gas-phase value in order to ascertain the effect of matrix solvation on the vibrational potential function. Gas-phase data, of course, are not presently available. Observation of possible krypton matrix counterparts in a krypton resonance photoionization experiment at 1660 and 1655 cm^{-1} ($A = 0.01$) does, however, provide some information. For the carbocations CF_3^+ and $CHBr_2^+$, the argon–krypton matrix differences of 5–10 cm^{-1} are only slightly larger than the argon–krypton matrix differences of 3–4 cm^{-1} for the CF_3 and $CHBr_2$ free radicals.[1,12,13] This suggests that the gas–argon difference should be on the order of 10 cm^{-1} for ions like CF_3^+ and $CHBr_2^+$. Some support for this argument is found in the gas-phase measurement of ν_1 and ν_3 for the CF_3 radical at 1090 and 1259 ± 2 cm^{-1}, respectively,[14] only 3–8 cm^{-1} above the argon matrix values and 6–11 cm^{-1} above the krypton matrix values,[12] and in the molecule isoelectronic with CF_3^+, namely, BF_3, which exhibits boron isotopic ν_3 fundamentals in the gas phase only 7 cm^{-1} above the argon matrix values.[11,15] This leads to a prediction that ν_3 of CF_3^+ will absorb near 1675 ± 10 cm^{-1} in the gas phase.

(12) Andrews, L.; Keelan, B. W., unpublished results, 1979. ν_1 and ν_3 of CF_3 in solid krypton at 1084 and 1248 ± 1 cm^{-1}.
(13) Andrews, L.; Prochaska, F. T.; Ault, B. S. *J. Am. Chem. Soc.* 1979, *101*, 9.
(14) Carlson, G. L.; Pimentel, G. C. *J. Chem. Phys.* 1966, *44*, 4053.

Conclusions

This study has developed an electric arc discharge technique for generating unstable ions and radicals for matrix isolation investigations. A comparison between the electric arc technique and argon resonance photolysis shows that, although the two methods are similar in most respects, the former has a greater range of intermediary products which it can produce. As a result of the ability of this new technique to produce higher yields of certain products under suitable conditons, the $\nu_1 + \nu_4$ combination band for $^{12}CF_3^+$ at 1624 cm^{-1} was identified for the first time.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation under Grant CHE 79-10966.

(15) Miller, J. H.; Andrews, L., unpublished results, 1978. ν_3 of $^{10}BF_3$ = 1498 cm^{-1} and ν_3 of $^{11}BF_3$ = 1447 cm^{-1} in solid argon from expanded scale spectra.

Better Estimates of Exponential Decay Parameters

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For simple exponential decay counting data collected in a finite number of channels, the maximum likelihood estimator (MLE) provides the simplest and, in an asymptotic sense, equal best (with least squares) estimator of the lifetime parameter. Both methods are more efficient, in a statistical sense, than the method of moments. The MLE algorithm is so simple it can be performed graphically or on a hand calculator. It could be hard-wired (ROM) into data collection units. *A minimization procedure is unnecessary.* We provide an expression for obtaining the optimal channel width (TAC range) for data collection.

Introduction

While chemists quickly adopt the most recent instrumental innovations for producing chemical data, the methods of analysis of that data have remained traditional and lack new statistical input.[1,2]

Standard parametric techniques were adopted and have remained unchallenged. As these methods become hard-wired into our calculators, there will be even less chance of having something better adopted. It is not generally realized that all of the standard methods of estimation (e.g., maximum likelihood and least squares) are ad hoc.[3] There are statistical theories which justify their use for large samples, but for small samples there are very few theoretical criteria for assessing estimators.

The reason for this is that in small samples the distribution of the estimators is usually not normal and then there may not be an agreed method of comparing them. In this paper we shall look at one particular model common to several areas of chemistry and the various methods of fitting data to it. The model is for a first-order process which follows an exponential decay law, be it in kinetics or in the area that we are particularly concerned with, single photon decay spectroscopy.

It is perhaps not fully appreciated that, where an experimenter wishes to estimate a parameter θ for a model for which he has data, he has in fact a choice. Suppose $\hat{\theta}_1, \hat{\theta}_2, ..., \hat{\theta}_n$ are different estimators which yield different numerical values. Which one is "best"? Sometimes the only way to give anything like a definite answer is to examine the asymptotic (i.e., large-sample) properties of the estimators. Thus, if n denotes the sample size and $n^{1/2}(\hat{\theta}_i - \theta)$ has a limiting normal $N(0,\sigma_i^2)$ distribution for $1 \le i \le n$, then $\hat{\theta}_i$ is "better" than $\hat{\theta}_j$ if $\sigma_i^2 < \sigma_j^2$. However, an estimator which performs "well" for large samples can behave erratically with more realistic small samples. Moreover, two estimators which appear to be computed in very different ways from the sample values can be asymptotically equivalent. We shall give an example of this phenomenon. Again, for realistic small samples, their behavior need not be equivalent.

