

Reactive Scattering from Solid Surfaces Treatment of Lock-in Detector Signals from Modulated Molecular Beams

JAMES A. SCHWARZ* AND ROBERT J. MADIX†

Received May 13, 1968; revised July 23, 1968

The lock-in detector signals for modulated molecular beams reactively scattered from solid surfaces were investigated. For a simple first order adsorption-desorption for the surface reaction it was found that the phase lag for the product signal rapidly shifts to lower values in that region of the surface temperature at which the product desorption rate "resonates" with the beam modulation rate. At higher chopping frequencies the phase correction for the dispersion of the beam packet becomes significant. For the reaction rate constants and the wide range of modulation frequencies investigated, the logarithm of the product signal plotted against the reciprocal of the surface temperature is linear with a slope proportional to the product desorption energy without correction of signal intensity for beam dispersion.

INTRODUCTION

Information processing by tuned amplification and phase-sensitive demodulation has become a useful and powerful technique in extracting low-level signals from high noise backgrounds in molecular beam experiments (1). The analysis and application of these techniques to the study of gas-solid interactions has been limited almost exclusively to nonreacting systems (2-6).

In the following analysis the potential of modulated molecular beams for the study of high-temperature gas-solid reactions is examined. Calculations are presented which illustrate how the rate constant for a first order surface reaction can be determined from reaction product signal amplitudes and phase-lag measurements. The limitations of the technique are indicated and suggestions for interpreting experimental data are made.

FORMULATION

Consider the following elementary reaction sequence

* Department of Chemistry, Stanford University, Stanford, California.

† Department of Chemical Engineering, Stanford University, Stanford, California.



describing the overall reaction process



The incident gas molecules A_2 adsorb dissociatively on the substrate S , with a probability α to form bound atoms $A_{(a)}$ which subsequently evaporate as product, $SA_{(g)}$, according to first order kinetics.

Experimental observations of the sticking probability, α , of diatomic molecules on metal or semiconductor surfaces show α to be nearly independent of surface coverage of adsorbed species at low coverage and roughly linearly dependent on coverage at coverages approaching a monolayer (7). These two regions are separated, in most cases, by a knee in the α versus coverage curve. Consequently, in a region of coverage away from the knee α depends linearly on the surface coverage according to

$$\alpha = \alpha_0(1 - a\theta_a), \quad (4)$$

where α_0 is the sticking probability on the bare surface, θ_a is the fraction of the surface sites occupied by A atoms, and a is a constant characteristic of the region

of coverage. For θ_a near zero, $\alpha = \alpha_0$. In any event, in principle, the peak-to-peak variation in beam intensity striking the surface can be made small compared to the dc intensity and the dependence of α on θ_a can be linearized about some value of θ_a according to Eq. (4). Practically, one must take care to avoid surface coverages in the vicinity of the knee in the α versus coverage plot.

ANALYSIS

Let $G(t - t'')$ be the fraction of molecules that pass uninterrupted by the beam chopper at time $t - t''$ where t'' is the time of flight of a beam molecule between the chopper and the target surface. Then the fractional contribution to the flux at the surface at t compared to the total efflux from the effusion orifice is

$$\Gamma_i(t) = \int_0^\infty \int_{\Omega_1} G(t - t'') P_3(t'') d\Omega dt'' \quad (5)$$

$G(t - t'')$ is proportional to the open area of the effusion orifice seen by the scattering surface as a function of time. For a vibrating reed chopper (8)

$$G(t - t'') = \frac{2R_m}{\pi R} \left[\frac{\pi R}{4R_m} - \cos \omega(t - t'') \right] \quad (6)$$

where R is the radius of effusion orifice; R_m , maximum extension of the chopper reed; and T_0 , is the period of modulation.¹ As previously described (3) $P_3(t'')$ is the normalized distribution function associated with Maxwellian beams, giving the fraction of molecules that have reduced velocities z , between z and $z + dz$ that contribute to the total flux at time t . The solid angle subtended by the solid surface at the effusion orifice is given by Ω_1 . If the integration over the solid angle is assumed to contribute only a geometric factor of Ω_1 to the integral of Eq. (5) $\Gamma_i(t)$ may be evaluated directly. For a well-collimated beam this assumption is nearly correct. The result is

