

GENERAL PHYSICS



# I. MOLECULE MICROSCOPY

## Academic and Research Staff

Prof. John G. King  
Dr. John W. Peterson

Dr. James C. Weaver  
Frank J. O'Brien

## Graduate Students

H. Fred Dylla  
Joseph A. Jarrell

Steven R. Jost  
Dusan G. Lysy

Bruce R. Silver  
Peter W. Stephens

### A. FACTORS AFFECTING RESOLUTION OF SCANNING DESORPTION MOLECULE MICROSCOPY

Joint Services Electronics Program (Contract DAAB07-71-C-0300)  
James C. Weaver

#### 1. Introduction

We are investigating two types of desorption for Scanning Desorption Molecule Microscopy (SDMM): desorption by spatially localized heating that causes a rise in the evaporation rate, and electron-stimulated desorption (ESD) which is a direct single-particle interaction between an incident low energy (~500 eV) electron and an adsorbed molecule. In each case we make order-of-magnitude estimates of the expected resolution,  $d$ , and also of the factors that affect  $d$ . In both cases we assume that the technique of neutral molecule surface staining<sup>1</sup> can be used to give a local stain coverage within a minimum resolvable area (MRA) of  $f\sigma_0$ , where  $\sigma_0 \approx 10^{15}$  molecules-cm<sup>-2</sup> corresponds to one monolayer, and  $f$  is the initial fractional coverage.

#### 2. Resolution Limitations with ESD Caused by Desorption Times

The desorption rate  $\dot{N}$  per area by ESD<sup>2</sup> is

$$\dot{N} = NQJ/e \quad (1)$$

where  $N$  is the number of adsorbed species per area,  $Q$  is the ESD total desorption cross section (of ions and neutrals),  $J$  is the current density of the electron beam, and  $e = 1.6 \times 10^{-19}$  coulombs. The rate is independent of area, and the time constant for ESD is

$$\tau_{\text{ESD}} = e/QJ. \quad (2)$$

Typically  $Q \lesssim 10^{-16}$  cm<sup>2</sup>, with values often in the range  $10^{-18}$  cm<sup>2</sup>- $10^{-20}$  cm<sup>2</sup> (at least for chemisorbed species, but probably somewhat larger for physisorbed species.<sup>2</sup>) In Table I-1 typical expected values of  $\tau_{\text{ESD}}$  are given for a range of current densities

## (I. MOLECULE MICROSCOPY)

for several values of  $Q$ . State-of-the-art values of  $J \approx 10^2 \text{ A-cm}^{-2}$  should be attainable in small spot sizes by the use of field-emitting tips,<sup>3</sup> although initially we are using thermionic sources for which  $J$  (at the sample) is of the order of  $1 \text{ A-cm}^{-2}$ . As a rough estimate we note that in a time  $\Delta t = 5 \tau_{\text{ESD}}$

Table I-1. Typical values of  $\tau_{\text{ESD}}$ .

J (amp-cm <sup>-2</sup> )	$\tau_{\text{ESD}}$ (s)		
	$Q = 10^{-16} \text{ cm}^2$	$Q = 10^{-18} \text{ cm}^2$	$Q = 10^{-20} \text{ cm}^2$
$10^{-2}$	$2 \times 10^{-1}$	$2 \times 10^1$	$2 \times 10^3$
$10^0$	$2 \times 10^{-3}$	$2 \times 10^{-1}$	$2 \times 10^1$
$10^2$	$2 \times 10^{-5}$	$2 \times 10^{-3}$	$2 \times 10^{-1}$

