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Citation: *The Journal of Chemical Physics* **72**, 3686 (1980); doi: 10.1063/1.439579

View online: <http://dx.doi.org/10.1063/1.439579>

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Infrared multiphoton decomposition: A comparison of approximate models and exact solutions of the energy-grained master equation

John R. Barker

Chemical Kinetics Department, SRI International, Menlo Park, California 94025

(Received 4 October 1979; accepted 6 December 1979)

The approximate "thermal" model and "continuum" model have been compared to exact calculations, and neither gives satisfactory results. In particular, the thermal model is based on an inaccurate and unphysical approximation to the correct molecular density of states, as well as a restrictive expression for the absorption cross sections. As an alternative to the approximate models, the exact stochastic method gives exact results and can be implemented using small computers or programmable pocket calculators. The results obtained from this method are exact and precision depends only upon the number of "trajectories" calculated. It was discovered that the yield versus fluence results from exact numerical integration of the master equation approximately conform to a cumulative log-normal distribution function in decomposition time or fluence. Thus, to a good degree of approximation, computed yield versus fluence results can be expressed simply in terms of a mean and a dispersion parameter. This suggests that the use of probability graph paper and the log-normal distribution function may prove to be a useful means for the presentation and analysis of experimental and computed data. Moreover, deviation from the log-normal distribution may indicate that the simple master equation is not a sufficient description of the experimental results.

INTRODUCTION

Unimolecular reactions traditionally have been studied through the use of thermal activation, chemical activation, and photoactivation.¹ Infrared laser-induced multiple photon absorption offers still another method for investigating the rates and dynamics of such reactions, although this approach is not, as yet, sufficiently well characterized to be useful. For the analysis of unimolecular reaction systems, the energy-grained master equation method has proved to be very effective, and it is a natural extension to apply this method for the analysis of multiphoton activation.^{2,3} Recently, consideration has been given to the propriety and validity of using the master equation for multiphoton activation and it has become clear that it cannot be used under all circumstances,⁴⁻⁷ but it shows promise for many systems, and it may find considerable use. However, the important question of validity will not be addressed in this paper.

The purpose of this work is to compare several approximate solutions of the master equation in its simplest form. The approximate methods require various assumptions that may, or may not, be consistent with physical reality. Following a brief introduction to the energy-grained master equation (EGME), the approximate methods of Yablonovitch and co-workers,⁸ and that of Fuss,⁹ will be compared to exact solutions of the EGME obtained by numerical integration according to the Gear procedure.^{3,10,11} It will be shown that although the Yablonovitch "thermal" model was derived using a nonphysical and inaccurate expression for the density of states, compensating errors give rough agreement with the exact EGME when certain restrictive conditions are met. The Fuss model is shown to be more general in some of its assumptions, but it does not give good results for the case tested.

Following the discussion of the approximate methods, the exact stochastic algorithm developed by Gillespie¹²

is described, and its usefulness demonstrated. Since this method is both exact and completely general, its use is recommended in place of the approximate methods when restriction of computer memory or user inclination precludes use of exact numerical integration. In this regard, it should be pointed out that all of the results given here for the exact stochastic method were obtained using a programmable hand calculator (Texas Instruments, TI-59) and printer (PC 100A), illustrating the convenience and tractability of this method. Finally, procedures for comparisons with experimental data will be discussed briefly.

Energy-grained master equation (EGME) (Refs. 2-4)

The EGME is a coupled set of differential rate equations describing the rates of change of the numbers (or concentrations) of species with internal energy in the energy band E_i to $E_i + \Delta E$. The grain size (ΔE) can be defined arbitrarily, but it is often chosen on the basis of computing machine size or on the basis of convergence criteria (i.e., the solutions show no perceptible change when ΔE is reduced below some value). For infrared multiphoton activation, ΔE is usually chosen to equal the infrared photon quantum $\hbar\omega$; for a CO₂ laser this quantum ranges from ~ 900 to 1000 cm^{-1} . For multiphoton activation under collision-free conditions, the differential equation describing the rate of change of population N_i in level i is

$$\frac{dN_i}{dt} = C_{i-1}^a N_{i-1} + C_i^e N_{i+1} - (C_i^a + C_{i-1}^e) N_i - k_i N_i, \quad (1)$$

where C_i^a is the effective first-order rate constant for absorption from level i to $i+1$, and C_i^e is the effective first-order rate constant for stimulated emission from level $i+1$ to i . Thus,

$$C_i^a = \sigma_i I / \hbar\omega, \quad (2a)$$

$$C_i^e / C_i^a = g_i / g_{i+1}, \quad (2b)$$

where σ_i is the absorption cross section for the i to $i+1$ transition, I is the laser intensity, $\hbar\omega$ is the photon energy, and g_i is the number of states with energies within the laser linewidth δE centered at energy $i\hbar\omega$ (degeneracy of level i):

$$g_i = \int_{E_{i-1}/2\delta E}^{E_{i+1}/2\delta E} \rho(E) dE. \quad (3)$$

For narrow laser lines, g_i is simply proportional to the density of vibrational states at energy E_i , $\rho(E_i)$, and the ratio of state degeneracies equals the ratio of the densities of states:

$$g_i/g_{i+1} = \rho(E_i)/\rho(E_{i+1}). \quad (4)$$

The specific rate constant for unimolecular decomposition k_i can be calculated using RRKM theory¹ or can be approximated by methods such as quantum RRK theory.^{1,13}

As written, the EGME includes only single photon incoherent interactions, but a more complete description would include coherent multiple photon transitions and inhomogeneous effects.⁴⁻⁷ These effects will not be included here, but they could be accommodated by the exact stochastic method and not by either of the approximate models. It is important to note that deviation of experimental data from the predictions of the EGME reflect the fact that the EGME is an oversimplified description of the phenomenon.