¹This form of $G(t - t'')$ is valid only for $R_m < \frac{1}{4}\pi R$.

$$\Gamma_i(t) = \Omega_1 \left[\frac{1}{2} - \frac{2}{\pi} \frac{R_m}{R} A_3(X_1) \cos(\omega t - \lambda) \right] \quad (7)$$

with

$$\lambda = \tan^{-1} \left[\frac{K_3(X_1)}{I_3(X_1)} \right] \quad (8)$$

where

$$A_n(X) = \frac{2}{\Gamma[\frac{1}{2}(n+1)]} [K_n^2(X) + I_n^2(X)]^{1/2} \quad (9)$$

$$I_n(X) = \int_0^\infty z^n \exp(-z^2) \cos \frac{X}{z} dz \quad (10)$$

$$K_n(X) = \int_0^\infty z^n \exp(-z^2) \sin \frac{X}{z} dz \quad (11)$$

$$X = \omega L / \bar{C} \quad (12)$$

$$\bar{C} = (2R_b T / M)^{1/2} \quad (13)$$

In Eq. (9), $n = 3$ and $X = X_1 = \omega L_1 / \bar{C}$ and $\bar{C} = \bar{C}_1 = (2R_b T_1 / M_1)^{1/2}$. L_1 is the distance from the chopper reed to the surface; R_b is the gas constant; T_1 is the beam gas temperature; M_1 is the molecular weight of the beam gas species; and ω is the modulation frequency.

For products leaving the surface at time $(t^* - t''')$, the instantaneous number density of molecules at the detector at time t^* is (5, p. 1092)

$$S(t^*) = \int_0^\infty \int_{\Omega_2} \Gamma_d(t^* - t''') P_2(t''') d\Omega dt''' \quad (14)$$

where $P_2(t''')$ is the number density distribution function for a Maxwellian beam. As before the solid angle integral will yield a numerical factor Ω_2 which is the solid angle defined by the detector as seen by the surface. From Eqs. (2)–(4) the rate at which products leave the surface, Γ_d , is given by the solution of the differential equation

$$\frac{d\Gamma_d}{dt} + \left[\frac{2a\alpha_0\Gamma_i(t)}{N_t} + k_d \right] \Gamma_d = 2\alpha_0 k_d \Gamma_i(t) \quad (15)$$

In Eq. (15) N_t is the total number of surface sites/cm², and k_d is the phenomenological first order desorption rate constant.

Here it is assumed that the product beam leaves the surface at the surface temperature with a spatial distribution independent of the gas or surface temperatures. As the distribution of product flux from the surface is probably cosine, this assumption is not severe. In principle any product spatial distribution function can be included in Eq. (14) for integration over Ω_2 .

The general solution of Eq. (15) is

$$\Gamma_d(\xi) = C \exp \varphi(\xi) + \exp \varphi(\xi) \int \exp[-\varphi(\xi')] f(\xi') d\xi' \quad (16)$$

where

$$\varphi(\xi) = -A\xi + B \sin(\omega\xi - \lambda) \quad (17)$$

$$f(\xi) = 2k_d\alpha_0\Omega_1 \left[\frac{1}{2} - \frac{2R_m}{\pi R} A_3(X_1) \cos(\omega\xi - \lambda) \right] \quad (18)$$

$$A = \frac{\alpha_0\Omega_1 a}{N_t} + k_d \quad (19)$$

$$B = \frac{2\alpha_0\Omega_1 a}{Nt} \frac{2R_m}{\pi R} A_3(X_1) \frac{1}{\omega} \quad (20)$$

The constant of integration, C , need not be specified uniquely. This term is exponentially damped and corresponds physically to the initial start up of the beam. For low surface coverage B is small (because a is small) and the obvious expansion of the exponential functions is made. In the steady state and to the first order in B .

