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ANALYSIS OF NONLINEAR REACTIONS IN MODULATED MOLECULAR BEAM-SURFACE EXPERIMENTS

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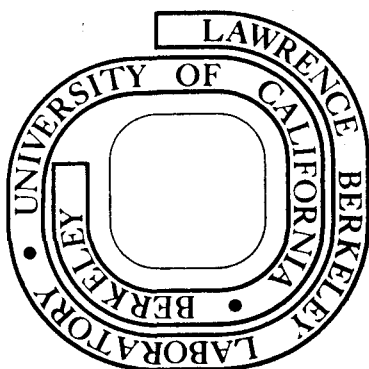
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ANALYSIS OF NONLINEAR REACTIONS IN  
MODULATED MOLECULAR BEAM-SURFACE EXPERIMENTS

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ABSTRACT

An approximate method of analyzing nonlinear reaction models in modulated molecular beam surface kinetic studies is developed. The exact method for treating nonlinear surface mechanisms is tedious and almost always requires computer analysis. The proposed approximate method is a simple extension of the Fourier expansion technique valid for linear surface reactions; it quickly provides analytical expressions for the phase lag and amplitude of the reaction product for any type of nonlinear surface mechanism, which greatly facilitates comparison of theory and experiment. The approximate and exact methods are compared for a number of prototypical adsorption-desorption reactions which include coverage-dependent adsorption and desorption kinetics of order greater than unity. Except for certain extreme forms of coverage-dependent adsorption, the approximate method provides a good representation of the exact solution. The errors increase as the nonlinearities become stronger. Fortunately, when the discrepancy between the two methods is substantial, the reaction product signal is so highly demodulated that reliable experimental data usually cannot be obtained in these regions anyway.

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Recent reviews (1,2) have shown that the combination of modulated molecular beams, mass spectrometry, and high vacuum techniques provides a powerful tool for studying heterogeneous or catalytic gas/solid reactions in a degree of detail unattainable by conventional chemical kinetic methods. One of the main problems with the modulated beam experiments is the interpretation of the experimental results (i.e., the phase and amplitude of the reaction product signal). The procedure is a circular one; a reaction mechanism is assumed and theoretical values of the phase and amplitude are calculated. The theoretical values are compared with the data. If agreement is unsatisfactory, a new or modified surface mechanism is assumed and the process is repeated until theory and data agree.

For linear surface processes, translation of the reaction model to predicted phase and amplitude is relatively simple (1,3). The concentrations of all species involved in the reaction and the gating function of the molecular beam are represented by the fundamental modes of their Fourier expansions, which are then substituted into the surface mass balances representing the proposed mechanism. The resultant algebraic equation is solved for the fundamental mode of the product vaporization rate, which is a complex number. By converting the complex quantity to polar form, the phase and amplitude predicted by the model can be identified.

For nonlinear surface reaction mechanisms, the laborious process of solving the surface kinetic equations in the time domain followed by Fourier analysis of the product waveform for the fundamental mode is required for an exact solution (2,4). The computational manipulations involved in analyzing even the simplest nonlinear processes by this method are substantial, with the result that the trial-and-error process of hunting for the mechanism which best fits the data is inordinately time consuming. We have found that this laborious procedure is

unnecessary; certain nonlinear processes can be treated approximately by simple extension of the methods developed for analyzing linear reaction mechanisms; with an enormous saving in data analysis time and effort.

The approximate method involves expanding in complete Fourier series all pertinent time dependent quantities appearing in the surface mass balance representing the reaction mechanism. Thus, the gating function is written as:

$$g(t) = \frac{1}{2} [1 + g_1 \cos \omega t + g_2 \cos 2\omega t + \dots] \quad (1)$$

The corresponding sine series (or, equivalently, a phase lag in the cosine terms of Eq. (1)) does not appear because the gating function forms the reference signal, which by definition has zero phase lag. Assuming for simplicity that there is but one adsorbed species in the reaction mechanism, the expansion of its surface concentration,  $n(t)$ , in a complete Fourier series is:

$$n(t) = n_0 + N_1 \cos(\omega t - \phi_1) + N_2 \cos(2\omega t - \phi_2) + \dots \quad (2)$$

When Eqs. (1) and (2) are substituted into the time dependent surface mass balance for a particular reaction mechanism, the coefficients of  $\cos \omega t$ ,  $\sin \omega t$ ,  $\cos 2\omega t$ ,  $\sin 2\omega t, \dots$  and the zero order term must each be equated to zero. If the surface process is linear, the coefficients of  $\cos \omega t$  and  $\sin \omega t$  contain only the amplitude factor  $N_1$  and the phase lag  $\phi_1$ . These quantities, which are determined experimentally by the phase sensitive detection method, are thus uniquely determined theoretically. However, when the surface reaction is nonlinear, the coefficients of  $\cos \omega t$  and  $\sin \omega t$  contain  $n_0$ , the higher order amplitude factors  $N_2, N_3, \dots$  and the higher order phase lags  $\phi_2, \phi_3, \dots$ . The presence of these higher order coefficients in the fundamental mode solutions prevents ready determination of  $N_1$  and  $\phi_1$ .