"Thermal" model

In this approach,⁸ suitable functional forms for σ_i , g_i , and k_i are substituted into Eqs. (1) and (2), and the master equation assumes a form that has a simple closed solution for the populations of the various energy levels. Yablonoitch and co-workers⁸ noted that the decomposition reaction merely acts as a perturbation to the population distribution, if the extent of decomposition is small, and thus they neglected k_i . They also assumed that g_i is of a mathematical form similar to that in QRRK theory, thus giving a simple expression for the ratios g_i/g_{i+1} . Unfortunately, although the functional form of QRRK theory was adopted, the improper usage of that functional form leads to gross errors in g_i , as will be discussed below.

The third approximation made is a special assumption concerning the absorption cross section σ_i . For the purpose of solving the master equation, it was assumed that a "net" cross section σ_e remains constant, regardless of the internal energy in the molecule:

$$\sigma_e = \text{const} = \sigma_i - (g_{i-1}/g_i) \sigma_{i-1}. \quad (5)$$

By inductive reasoning, it can be shown that

$$\sigma_i = \sigma_e \left(1 + \frac{1}{g_i} \sum_{k=0}^{i-1} g_k \right). \quad (6)$$

This functional form for σ_i displays an *increase* in σ_i with increasing internal energy in the molecule. Although this functional dependence is not implausible, the authors acknowledge that it is unrealistic for SF₆ (Ref. 8); it also has been shown to be inappropriate for other species^{2,3} and appears to contradict theoretical

considerations.^{4(a),4(b)} Thus, although Eq. (5) may be appropriate for some molecules, for many cases it is inappropriate, and the "thermal" model will fail.

Although the restrictive assumption concerning σ_i severely limits the usefulness of the model, the most troubling feature is the misuse of QRRK theory. According to normal usage of QRRK theory,^{1,13,14} the vibrational state density of a molecule can be approximated by assuming that all of the molecular vibrations have the same frequency $\langle\nu\rangle$, defined as the geometric mean frequency of all modes.¹⁴ The usual combinatorial analysis then gives the state degeneracy for energies corresponding to each multiple (n) of this average frequency $\langle\nu\rangle$:

$$g_n = \frac{(n+s-1)!}{n!(s-1)!} = \frac{\Gamma(n+s)}{\Gamma(n+1)\Gamma(s)}, \quad (7)$$

where s is the number of vibrational modes; the gamma function expression is a useful interpolation formula for noninteger values of n . The important point here is that *the molecular geometric mean frequency $\langle\nu\rangle$ is not the same as the laser frequency ν_1 and substitution of ν_1 for $\langle\nu\rangle$ usually gives grossly inaccurate values for g_n* . For internal energies corresponding to i laser quanta, the correct expression for the QRRK density of states is

$$\rho(E_n) = \frac{g_n}{\langle\nu\rangle} = \frac{1}{\langle\nu\rangle} \frac{\Gamma(n+s)}{\Gamma(n+1)\Gamma(s)}, \quad (8a)$$

where

$$n = i\nu_1/\langle\nu\rangle. \quad (8b)$$

Note that Eq. (8b) explicitly takes cognizance of the difference between the average molecular quantum and that of a laser photon.

For the purpose of solving the master equation in closed form, Yablonoitch and co-workers did not use Eq. (8), but instead used Eq. (7), substituting i for n :

$$g_i = \frac{(i+s-1)!}{i!(s-1)!}. \quad (9)$$

Note that the only molecular parameter appearing in Eq. (9) is s , the number of oscillators. Thus, molecules with vastly different molecular frequencies are assumed to have identical densities of states (e.g., CH₄ and Cl₄), a nonphysical result. Moreover, if the laser frequency is changed, a different number of laser photons will correspond to the same molecular internal energy (e.g., CO₂ laser vs HF laser); according to Eq. (9), the density of states of the molecule will have altered at a given internal energy—a nonphysical result. These comments are intended to illustrate the nonphysical consequences of the improper use of the QRRK theory. Quantitatively, comparisons have been made for CF₃I. The error in the density of states for CF₃I is shown in Fig. 1 for 1070 cm⁻¹ laser photons (the molecular geometric mean quantum energy is 569 cm⁻¹, similar to that of SF₆). Note that the ordinate is logarithmic and that the density of states according to Eq. (8) is relatively accurate, but Eq. (9) diverges systematically from the exact density of states and is in error by a factor of ~300 at the reaction threshold. Because only the ratios g_i/g_{i-1} are important, however, the effect of this

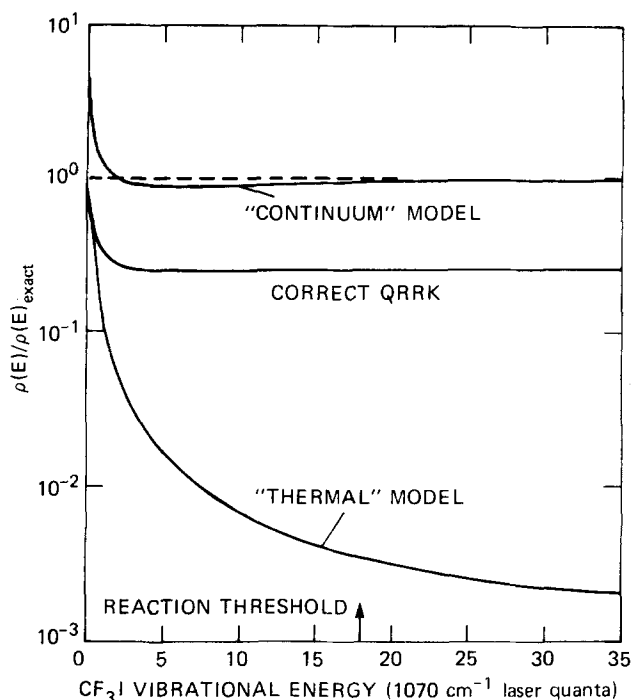


FIG. 1. Comparison of approximate expressions for the vibrational density of states as functions of the internal energy of CF_3I .

poor approximation is moderated, as discussed below.