$$\Gamma_d(t) = 2k_d\alpha_0\Omega_1 \left[\frac{1}{2k_d} - \frac{2R_m}{\pi R} \frac{A_3(X_1)}{(k_d^2 + \omega^2)^{1/2}} \cos(\omega t - \theta) \right] \quad (21)$$

where

$$\theta = \tan^{-1} \left[\frac{\omega I_3(X_1) + k_d K_3(X_1)}{k_d I_3(X_1) - \omega K_3(X_1)} \right] \quad (22)$$

From Eq. (14) we then have

$$S(t^*) = 2k_d\alpha_0\Omega_1\Omega_2 \left\{ \frac{1}{2k_d} - \frac{2R_m}{\pi R} \frac{A_3(X_1)A_2(X_2)}{(k_d^2 + \omega^2)^{1/2}} \cos(\omega t^* - (\theta + \lambda)) \right\} \quad (23)$$

where

$$\lambda = \tan^{-1} \left[\frac{K_2(X_2)}{I_2(X_2)} \right] \quad (24)$$

Analogous to Eqs. (12) and (13)

$$X_2 = \omega L_2 / \bar{C}_2 \quad (25)$$

$$\bar{C}_2 = (2R_b T_2 / M_2)^{1/2} \quad (26)$$

where L_2 is the distance from the surface to the detector, R_b is the gas constant, $T_2 = T_s$ the surface temperature, and M_2 is the molecular weight of the product. When this signal is demodulated and averaged in the lock-in detector (5, p. 1093) a maximum dc signal $\mathfrak{F}(S)$ is obtained when the phase, φ_R , is

$$\varphi_R = \pm \left[\tan^{-1} \left[\frac{\omega I_3(X_1) + k_d K_3(X_1)}{k_d I_3(X_1) - \omega K_3(X_1)} \right] + \tan^{-1} \left[\frac{K_2(X_2)}{I_2(X_2)} \right] \right] \quad (27)$$

and then

$$\mathfrak{F}^2(S) \sim \frac{k_d A_3(X_1) A_2(X_2)}{[k_d^2 + \omega^2]^{1/2}} \quad (28)$$

This is a general solution, dependent only on the existence of a linearizeable coverage-dependent sticking probability and holds over that region of surface coverage in which the sticking probability can be described by Eq. (4), and the expansion of Eq. (16) is valid. In the derivation of Eqs. (27) and (28) k_d was assumed large compared to $\alpha_0\Omega_1 a / N_t$.

DISCUSSION

In Figs. 1 and 2 the phase lag and logarithm of the amplitude of the product signal were plotted as a function of $1/T_s$ under conditions corresponding approximately to those reported experimentally (9). A first order desorption rate constant given by $k_d = 10^{13} \exp(-40,000 \text{ cal}/RT_s)$ sec⁻¹ was assumed. Three convenient beam

²For the first order kinetic scheme discussed here, the amplitude and phase lag are independent of the gating function [Eq. (6)] provided that it is periodic. The reason for this is because the lock-in detector responds only to the tuned harmonic of the Fourier transform of the process signal.