Instead of using sines and cosines, the Fourier representation of the gating function and the concentration of the surface intermediate may be expressed as complex exponentials using the relation:  $e^{i\omega t} = \cos\omega t + i \sin\omega t$ . In nonlinear processes, the amplitude and phase of each harmonic will be a function of the amplitudes and phases of all other harmonics. The complete expansions of the gating and surface concentration functions, (Eqs. (1) and (2)), cannot be approximated by truncated Fourier expansions without introducing some error. However, because of the simplicity of using such truncations, we have explored the accuracy of expansions of the type:

$$g(t) = \frac{1}{2} [1 + g_1 e^{i\omega t}] \quad (3)$$

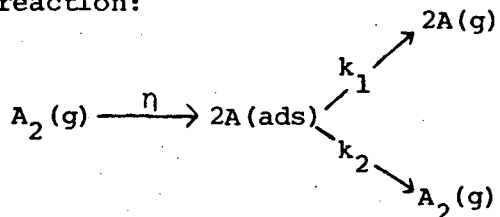
for the gating function, and:

$$n(t) = n_0 + \bar{n}_1 e^{i\omega t} \quad (4)$$

for the surface intermediate. The essential difference between the approximate nonlinear analysis and the treatment of linear reactions is that in the former the steady state terms in the Fourier expansions are retained. Comparisons are made for several simple nonlinear surface reactions for which exact solutions are available. Since Eqs. (3) and (4) are sufficient to reproduce the exact solutions in the linear case, we start with a weakly nonlinear system and proceed through increasingly strong nonlinearities.

### 1. Adsorption and Parallel First and Second Order Desorption

The reaction:



represents the dissociative adsorption of a diatomic molecule on a surface followed by competitive desorption as atoms and molecules. The surface mass balance on the concentration of adsorbed atoms (denoted by  $n$ ) is:

$$\frac{dn}{dt} = 2\eta I_0 g(t) - k_1 n - 2k_2 n^2 \quad (5)$$

Here  $\eta$  is the sticking probability (assumed to be independent of  $n$ ) and  $I_0$  is the intensity of the molecular beam of  $A_2$  striking the surface.  $k_1$  and  $k_2$  are the first and second order desorption rate constants, respectively.

Eqs. (3) and (4) are substituted into Eq. (5) and the coefficients of the zeroth and first powers of  $e^{i\omega t}$  are collected and equated independently to zero. For the dc component and the fundamental mode, there results:

$$n_0 = \left[ \sqrt{k_1^2 + 8k_2\eta I_0} - k_1 \right] / (4k_2) \quad (6)$$

$$\bar{n}_1 = \frac{\frac{1}{2}\eta I_0 g_1}{i\omega + k_1 + 4k_2 n_0} \quad (7)$$

The theoretical phase and amplitude depend upon the reaction product that is detected. If atom vaporization is considered, the reaction product vector, described by the apparent reaction probability  $\epsilon$  and the phase lag  $\phi$ , is:

$$\epsilon e^{-i\phi} = \frac{k_1 \bar{n}_1}{\frac{1}{2} I_0 g_1} = \frac{\eta k_1}{i\omega + k_1 + 4k_2 n_0} \quad (8)$$



where the subscript "1" on the phase lag symbol has been removed because only the fundamental mode of the output signal is considered. Casting Eq. (8) into polar form and identifying  $\epsilon$  and  $\phi$  yields:

$$\epsilon = \eta \left[ 1 + \frac{b}{2} + \left( \frac{\omega}{k_1} \right)^2 \right]^{-1/2} \quad (9)$$

and

$$\tan \phi = \frac{\omega/k_1}{\sqrt{1 + b/2}} \quad (10)$$

where

$$b = 16\eta I_0 k_2 / k_1^2 \quad (11)$$

Eqs. (1) and (10) reproduce the plots on Figs. 4 and 5 of Ref. 5 with high accuracy.

## 2. Adsorption and $m^{\text{th}}$ order desorption

The surface mass balance for this class of reactions is:

$$\frac{dn}{dt} = \eta I_0 g(t) - k_n^m \quad (12)$$

Substitution of Eqs. (3) and (4) into Eq. (12) permits  $n_0$  and  $\bar{n}_1$  to be determined. The fundamental mode of the desorbed product flux referenced to the impinging reactant flux (i.e., the reaction product vector) is:

$$\epsilon e^{-i\phi} = \frac{m k n_0^{m-1} \bar{n}_1}{\frac{1}{2} I_0 g_1} \quad (13)$$

from which the amplitude factor (the apparent reaction probability) and the reaction phase lag may be identified as:

$$\epsilon = \frac{\eta}{\left[ 1 + \left( \frac{\omega}{k_{\text{eff}}} \right)^2 \right]^{1/2}} \quad (14)$$

$$\tan\phi = \frac{\omega}{k_{\text{eff}}} \quad (15)$$

For second order desorption ( $m = 2$ ),

$$k_{\text{eff}} = (2\eta I_0 k)^{1/2} \quad (16)$$

and for third order desorption ( $m = 3$ ):

