not included in his analysis. Together with a clever transformation of variables, he demonstrates an integral relationship designated as the "Photochromic Function." In Ohtsuka's (Ref. 11) formulation of the rate equations, pertaining to laser beam propagation, there is no distinction made between absorption coefficients since both probe and excitation wavelengths are the same. In addition, his analysis assumes the condition equivalent to setting $\sigma_{L1}\ \Phi_{L1} = \sigma_{U1}\ \Phi_{U1}$.

It is advantageous to introduce other variables and parameters in the rate equations. Let

$$J_1 = I_1 e^{\alpha x},\ J_1(0,t) = A_1,\ J_2 = I_2 e^{\beta x},\ J_2(0,t) = A_2,$$

$$\eta = N_U/N_o,\ \eta(y,0) = 0, y = N_o \sigma_{L1} x \tag{6}$$

Equations (2), (3), and (4a) become

$$\frac{\partial J_1}{\partial y} = -\left[1 + \left(\frac{\sigma_{U1}}{\sigma_{L1}} - 1\right) \eta\right] J_1 \tag{7}$$

$$\frac{\partial J_2}{\partial y} = -\left[\left(\frac{\sigma_{L2}}{\sigma_{L1}} + \frac{\sigma_{U2} - \sigma_{L2}}{\sigma_{L1}}\right) \eta\right] J_2 \tag{8}$$

$$\begin{aligned}\frac{\partial \eta}{\partial t} = {} & \sigma_{L1}\ \Phi_{L1}\ (1-\eta)\ J_1 \exp(-\alpha y/N_o\sigma_{L1}) - \sigma_{U1}\ \Phi_{U1}\ \eta\ J_1 \exp(-\alpha y/N_o\sigma_{L1}) \\ & + \sigma_{L2}\ \Phi_{L2}\ (1-\eta)\ J_2 \exp(-\beta y/N_o\sigma_{L1}) - \sigma_{U2}\ \Phi_{U2}\ \eta\ J_2 \exp(-\beta y/N_o\sigma_{L1}) \\ & - \eta/\tau \end{aligned} \tag{9}$$

With the further substitutions

$$J_{10} = 1/\tau\ \sigma_{L1}\ \Phi_{L1},\ J_{20} = 1/\tau\ \sigma_{L2}\ \Phi_{L2},\ \lambda = t/\tau$$

$$p = J_1/J_{10},\ p(0,\lambda) = A_1/J_{10},\ s = J_2/J_{20},\ s(0,\lambda) = A_2/J_{20}$$

$$K_1 = \sigma_{U1}\ \Phi_{U1}/\sigma_{L1}\ \Phi_{L1},\ K_2 = \sigma_{U2}\ \Phi_{U2}/\sigma_{L2}\ \Phi_{L2}, \tag{10}$$

$$a_1 = (\sigma_{U1}/\sigma_{L1}) - 1,\ a_2 = \sigma_{L2}/\sigma_{L1},\ a_3 = (\sigma_{U2} - \sigma_{L2})/\sigma_{L1}$$

Equations (7) through (9) are reduced to

$$\frac{\partial p}{\partial y} = - (1 + a_1 \eta) p \tag{11}$$

$$\frac{\partial s}{\partial y} = - (a_2 + a_3 \eta) s \tag{12}$$

$$\frac{\partial \eta}{\partial \tau} = (1-\eta-K_1 \eta) p \exp (-\alpha y/N_o \sigma_{L1})$$

$$+ (1-\eta-K_2 \eta) s \exp (-\beta y/N_o \sigma_{L1}) - \eta \tag{13}$$

Further simplifications can be made. Introduce the new variable $q(y,\lambda)$ from

$$p = q \cdot \exp (-y) \tag{14}$$

where

$$q(0,\lambda) = A_1/J_{10} \tag{15}$$

Also introduce another variable $r(y,\lambda)$ using

$$s = r \cdot \exp (-a_2 y) \tag{16}$$

where

$$r(0,\lambda) = A_2/J_{20} \tag{17}$$

In terms of the new set of dependent variables q, r, and η and independent variables y and λ, the rate equations, Eqs. (11), (12), and (13) reduce to

$$\frac{\partial}{\partial y} \ln q = - a_1 \eta \tag{18}$$

$$\frac{\partial}{\partial y} \ln r = - a_3 \eta \tag{19}$$

$$\frac{\partial \eta}{\partial \lambda} = (1-\eta)\, q\, e^{-b_1 y} - K_1\, \eta\, q\, e^{-b_1 y}$$

$$+ (1-\eta) r\, e^{-b_2 y} - K_2\, \eta\, r\, e^{-b_2 y} - \eta \qquad (20)$$

where the constants

$$b_1 = 1 + (\alpha / N_o\, \sigma_{L1}), \; b_2 = a_2 + (\beta / N_o\, \sigma_{L1}) \qquad (21)$$

A FIRST INTEGRATION

An important integral is obtained by eliminating the common η - term in Eqs. (18) and (19). Integration with respect to the y - variable results in

$$r = C\, q^{\nu}, \; \nu \equiv a_3/a_1 = (\sigma_{U2} - \sigma_{L2})/(\sigma_{U1} - \sigma_{L1}) \qquad (22)$$

As a consequence of the boundary conditions imposed on the variables q and r, the arbitrary function of integration in Eq. (22) is just a constant C. Note that if both excitation and probe beams are of different wavelength (implying unequal absorption coefficients) one expects that in general the ratio $\nu \neq 1$. However, for equal wavelengths the ratio is identically unity (Ref. 11).

The three first order partial differential equations in Eqs. (18) through (20) are reduced to the pair of equations.

$$\frac{\partial}{\partial y} \ln q = - a_1\, \eta$$

$$\frac{\partial \eta}{\partial \lambda} = (1-\eta)\, q\, e^{-b_1 y} - K_1\, \eta\, q\, e^{-b_1 y} \qquad (23)$$

$$+ (1-\eta)\, C\, q^{\nu}\, e^{-b_2 y} - K_2\, \eta\, C\, q^{\nu}\, e^{-b_2 y} - \eta$$

The two level system is now described in terms of the variables q, r, and η, governed by Eqs. (22) and (23).