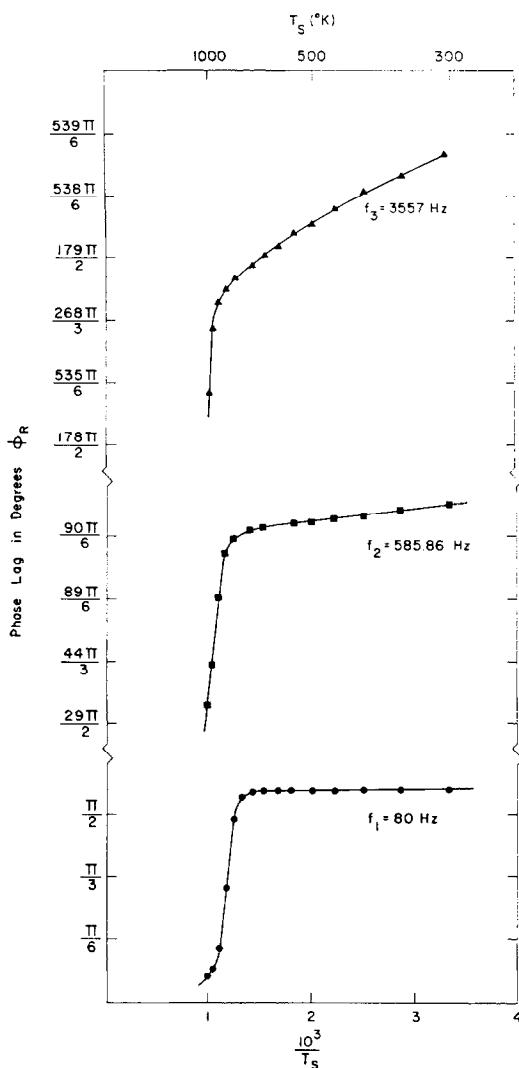


FIG. 1. The phase lag, φ_R (Eq. 27) at the various beam modulation frequencies plotted against the reciprocal of the surface temperature.

modulation frequencies were chosen: $f_1 = 80$ Hz, $f_2 = 585.86$ Hz, $f_3 = 3557$ Hz. Dimensions were taken as follows: chopper-to-surface distance of 15 cm, surface-to-detector distance of 4 cm. An incident reactant gas with $M_1 = 32$ g/g mole, and $T_1 = 300^\circ\text{K}$, and for convenience, a product beam with $M_2 = 3 M_1$ was assumed. The product temperature was taken equal to the surface temperature over the range $300^\circ \leq T_s \leq 1000^\circ\text{K}$.

Several interesting features were immediately apparent from the calculations.

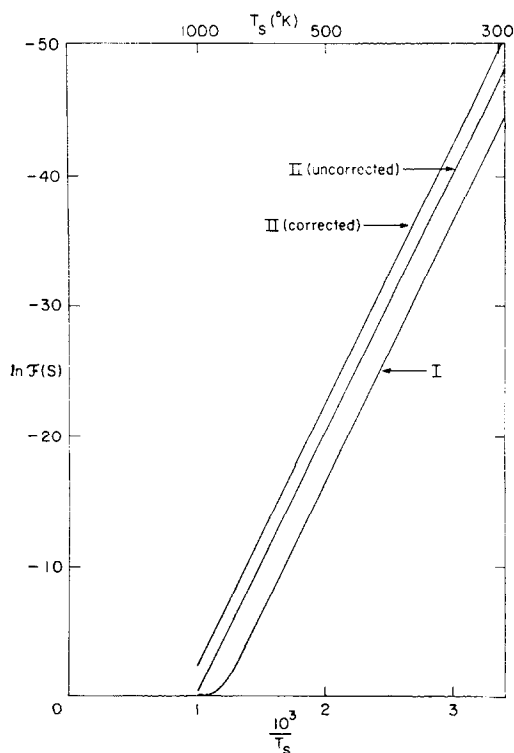


FIG. 2. Logarithm of the signal strength [Eq. (28)] at the various beam modulation frequencies plotted against the reciprocal of the surface temperature: curve I, $f_1 = 80$ Hz; curve II (uncorrected for beam dispersion), $f_3 = 3557$ Hz; curve II (corrected for beam dispersion), $f_3 = 3557$ Hz.

The total phase lag calculated, Eq. (27), consisted of a time-of-flight delay, a surface residence time, and a correction for the dispersion of the beam packet due to the velocity distribution of the beam particles. Since the time delay associated with these events is independent of the modulation rate at a given surface temperature, a larger phase lag must be measured at a higher chopping frequency. The relation

$$\frac{(\varphi_R)_i}{(\varphi_R)_0} = \frac{T_0}{(T_0)_i} \quad (29)$$

determined the phase lag for any modulation period $(T_0)_i$, once the phase lag is known at some period T_0 . For modulation rates of the order of 80 Hz and rate constants of the magnitude assumed here $(\varphi_R)_0 < 360^\circ$. In Fig. 1 the phase angles for the modulation rates assumed here have

been plotted in their appropriate quadrants modulo $2\pi[(T_0)_i/T_0]$.