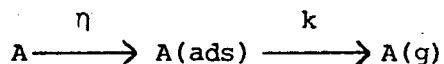
$$k_{\text{eff}} = \left( \frac{81}{4} k \eta^2 I_0^2 \right)^{1/3} \quad (17)$$

We have obtained the exact solutions for this general class of reactions by the method outlined at the beginning of this paper and have compared the calculated amplitudes and phases with those predicted by Eqs. (14) and (15) of the approximate method. The results are shown in Fig. 1 for  $m = 2$  and  $m = 3$ .

For second order desorption, the maximum deviation of the approximate solution from the exact result is 5% in the amplitude and  $3^\circ$  in phase. For third order desorption, the corresponding errors are 6% and  $4^\circ$ . These cases represent rather severe tests of the approximate method because of the strong nonlinearity in the desorption steps. If the reaction mechanism contains linear terms (such as diffusion) in addition to the nonlinear steps, the effect of the latter is reduced and the agreement between the approximate and exact solution methods is improved.

### 3. Langmuir Adsorption-Desorption

A class of nonlinear reactions involving coverage-dependent adsorption followed by simple desorption may be written as:



In the simplest case, the sticking probability varies linearly with the fraction of unoccupied surface and the mass balance on adsorbed atoms is:

$$\frac{dn}{dt} = \eta_0 (1-\theta) I_0 g(t) - kn \quad (18)$$

where  $\eta_0$  is the bare surface sticking probability and  $\theta = n/N_s$  is the coverage,  $N_s$  being the site density on the surface. In an equilibrium system, this mechanism leads to the Langmuir adsorption isotherm. Solution of Eq. (18) for the fundamental mode of the coverage  $\theta$  by substitution of Eqs. (3) and (4) and referencing the desorption flux to the incident flux yields:

$$\epsilon = \frac{\eta_0}{(1 + q/2)^2} \left\{ 1 + \left( \frac{\omega/k}{1 + q/2} \right)^2 \right\}^{-\frac{1}{2}} \quad (19)$$

$$\tan\phi = \frac{\omega/k}{1 + q/2} \quad (20)$$

where:

$$q = \frac{\eta_0 I_0}{k N_s} \quad (21)$$

Comparison of the approximate solutions for  $\epsilon$  and  $\phi$  given by Eqs. (19) and (20) with the exact solution is shown in Fig. 2. The two solution methods give identical results for  $q = 0$ , in which case the coverage is zero and the process is linear. Even for substantial coverages (large  $q$ ), the approximate method follows the exact solution reasonably well. The largest errors in amplitude occur in

regions of large  $q$  and small  $\omega/k$ . At  $q = 3$ , for example, the approximate method predicts amplitude factors which are as much as  $\sim 35\%$  lower than the correct values. Because of these discrepancies, it is of interest to examine how interpretation of data collected from a modulated molecular beam experiment would be affected by using the approximate theory. We suppose that the surface processes are actually those of Langmuir adsorption-desorption and concentrate upon the amplitude data only. Three types of experiments are usually conducted in a molecular beam experiment: surface temperature variations, beam intensity variation, and modulation frequency variation, each with the other two variables held constant. Typical trajectories for these three types of experiments are shown in the lower part of Fig. 2. The arrows indicate the direction followed as the indicated variable is increased.

Each point on the line labelled "temperature variation" in Fig. 2 corresponds to a different surface temperature  $T$ . Assuming Arrhenius form of the desorption rate constant  $k$ , the abscissa of Fig. 2 is related to  $T$  by:  $\omega/k = A \exp(E/RT)$ , where  $A$  is the ratio of the fixed modulation frequency and the pre-exponential factor of  $k$ .  $E$  is the activation energy for desorption and  $R$  is the gas constant. Since the beam intensity is fixed in this series of experiments, Eq. (21) shows that the parameter  $q$  is also of the form:  $q = B \exp(E/RT)$ . At sufficiently high temperature,  $\omega/k$  and  $q$  approach the small values of  $A$  and  $B$ , respectively; in this limit, the temperature variation of the measured amplitude approaches that characteristic of simple adsorption-desorption on a bare surface. As temperature is reduced, both  $\omega/k$  and  $q$  are simultaneously increased, and the temperature variation curve in Fig. 2 begins to deviate from the  $q = 0$  curve. The temperature variation curve cuts the  $\epsilon(\omega/k, q)$  family of theoretical curves in regions where there is not much difference between the approximate and exact analyses of this surface reaction model.