REDUCTION TO A SECOND-ORDER EQUATION

For purposes of numerical evaluation, it is more convenient to deal with a single higher order differential equation rather than with a pair of first order equations. Equations (23) are combined to form a second order partial differential equation in terms of one of the variables, q or η. By far the simplest equation is obtained if the η variable is eliminated from the pair of equations. In terms of a new variable z, where

$$\ln q = z + b_1 y \tag{24}$$

one finally has the lengthy general result

$$\begin{aligned} \frac{\partial^2 z}{\partial y \partial \lambda} = &- (1+K_1) \left[\frac{\partial e^z}{\partial y} + b_1 e^z \right] - a_1 e^z - \frac{\partial z}{\partial y} - b_1 \\ &- a_1 C e^{\nu z} e^{\nu b_1 y} e^{-b_2 y} \left[1 + \left(\frac{1+K_2}{a_1} \right) \left(\frac{\partial z}{\partial y} + b_1 \right) \right] \end{aligned} \tag{25}$$

This second order partial differential equation is obviously "highly nonlinear" and can only be solved numerically. As an alternative we will consider simplifications that are practical as well as physically meaningful.

Assume that interactions with the probe beam can be neglected. That is, terms in Eq. (4a) containing the absorption cross-sections σ_{L2}, σ_{U2} are to be neglected in this analysis. The net result is to discard the last term in Eq. (25). (Surely if there is no probe light then $C = 0$ and this term will vanish.) With this assumption and the transformation

$$\begin{aligned} u\,(y,\lambda) &= \ln\,(1+K_1) + z \\ &= \ln \left[\tau\,(\sigma_{L1}\,\phi_{L1} + \sigma_{U1}\,\phi_{U1}) \right] + \ln I_1\,(x,t) \end{aligned} \tag{26}$$

then Eq. (25) reduces to

$$\frac{\partial^2 u}{\partial y \partial \lambda} = - \left[(1+e^u) \frac{\partial u}{\partial y} + b_3 e^u + b_1 \right]$$

or, dividing by b_1

$$\frac{\partial^2 u}{\partial (b_1 y) \partial \lambda} = - \left[(1+e^u) \frac{\partial u}{\partial (b_1 y)} + \frac{b_3}{b_1} e^u + 1 \right] \tag{27}$$

where

$$b_3 = \frac{a_1 + (1+K_1)\, b_1}{(1+K_1)} = \frac{\sigma_{U1} (\phi_{L1} + \phi_{U1})}{\sigma_{L1} \phi_{L1} + \sigma_{U1} \phi_{U1}} + \frac{\alpha}{N_o \sigma_{L1}} \tag{28}$$

The η- variable is related to the quantity u as

$$\eta = (-b_1/a_1) \left(1 + \frac{\partial u}{\partial (b_1 y)}\right) \tag{29}$$

Equation (27) can be integrated numerically, subject to the initial-boundary conditions

$$u\,(0,\lambda) = \ln \left[\tau \, (\sigma_{L1} \phi_{L1} + \sigma_{U1} \phi_{U1}) \right] + \ln A_1$$

$$\left. \frac{\partial u}{\partial (b_1 y)} \right|_{\lambda = 0} = - (a_1 \; \eta \; (y,0) + b_1) / \, b_1 = - 1 \tag{30}$$

where a zero initial value for the upper level population has been assumed in Eq. (5) (note that this assumption for the initial population distribution can be altered without modification of any prior results). Equation (27) is recognized as a hyperbolic partial differential equation in canonical form.

With no probe beam present there are six material constant groups that must be known in order to achieve a numerical solution. Specifically, these quantities are b_1, K_1, and a_1 -- terms that appear explicitly in Eqs. (27) and (28). In addition, the scaling quantities $N_o \sigma_{L1}$, τ, and the constant term in the boundary condition of Eq. (30), (namely, $\sigma_{L1} \Phi_{L1} + \sigma_{U1} \Phi_{U1}$) must also be given. Furthermore, if a weak probe beam is present in the system, then a seventh constant must be known, namely ν. Note that the quantities A_1 and A_2 are experimentally controlled parameters independent of the material understudy. Likewise, the thickness of the sample, x, is assumed known. In the following sections, we present a few experimental procedures that can be used to determine some of these needed constants from a given material sample.

EVALUATION OF THE MATERIAL CONSTANTS

This section discusses several experimental methods that are useful for material parameter estimation. Specific photochromic data are presented as a convenient means to illustrate the procedures.

STEADY STATE SOLUTION

The steady state conditons are found from Eq. (27). Setting the partial derivative with respect to λ equal to zero and separating variables leads to

$$\frac{1 + e^{\bar{u}}}{(b_1/b_3) + e^{\bar{u}}} \frac{d\bar{u}}{dy} = - b_3 \qquad (31)$$

where the - symbol denotes the steady state value of the variable, (e.g., $\lim u(y,\lambda) \equiv \bar{u}$ as $t \to \infty$). With the substitution

$$w = (b_1/b_3) + e^{\bar{u}} \qquad (32)$$

one has

$$\left[\frac{1}{w-(b_1/b_3)} - \frac{1-(b_1/b_3)}{w} \right] dw = - b_1 \, dy$$

Upon integration,

$$\bar{u} - (1-(b_1/b_3)) \cdot \ln \left[e^{\bar{u}} + (b_1/b_3) \right] = - b_1 y + \text{const} \qquad (33)$$

The constant of integration is evaluated using the boundary conditon at $y = 0$; namely, Eq. (5c).