There is a very large statistical literature on choosing the "best" estimator.[4] The various estimators presently

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(1) A. E. W. Knight and B. K. Selinger, *Spectrochim. Acta, Part A*, 27, 1223 (1971).
(2) A. E. W. Knight and B. K. Selinger, *Aust. J. Chem.*, **26**, 1 (1973).
(3) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw Hill, New York, 1969.

in use were originally suggested on the basis of intuition, and only later were precise efficiencies derived. Other things being equal, application of Occam's razor favors the estimator which is most easily computed.

We shall examine the case of single photon data for exponential decay, and three common estimators. These are the minimum χ^2 estimator (least squares), the maximum likelihood estimator, and the method of moments.

There are three commonly used variants of the minimum χ^2 estimator:[4] (a) Pearson's "exact" χ^2, which minimizes $\sum\{(o-e)^2/e\}$ (here o = observed and e = expected), (b) Neyman's "reduced" χ^2, which minimizes $\sum\{(o-e)^2/o\}$ (simulations have shown that for small samples this estimator becomes erratic[5]), and (c) the "likelihood" χ^2, which minimizes $2\sum o \log (o/e)$. All three quantities have asymptotic χ^2 distributions. The likelihood χ^2 has defining equations which are identical with those of the maximum likelihood estimator (MLE). Thus, the MLE can be regarded as a minimum χ^2 estimator.

The Model

The emission times of particles (including photons) emitted at random by an exponentially decaying source may be described by an inhomogeneous Poisson process with intensity function $\lambda(t) = A \exp(-t/\tau)$, $t \geq 0$, where A and τ are fixed positive parameters. Let $\Lambda(t) = \int_0^t \lambda(u)\,du = A\tau\{1-\exp(-t/\tau)\}$, and suppose that the particles are recorded by m counters, or channels, each of width T time units. (That is, all particles arriving between time $(i-1)T$ and iT are recorded in the ith channel, where $1 \leq i \leq m$.) Suppose N_i particles are recorded by the ith channel. The variables N_i are independently Poisson distributed with respective parameters $\Lambda(iT) - \Lambda\{(i-1)T\} = A\tau \exp(-iT/\tau)\{\exp(T/\tau)-1\}$.

Maximum Likelihood

The *likelihood* of the observed sample $N_1, ..., N_m$ is given by L where

$$L = \prod_{i=1}^{m} [\Lambda(iT) - \Lambda\{(i-1)T\}]^{N_i} \exp[-\{\Lambda(iT) - \Lambda[(i-1)T]\}]/(N_i!) \quad (1)$$

With $N = \sum_{i=1}^{m} N_i$, we obtain

$$\log L = N\{\log A + \log \tau + \log [\exp(T/\tau) - 1]\} - (T/\tau)\sum_{i=1}^{m} iN_i - A\tau\{1-\exp(-mT/\tau)\} - \log\{\prod_{i=1}^{m}(N_i!)\}$$

When $\partial \log L/\partial A = 0$

$$A = N/\{\tau[1-\exp(-mT/\tau)]\} \quad (2)$$

and when $\partial \log L/\partial \tau = 0$

$$N\{(\tau/T) - \exp(T/\tau)/[\exp(T/\tau)-1]\} + \sum_{i=1}^{m} iN_i - A\tau\{(\tau/T)[1-\exp(-mT/\tau)] - m\exp(-mT/\tau)\} = 0 \quad (3)$$

Substituting eq 2 into eq 3, we obtain

$$1 + \{\exp(T/\tau)-1\}^{-1} - m\{\exp(mT/\tau)-1\}^{-1} = N^{-1}\sum_1^m iN_i \quad (4)$$

The MLE $\hat{\tau}$ is given by the solution of eq 4, and the MLE $\hat{A}$ is given by eq 2. Rewriting eq 4 with $\bar{\nu} = N^{-1}\sum_1^m iN_i$ (the channel with the "average" number of arrivals) and $x = T/\tau$ gives

$$1 + (e^x - 1)^{-1} - m(e^{mx}-1)^{-1} = \bar{\nu} \quad (5)$$

The left-hand side of eq 5 is a function only of the parameter τ (it does not involve the data). The right-hand side of eq 5 is a function only of the data (it does not involve the parameter τ). Equation 5 thus lends itself to graphical solution (see Figure 1) or tabulation. (The left-hand side is strictly monotone decreasing, and eq 5 admits a unique solution as long as the source is decaying, i.e., $\bar{\nu}\ \langle {}^1/_2(m+1)$.) For a value of $\bar{\nu}$ observed from the data, there is a corresponding unique value of x, e.g., $\hat{x}$, defined by eq 5 and quickly derived from Figure 1. This gives $\hat{T} = T/\hat{x}$, and then $\hat{A}$ follows from eq 2. Any of the common iterative techniques (e.g., Newton–Rhapson) gives a numerical solution.