The vertical line with arrows in Fig. 2 represents a trajectory of a beam intensity variation experiment. In this case, the experimental parameters may place the system in a region of the  $\epsilon(\omega/k, q)$  plot where the approximate method is in significant error. The following effects on interpretation of the data would be expected. Since we have supposed that the reaction mechanism is a perfect Langmuir adsorption-desorption process, it should be possible to select values of  $\eta_0$ ,  $k$  and  $N_s$  for which the amplitude versus beam intensity data fit the exact theory. On the other hand, if Eq. (19) is used for interpreting these data, deviations between theory and experiment will appear at high beam intensities. Since molecular beam data (in common with most chemical kinetic data) are usually not of very high precision, the effect of utilizing the approximate theory instead of the exact theory would most probably be the determination of somewhat different parameters ( $\eta_0$ ,  $k$  and  $N_s$  for the beam intensity variation experiment) in the two cases.

The major difference between the effect of modulation frequency changes in the approximate and exact theories is the magnitude of the change in  $\epsilon$  over a given frequency range. Suppose, for example, that measurements of amplitude versus frequency exhibit a factor of  $\sim 6$  decrease as the frequency is increased by a factor of 100 (e.g., for the range  $0.1 \leq \omega/k \leq 10$  in Fig. 2). If the approximate theory were used in interpreting these data, one would decide from the plots of Fig. 2 that the correct value of  $q$  is  $\sim 1$ . However, if the exact theory were used to interpret the same data, the curve for  $q \approx 3$  would provide the observed factor of 6 change in  $\epsilon$  over the modulation frequency range studied.

The magnitude of the errors incurred in interpreting molecular beam data with the approximate theory instead of the exact solution of coverage-dependent surface mechanisms increases as the beam intensity parameter  $q$  increases. However, there is a natural limitation to the maximum values of  $q$  which can be explored by the molecular beam experiment. As  $q$  becomes large (whether due to a

2 6 5 8 0 2 6 0 0 0

temperature decrease or to a beam intensity increase) the apparent reaction probability  $\epsilon$  diminishes and the reaction product signal becomes more difficult to detect above noise and background. Thus the large- $q$  regions where the approximate theory begins to fail often correspond to regimes where the experimental data are poor because of signal detection limitations.

#### 4. Generalized Coverage-Dependent Adsorption-Desorption

The general class of first order reaction with adsorption probabilities dependent on the coverage are included in the surface mass balance:

$$\frac{dn}{dt} = \eta(\theta) I_0 g(t) - kn \quad (22)$$

The adsorption probability can be expressed as a Taylor series about the mean coverage,  $\bar{\theta}$ :

$$\eta(\theta) = \eta(\bar{\theta}) + \left(\frac{d\eta}{d\theta}\right)_{\bar{\theta}} (\theta - \bar{\theta}) + \frac{1}{2} \left(\frac{d^2\eta}{d\theta^2}\right)_{\bar{\theta}} (\theta - \bar{\theta})^2 + \dots \quad (23)$$

and may be approximated to lowest order in  $(\theta - \bar{\theta})$  as a linearized adsorption probability,

$$\eta(\theta) \approx \bar{\eta} [1 - a(\theta - \bar{\theta})] \quad (24)$$

where

$$a = -\frac{1}{\bar{\eta}} \left(\frac{d\eta}{d\theta}\right)_{\bar{\theta}} \quad (25)$$

and  $\bar{\eta} = \eta(\bar{\theta})$ .

The mean coverage appearing in Eqs. (24) and (25) is defined by:

$$\bar{\theta} = \frac{\omega}{2\pi} \int_{-\pi/\omega}^{\pi/\omega} \theta(t) dt \quad (26)$$

The amplitude and phase may be evaluated to one of three levels of accuracy.

### Fully linear analysis

In the least accurate, or "fully linear" level of approximation, the linearized adsorption probability, Eq. (24), is combined with the approximate solution of Eq. (22) using Eqs. (3) and (4). The following phase lag and apparent reaction probabilities are obtained by equating the coefficient of  $e^{i\omega t}$  to zero:

$$\epsilon = \frac{\bar{\eta}}{(1 + q'/2)^2} \left[ 1 + \left( \frac{\omega/k}{1 + q'/2} \right)^2 \right]^{-\frac{1}{2}} \quad (27)$$

$$\tan\phi = \frac{\omega/k}{1 + q'/2} \quad (28)$$

where:

$$q' = a \left( \frac{\bar{\eta}}{\eta_0} \right) q = \frac{a\bar{\eta}I_0}{kN_s} \quad (29)$$

The time-independent term obtained by substituting Eqs. (3), (4), and (24) into Eq. (22) provides the following relation between the mean coverage and the sticking probability at the mean coverage:

$$\bar{\theta} = \theta_0 = \frac{\bar{\eta}I_0}{2kN_s} \quad (30)$$

where the first equality is a consequence of Eq. (26). Simultaneous solution of Eq. (30) and the known variation of the sticking probability with coverage,  $\eta(\theta)$ , yields the appropriate value of  $\bar{\eta}$  to be used in Eqs. (27) and (29).

### The quasilinear analysis

When the linearized sticking probability of Eq. (24) is utilized in the exact solution method, the resulting model predictions are called "quasilinear".