an exponential decay (of the coverage of adsorbed molecules) will be ~99% complete. We could, of course, use  $\Delta t = \tau_{\text{ESD}}$ , but here we estimate the maximum acceptable  $\tau_{\text{ESD}}$  conservatively by using  $\Delta t = 5 \tau_{\text{ESD}}$ . We thus estimate the maximum acceptable  $\tau_{\text{ESD}}$  by noting that a fairly good micrograph containing  $10^5$  MRA with an assumed maximum acceptable exposure time,  $t_{\text{exp}}$ , of  $10^3$  seconds gives  $\Delta t_{\text{max}} = \text{maximum time/MRA} = t_{\text{exp}}/N_{\text{MRA}} = 10^{-2} \text{ s} \approx 5 \tau_{\text{ESD}}$ ; therefore,  $\tau_{\text{ESD, max}} = 2 \times 10^{-3} \text{ s}$ . If, for example,  $J_{\text{max}} \approx 10^2 \text{ A-cm}^{-2}$ , complete desorption is possible only if  $Q \gtrsim 10^{-18} \text{ cm}^2$ , so that adsorbed species with  $Q \lesssim 10^{-18} \text{ cm}^2$  may not be accessible to SDMM by ESD under these conditions. For our initial  $J \approx 1 \text{ A-cm}^{-2}$  we shall need  $Q \approx 10^{-16} = Q_{\text{max}}$ , a cross section that probably will only be found for physisorbed stain molecules,<sup>2</sup> or we shall have to be content with fewer than  $10^5$  MRA in a micrograph. In short, both long exposure times and high current densities will be needed in order to sample most of the adsorbed molecules within an MRA by ESD.

### 3. Electron Radiation Damage

Apparently a very crude rule of thumb<sup>4</sup> is that damage becomes appreciable in electron microscopy of organic molecules when the integrated electron radiation reaches  $\sigma^* \approx 10^{-1} \text{ coulomb-cm}^{-2}$ . For an MRA irradiated for ESD we expect

$$\sigma_{\text{ESD}}^* = J\Delta t \approx 5 J\tau_{\text{ESD}} = 5 e/Q. \quad (3)$$

Thus, if electron radiation damage is to be kept below  $\sigma^* \approx 10^{-1} \text{ coulomb-cm}^{-2}$ , we need

$$Q > 5 e/\sigma_{\text{ESD}}^* \approx 10^{-17} \text{ cm}^2, \quad (4)$$

(I. MOLECULE MICROSCOPY)

which is equal to  $10^{-1}$  of the largest known ESD cross section,  $Q \approx 10^{-16} \text{ cm}^2$  (approximately equal to the "geometric" cross section of an atom). This somewhat pessimistic estimate of the damage is not surprising because, almost by definition, ESD is a damaging interaction, being a direct electron-molecule process that results in bond breakage and the ejection of a molecule or ion from a surface. Apparently organic molecules are sensitive to electron radiation at levels below those needed for ESD of chemisorbed species, although one should be cautioned that the method one uses to measure damage may significantly affect the actual numerical value obtained for  $\sigma^*$ . For physisorbed molecules, however, a case that thus far has been only slightly studied,<sup>2</sup>  $Q$  appears to be larger, often  $>10^{-17} \text{ cm}^2$ . Thus physisorbed neutral molecule surface stains may be useful for samples containing primarily organic molecules, whereas both physisorbed and chemisorbed molecules may be useful for metal and semiconductor samples where  $\sigma_{\text{max}}^*$  is larger.

In summary, if  $\sigma^* \approx 10^{-1} \text{ coulomb-cm}^{-2}$  holds as a threshold for organic molecules it appears that SDMM with ESD using chemisorbed stains will not work for samples composed mainly of organic molecules at high resolution where, from signal-to-noise considerations (see below), we expect that it will be necessary to desorb most of the adsorbed molecules from an MRA. Nevertheless, SDMM with ESD should certainly be considered for the study of metals and semiconductors, since (i) such samples should be much less sensitive to damage and (ii), metals have such a large thermal diffusivity that local heating for thermal desorption seems highly unlikely.<sup>5</sup>

4. Signal-to-Noise Ratio and Resolution

For both thermal and ESD approaches the maximum number of desorbed molecules,  $\Delta n_{\text{max}}$ , decreases with the resolution,  $d$  squared, that is,  $\Delta n_{\text{max}} \approx f \sigma_o d^2$ , where  $d$  is the diameter of the MRA. Since most desorbed molecules will be neutral, we use the usual estimate for the maximum signal  $\Delta n_{\text{s, max}}$ , with solid angle  $\Omega$  and universal ionizer efficiency  $\epsilon$ , that is,  $\Delta n_{\text{s, max}} = \epsilon(\Omega/\pi) \Delta n_{\text{max}}$ . In Table I-2,  $\epsilon = 10^{-3}$  and  $\Omega/\pi = 10^{-3}$  have been used, since they are currently attainable values. It is clear

Table I-2. Maximum detected molecules,  $\Delta n_{\text{s, max}}$ .