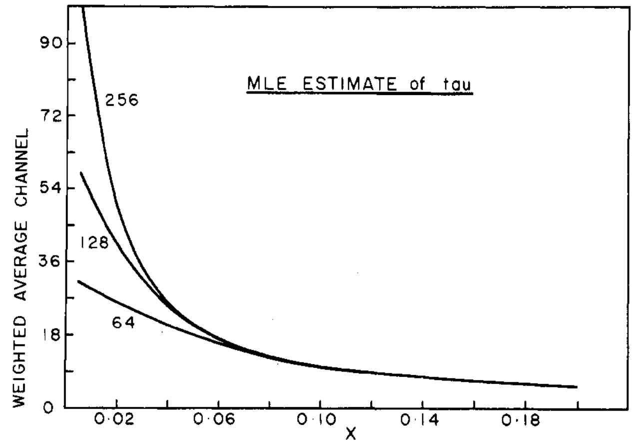

Figure 1. Maximum likelihood estimate for a single exponential for three values of the number of channels (m = 64, 128, and 256). Horizontal axis: $x = T/\tau$. Vertical axis: right-hand side of eq 4.

Least Squares

We now examine Pearson's χ^2, which minimizes $\sum\{(o-e)^2/e\}$. As before, the model gives

$$E(N_i) = \Lambda(iT) - \Lambda\{(i-1)T\} = A\tau\exp(-iT/\tau)\{\exp(T/\tau)-1\}$$

For the case where T/τ is small, the discrete nature of collection in channels may be ignored and the data considered to be continuous. This suggests the approximation $\exp(T/\tau) - 1 \simeq T/\tau$, which is commonly used in the literature.[2] Thus we minimize

$$S = \sum_{i=1}^{m}\{(o-e)^2/e\} \simeq \sum_1^m\{N_i - AT\exp(-iT/\tau)\}^2/\{AT\exp(-iT/\tau)\} = S'$$

Now when $\partial S'/\partial A = 0$

$$\sum_{i=1}^{m} N_i^2 \exp(iT/\tau) = (AT)^2 \sum_{i=1}^{m}\exp(-iT/\tau) \quad (6)$$

and when $\partial S'/\partial \tau = 0$

$$\sum_{i=1}^{m} iN_i^2\exp(iT/\tau) = (AT)^2\sum_{i=1}^{m} i\exp(-iT/\tau) \quad (7)$$

Dividing eq 6 by eq 7 eliminates the parameter A, to give

$$\{\sum_{i=1}^{m} N_i^2\exp(iT/\tau)\}/\{\sum_{i=1}^{m} iN_i^2\exp(iT/\tau)\} = \{\sum_{i=1}^{m}\exp(-iT/\tau)\}/\{\sum_{i=1}^{m} i\exp(-iT/\tau)\}$$

(4) See, for example, J. Berkson, *Annal. Stat.* 8, 457 (1980).
(5) D. C. Robinson, "An Evaluation of Least Squares Methods of Analysing Decay Data", AERE (UK), 1968, no. RJ911.
(6) M. G. Kendall and A. Stuart, "The Advanced Theory of Statistics", Vol. 2, 3rd ed., Griffin, London, 1973, p 57.
(7) B. Selinger, C. Harris, and A. Kallir in "NATO Advanced Study Institute on Time-Resolved Spectroscopy in Biology and Biochemistry", Plenum Press, in press.

which can be rewritten as

$$\frac{\exp(T/\tau)}{\exp(T/\tau) - 1} - \frac{m}{\exp(mT/\tau) - 1} = \{\sum_{i=1}^{m} iN_i^2 \exp(iT/\tau)\}/\{\sum_{i=1}^{m} N_i^2 \exp(iT/\tau)\} \quad (8)$$

by noting that

$$(\sum_{i=1}^{m} ie^{-ix})/(\sum_{i=1}^{m} e^{-ix}) = -\frac{\mathrm{d}}{\mathrm{d}x}\{\log (\sum_{i=1}^{m} e^{-ix})\} = -\frac{\mathrm{d}}{\mathrm{d}x}[\log \{(1 - e^{-mx})/(e^x - 1)\}]$$

The estimate $\hat{A}$ can be obtained by inverting either eq 6 or 7:

$$\hat{A} = [\{\exp(T/\hat{\tau}) - 1\} \times \{\sum_{i=1}^{m} N_i^2 \exp(iT/\hat{\tau})\}/(T^2\{1 - \exp(-mT/\hat{\tau})\})]^{1/2}$$

One can note immediately that the usual "least-squares" estimator (LSE) of τ, the solution of eq 8, is much more complicated than the MLE, the solution of eq 5. More important is the fact that in eq 8 the data and parameter are *not* separated. Its solution (except for very small m) cannot be found graphically and must be obtained on a high-speed computer. Finally, eq 8 is derived for an "approximate" model in which T/τ (the channel width as a function of lifetime) is very small. Curiously, the least-squares estimator on the *exact* model still yields eq 8, and the MLE on the *inexact* model still yields eq 5. However, the associated estimators of A are not even consistent under the inexact model (see ref 8).

Method of Moments

The "method of moments" estimator has attracted a dedicated following, although in a general statistical context it would normally be considered only when other estimators adopt an intractable form. We shall show in the next section that the method of moments estimator *can be much less efficient* than the MLE, while being no easier to compute than the MLE for the present problem.