### Exact

In the present case, the "exact" solution refers to the results obtained by

2 6 5 8 0 2 4 0 0 0 0

solving Eq. (23) exactly using the exact functional dependence of sticking probability on coverage rather than the linearized form of Eq. (24).

#### Adjacent site adsorption

To illustrate the accuracy of the fully linearized and quasilinear approximations just described, we consider the common case of adsorption occurring on  $m$  adjacent sites. Here, the sticking probability is given by:

$$\eta(\theta) = \eta_0 (1 - \theta)^m \quad (31)$$

Application of Eqs. (25) and (26) gives:

$$\bar{\eta} = \eta_0 (1 - \bar{\theta})^m \quad (32)$$

and

$$a = \frac{m}{1 - \bar{\theta}} \quad (33)$$

For  $m = 0$ , all three calculation methods give the same result, since the problem is linear. When  $m = 1$ , the mechanism reverts to adsorption following the Langmuir isotherm, which was analyzed in the preceding section. In this case, the quasilinear method is identical to the exact method. For  $m \geq 2$ , however, all three methods yield different results, as shown for  $m = 2$  and  $q = 1$  in Fig. 3. The fully linearized method is in error by as much as 33% in amplitude and  $7^\circ$  in phase. The corresponding errors incurred by using the quasilinear analysis are 6% and  $3^\circ$ .

Under even more adverse circumstances, the discrepancies between the three solutions can become much larger. Such a situation arises in the limit:  $\omega/k \rightarrow \infty$  but  $\omega/q'k \rightarrow 0$ . In this limit, Eqs. (27) and (28) yield:

$$\epsilon/\bar{\eta} = (1 + q'/2)^{-2}; \quad \phi = 0^\circ$$

On the other hand, the quasilinear analysis in the same limit yields:



$$\epsilon/\bar{\eta} = (1 + q')^{-1} (1 + \omega^2/k^2)^{-1/2}; \quad \phi = 90^\circ$$

The phase lags differ by  $90^\circ$ , but since both  $q'$  and  $\omega/k$  are large, this divergence only occurs when the amplitude approaches zero, and the quality of the experimental data suffers from the approach to the signal detection limit.

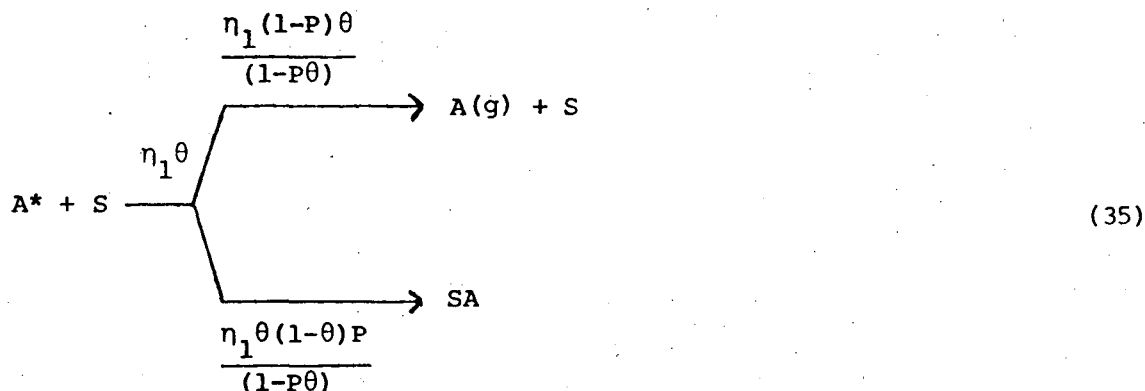
#### A pathological case

It is not at all difficult to construct physically reasonable models for the coverage-dependence of the adsorption probability for which the fully linearized and quasilinear analyses are both in substantial error. One such mechanism involves adsorption by two parallel routes, the first by direct chemisorption on vacant sites and the second by physisorption on the chemisorbed reactant. The adsorption steps of this mechanism may be written as:



where  $SA$  and  $A^*$  are chemisorbed and physisorbed species, respectively, and  $\theta$  is the fraction of sites on which chemisorption has occurred.  $\eta_0(1-\theta)$  and  $\eta_1\theta$  are the adsorption probabilities for chemisorption and physisorption, respectively.

The conversion of a physisorbed species to a chemisorbed one is assumed to occur via a hopping mechanism, with a characteristic time  $t_H$  for hopping to an adjacent site, and  $t_D$  for desorption of the physisorbed species. Conversion occurs when a vacant site is reached. The probability of desorption of a physisorbed species during a single hop is therefore  $1 - \exp(-t_H/t_D)$ , and the probability of conversion from physisorbed to chemisorbed state is  $(1 - \theta)\exp(-t_H/t_D)$ . Considering all such hops until the physisorbed species has either desorbed or been chemisorbed, the ultimate fate of the physisorbed species can be described by:



where  $P = \exp(-t_H/t_D)$ . The sticking probability to be used in Eq. (22) for this particular mechanism is:

$$\eta(\theta) = \begin{cases} \eta_0 (1-\theta) + \frac{\eta_1 \theta (1-\theta)P}{1-P\theta} & \text{for } \theta < 1 \\ 0 & \text{for } \theta > 1 \end{cases}
 \tag{36}$$