When the approximations and assumptions described above are incorporated into Eq. (1), the result is

$$\frac{dN_i}{dt} = \frac{AI}{s} (i+s-1) N_{i-1} + \frac{AI}{s} (i+1) N_{i+1} - \frac{AI}{s} (2i+s) N_i, \quad (10)$$

where the constant A is proportional to σ_e . This set of equations can be solved^{8,18} in closed form to give a population distribution formally similar to the thermal distribution

$$W_i = \frac{1}{Z} \exp(-i\beta\hbar\omega) \frac{(i+s-1)!}{i!(s-1)!}, \quad (11a)$$

$$Z = [1 - \exp(-\beta\hbar\omega)]^{-s}, \quad (11b)$$

and the parameter β is given by the energy conservation equation

$$\frac{s\hbar\omega}{\exp(\beta\hbar\omega) - 1} = \sigma_e \int_0^t I dt = \sigma_e \phi, \quad (11c)$$

where ϕ is the "fluence": total energy per cm^2 incident on the molecule. Note that in Eq. (11c), $d\phi$ can be substituted for $I dt$ if the rate constants k_i are neglected.

In Eq. (11a), Z plays the role of a partition function and the combinatorial factor is the state degeneracy. If the state degeneracies in Z and in the combinatorial factor are both in error by the same multiplicative factor, the errors cancel and Eq. (11) gives a fair approximation to the correct solution despite the improper use of QRRK theory. Reference to Fig. 1 shows this cancellation of errors is never perfect, but will be most complete for low values of β (high "temperatures") and high values of i . For high β and/or low values of i , cancellation is not

complete and Eq. (11) becomes a poor approximation. Thus, the acceptable range of validity is for "low" extents of decomposition [because of neglect of effects due to the k_i term in Eq. (1)], but not "too low" (because of improper use of QRRK theory). Calculations of average number of photons absorbed (i.e., average excitation energy of the ensemble) will be inaccurate at low levels of excitation and at high levels, but may be tolerably accurate at intermediate degrees of excitation. Unfortunately, the range of tolerable accuracy is not readily assessed. In Fig. 2, the fraction of CF_3I molecules above the decomposition threshold according to Eq. (11) is compared to the solution obtained using the exact stochastic method (see below) that incorporated the Whitten-Rabinovitch¹⁶ density of states and used an approximate form of Eq. (6) in which only the first term of the summation was retained. At high fluences, Eq. (11) breaks down, but for yields less than 10%, it gives a good approximation to the exact results.

After this paper was submitted, a letter appeared in which the thermal model was considered from a more formal and general point of view. The authors came to conclusions similar to those discussed here.¹⁷

During the past several years, the thermal model has served a useful purpose in exploring some of the dynamical features of multiple photon excitation, and it has generated much interest, but for calculational purposes, better methods are available. Considering the unphysical approximations and assumptions inherent in this model and the consequently uncertain ranges of validity for different molecules and fluences, it is recommended that the exact stochastic method¹² (described below) be used for small-scale calculations and that exact numerical integration be used when necessary.

Continuum model

The model developed by Fuss⁹ may be termed a "continuum" model, because it is developed using continuum functions and the idea of discrete levels is abandoned. This is analogous to the classical RRK theory as contrasted with the "thermal" model which employed the quantum RRK approach. Retaining, for the moment,

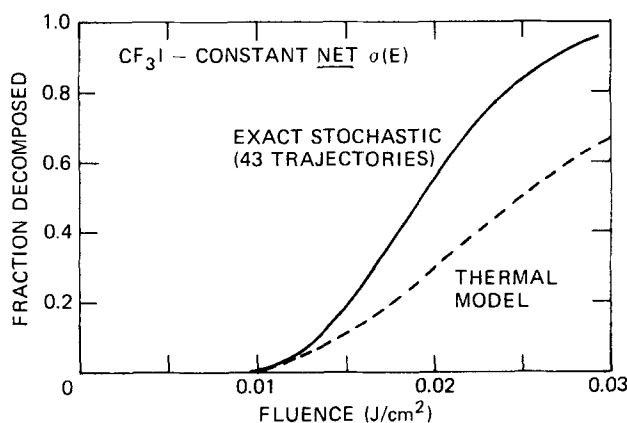


FIG. 2. Thermal model results for yield versus fluence compared to exact results.

discrete levels and neglecting the rate constants k_i , as in the thermal model, Eq. (1) can be written

$$\frac{dN_i}{dt} = -\frac{I\sigma_i}{\hbar\omega} \left(N_i - \frac{g_i}{g_{i+1}} N_{i+1} \right) + \frac{i\sigma_{i-1}}{\hbar\omega} \left(N_{i-1} - \frac{g_{i-1}}{g_i} N_i \right). \quad (12)$$

Defining $n_i = N_i/g_i$ and $d\phi = I dt$, Eq. (12) can be written

$$\frac{d(g_i n_i)}{d\phi} = -\frac{g_i \sigma_i}{\hbar\omega} (n_i - n_{i+1}) + \frac{g_{i-1} \sigma_{i-1}}{\hbar\omega} (n_{i-1} - n_i). \quad (13)$$