The variable $u(y,\lambda)$ and the originally introduced quantity $I_1(x,t)$ are related by

$$u = \ln \left[\tau \left(\sigma_{L1} \phi_{L1} + \sigma_{U1} \phi_{U1} \right) \right] + \ln I_1 \tag{34}$$

Thus, at the entrance face x = 0 the steady state value

$$\begin{aligned} \bar{u}\,(0) &= \ln \left[\tau \left(\sigma_{L1} \phi_{L1} + \sigma_{U1} \phi_{U1} \right) \right] + \ln A_1 \\ &= \ln \left[(1+K_1)/J_{10} \right] + \ln A_1 \end{aligned} \tag{35}$$

Using this result to evaluate the constant term in Eq. (33), one finally has

$$\begin{aligned} \ln\left(\bar{I}_1/A_1\right) - \left(1 - (b_1/b_3)\right) \ln \left\{ (\bar{I}_1/A_1) + b_5 \right\} \\ = - b_1\, y - \left(1 - (b_1/b_3)\right) \ln \left\{ 1 + b_5 \right\} \end{aligned} \tag{36}$$

where $\bar{I}_1$ is the steady state value of I_1 measured after the excitation beam has traversed a distance x through the material. The constant b_5 is defined as

$$\begin{aligned} b_5 &\equiv b_1\, J_{10}/b_3\, A_1\, (1 + K_1) \\ &= \frac{A_1}{\tau} \; \frac{(N_o \sigma_{L1} + \alpha)}{\alpha(\sigma_{L1}\phi_{L1} + \sigma_{U1}\phi_{L1}) + N_o \sigma_{L1} \sigma_{U1} (\phi_{L1} - \phi_{U1})} \end{aligned} \tag{37}$$

The quantities b_1, b_3, and b_5 are known in terms of the material constants whereas $\bar{I}_1$, A_1, and x are experimentally controlled or measured values. In principle, Eq. (36) can be used to help evaluate the material constants from experimental data. Unfortunately, the functional form of this equation only all allows for "trial-and-error" estimates.

A useful simplification is possible if we consider a "small signal approximation" where $\bar{I}_1 = A_1 (1-i)$ for which $i \ll 1$. The logarithmic terms in Eq. (36) can be replaced with the approximations

$$\ln (1-i) \simeq - i$$

$$\ln (1+b_5-i/1+b_5) \simeq - i/(1+b_5)$$

with which Eq. (36) simplifies to

$$i \simeq \frac{b_1 b_3 (1+b_5)}{b_1 + b_3 b_5} y = \text{constant} \cdot y \qquad (38a)$$

Thus, for the "small signal case," the fractional change in transmitted excitation light is linearly proportional to the thickness y. The slope of this linear relation can be easily related to several material constants

$$\frac{b_1 b_3 (1+b_5)}{b_1 + b_3 b_5} = \frac{A_1 a_1}{A_1 (1+K_1) + J_{10}} + 1 + \frac{\alpha}{N_o \sigma_{L1}} \qquad (38b)$$

SIMULTANEOUS TWO-BEAM INTENSITY MEASUREMENTS

Figure 2 shows the experimental system used to measure the transmitted light levels in both excitation and probe beams after passage through a specific photochromic absorber sample. The argon laser 448 nm line was used for sample excitation and the helium-neon laser 633 nm line served as the probe light in this demonstration. A photochromic film similar to that employed by Baldwin (Ref. 8) (type 63•071, American Cyanamid Co.), was used in these demonstrations. The wavelength sensitivity of this material is well suited for use with the blue-green argon laser lines for excitation together with the helium-neon light as a probe beam. Both laser beams were spatially filtered, expanded, and collimated to illuminate uniformly a portion of the film. A beam splitter directed both beams onto the film and shutters were used to control exposure times. Transmitted beams were separated using narrow band pass filters and detectors monitored the individual changing beam intensities in time.

At every instant in time the excitation and probe beam intensities, after passing through the absorber, are related by Eq. (22). In terms of the measured beam intensities one derives from Eq. (22) and the boundary conditions of Eq. (5) the result

$$\ln I_2 = \nu \ln I_1 + [\ln A_2 - \nu \ln A_1 + y\,(\nu\, b_1 - b_2)] \qquad (39)$$

Thus, a plot of the quantities $\ln I_2$ vs $\ln I_1$ should be linear with slope ν and intercept equal to the value of the last three bracketed terms in Eq. (39). Figure 3 illustrates how well a straight line represents the demonstration experimental results. The least square fit value of $\nu = -0.66$ falls within Baldwin's range of values ($\nu = -0.65$ to -0.95). No numerical estimates were obtained from the intercept value in this demonstration since the experimental data were not corrected for reflectivity losses at the front face of the photochromic film and only relative beam intensities were measured.

POST-EXCITATION DECAY

The time constant τ can be found from decay measurements of the excited state population after removal of the excitation beam. The probe beam is used to monitor the decay rate. We first assume that the interaction between probe radiation and excited state population can be neglected as a consequence of using a very weak probe beam or of small cross section values. The rate equations similar to Eqs. (19) and (20) are now

$$\frac{\partial}{\partial y} \ln r = - a_3 \eta \tag{40}$$

$$\frac{\partial \eta}{\partial \lambda} = - \eta \tag{41}$$

with the initial distribution $\eta\ (y,0) \equiv \eta_o\ (y) \neq 0$. That is, an excited state population is created and exists at the time when the excitation beam is just removed. The decrease in excited state population density affects the probe light transmission characteristics.

Integration of Eq. (41) is straightforward, resulting in the well-known exponential decay, $\eta\ (y,\lambda) = \eta_o\ (y) \exp\ (-\lambda)$. Substituting this result into Eq. (40) and integrating with respect to the y-variable finally yields

$$\ln I_2 = \ln S_2 + a_3 \left[1 - e^{-t/\tau}\right] \int_0^y \eta_o\ (y)\ dy \tag{42}$$

The quantity $S_2 \equiv I_2\ (y,0)$ represents the initial probe light intensity level transmitted through the absorber.