The expression for "a" needed in the fully linear

$$a = \frac{\eta_1 (1-P) - (\eta_1 - \eta_0) (1 - P\bar{\theta})}{(1-P\bar{\theta}) (1-\bar{\theta}) \{ \eta_1 - [\eta_1 - \eta_0] [1 - P\bar{\theta}] \}}
 \tag{37}$$

The pathological nature of this reaction mechanism (from the point of view of the approximate method of solving the surface mass balance) can immediately be seen by examining the limit in which hopping of the physisorbed species is rapid (i.e.,  $P \approx 1$ ) and in which  $\eta_0 = \eta_1$ . In this instance, Eqs. (36) and (37) reduce to:

$$\tilde{\eta} = \begin{cases} \eta_0 & \text{for } \theta < 1 \\ 0 & \text{for } \theta > 1 \end{cases}
 \tag{38}$$

and

$$a = 0$$

Thus, the fully linearized approximation predicts no effect of the coverage dependent adsorption probability on the amplitude attenuation and the phase lag. These quantities are governed entirely by the desorption kinetics (i.e., by the magnitude of the rate constant  $k$ ). Examination of the exact solution method shows that when  $\bar{\theta} \rightarrow 1$ , the phase lag and amplitude attenuation are controlled almost completely by the adsorption process, with little contribution from the desorption step. The approximate method of solving the surface mass balance fails dramatically for this particular case, and the exact method must be used when the mechanism exhibits singularities of the type evident from Eq. (38).

### Conclusions

Although the proposed method of analyzing nonlinear surface reaction mechanisms in modulated molecular beam experiments is not exact, the errors introduced by the use of the truncated Fourier expansions represented by Eqs. (3) and (4) are usually well within the precision of phase and amplitude measurements. The new method, however, is substantially faster to use than the exact solution technique, and in addition, produces analytical formulae which are useful in visualizing trends as various parameters (temperature, beam intensity, frequency) are changed. The method appears to be general and applicable to any nonlinear kinetic process. The second harmonic of the reaction product signal is as easily calculated as the first harmonic, or fundamental mode. The presence of a second harmonic contribution (either in the data or in the model calculation) is a sensitive test of the linearity of the system. Surface processes in which all elementary steps are first order produce modulated reaction product signals which have no even harmonic content. The application of this method to parametric nonlinearities introduced through the dependence of the adsorption probability on the coverage appears to be less sound, giving results which may be both quantitatively and qualitatively in error. Even in these situations, however, the

large errors appear to occur only when the signal is strongly attenuated, and hence may be lost due to signal detection limits.

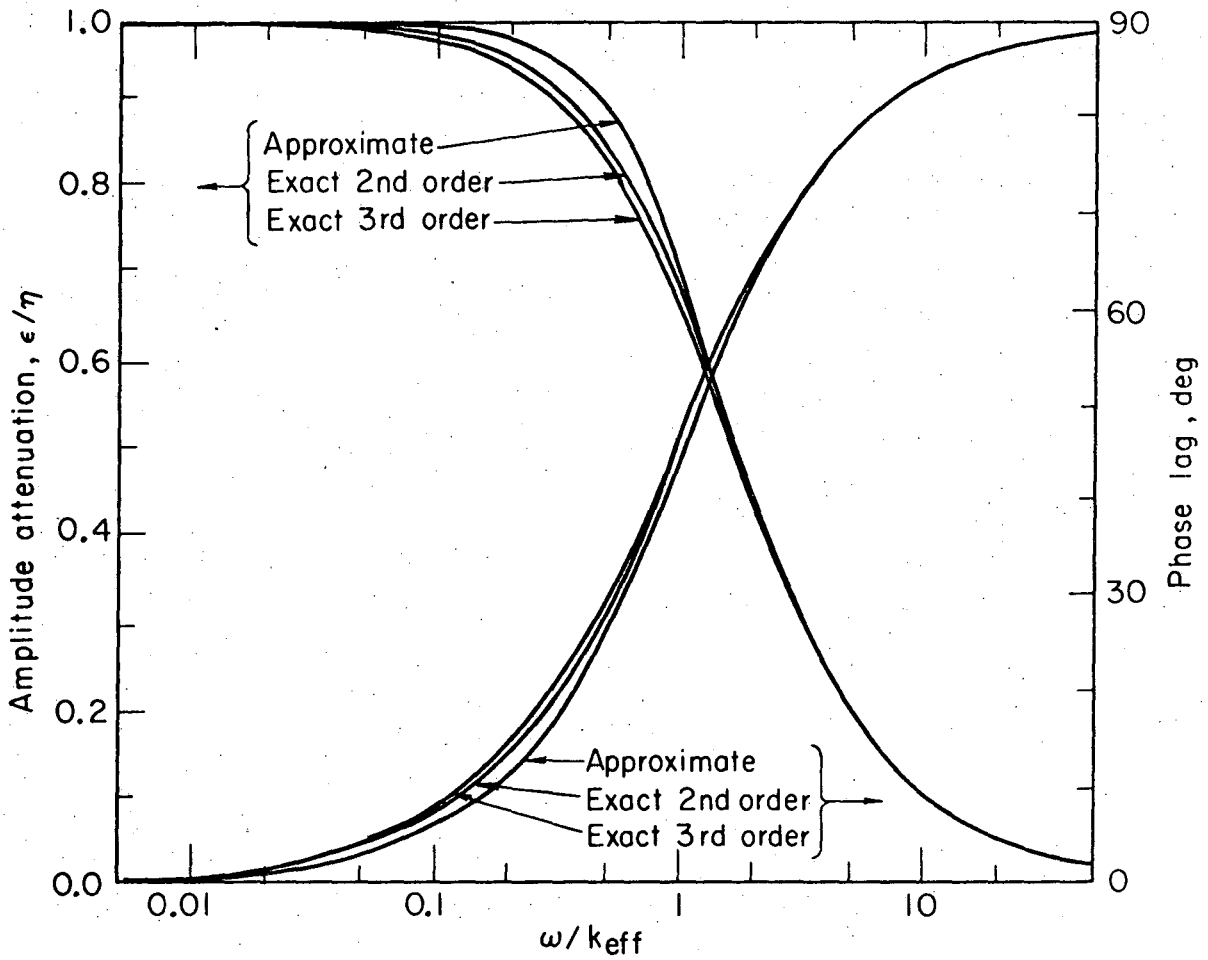
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FIGURE CAPTIONS