If expressed as a difference equation, Eq. (13) takes the form

$$\frac{dn_i}{d\phi} = \frac{1}{g_i} \Delta \left(g_{i-1} \frac{\sigma_{i-1}}{\hbar\omega} \Delta n_{i-1} \right), \quad (14)$$

where Δ is defined by $\Delta n_i = n_{i+1} - n_i$. At this point, the difference equation is written as the corresponding partial differential equation for continuous functions and the idea of discrete levels is abandoned:

$$\frac{\partial n_\epsilon}{\partial \phi} = \frac{1}{g_\epsilon} \frac{\partial}{\partial \epsilon} \left(g_\epsilon \frac{\sigma_\epsilon}{\hbar\omega} \frac{\partial n_\epsilon}{\partial \epsilon} \right), \quad (15)$$

where ϵ is a continuous variable identifiable with level index i . As Fuss clearly points out, "replacement of differentials is justified only for $\epsilon \gg 1$; that is, for high excitation."

In the continuum model, σ_ϵ and g_ϵ can be defined in relatively general ways:

$$\sigma_\epsilon = \sigma_0(\epsilon + c)^\alpha, \quad (16)$$

$$g_\epsilon = g_0(\epsilon + c)^{s-1}, \quad (17)$$

where $\alpha < 2$ gives a solution of Eq. (15). Note that if $c = aE_\epsilon/\hbar\omega$, g_ϵ assumes the Whitten-Rabinovitch form, which is relatively accurate, especially for $\epsilon \gg 1$, as illustrated in Fig. 1.

Using Eqs. (16) and (17) and employing the proper boundary conditions, Fuss⁹ shows that the fraction of molecules with energies in excess of reaction threshold ϵ_d is given by

$$P = \frac{\beta'}{\Gamma(ms)} \frac{1}{\epsilon_0^s} \int_{\epsilon_d}^{\infty} \epsilon'^{s-1} \exp\left(-\frac{\epsilon'^{\beta'}}{\epsilon_0^{\beta'}}\right) d\epsilon', \quad (18)$$

where

$$\beta' = 2 - \alpha, \quad m = 1/\beta', \quad \epsilon_0 = (\beta'^2 \sigma_0 \phi)^m.$$

For integer values of ms , Eq. (18) can be integrated in closed form to give

$$P = \exp\left(-\frac{\phi_0}{\phi}\right) \left[1 + \frac{1}{1!} \left(\frac{\phi_0}{\phi}\right) + \frac{1}{2!} \left(\frac{\phi_0}{\phi}\right)^2 + \cdots + \frac{1}{(ms-1)!} \left(\frac{\phi_0}{\phi}\right)^{ms-1} \right], \quad (19)$$

where $\phi_0 = \epsilon_d^{\beta'}/(\beta'^2 \sigma_0)$. This model results in a set of "universal" curves that can be used for data analysis, or, given appropriate input parameters, predictions can be made.

For the purpose of comparing Eqs. (18) or (19) with the results of an exact numerical integration of the master equation, the constant c in Eqs. (16) and (17) was chosen to correspond to the Whitten-Rabinovitch approximation⁸ and, in the exact calculation, exact densi-

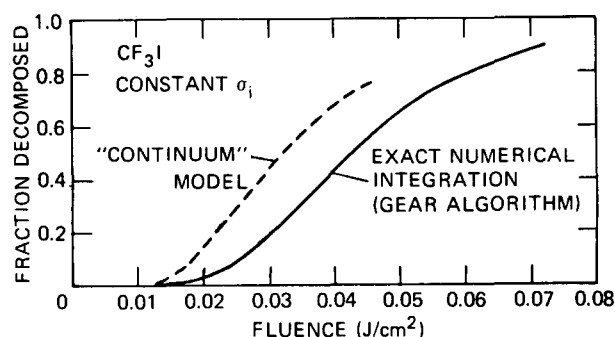


FIG. 3. Continuum model results for yield versus fluence compared to exact results.

ties of states were used. Specifically, for CF_3I ,

$$c = \frac{aE_\epsilon}{\hbar\omega} = \frac{(0.96)(3038 \text{ cm}^{-1})}{1070 \text{ cm}^{-1}},$$

where the Whitten-Rabinovitch parameter (a) was chosen for the reaction threshold. The resulting density of states is a good approximation and is shown in Fig. 1. The absorption cross section was assumed to be constant ($\alpha = 0$):

$$\sigma = 1.6 \times 10^{-17} \text{ cm}^2.$$

The reaction threshold was assumed to be 18462 cm^{-1} , giving $\phi_0 = 3.67 \times 10^{19} \text{ photons/cm}^2$.

Calculations were made for simulated laser pulses of constant intensity ($I/\hbar\omega = 4.67 \times 10^{26} \text{ photons/cm}^2 \text{ sec}$) and variable duration, and the resulting fraction of molecules dissociated after pulses of different fluence are presented in Fig. 3. The exact numerical integration was performed using the Gear algorithm.¹¹ Note that in the exact calculation, rate constants k_i were not neglected, but were obtained from RRKM theory.¹

Inspection of Fig. 3 shows that the continuum model consistently predicts too much dissociation. Moreover, the shapes of the exact curve is not well reproduced by the model, since neither a constant displacement nor a proportional shift of the fluence scale will superimpose the two. It is interesting to note that the thermal model, for its narrowly defined conditions, appears to give better results than the continuum model.

Note that in the continuum model, the parameter s has significance only when the parameter c [Eq. (17)] is chosen as above to give a good approximation for the density of states; if $c = 0$, s must vary to compensate for the consequent poor approximation for g_ϵ and loses any quantitative significance, although s may be employed as a curve-fitting parameter. This result is familiar from classical RRK theory¹ and has been misinterpreted in Ref. 7.