		f		
		$10^{-2}$	$10^{-1}$	$10^0$
d (cm)	$10^{-2}$	$10^3$	$10^4$	$10^5$
	$10^{-4}$	$10^{-1}$	$10^0$	$10^1$
	$10^{-6}$	$10^{-5}$	$10^{-4}$	$10^{-3}$

(I. MOLECULE MICROSCOPY)

that  $\epsilon$  and  $\Omega$  must be improved in order to reach high resolutions. We can estimate that if all the molecules are desorbed from an MRA, then

$$\Delta n_s \approx f \sigma_o d^2 \epsilon (1 - \cos^2 \beta), \quad (5)$$

where  $\beta$  is the half-angle subtended by the universal ionizer (UI), as shown in Fig. I-1. Here we have used  $A_{UI} = \pi R^2$ , the UI aperture area, and the sample-UI separation  $\ell$  in the effusion equation

$$N(\beta) = \dot{N}_{total} \int_0^\beta \frac{dA(\theta) \cos \theta}{\pi q^2(\theta)}. \quad (6)$$

The geometry is illustrated in Fig. I-2, where  $dA(\theta) = 2\pi r(\theta) dr(\theta)$ .

If we can repetitively apply and desorb stain molecules  $N_D$  times at each MRA, our signal becomes  $\Delta n_s \approx N_D f \sigma_o d^2 \epsilon (1 - \cos^2 \beta)$ . Initially we shall use  $N_D = 1$ , but it is of interest to consider the ultimate resolution for cases in which  $N_D > 1$  and the background pressure  $p_b$  is negligible. How large can  $N_D$  be? <sup>5</sup> Certainly the total time to obtain a picture,  $t_{exp}$ , must be reasonable. Suppose a complete picture contains  $N$  minimum resolvable areas. Then the time allowed for each MRA desorption cycle is  $\Delta t = t_{exp}/NN_D$ , with  $N_D = t_{exp}/N\Delta t$ . But we can also relate  $\Delta t$  in an approximate

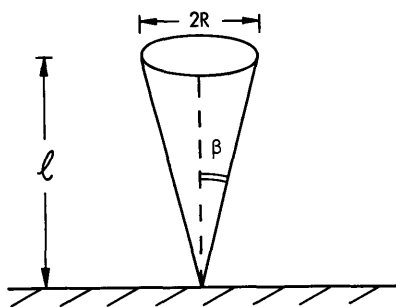


Fig. I-1. Geometry locating universal ionizer (UI) with respect to sample surface.  $2R$  is the UI aperture,  $\ell$  its distance from the sample and the half-angle subtended by the aperture.

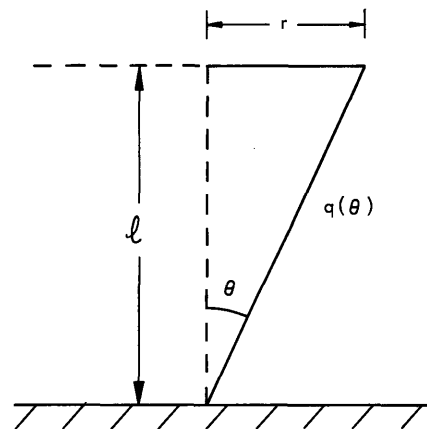


Fig. I-2. Geometry used to calculate the fraction of molecules accepted by the universal ionizer.

way to the transit time for desorbed molecules to reach the UI. Thus  $\Delta t \geq a\ell/\bar{v}$ , where  $\bar{v}$  is the mean velocity of a desorbed molecule and the choice  $a \approx 4$  allows for the spread of transit times in the case of thermal desorption. (For ESD  $\bar{v}$  is probably larger than

the thermal case, but the actual velocity distribution is unknown.) For thermal desorption, since  $T$  rises momentarily to  $\sim 300^\circ\text{K}$  in the case of adsorbed water, we estimate  $\bar{v} \approx \sqrt{3kT/m} \approx (3 \times 10^5) M^{-1/2} \text{ cm-s}^{-1}$ ; hence,  $\Delta t \approx (3 \times 10^{-6}) a \ell M^{1/2}$ . Using this, we can substitute for  $N_D$  in the equation for  $\Delta n_s$  and then solve for the resolution,  $d$ .