There being two unknown parameters, A and τ, the method of moments estimator would usually be obtained by equating the first two sample moments to the population moments (alternatively the approximate model can be used). Now

$$E(N_i) = \Lambda(iT) - \Lambda\{(i - 1)T\}$$

$$E(N_i^2) = \Lambda(iT) - \Lambda\{(i - 1)T\} + [\Lambda(iT) - \Lambda\{(i - 1)T\}]^2 \approx [\Lambda(iT) - \Lambda\{(i - 1)T\}]^2$$

for large A. Perhaps the simplest form of the method of moments estimator is defined by the equations

$$\sum_{i=1}^{m} N_i = \sum_{i=1}^{m} [\Lambda(iT) - \Lambda\{(i - 1)T\}]$$

$$\sum_{i=1}^{m} N_i^2 = \sum_{i=1}^{m} [\Lambda(iT) - \Lambda\{(i - 1)T\}]^2$$

That is

$$N = A\tau\{1 - \exp(-mT/\tau)\}$$

$$\sum_{i=1}^{m} N_i^2 = A^2\tau^2\{\exp(T/\tau) - 1\}\{1 - \exp(-2mT/\tau)\}/\{\exp(T/\tau) + 1\}$$

Eliminating A from the last two equations, we obtain

$$\frac{\{\exp(T/\tau) - 1\}\{\exp(mT/\tau) + 1\}}{\{\exp(T/\tau) + 1\}\{\exp(mT/\tau) - 1\}} = N^{-2} \sum_{i=1}^{m} N_i^2 \quad (9)$$

The moment estimator $\tilde{\tau}$ of τ is the solution of this equation, while $\tilde{A}$ is given by

$$\tilde{A} = N/\{\tilde{\tau}[1 - \exp(-mT/\tilde{\tau})]\} \quad (10)$$

Equation 9 also lends itself to graphical solution (see Figure 2). If the approximate model is used, eq 9 is *still* obtained but eq 10 is not. The estimator of A obtained is now not consistent (see ref 8). We note that eq 9 (defining the moment estimator of τ) is no less complex than eq (5) (defining the MLE of τ). There is thus no justification on the grounds of simplicity for using the method of moments.

Comparison of Estimators

So far we have examined three estimators of τ, which give three different estimates. It can be shown that the MLE of τ and the least-squares estimator of τ are both statistically consistent and asymptotically efficient. What this means is that both converge to the true parameter value as the sample sizes increase indefinitely, and both attain the Cramér–Rao variance lower bound[6] in an asymptotic sense.

However, the least-squares estimator of A is not even consistent under the inexact model, let alone efficient (see ref 8). Fortunately there is often no experimental interest in the parameter A.

Theorem 1 describes the asymptotic behavior of either the ML or LS estimator of τ.

Theorem 1. Let $\hat{\tau}$ denote either the ML or LS estimator of τ. Then as $A \to \infty$, $A^{1/2}(\hat{\tau} - \tau)$ is asymptotically normally distributed with zero mean and variance equal to

$$(\tau^3/T^2) \times \left\{\frac{\exp(T/\tau)[1 - \exp(-mT/\tau)]}{[\exp(T/\tau) - 1]^2} - \frac{m^2}{[\exp(mT/\tau) - 1]}\right\}^{-1} \quad (11)$$

The proof is given in Appendix A.

In order to compare the maximum likelihood and least-squares estimates with the moment estimator, it is first necessary to derive the asymptotic behavior of the estimator defined by eq 9.

Theorem 2. Let $\tilde{\tau}$ be the moment estimator, defined by eq 9. Then as $A \to \infty$, $A^{1/2}(\tilde{\tau} - \tau)$ is asymptotically normally distributed with zero mean and variance equal to

$$(\tau^3/T^2)(e^{T/\tau} - 1)^2(1 - e^{-mT/\tau})\left\{\frac{(e^{T/\tau} + 1)^2(1 + e^{mT/\tau} + e^{2mT/\tau})}{1 + e^{T/\tau} + e^{2T/\tau}} - (1 + e^{mT/\tau})^2\right\}\{m(e^{T/\tau} - 1) - (e^{2mT/\tau} - 1)e^{-(m-1)T/\tau}/(e^{T/\tau} + 1)\}^{-2} \quad (12)$$

The proof is given in Appendix B.

(8) Note on statistical consistency: Ideally an estimator $\hat{A}$ or A should have the property that $\hat{A}/A \to 1$ as the sample sizes increase indefinitely (i.e., as $A \to \infty$). This is called *consistency*, and the ML, LS, and moment estimators of A derived under the exact Poisson process model exhibit this property. However, when the estimators are derived under the often-used inexact model, $\hat{A}/A$ converges to a function of τ which is generally close to 1 but does not equal 1. Roughly speaking, the estimator $\hat{A}$ is trying to adjust itself to take a value which would make the inexact model closer to the exact model. Fortunately, this effect does not occur with the estimators of τ, which assume the same form under either the exact or inexact model. As the sample size increases indefinitely, $\hat{\tau} \to \tau$ no matter which of the two models is used in its derivation.