The reason for the discrepancy between the exact calculation results and those of the continuum model probably lies in replacing differences by differentials in Eq. (14). In the continuum model, g_ϵ is a good approximation and σ is identical to that used in the exact calculation, thus neither of these functions can be the cause of the discrepancies observed. Although the specific rate

constants for decomposition have been neglected in the continuum model, they represent only a minor perturbation for extents of decomposition less than 10%. Thus, the replacement of differences by differentials is probably the cause of the discrepancy.

In conclusion, it is clear that the continuum model is not satisfactory and it is recommended that either the exact stochastic method described below or exact integration of the coupled equations be used instead, if accurate results are desired.

EXACT STOCHASTIC METHOD

Unlike the two approximate solutions of the master equation that were presented above, the stochastic method developed by Gillespie¹² gives an exact solution for the complete set of equations. This exact stochastic method bears the same relationship to numerical solutions of the master equation as Monte Carlo integration does to numerical integration of the equations of motion for an ensemble of molecules. Thus, results can be obtained with any desired degree of precision merely by increasing the number of "trajectories" calculated, where the "trajectories" are Markovian random walks over the energy levels of the molecule. Although this may be a time-consuming procedure for some problems, there are also some advantages, as discussed (along with the disadvantages) by Gillespie.¹² For present purposes, the primary advantages are (i) the method is *exact*; (ii) the stochastic simulation program occupies very little computer memory; and (iii) the method is easy to program on a programmable calculator or small computer. Thus, stochastic simulations are feasible for fairly large problems even when major computer facilities are not available. Since many research groups have small computers that are not large enough to accommodate codes for exact numerical integration of the master equation, the exact stochastic method of Gillespie is a "happy" alternative. It should be pointed out again, that all of the results presented in this paper were calculated on the TI-59 programmable pocket calculator.

For a full description of the exact stochastic method, including a computing flow diagram, the lucid discussion by Gillespie^{12(b)} should be consulted, but the essential features will be outlined here, specifically for multiphoton excitation and dissociation.

Consider a molecule in a laser field. This molecule has available three "reaction channels": stimulated absorption and stimulated emission of a photon, and irreversible decomposition to form products. The basic idea of the stochastic method is to define a joint probability function that is the product of two terms: one term is the probability that a molecule in a particular state at time t will not undergo reaction during the next time interval τ ; the second term is the probability that a reaction will occur by way of reaction channel λ in the time interval $t + \tau$ to $t + \tau + d\tau$. Gillespie shows that this joint probability density function is given by

$$P(\tau, \lambda) = \begin{cases} a_\lambda \exp(-a_0 \tau), & 0 \leq \tau \leq \infty, \quad \lambda = 1, 2, 3, \\ 0, & \text{otherwise,} \end{cases} \quad (20)$$

where $a_0 \equiv \sum_{j=1}^3 a_j$, for the three channels. For the present application, the probability density a_λ is equal to the effective first-order rate constants for absorption, stimulated emission, and decomposition, as expressed in Eq. (1).

To make use of these ideas, two random numbers (r_1 and r_2) are selected from the unit-interval uniform distribution. Given the molecule in some particular state i at time t , a random time interval τ is generated and the next "reaction" will occur at time $t + \tau$:

$$\tau = (1/a_0) \ln(1/r_1), \quad (21)$$

and the time is increased to $(t + \tau)$. The reaction channel λ is selected through use of the second random number by taking λ to be that integer for which

$$\sum_{\mu=1}^{\lambda-1} a_\mu < r_2 a_0 \leq \sum_{\mu=1}^{\lambda} a_\mu. \quad (22)$$

Depending upon λ , i is changed by $+1$ or -1 (absorption or stimulated emission), or decomposition to form products will have taken place, at which time the "trajectory" is stopped. As outlined in detail by Gillespie, for each trajectory this procedure is repeated until decomposition has taken place. At each step, provision may be made to print out n , the number of iterations, t , the reaction time elapsed, and i , the energy level of the molecule. For the multiphoton case, knowledge of t and the intensity gives the fluence and i gives the net number of photons absorbed at time t . For the calculations reported here, all "trajectories" were started from the zero energy level.

By repeating this procedure for many "trajectories" an ensemble average is constructed, from which average population distributions and average net numbers of photons absorbed $\langle n \rangle$ can be obtained to any degree of accuracy desired, merely by increasing the number of trajectories computed. As will be shown below, values for $\langle n \rangle$ and relative yield as a function of fluence can be obtained with good precision, using relatively few trajectories. More detailed information, such as population distributions as functions of time or fluence, require many more trajectories for reasonable results. Since $\langle n \rangle$ and yield versus fluence simulations may be generated using relatively few trajectories, this is a convenient technique for performing exact calculations with little computing power.

To facilitate the use of the stochastic method, it helps to have some idea of the distribution of decomposition times t_d for molecules exposed to a constant intensity. By examining the exact integration results, it was observed that the ensemble distribution of decomposition times is surprisingly well represented by a log-normal distribution function

$$P(x) = [t_d \sigma_t (2\pi)^{1/2}]^{-1} \exp[-(x - \mu_t)^2 / 2\sigma_t^2], \quad (23)$$

where $x = \ln t_d$. The fraction of molecules decomposed $F(t)$ in the time interval 0 to t is

$$F(t) = \int_0^t P(t_d) dt_d \quad (24)$$

where $F(t)$ is the cumulative distribution function¹⁸ corresponding to Eq. (23). These distributions are char-

acterized by an average μ_t and a dispersion parameter σ_t , which can be approximated very simply by tabulating the logarithms of the decomposition times for a number of trajectories and calculating the average and the standard deviation, which may be identified with μ_t and σ_t , respectively.