The change of the helium-neon probe light after excitation of the photochromic absorber was measured in the demonstration experiment previously mentioned. Figure 4 illustrates the variation of the probe beam light level at several points in time after the excitation beam is removed. In accord with Eq. (42) the quantity $\ln I_2$ should vary as an exponential function of time. The curves shown in the figure represents matches to the experimental data points using the functional form of Eq. (42) for three values of τ. A value of $\tau = 1900$ sec was found to offer the best overall curve fit. This estimated value for τ is higher than that reported by Baldwin (Ref. 8), namely, $1100 \lesssim \tau \lesssim 1400$ sec.

A less restrictive model allows for an interaction between the probe radiation and the level populations. As a practical measure assume now that the interaction involves only the excited level by setting $\sigma_{L2} = 0$ in Eqs. (8) and (9). Since $I_1\ (x,t) = J_1\ (x,t) = 0$ after excitation one has

$$\begin{aligned} \frac{\partial J_2}{\partial y} &= -\ a_3\ \eta\ J_2 \\ \frac{\partial \eta}{\partial \lambda} &= -\ \tau\ \sigma_{U2}\ \Phi_{U2}\ J_2\ \eta e^{-\beta y/N_o\ \sigma_{L1}} - \eta \end{aligned} \qquad (43)$$

The quantity J_2 cannot be normalized as before with respect to the J_{20}-term since the latter is not defined when $\sigma_{L2} = 0$, (see Eqs. (10)). Instead, we normalize with respect to the quantity $\tau\ \sigma_{U2}\ \Phi_{U2}$ by defining

$$S \equiv \tau\ \sigma_{U2}\ \Phi_{U2}\ J_2 \qquad (44)$$

With this substitution Eq. (43) becomes

$$\begin{aligned} \frac{\partial S}{\partial y} &= -\ a_3\ \eta\ S \\ \frac{\partial \eta}{\partial \lambda} &= -\ S\ \eta\ e^{-\beta y/N_o\ L1} - \eta \end{aligned} \qquad (45)$$

If the quantity β is zero or can be neglected then the coupled Eqs. (45) can be integrated.

With the transformations

$$S = e^Q,\ \eta = e^v \qquad (46)$$

Equations (45) finally reduce to

$$\frac{\partial Q}{\partial y} = -a_3\ e^v\ \ ,\ \ \frac{\partial v}{\partial \lambda} = -\ (1 + e^Q) \qquad (47)$$

Differentiation of the first of Eqs. (47) with respect to λ yields

$$\frac{\partial^2 Q}{\partial\lambda\, \partial y} = - \frac{\partial}{\partial y} (Q + e^Q) \tag{48}$$

Integration first with respect to y and then with respect to λ results in

$$\int \frac{dQ}{Q+e^Q+C} = - \lambda + f (y) \tag{49}$$

where C is evaluated from the boundary conditions at $y = 0$ and is given by

$$C = - \ln \left[A_2\, \tau\, \sigma_{U2}\, \phi_{U2}\right] - A_2\, \tau\, \sigma_{U2}\, \phi_{U2} \tag{50}$$

Finally, in terms of the variable J_2, one has

$$\int_{J_2(y,0)}^{J_2(y,\tau)} \frac{d\, J_2}{J_2 \left[\ln(J_2/A_2)+\tau\sigma_{U2}\phi_{U2}(J_2-A_2)\right]} = -\lambda+f(y) \tag{51}$$

The integral is to be evaluated numerically. The combination of terms $\tau\, \sigma_{U2}\, \phi_{U2}$ appear as a single item to be determined utlimately from the numerical integration and match to the experimental data. The arbitrary function of integration f(y) can be found from the steady-state properties, i.e., $\eta\, (y,\infty) = 0$ and $J_2\, (y,\infty) = A_2$. Thus, with the above mentioned approximations the material constants τ and $\tau\, \sigma_{U2}\, \phi_{U2}$ can be found from experimental data. (Note that Mohn's (Ref. 9) treatment of optical bleaching for a photochromic material suggests an approximation for which Eq. (51) can be integrated to estimate the material constants. When applicable, this estimated value could be used in a recursive fashion to refine the numerical integration.)

LINEARIZED PARTIAL DIFFERENTIAL EQUATION APPROXIMATION

We consider simplifications to the second order equation, Eq. (27). As a first assumption set $\alpha = 0$. Consider an expansion of the quantity u about a particular quiescent value of I_1, say $< I_1 >$, in the form

$$u = \ln [\tau (\sigma_{L1} \phi_{L1} + \sigma_{U1} \phi_{U1}) < I_1 >] + \ln I_1/<I_1> \quad (52)$$

using Eq. (26). The small signal approximation $I_1 \simeq < I_1 > + \delta$ suggests that

$$u \simeq \ln [\tau(\sigma_{L1} \phi_{L1} + \sigma_{U1} \phi_{U1}) <I_1>] + \ln (1+\delta/<I_1>) \quad (53)$$

$$\simeq u_o + \delta/< I_1 >$$

where u_o is a constant. With this simplification Eq. (27) becomes

$$\frac{\partial^2 u}{\partial y \, \partial \lambda} \simeq - [(1 + e^{u_o}) \frac{\partial u}{\partial y} + b_3 e^{u_o} + b_1] \quad (54)$$

Equation (54) is a linear partial differential equation which can be readily integrated subject to the initial-boundary conditions of Eq. (30). The solution for this linearized problem, expressed in terms of the quantity I_1 (x,t), can be written as

$$\ln I_1 \simeq \ln A_1 - \left[\frac{\dfrac{a_1\langle I_1\rangle}{J_{10}}}{1+(1+K_1)\langle I_1\rangle/J_{10}} + 1 \right] y$$

$$+ \frac{a_1\langle I_1\rangle/J_{10}}{1+(1+K_1)\langle I_1\rangle/J_{10}}\, y \exp\left[- \left(1 + \frac{(1+K_1)\langle I_1\rangle}{J_{10}} \right) \lambda \right] \tag{55}$$

(Note, the second term in Eq. (55) would be identical to a "small signal" steady state result of Eq. (38) in accord with the assumptions $\langle I_1\rangle \simeq J_{10} \simeq A_1$. The last term in Eq. (55) vanishes in steady state.)