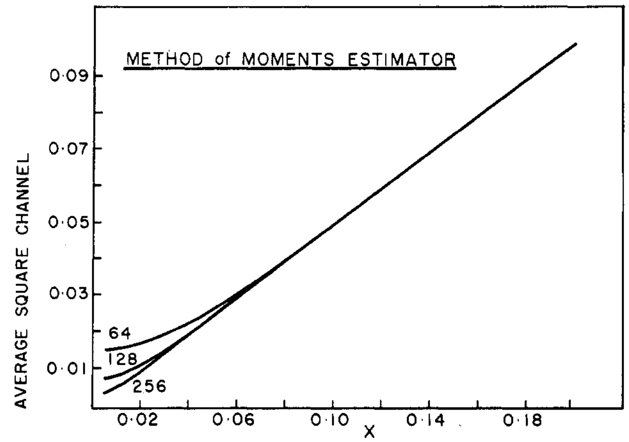

Figure 2. Method of moments estimate for a single exponential for three values of the number of channels (m = 64, 128, and 256). Horizontal axis: $x = T/\tau$. Vertical axis: right-hand side of eq 9.

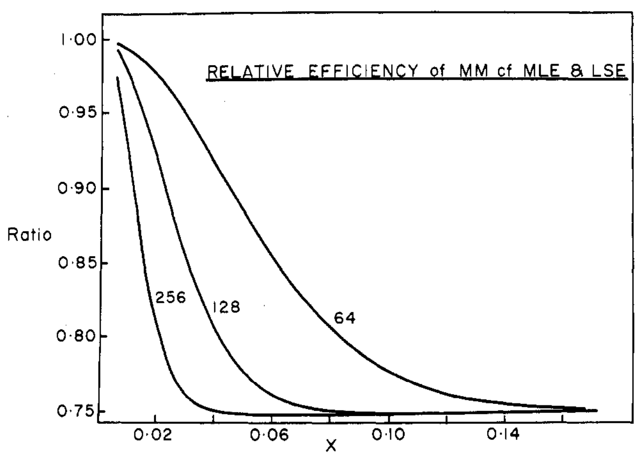

Figure 3. Relative efficiency of the method of moments compared to the maximum likelihood (or least-squares) estimators for three values of the number of channels (m = 64, 128, and 256). Horizontal axis: $x = T/\tau$. Vertical axis: eq 11/eq 12.

The variance of the moment estimator $\bar{\tau}$ can be significantly greater than that of either the MLE or LSE, $\hat{\tau}$. The ratio of the asymptotic variance of $\hat{\tau}$ to the asymptotic variance of $\bar{\tau}$ is the efficiency of $\bar{\tau}$ and is plotted in Figure 3.

Optimal Channel Width

A question of considerable practical interest is the optimal channel width to be used in an experiment.[7] In order to compare the performances of estimators derived by using different channel widths, we shall suppose that the amplitudes are adjusted so that the total (expected) numbers of counts in the TAC range are the same. The expected number of counts equals

$$\Lambda(mT) = A\tau\{1 - \exp(-mT/\tau)\} = C$$

and so the amplitude A should be adjusted to

$$A = C/\{\tau[1 - \exp(-mT/\tau)]\}$$

With this substitution the asymptotic variance of $(\hat{\tau} - \tau)$ may be seen from Theorem 1 to equal

$$\sigma^2 = \tau^4/\left[CT^2\left\{\frac{\exp(T/\tau)}{[\exp(T/\tau) - 1]^2} - \frac{m^2\exp(mT/\tau)}{[\exp(mT/\tau) - 1]^2}\right\}\right]$$

TABLE I: x Value Minimizing $g_m(x)$

m	64	128	256	512
$x_0(m)$	0.1947	0.1094	0.0606	0.0331

The relative standard error of $\hat{\tau}$, i.e., the ratio of the standard deviation of $\hat{\tau}$ to τ, is given by

$$\rho = \sigma/\tau = C^{-1/2}\tau(\tau/T)\left\{\frac{\exp(T/\tau)}{[\exp(T/\tau) - 1]^2} - \frac{m^2\exp(mT/\tau)}{[\exp(mT/\tau) - 1]^2}\right\}^{-1/2}$$

Setting

$$g_m(x) = x^{-1}\left\{\frac{\exp(x)}{[\exp(x) - 1]^2} - \frac{m^2\exp(mx)}{[\exp(mx) - 1]^2}\right\}^{-1/2} \quad (13)$$

gives $\rho = C^{-1/2}\tau g_m(T/\tau)$. The function g_m has a unique minimum, and the value $x_0(m)$ which minimizes g_m is given in Table I. The optimal choice of channel width T is given by

$$T_0 = \tau x_0(m)$$

That is, *for fixed m the optimal channel width is proportional to the parameter* τ. Having established an approximate τ, one can optimally adjust the experiment. This method is valid for either the MLE or LSE, and also (with a change in the proportionality constant) for the ME.

The function g_m is plotted in Figure 4. It is clear that choosing T a little too large (that is, $T/\tau > x_0(m)$) does not have an appreciable effect on the error of the estimator, although choosing T too small can make a difference. When background is present, there has been a tendency to increase T/τ so as to increase the significance of counts in later channels. This is now seen as being acceptable.