Although it is not obvious why such a distribution function works so well, it is a very convenient result, since many pocket calculators can be programmed to compute $P(x)$ and $Q(x)$; indeed, the TI-59 is internally programmed to compute these functions. Not only is this result convenient for use with the exact stochastic method, but it may prove to be a powerful method for presenting and analyzing real experimental data, as briefly discussed below.

"Fluence" may be substituted for "time" in the preceding discussion, since the dissociation yield depends almost exclusively on fluence, rather than intensity. Thus, as long as the order of the intensity in the EGME is unity, Eqs. (23) and (24) may be used with fluence rather than with time, to an excellent approximation.

Quantitative demonstrations of the suitability of Eqs. (23) and (24) are presented in Figs. 4 and 5 in which "probability" graph paper has been employed.¹⁸ On probability paper, a plot of the cumulative normal distribution yields a straight line. The relative yield versus $\ln t$ data calculated by the Gear numerical integration method give nearly straight lines, regardless of the power dependence of the absorption cross section, for the two model calculations that will now be described.

The model calculations were performed for CF_3I , using densities of states from the Whitten-Rabinovitch approximation, and decomposition rate constants k_i from QRRK theory according to the equation

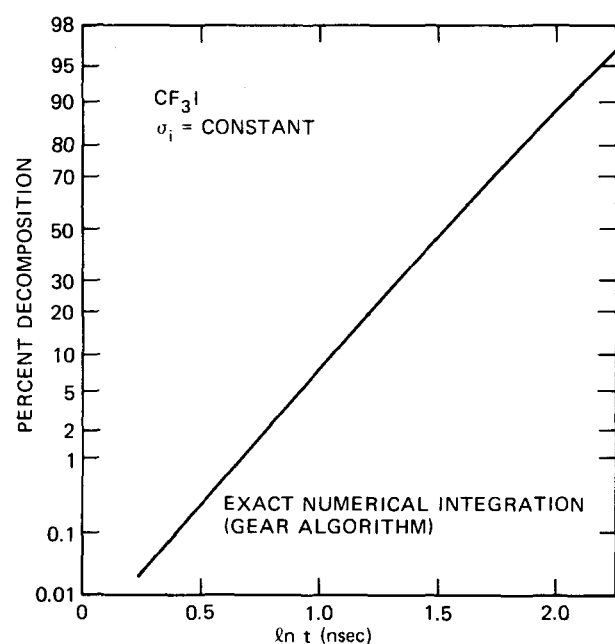


FIG. 4. Constant absorption cross section results for yield versus time plotted on probability graph paper in terms of $\ln t$.

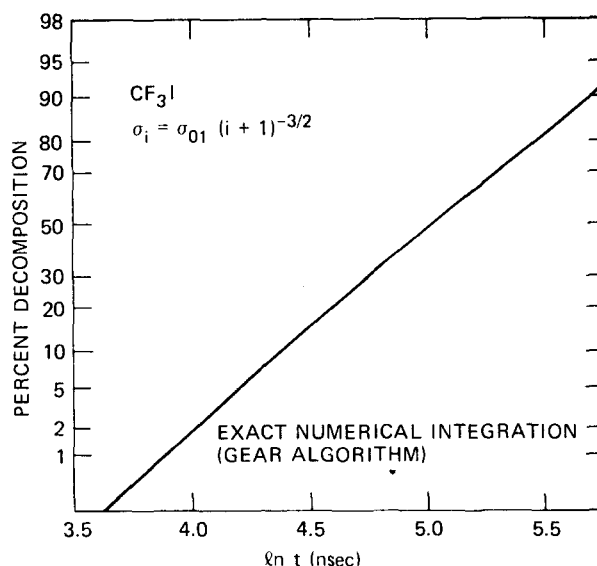


FIG. 5. Variable absorption cross section results for yield versus time plotted on probability graph paper in terms of $\ln t$.

$$k(E_i) = A \frac{\Gamma(n+1) \Gamma(n-m+s)}{\Gamma(n-m+1) \Gamma(n+s)}, \quad (25)$$

where A is the preexponential factor of the high-pressure unimolecular rate constant ($3.16 \times 10^{15} \text{ sec}^{-1}$), s is the number of oscillators (9), n is the number of molecular quanta (geometric mean frequency of the molecule) corresponding to i laser photons, and m is the number of molecular quanta corresponding to the reaction threshold. Specifically, for CF_3I

$$n = i(1070 \text{ cm}^{-1}/569.4 \text{ cm}^{-1}),$$

$$m = (18642 \text{ cm}^{-1}/569.4 \text{ cm}^{-1}).$$

(Note that the use of gamma functions rather than factorials permits use of the QRRK theory over a continuous range of excitation energies and for any reaction threshold energy.) These choices for densities of states and specific decomposition rate constants were governed by a desire for simplicity as well as accuracy. Exact counts of states and RRKM theory could have been used, but would not have affected the results in a substantial way. The Whitten-Rabinovitch approximation was accurate to within 20% of the exact density of states¹⁹ at $i=1$ and it was accurate to within 1% at the reaction threshold. The QRRK rate constants agreed with RRKM theory to within a factor of 3 at all energies; the discrepancy was mainly caused by a shift in the critical energy for reaction predicted by RRKM theory, due the Waage-Rabinovitch centrifugal correction,¹ which was not applied to the QRRK rate constants. Considering the uncertainties in the reaction threshold and A factor for this reaction, QRRK theory is a suitable approximation. These approximate methods are to be recommended for routine calculations.