Figure 5 shows several measured I_1 - t data points from the demonstration experiment and a curve fit determined from the functional form of Eq. (55) as A + B exp (-Ct). The constants A, B, and C were evaluated from the measurements at the later time intervals t = 400, 500, and 600 sec. From the computed exponential factor, C, and using the value $\tau \simeq 1900$ sec obtained previously, one find that the quantity $(1+K_1)\ \langle I_1\rangle/J_{10} \simeq 3$. For example, assuming the value $K_1 \simeq 1$ and $\langle I_1\rangle$ of the order of 1 μ watt/cm^2, one finds that J_{10} is also of the order of 1 μ watt/cm^2. (Baldwin's (Ref. 8) equivalent value for J_{10} is about 20 μ watts/cm^2.) In addition, the computed value of B in the above mentioned exponential form leads to an estimate of the product $a_1\ y \simeq - 10$. This result implies that the ratio σ_{UL}/σ_{L1} is much less than unity as expected (see Eq. (10)).

SUMMARY

The accomplishments of this work are threefold: First, general rate equations have been developed either as a pair of first order or a single second order partial differential equations. As previously noted, these equations have a broad scope and are useful to model absorption phenomena and energy level population changes. The procedure was shown to be valuable for the identification of significant material constant groupings as characteristic constants; that is, several scale parameters and non-dimensional groups are new physical insights to the problem. Secondly, the reduction of the descriptive equations to a hyperbolic partial differential equation in canonical form is another important result that implies relative simplicity and accuracy for numerical evaluations. In addition, an integral solution was derived relating probe and exictation beam intensities in the form of a time-independent power law (see Eqs. (22) or (39)). This result suggests a new experimental technique for monitoring the excitation beam. Finally, several experimental methods were presented in which the calibration test data could be analyzed to estimate a number of material constants. A photochromic was used as a convenient demonstration media.

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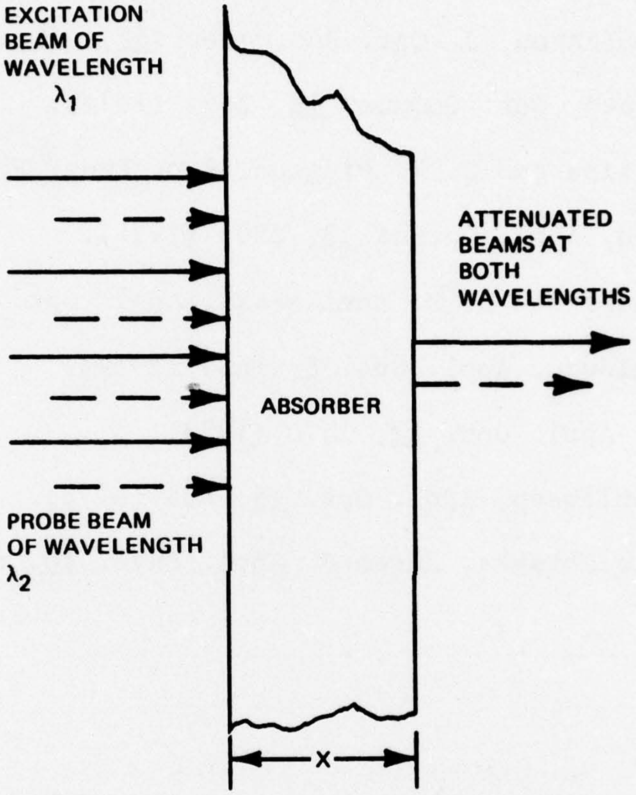