Conclusion

For a single exponential decay there appears to be no good reason to use a method other than the simple algorithm derived from the MLE. While the traditional inexact model does not distort the estimate of τ, the estimates of the amplitude are statistically inconsistent. We derive an analytical answer for the choice of the optimum channel width (TAC range).

Appendix A

Proof of Theorem 1. Asymptotic normality may be proved after some tedious algebra by inverting the Taylor series expansions of eq 4 or 8. (This technique is used in the proof of Theorem 2 in Appendix B.) We shall only derive the asymptotic variance and do this by inverting an information matrix. (A Taylor expansion of eq 8 shows that the least-squares estimator is asymptotically efficient.)

It is mathematically convenient to change variable from (τ,A) to (α,B), where $\alpha = 1/\tau$ and $B = A\tau$. Then the log likelihood becomes

$$\log L = N\{\log B + \log(e^{\alpha T} - 1)\} - \alpha T\sum_{i=1}^{m} iN_i - B(1 - e^{-m\alpha T}) - \log\{\prod_1^m(N_i!)\}$$

whence

$$-\frac{\partial^2 \log L}{\partial \alpha^2} = T^2\left\{\frac{Ne^{\alpha T}}{(e^{\alpha T}-1)^2} - Bm^2e^{-m\alpha T}\right\}$$

$$-\frac{\partial^2 \log L}{\partial B^2} = \frac{N}{B^2}$$

$$-\frac{\partial^2 \log L}{\partial \alpha\, \partial B} = mTe^{-m\alpha T}$$

Since $E(N) = B(1 - e^{-m\alpha T})$ then

$$-E\left\{\frac{\partial^2 \log L}{\partial \alpha^2}\right\} = BT^2\left\{\frac{e^{\alpha T}(1-e^{-m\alpha T})}{(e^{\alpha T}-1)^2} - m^2e^{-m\alpha T}\right\}$$

$$-E\left\{\frac{\partial^2 \log L}{\partial B^2}\right\} = (1-e^{-m\alpha T})/B$$

$$-E\{\partial^2 \log L/(\partial \alpha\, \partial B)\} = mTe^{-m\alpha T}$$

The inverse of the information matrix for this parametrization is therefore equal to

$$\mathbf{V}^{-1} = -\begin{bmatrix} E\{\partial^2 \log L/\partial\alpha^2\} & E\{\partial^2 \log L/(\partial\alpha\,\partial B)\} \\ E\{\partial^2 \log L/(\partial\alpha\,\partial B)\} & E\{\partial^2 \log L/\partial B^2\} \end{bmatrix}^{-1}$$

$$= D^{-1}\begin{bmatrix} (1-e^{-m\alpha T})/B & -mTe^{m\alpha T} \\ -mTe^{-m\alpha T} & BT^2\left\{\dfrac{e^{\alpha T}(1-e^{m\alpha T})}{(e^{\alpha T}-1)^2} - m^2e^{-m\alpha T}\right\} \end{bmatrix}$$

where $D = T^2\{e^{\alpha T}(1-e^{-m\alpha T})^2/(e^{\alpha T}-1)^2 - m^2e^{-m\alpha T}\}$ is the determinant of **V**. The asymptotic variance of $\hat{\alpha}$ equals the top left-hand element in this matrix:

$$\sigma_\alpha^2 = (1-e^{-m\alpha T})/BD = 1\bigg/\left[A\tau T^2\left\{\frac{e^{T/\tau}(1-e^{-mT/\tau})}{(e^{T/\tau}-1)^2} - \frac{m^2}{e^{mT/\tau}-1}\right\}\right]$$

Now, $\hat{\tau} = 1/\hat{\alpha} = 1/\{\alpha[1 + (\hat{\alpha}-\alpha)/\alpha]\} \simeq \alpha^{-1}\{1-(\hat{\alpha}-\alpha)/\alpha\}$. Therefore, $\hat{\tau} - \tau \simeq -\tau^2(\hat{\alpha}-\alpha)$, and so $\hat{\tau}$ has asymptotic variance $\sigma_\tau^2 = \tau^4\sigma_\alpha^2$. This completes the proof.

Appendix B

Proof of Theorem 2. Again it is convenient to make the change of variable $\alpha = 1/\tau$. Equation 9 of the text may then be rewritten as

$$g(\alpha) = 0$$

where

$$g(\alpha) = (e^{\alpha T}+1)(e^{m\alpha T}-1)\sum N_i^2/A^2 - (e^{\alpha t}-1)(e^{m\alpha T}+1)N^2/A^2$$