The absorption cross section for the 0-1 transition was assumed to be $1.63 \times 10^{-17} \text{ cm}^2$ and the constant laser intensity (flux) was $4.673 \times 10^{26} \text{ photons cm}^{-2} \text{ sec}^{-1}$ for 1070 cm^{-1} photons. This corresponds a fluence of 1 J/cm^2 for a 100 nsec pulse.

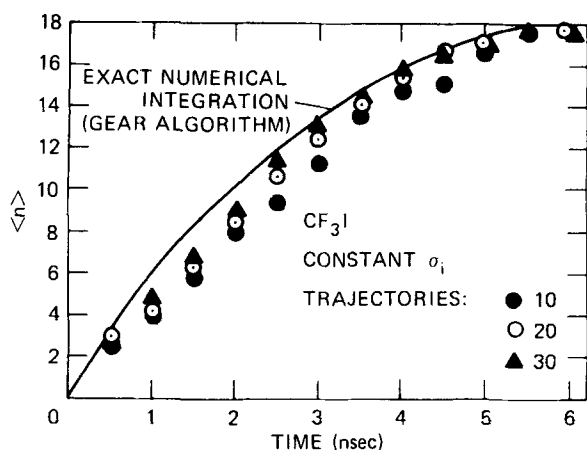


FIG. 6. Constant absorption cross section results for average number of photons absorbed as a function of time.

Calculations were performed for two different test cases: constant absorption cross section (as in the comparison with the continuum model) and cross section that decreased with internal molecular excitation:

$$\sigma_i = \sigma_{0-1}(i+1)^{-3/2}. \quad (26)$$

The second test case happens to give fair agreement with experimental data recently obtained in this laboratory.⁵ Calculations were performed in two modes. In the first mode, every step of each trajectory was recorded and from these data the average net numbers of photons absorbed during the course of the laser pulse were calculated. Thus, these calculations correspond to the time history of $\langle n \rangle$ during the laser pulse. In the second mode, only the times (fluences) at which the molecules decomposed were recorded, and from this data, relative yield as a function of time (fluence) was obtained.

In Fig. 6 is presented the average number of photons absorbed as a function of time for constant absorption cross section. The reaction threshold is in the vicinity of $i = 18$ and $\langle n \rangle = 18$ at ~ 5.4 nsec. According to Fig. 7, 65% of the molecules have already dissociated at this

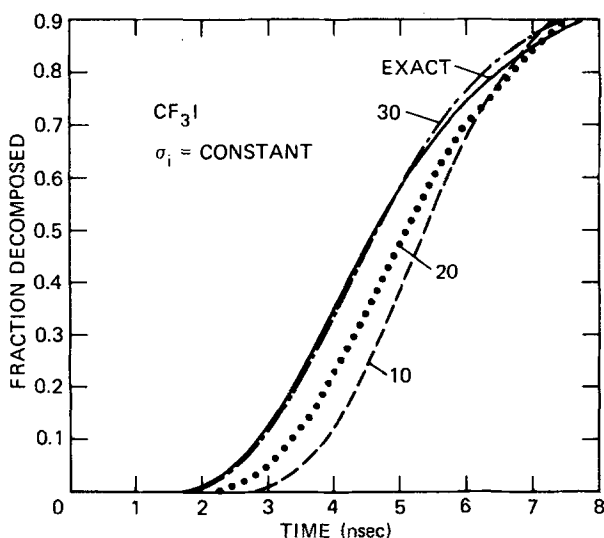


FIG. 7. Constant absorption cross section results for yield versus time.

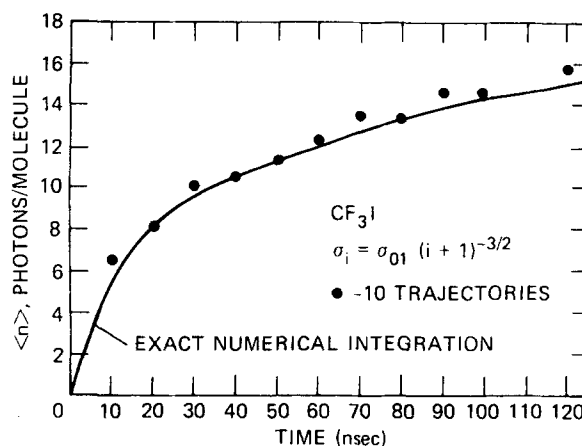


FIG. 8. Variable absorption cross section results for average number of photons absorbed as a function of time.

time, reflecting the asymmetry of the population distribution.

These figures show that the exact stochastic method gives good agreement with the exact results, when enough trajectories are utilized. Based upon the results obtained in this study, it seems that a minimum of 30 trajectories is necessary for moderate accuracy, but the actual number of trajectories necessary depends upon the accuracy desired and upon the actual history of the sequence of random numbers used. As an aid in estimating the accuracy of the stochastic method, one can assume that the errors in μ_t and σ_t decrease linearly with $j^{-1/2}$, where j is the number of trajectories computed. A plot of μ_t or σ_t vs $j^{-1/2}$ often gives a straight line whose intercept at $j^{-1/2} = 0$ can serve as an estimate for the asymptotic value for μ_t and σ_t . This method must be used with caution, however, since fluctuations can lead to incorrect extrapolated values.

As an example of typical behavior, values for μ_t and σ_t for different total numbers of trajectories are presented in Table I along with the parameters characterizing the exact integration results. For 30 trajectories, μ_t and σ_t are close to the exact values, demonstrating satisfactory convergence. But caution should be observed, since a simple linear regression analysis of μ_t vs $j^{-1/2}$ gives an asymptotic limit $(\mu_t)_\infty = 1.364$, in very poor agreement with the exact results. If the correct answer had not been known, more trajectories would have been calculated to insure that fluctuations did not substantially affect the asymptotic values for μ_t and σ_t .