Fig. 1 Geometry of the Absorption Process

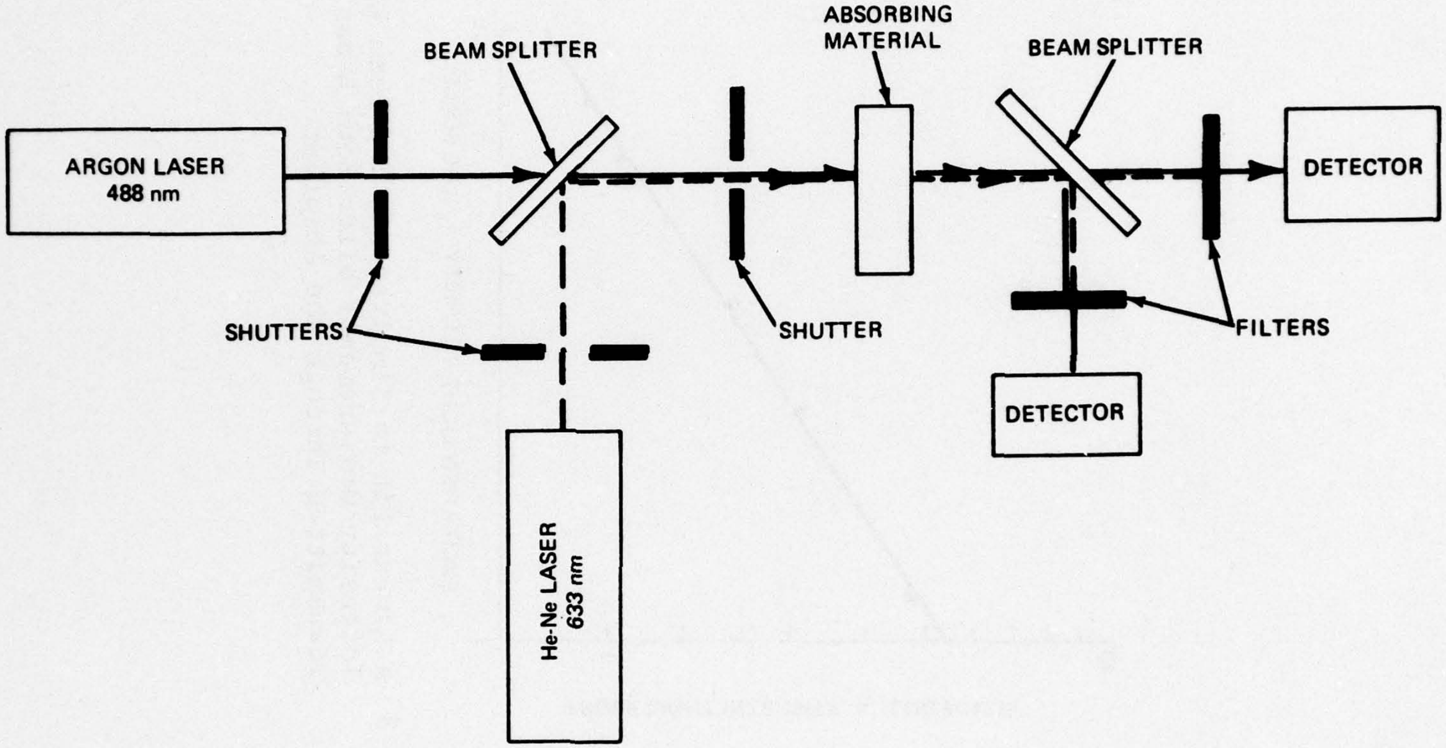

Fig. 2 Optical System to Measure Attenuation of Collimated Excitation (488 nm) and Probe (633 nm) Beams Traversing a Two-Level Photochromic Absorber

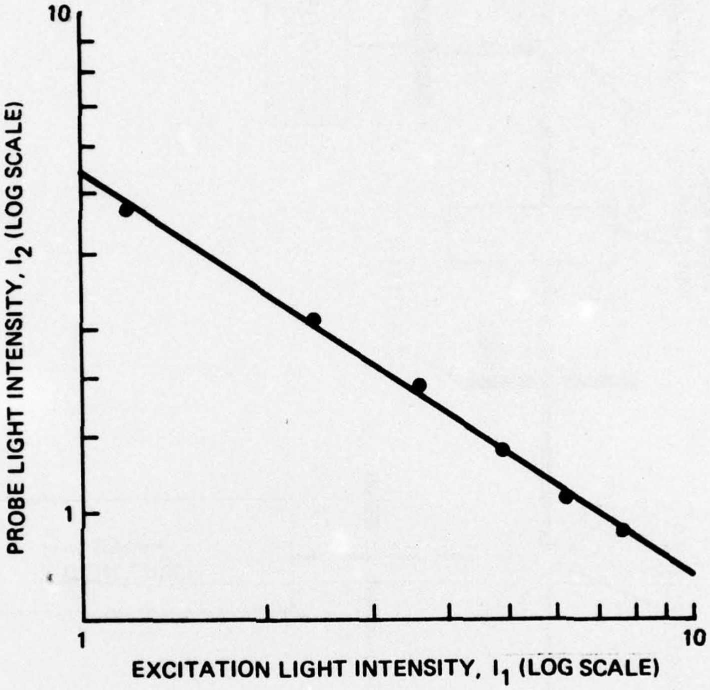

Fig. 3 A Linear Fit to Simultaneous Two-Beam Light Intensity Measurements after Both Beams are Transmitted Through the Absorber

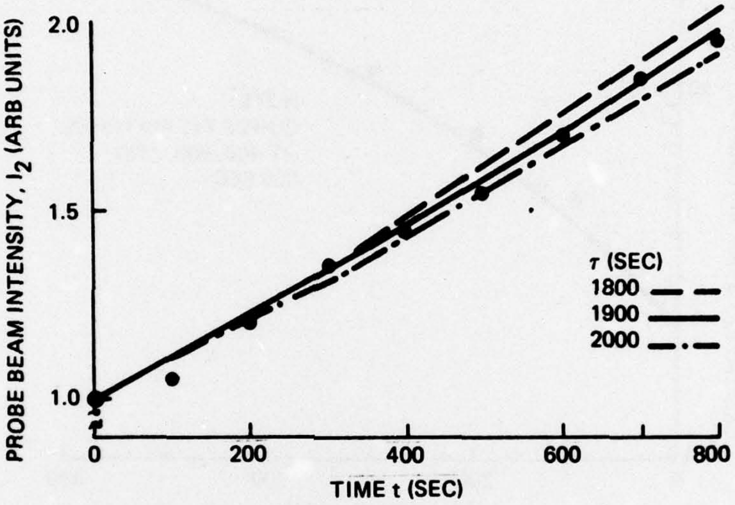

Fig. 4 Measured Changes of the Probe Light Level Transmitted Through the Absorber after Excitation and Several Comparison Exponential Time Functions.

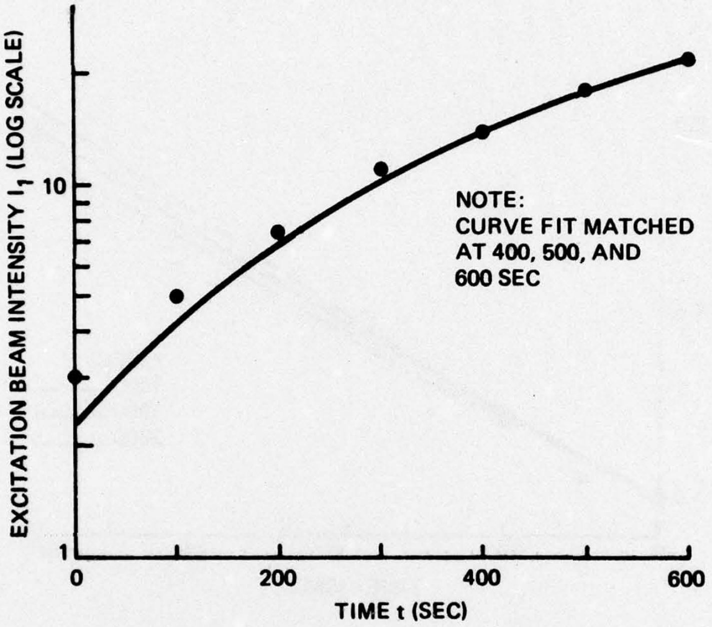

Fig. 5 A Comparison of Measured Excitation Light Levels Transmitted Through the Absorber with a Linear Approximation Solution