Now

$$g'(\alpha) = T\{e^{\alpha T}(e^{m\alpha T}-1) + (e^{\alpha T}+1)me^{m\alpha T}\}\sum N_i^2/A^2 - T\{e^{\alpha T}(e^{m\alpha T}+1) + (e^{\alpha T}-1)me^{m\alpha T}\}N^2/A^2 \rightarrow T\{e^{\alpha T}(e^{m\alpha T}-1) + (e^{\alpha T}+1)me^{m\alpha T}\} \times \sum_{i=1}^{m} \tau^2(e^{\alpha T}-1)^2e^{-2i\alpha T} - T\{e^{\alpha T}(e^{m\alpha T}+1) + (e^{\alpha T}-1)me^{m\alpha T}\}\tau^2(1-e^{-m\alpha T})^2$$

as $A \rightarrow \infty$. (This last result states in effect that $g'(\alpha)$

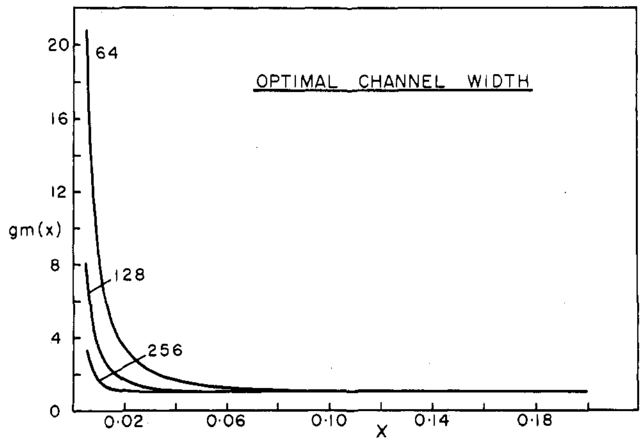

Figure 4. The optimal channel width for fitting a single exponential for three values of the number of channels (m = 64, 128, and 256). Horizontal axis: $x = T/\tau$. Vertical axis: eq 13.

converges in measure as $A \rightarrow \infty$.) The quantity on the right here equals

$$\tau^2T[(e^{\alpha T}-1)^2(1-e^{-2m\alpha T}) \times (e^{2\alpha T}-1)^{-1}\{e^{\alpha T}(e^{m\alpha T}-1) + (e^{\alpha T}+1)me^{m\alpha T}\} - (1-e^{-m\alpha T})^2\{e^{\alpha T}(e^{m\alpha T}+1) + (e^{\alpha T}-1)me^{m\alpha T}\}]$$

$$= \tau^2T(1-e^{-m\alpha T})\left[\frac{e^{\alpha T}-1}{e^{\alpha T}+1}(1+e^{-m\alpha T}) \times \{e^{\alpha T}(e^{m\alpha T}-1) + (e^{\alpha T}+1)me^{m\alpha T}\} - (1-e^{-m\alpha T})\{e^{\alpha T}(e^{m\alpha T}+1) + (e^{\alpha T}-1)me^{m\alpha T}\}\right]$$

Writing $(e^{\alpha T}-1)/(e^{\alpha T}+1)$ as $1 - 2/(e^{\alpha T}+1)$, we may simplify this to

$$2\tau^2T(1-e^{-m\alpha T})\left[m(e^{\alpha T}+e^{m\alpha T}) - (1+e^{-m\alpha T})\left\{\frac{e^{\alpha T}(e^{m\alpha T}-1)}{e^{\alpha T}+1} + me^{m\alpha T}\right\}\right] = 2\tau^2T(1-e^{-m\alpha T})\{m(e^{\alpha T}-1) - (e^{2m\alpha T}-1)e^{-(m-1)\alpha T}/(e^{\alpha T}+1)\} = h(\alpha)$$

Therefore

$$g'(\alpha) \rightarrow h(\alpha) \qquad \text{(I)}$$

as $A \rightarrow \infty$.

Let $Z_i = (N_i - EN_i)/(EN_i)^{1/2}$. The variables $Z_1, Z_2, ..., Z_m$ are independent with zero mean and unit variance, and asymptotically normally distributed. Moreover

$$\sum_1^m N_i^2 = \sum_1^m \{EN_i + Z_i(EN_i)^{1/2}\}^2 = \sum_1^m (EN_i)^2 + 2\sum_1^m Z_i(EN_i)^{3/2} + \sum_1^m Z_i^2 EN_i \qquad \text{(II)}$$

$$N^2 = \{EN + \sum_1^m Z_i(EN_i)^{1/2}\}^2 = (EN)^2 + 2(EN)\sum_1^m Z_i(EN_i)^{1/2} + \{\sum_1^m Z_i(EN_i)^{1/2}\}^2 \qquad \text{(III)}$$

Now

$$(e^{\alpha T} + 1)(e^{m\alpha T} - 1)\{\sum_1^m (EN_i)^2 + \sum_1^m Z_i^2 EN_i\}/A^2 - (e^{\alpha T} - 1)(e^{m\alpha T} + 1)[(EN)^2 + \{\sum_1^m Z_i(EN_i)^{1/2}\}^2]/A^2 = (e^{\alpha T} + 1)(e^{m\alpha T} - 1)\{\sum_1^m \tau^2(e^{\alpha T} - 1)^2 e^{-2i\alpha T} + O_p(A^{-1})\} - (e^{\alpha T} - 1)(e^{m\alpha T} + 1)\{\tau^2(1 - e^{-m\alpha T})^2 + O_p(A^{-1})\} = O_p(A^{-1}) \quad \text{(IV)}$$

as $A \to \infty$. Substituting the expansions II–IV into the formula for $g(\alpha)$, we deduce that