As shown in Fig. 1 there is a sudden change in the phase of the product signal (relative to the incident beam) with surface temperature which is especially noticeable for the lowest modulation frequency. This effect arises when the desorption rate constant "resonates" with the chopping frequency. The phase lag at 80 Hz is sensitive to surface temperature only over a narrow range of surface temperatures due to the exponential dependence of k_d on T_s . The fact that the curves at higher chopping frequency show a more gradual phase shift with T_s is due to the increased importance in the time of flight from surface to detector. The change in phase shift is broadened and shifted to higher values of the surface temperature by increasing the chopping rate.

An Arrhenius plot of the product signal strength against the surface temperature yields the activation energy for the desorption without significant correction for dispersion of the beam. The curve labeled uncorrected in Fig. 2 was calculated from Eq. (28) with $A_1(X_1) = A_2(X_2) = 1$. The absolute error in E_a for this approximation is 0.5%. However, for sufficiently high temperatures and low modulation rates, the denominator of Eq. (28) approaches k_d and therefore the temperature variation becomes characteristic of the amplitude dispersion function $A_2(X_2)$. For low modulation rates $A_2(X_2)$ is essentially constant. The rapid leveling off of curve I in Fig. 2 indicates this condition.

SUMMARY

The purpose of this investigation was to examine in detail the information that can be obtained from the lock-in detector signals of modulated molecular beams reactively scattered from solid surfaces. For a first order adsorption and desorption and in the region of low surface coverage, the product signal strength and phase relative to the incident beam were found to depend primarily on the kinetic parameters char-

acterizing the surface reaction, the solid temperature, and the beam's modulation frequency. For typical gas-solid desorption energies ($20,000 < E_a < 40,000$ cal/mole) and Arrhenius pre-exponential factors of the order 10^{13} sec⁻¹, it was found that the product phase lag at low modulation frequencies (<100 Hz) rapidly shifted to lower values in that range of surface temperature at which the product desorption rate was comparable to the beam modulation rate. At higher modulation frequencies the dispersion of the beam packet became significant, and the phase-lag change with surface temperature was broadened and shifted to higher values of the surface temperature. For modulation frequencies less than 3600 Hz. and with the conditions cited for this model, the logarithm of the signal strength plotted against the reciprocal of the surface temperature is proportional to the desorption energy for the gas-solid reaction without correction for beam dispersion.

REFERENCES

1. For example, see FITE, W. L., AND DATZ, S., *Ann. Rev. Phys. Chem.* **14**, 61 (1963).
2. HARRISON, H., HUMMER, D., AND FITE, W. L., *J. Chem. Phys.* **41**, 2567 (1964).
3. HARRISON, H., HUMMER, D., AND FITE, W. L., Document 8097. Order from Chief, Photo Duplication Service, Library of Congress, Washington, D. C.
4. STICKNEY, R. E., LOGAN, R. M., YAMAMOTO, S., AND KECK, J. C., "Fundamentals of Gas-Surface Interactions" (H. Saltsburg, J. N. Smith, Jr., and M. Rogers, eds.) p. 422. Academic Press, 1967.
5. YAMAMOTO, S., AND STICKNEY, R. E., *J. Chem. Phys.* **47**, 1091 (1967).
6. DATZ, S., MOORE, G., AND TAYLOR, E., *Proc. Intern. Symp. Rarefied Gas Dynamics, 3rd, 1962* **1**, 347 (1963).
7. For example, see "Chemisorption" (D. O. Hayward and B. M. W. Trapnell, eds.), 2nd ed., p. 110. Butterworths (London), 1964.
8. SCHWARZ, J. A., AND MADIX, R. J., *Rev. Sci. Instr.*, to be published.
9. SMITH, J. N., JR., AND FITE, W. L., *Proc. Intern. Symp. Rarefied Gas Dynamics, 3rd, 1962* **1**, 430 (1963).