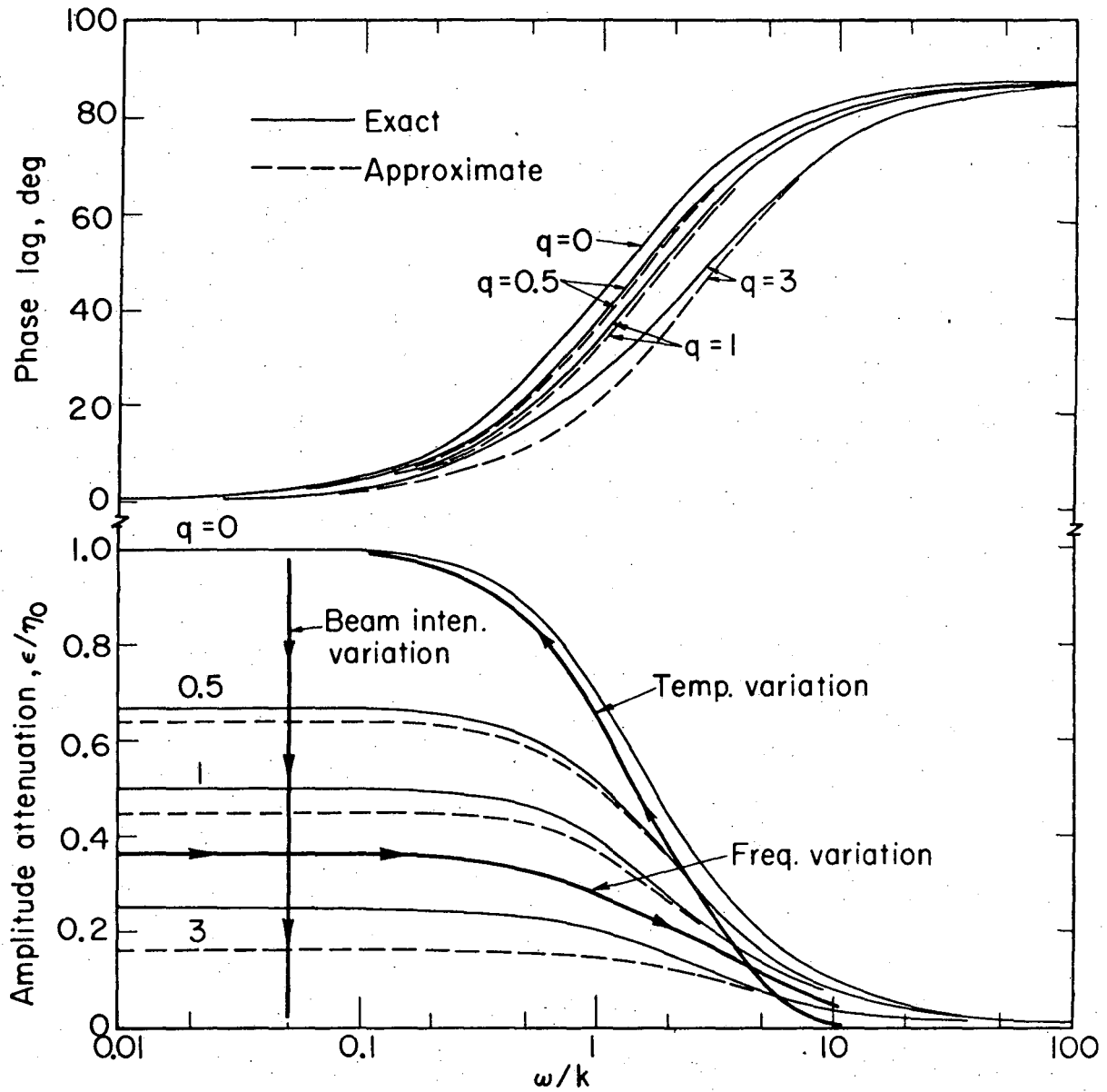
1. Phase lag and amplitude attenuation for first, second and third order desorption kinetics
2. Phase lag and amplitude attenuation for Langmuir adsorption-desorption
3. Phase lag and amplitude attenuation for adsorption probabilities depending upon  $(1-\theta)^m$ , where  $m = 0, 1, \text{ or } 2$ . The beam intensity parameter (Eq. (22)) is unity