$$g(\alpha) = 2(e^{\alpha T} + 1)(e^{m\alpha T} - 1)\sum_1^m Z_i(EN_i)^{3/2}/A^2 - 2(e^{\alpha T} - 1)(e^{m\alpha T} + 1)(EN)\sum_1^m Z_i(EN_i)^{1/2}/A^2 + O_p(A^{-1})$$

$$= (2\tau/A)\sum_1^m Z_i(EN_i)^{1/2}\{(e^{\alpha T} + 1)(e^{m\alpha T} - 1) \times (e^{\alpha T} - 1)e^{-i\alpha T} - (e^{\alpha T} - 1)(e^{m\alpha T} + 1)(1 - e^{-m\alpha T})\} + O_p(A^{-1})$$

$$= \{2\tau(e^{\alpha T} - 1)(e^{m\alpha T} - 1)/A\}\sum_1^m Z_i(EN_i)^{1/2}\{(e^{\alpha T} + 1)e^{-i\alpha T} - (1 + e^{m\alpha T})\} + O_p(A^{-1})$$

The series on the right is a sum of independent, zero-mean random variables, and it is readily proved that $A^{1/2}g(\alpha)$ is asymptotically normally distributed with zero mean and variance equal to

$$\{2\tau(e^{\alpha T} - 1)(e^{m\alpha T} - 1)\}^2\sum_1^m (EN_i/A)\{(e^{\alpha T} + 1)e^{-i\alpha T} - (1 + e^{-m\alpha T})\}^2 = \{2\tau(e^{\alpha T} - 1)(e^{m\alpha T} - 1)\}^2\tau(1 - e^{m\alpha T})\left\{\frac{(e^{\alpha T} + 1)^2(1 + e^{-m\alpha T} + e^{-2m\alpha T})}{e^{2\alpha T} + e^{\alpha T} + 1} - (1 + e^{-m\alpha T})^2\right\} = k(\alpha) \quad \text{(V)}$$

That is, $A^{1/2}g(\alpha)$ is asymptotically normal $N(0,k(\alpha))$.

Finally, observe that

$$0 = g(\hat{\alpha}) = g(\alpha) + (\hat{\alpha} - \alpha)g'(\alpha) + \tfrac{1}{2}(\hat{\alpha} - \alpha)^2 g''(\alpha) + ...$$

Inverting this expansion, we see that

$$\hat{\alpha} - \alpha \simeq -g(\alpha)/g'(\alpha)$$

As in the proof of Theorem 1, we have $\hat{\tau} - \tau \simeq -\tau^2(\hat{\alpha} - \alpha)$, and so

$$\hat{\tau} - \tau \simeq \tau^2 g(\alpha)/g'(\alpha)$$

Combining this with eq I and V we see that $A^{1/2}(\hat{\tau} - \tau)$ is asymptotically normally distributed with zero mean and variance equal to

$$\tau^4 k(\alpha)/\{h(\alpha)\}^2 = (\tau^3/T^2)(e^{\alpha T} - 1)^2(1 - e^{-m\alpha T}) \times \left\{\frac{(e^{\alpha T} + 1)^2(1 + e^{m\alpha T} + e^{2m\alpha T})}{1 + e^{\alpha T} + e^{2\alpha T}} - (1 + e^{m\alpha T})^2\right\} \times \{m(e^{\alpha T} - 1) - (e^{2m\alpha T} - 1)e^{-(m-1)\alpha T}/(e^{\alpha T} + 1)\}^{-2}$$

This completes the proof of Theorem 2.

Rate Coefficient for the Reaction of CH_3O_2 with NO from 218 to 365 K

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(Received: April 6, 1981)

The kinetics of reaction 1, $CH_3O_2 + NO \rightarrow CH_3O + NO_2$, were studied in the temperature range 218–365 K by using the flash photolysis of Cl_2 in the presence of CH_4 and O_2 as a source of CH_3O_2 radicals. These radicals were monitored by ultraviolet absorption. The rate coefficient $k_1 = (2.1 \pm 1) \times 10^{-12} \exp\{(380 \pm 250)/T\}$ cm^3 s^{-1} at 200-torr total pressure. The reaction is independent of pressure (70–600 torr, mostly CH_4) at 296 K.

Introduction

CH_3O_2 radicals are produced in the atmosphere from the oxidation of CH_4. In the stratosphere their principle loss process is the reaction with NO:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \quad (1)$$

However, in regions of low NO concentration, such as the clean troposphere, reaction 1 may also compete with other CH_3O_2-loss processes.[1]

The kinetics of reaction 1 at room temperature have now been measured directly by several groups.[2-6] The results of the various studies are summarized in Table I. In general the agreement is good. However, in one study[2] a significantly lower value for k_1 was found, but this has been explained.[5] In this paper we report our kinetic measurements of reaction 1 over the temperature range 218–365 K. Since this work was completed, Ravishankara et al. have also completed a temperature study of reaction 1.[6,7]

Experimental Section

Apparatus. The kinetics of reaction 1 were studied by using the flash photolysis–ultraviolet absorption technique. The system consists of four principle parts: the reaction cell, the flash unit, the analysis lamp, and the detection system.

The Pyrex reaction cell with quartz windows is 100 cm long and consists of three concentric chambers with an

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0022-3654/81/2085-2946$01.25/0