APPENDIX A - NUMERICAL INTEGRATION PROGRAM

To accommodate a numerical integration procedure, the hyperbolic differential equation of Eq. (27) can be expressed as

$$\frac{\partial^2 u}{\partial(b_1 y)\partial\lambda} = f(u, {}^{\partial u}/\partial(b_1 y)) \equiv f \qquad \text{(A-1)}$$

together with the initial value-boundary value conditions of Eq. (30) written as

$$\begin{aligned} u\,(o,\lambda) &= C \\ \frac{\partial u}{\partial(b_1 y)} &= -1 \end{aligned} \qquad \text{(A-2)}$$

at $\lambda = 0$ or equivalently

$$u\,(y, o) = -\, b_1 y + C \qquad \text{(A-3)}$$

For convenience set $b_1 = 1$, (*equivalent to redefining the y-variable*).

Integration of Eq. (A-1) in terms of the differential or step size $\Delta\lambda$ yields

$$\left.\frac{\partial u}{\partial y}\right|_{y,\lambda+\Delta\lambda} = \left.\frac{\partial u}{\partial y}\right|_{y,\lambda} + f\,\Delta\lambda \qquad \text{(A-4)}$$

Also the change in the u-variable for a step change y can be written as

$$u\left[(y+\Delta y), (\lambda+\Delta\lambda)\right] = u(y,(\lambda+\Delta\lambda)) + \left.\frac{\partial u}{\partial y}\right|_{y,\lambda+\Delta\lambda} \cdot \Delta y \qquad \text{(A-5)}$$

To obtain the recurrence formulas upon which the integration scheme is based let

$$\lambda = n \cdot \Delta\lambda \quad , \quad y = s \cdot \Delta y \qquad \text{(A-6)}$$

where n, s are integers. Thus, Eqs. (A-4) and A-5) become

$$\left.\frac{\partial u}{\partial y}\right|_{s,\ n+1} = \left.\frac{\partial u}{\partial y}\right|_{s,n} + f(s,n)\ \Delta\lambda \qquad \text{(A-7)}$$

$$u\ ((s+1),\ (n+1)) = u\ (s,(n+1)) + \left.\frac{\partial u}{\partial y}\right|_{s,n+1} \Delta y \qquad \text{(A-8)}$$

together with the initial value-boundary value conditions

$$u\ (o,n) = C$$

$$\left.\frac{\partial u}{\partial y}\right|_{s,o} = -\ 1 \text{ or } u(s,o) = -\ s \cdot \Delta\ y + C \qquad \text{(A-9)}$$

For simplicity in notation define

$$U_{s,n} = u(s,n)$$

$$D_{s,n} = \left.\frac{\partial u}{\partial y}\right|_{s,n} \qquad \text{(A-10)}$$

Finally, the recurrence formulas are

$$D_{s,n+1} = D_{s,n} + f\ (s,n)\Delta\lambda$$

$$U_{s+1,n+1} = U_{s,n+1} + D_{s,n+1} \cdot \Delta\ y \qquad \text{(A-11)}$$

$$U_{o,n} = C$$

$$U_{s,o} = -\ s \cdot \Delta y + C$$

representing a first order integration scheme. The numerical procedure consists of solving Eqs. (A-11) for the quantity $U_{s,n}$ over a range of values

$$s = 0 \text{ to } s_{max} \qquad n = 0 \text{ to } n_{max} \qquad \text{(A-12)}$$

A program for the solution of Eqs. (A-11) is given in Figure A-1. The interpretations of several program variable are stated in Table A-1. Initial-boundary conditions are stored on files, (see program statement 1242). The values of $U_{s,n}$ and $D_{s,n}$ computed during the run are also stored on files, (see program statement 1320). Solution of the recurrence equations is carried out between statements 1372 and 2220. An output file, (see statement 2050) consists of exponentiated u-values at a fixed value of n(orλ) over a range of s(or y) values.

At the starting value of the interger n, the change in the variable $U_{s,n}$ with s is calculated over the range of s-values and subsequently stored. The value of u is increased by unity and the computations are repeated. The final computed values of $U_{s,n}$ and $D_{s,n}$ are stored in file format, to be used as input values when the program is run again.

Note that in this version of the program only two steps in n are utilized due to computer storage limitations, i.e., N 9=2. To go beyond two steps requires program changes in the arguments of statement numbers 2140 and 3600.

TABLE A-1 - SIGNIFICANT PROGRAM VARIABLES

Computer Program Variable	Mathematical Equivalent
C	$\ln\left[\tau(\sigma_{L1}\phi_{L1} + \sigma_{U1}\phi_{U1})\right] + \ln A_1$
B	b_3/b_1
T	$\Delta\lambda$
L	Δy
M2	s_{max}
N9	n_{max}
M5	initial value of n
S1	s
N1,K	n
F	f
U(s1,K)	$U_{s,n}$
D(s1,K)	$D_{s,n}$
S	exp (U)/exp (C)
G3,G4	accuracy test variables

```
PHOTO5
1000 LONG U7,D7,S
1010 LONG D[1500,2],U[1500,2]
1020 LONG C,B,A,B4,T,L,M5,M2,G1,G2,F
1021 LONG F1
1030 DIM H$[8]
1031 DIM G$[8],F$[8]
1040 DIM U$[8],D$[8]
1050 DIM E$[8],W$[8]
1060 MAT D=ZER
1070 MAT U=ZER
1080 FILES *,*,*,*,*
1090 PRINT "INPUT BOUNDARY CONDITION C=?"
1100 INPUT C
1110 PRINT "INPUT PARAMETER B=?"
1120 INPUT B
1130 PRINT "TIME STEP T=? AND SPACE STEP L=?"
1140 INPUT T
1141 INPUT L
1150 PRINT "INPUT THE NUMBER OF STEPS IN L M2="
1160 INPUT M2
1170 PRINT "INPUT THE STARTING TIME STEP M5="
1180 INPUT M5
1185 PRINT
1186 PRINT "HOW MANY TIME STEPS N9?"
1187 INPUT N9
1190 C1=C
1200 B1=B
1210 T1=T
1220 L1=L
1230 M3=M5
1240 M4=M2
1242 PRINT "WHAT ARE THE INITIAL CONDITION FILE NAMES?"
1243 INPUT F$
1244 INPUT G$
1245 PRINT F$,G$
1246 ASSIGN F$,3,Y1
1248 ASSIGN G$,4,Y1
1250 PRINT "BOUNDARY CONDITION C=";C1
1260 PRINT " PARAMETER IN DIFF. EQ. B=";B1
1270 PRINT "TIME STEP T=";T1
1280 PRINT "SPACE STEP L=";L1
1290 PRINT "STARTING TIME STEP M5=";M3
1300 PRINT "NO. OF SPACE STEPS M2=";M4
```