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Fig. 1

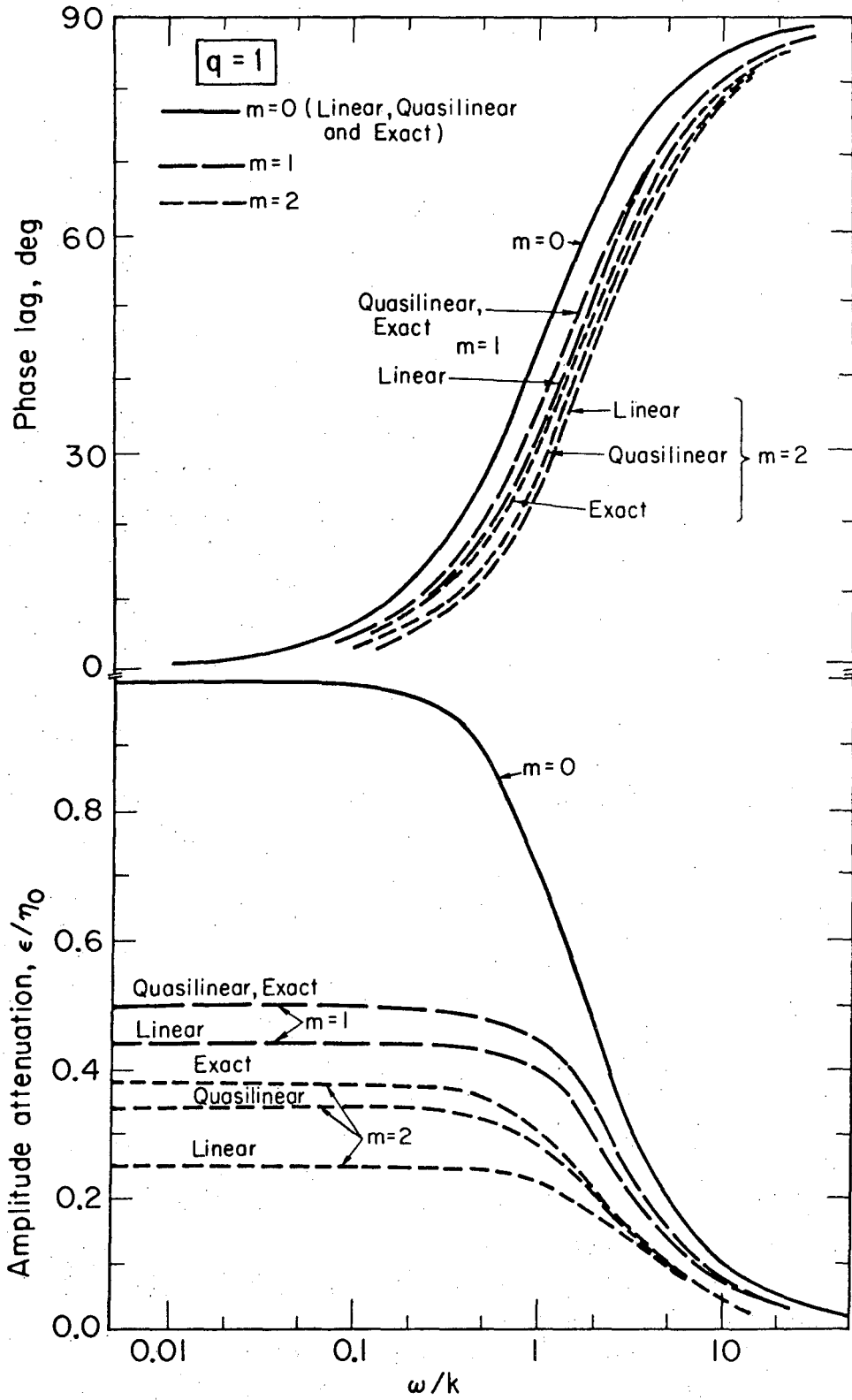
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Fig. 2





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Fig. 3

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