For the second demonstration of the exact stochastic method, the absorption cross section was assumed to decrease with internal energy according to Eq. (26). The results are presented in Figs. 8 and 9 and in Table

TABLE I. Distribution function parameters for exact stochastic method—constant absorption cross section results.

Trajectories	μ_t	σ_t
10	1.676	0.250
20	1.626	0.318
30	1.527	0.366
Numerical integration:	1.53	0.40

II. Again, the distribution function expressed by Eq. (24) gives an excellent representation of the calculated results. This time, however, fewer trajectories were necessary for convergence to the numerical integration results. For a complete treatment, more trajectories could be computed and the asymptotic behavior tested as described above.

Other calculations²⁰ have been performed using the exact stochastic method, and the two example cases given here appear to be representative. No pathological behavior has been observed, in complete agreement with Gillespie's discussion.

COMPARISONS TO EXPERIMENTAL DATA

Although it is not the purpose of the present work to compare EGME calculations with experimental data, it is worthwhile discussing how such comparisons might be made and what might be learned from them. Several examples of such comparisons have already been mentioned in the text.^{2,3}

For a proper comparison with calculated results, the experimental data must be corrected for the spatial intensity distribution of the laser beam, or, conversely, the calculated results must be properly convoluted with the intensity profile. This step is essential because the calculations are generally performed for a laser beam of uniform intensity, whereas experiments generally employ lasers with beams that are of high intensity at the center, tailing off on the wings. For Gaussian beams, the ingenious method described in Ref. 8(b) can be used for this purpose.

For simulation of the experiment, any method for exact solutions of the master equation is suitable, including the Gear integration procedure or Gillespie's exact stochastic method. Work in our group is currently underway²¹ to test the generality of the log-normal distribution function for the systematic presentation of the computed results. For a wide range of parameters encompassing practically all reasonable values for absorption cross sections, densities of states, reaction thresholds, and functional behavior of unimolecular rate

TABLE II. Distribution function parameters for exact stochastic method—variable absorption cross section results.

Trajectories	μ_t	σ_t
10	4.906	0.480
20	4.980	0.531
30	4.883	0.516
40	4.956	0.504
Numerical integration:	5.01	0.51

constants, the log-normal distribution appears to give a good representation of results calculated using the EGME.

When complete, this study will be presented in detail, but it appears that the log-normal distribution provides a good baseline of expected behavior if the EGME is an appropriate description of the physical system. In this sense, it can be viewed in a way similar to the "prior" distribution in surprisal analysis.²² Deviation from the log-normal distribution may reflect inadequacies of the simple EGME. Such deficiencies can include the neglect of inhomogeneous effects, coherent multiphoton transitions, collisional energy transfer, slow intramolecular vibrational energy redistribution, etc. Many of these effects can be included in a more detailed master equation.⁴

Thus, it appears that the need for a more complex master equation can be identified without performing calculations. One must simply plot the experimental data (corrected for the spatial profile of the laser beam) according to the log-normal distribution; deviation from the distribution would indicate that the simple EGME is insufficient for simulating the experiment.

SUMMARY

In the preceding sections, two simple approaches to approximate solutions of the energy-grained master equations have been discussed. The "thermal" model of Yablonoitch and co-workers⁸ has been shown to be based on a poor approximation to the molecular density of states and on a restrictive function for the absorption cross section, and is of limited usefulness. The "continuum" model of Fuss⁹ does not give sufficiently accurate results.

In contrast to the approximate methods, the exact stochastic method of Gillespie¹² gives a solution that is exact to any desired accuracy and it can be programmed easily and run on a small computer or programmable calculator. Two example calculations were presented that demonstrate the utility of the Gillespie method. It is recommended that the exact stochastic method be used for "quick" calculations.

In the course of the analysis of the results of exact numerical calculations, it was discovered that simple log-normal distribution function in decomposition time or fluence gives an excellent fit to the computed results. This suggests that to a good approximation yield versus fluence results can be expressed simply in terms of a

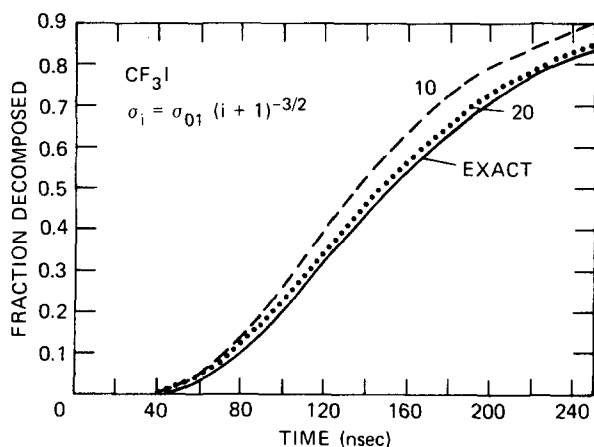


FIG. 9. Variable absorption cross section results for yield vs time.

mean and a dispersion parameter. For the computer results, presentation on "probability" graph paper is useful, suggesting that similar presentations of experimental data may also prove to be instructive in deciding when the simple EGME is an appropriate description of the phenomenon.

ACKNOWLEDGMENTS

Thanks go to AFOSR for financial support through Contract No. F49620-78C-0107. Stimulating conversations with D. M. Golden, M. Rossi, and A. C. Baldwin are gratefully acknowledged. Additional thanks go to A. C. Baldwin for running the exact numerical integration computer program.

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