Fig. A-1 Computer Program for the Solution of the Recurrence Formulas of Eq. (A-11) (1 of 3)

```
1301 PRINT
1302 PRINT " N9=";N9
1310 PRINT "START NEXT TIME STEP M5 = ";M5+N9
1311 PRINT
1320 PRINT " INPUT U$ AND D$ FILE NAMES"
1321 PRINT
1330 INPUT U$
1331 INPUT D$
1340 ASSIGN U$,1,Y1
1350 PRINT Y1;
1360 ASSIGN D$,2,Y1
1370 PRINT Y1;U$,D$
1371 PRINT
1372 FOR R7=1 TO N9
1380   Q9=0
1390   S1=1
1395   K=0
1400   FOR N1=1 TO M5+R7+1
1410     READ #3;F1
1412     IF K=2 THEN 1430
1415     IF N1<(M5+R7-2) THEN 1430
1417     K=K+1
1420     U[S1,K]=F1
1430   NEXT N1
1435   RESTORE #3
1440   FOR S1=1 TO (M2-1)
1450     READ #2;D7
1460     D[S1,1]=D7
1470   NEXT S1
1480   FOR S1=1 TO M2
1490     READ #1;U7
1500     U[S1,1]=U7
1510   NEXT S1
1520   K=1
1530   FOR S1=1 TO (M2-1)
1540     F=1+EXP(U[S1,K])
1550     F=(F*D[S1,K])+(B*EXP(U[S1,K]))+1
1560     F=-F
1570     D[S1,K+1]=D[S1,K]+F*T
1580     U[S1+1,K+1]=U[S1,K+1]+D[S1,K+1]*L
1590     G1=D[S1,K+1]-D[S1,K]
1600     G3=.0001
1610     IF G1>G3 THEN 1650
1620     G2=U[S1+1,K+1]-U[S1,K+1]
1630     G4=.0001
1640     IF G2<=G4 THEN 1690
1650     PRINT "ABOVE THRESHOLD"
1660     Q9=1
1670     PRINT C,B,T,L,M5,M2,S1
1680     S1=M2
1690   NEXT S1
1700   IF Q9=1 THEN 2220
1850   K=2
```

Fig. A-1 Computer Program for the Solution of the Recurrence Formulas of Eq. (A-11) (2 of 3)

```
1860   RESTORE #1
1870   RESTORE #2
1900   FOR J=1 TO M2
1910     A=U[J,K]
1920     PRINT #1;A
1930   NEXT J
1935   GOTO 3000
1940   FOR J=1 TO (M2-1)
1950     B4=D[J,K]
1960     PRINT #2;B4
1970   NEXT J
1980   PRINT #1;END
1990   PRINT #2;END
2000   RESTORE #1
2010   RESTORE #2
2040 NEXT R7
2050 PRINT "INPUT THE OUTPUT FILE NAME H$="
2060 INPUT H$
2061 PRINT
2070 CREATE Y1,H$,2,256
2080 IF Y1=0 THEN 2110
2090 PRINT " CAN'T OPEN THE H$ FILE"
2100 GOTO 2220
2110 ASSIGN H$,5,Y1
2120 PRINT Y1;H$
2130 FOR J=1 TO M2 STEP (M2/30)
2140   S=U[J,2]-C
2150   S=EXP(S)
2160   PRINT #5;S
2170   PRINT S
2180 NEXT J
2190 PRINT #5;END
2210 RESTORE #5
2215 PRINT #4;END
2220 END
3000 S1=M2
3100 FOR J=1 TO (M5+R7-2)
3200   READ #4;F1
3500 NEXT J
3600 F1=U[S1,2]
3700 PRINT #4;F1
3705 IF R7=N9 THEN 4000
3800 RESTORE #4
4000 GOTO 1940
```

Fig. A-1 Computer Program for the Solution of the Recurrence Formulas of Eq. (A-11) (3 of 3)

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4. TITLE (and Subtitle) ⑥ Partial Differential Rate Equations for a BiLevel Absorber, (12/1977)		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER RM 646
7. AUTHOR(s) ⑩ B. J. / Pernick		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Research Department, Grumman Aerospace Corporation Bethpage, New York 11714 ✓		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE ⑪ Dec [redacted] 77
		13. NUMBER OF PAGES 26 26 ⑫ 41p.
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. Key Words

20. Abstract

~~19. KEY WORDS~~ (Continue on reverse side if necessary and identify by block number)

The interaction of a directed beam of radiation with an absorber is described using a two level model; transmitted light intensities and level populations are treated as functions of temporal and spatial independent variables; and the general rate equations are given as partial differential equations. Additionally, combinations of material constants are identified as scale parameters

~~20. ABSTRACT (Continue on reverse side if necessary and identify by block number)~~

and used to express the rate equations in nondimensional form as a hyperbolic partial differential equation in cononical form. One integration yields a time-independent relationship between two transmitted beam intensities at different wavelengths. Also described are several calibration experiments to evaluate material parameters.

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