$$d_{\text{thermal}} \approx (1.7 \times 10^{-3}) \left[ \frac{N a \ell \Delta n_s}{t_{\text{exp}} f \sigma_o \epsilon (1 - \cos^2 \beta)} \right]^{1/2} M^{1/4} \text{ cm.} \quad (7)$$

Typical parameters for a SDMM with multiple stain-desorption cycles may be  $N = 300 \times 300 = 10^5$ ,  $t_{\text{exp}} = 10^3 \text{ s}$ ,  $\Delta n_s = 25$  for 5 shades of gray,  $a = 4$ ,  $f = 10^{-1}$ ,  $\sigma_o \approx 10^{15} \text{ cm}^{-2}$ ,  $\epsilon \approx 10^{-3}$ ,  $\beta \approx 3 \times 10^{-2}$ , since  $R = 1.5 \times 10^{-1} \text{ cm}$ , and  $\ell \approx 5 \text{ cm}$ . The corresponding resolution estimate is  $d \approx 10^{-4} \text{ cm}$  which is very reasonable, but  $N_D \approx 4 \times 10^1$  is required. (Initially we shall use  $N_D = 1$  and estimate the resolution from Fig. I-3 by noting that initially  $\Omega$  is  $10^2$  smaller than assumed there.) If we have somewhat higher coverage, say  $f = 3 \times 10^{-1}$ , and  $\epsilon = 10^{-2}$ , then  $d \approx 2 \times 10^{-5} \text{ cm}$ , and again  $N_D \approx 4 \times 10^1$ . Ultimately it seems reasonable to expect  $N = 300 \times 300 = 10^5$ ,  $\Delta n_s = 25$ ,  $a = 4$ ,  $t_{\text{exp}} = 10^3 \text{ s}$ ,  $f = 1$ ,  $\sigma_o \approx 10^{15} \text{ cm}^{-2}$ ,  $\epsilon = 10^{-2}$ ,  $A_{\text{UI}} \approx 1$  with  $R = 5 \times 10^{-1}$ , and  $M = 18$ , so that  $d \approx 10^{-7} \text{ cm} = 10 \text{ \AA}$ , with  $N_D \approx 4 \times 10^2$ . Here the resolution is at the atomic scale, and  $f = 1$  or  $f = 0$  is appropriate. We expect, of course, that this expression for  $d$  should be only a crude guide to achievable resolution, and it primarily shows the approximate dependence of  $d$  on instrument parameters when  $p_B$  is negligible.

## 5. Background Problems

If we include the background at the same mass number as the desorbed stain and consider only  $N_D = 1$ , we assume that in addition to the counted anisotropic flux  $\dot{n}_s$  of "signal molecules" in the UI there will be some counted isotropic flux of molecules of the same mass number,  $\dot{n}_B$ , and we treat this background as a partial pressure,  $p_B$ . Thus, if  $p_B$  is in mm Hg, the background count is given by

$$\Delta n_B \approx (3.5 \times 10^{22}) p_B \epsilon A_{\text{UI}} \Delta t / (MT)^{1/2}. \quad (8)$$

If we further assume that all background molecules are perfectly trapped by a cold surface after one pass through the UI, and use the aperture size of the Extra Nuclear Ionizer<sup>6</sup> with its efficiency  $\epsilon = 10^{-3}$ , we find that  $\Delta n_B \approx (4 \times 10^{16}) p_B \Delta t$ . Since the maximum signal is  $\Delta n_s = f \sigma_o \epsilon \Omega d^2 = A d^2$ , that is, the number of adsorbed molecules within an MRA multiplied by counting efficiency  $\epsilon \Omega / \pi$ , we can estimate the maximum signal-to-noise ratio,  $S/N$ , by setting the noise equal to the shot noise in the total count. Thus

(I. MOLECULE MICROSCOPY)

$$S/N = Ad^2 / (Ad^2 + Bp_B \Delta t)^{1/2}, \quad (9)$$

where  $B = (3.5 \times 10^{22}) \epsilon A_{UI} / (MT)^{1/2}$ . Typical estimates are shown in Fig. I-3.

This simple estimate implies that ESD, which requires  $\Delta t \approx 10^{-2}$ , has more stringent vacuum requirements than thermal desorption with its shorter heat pulse. We estimate that for a specimen modeled by polyethylene covered with a monolayer of water,

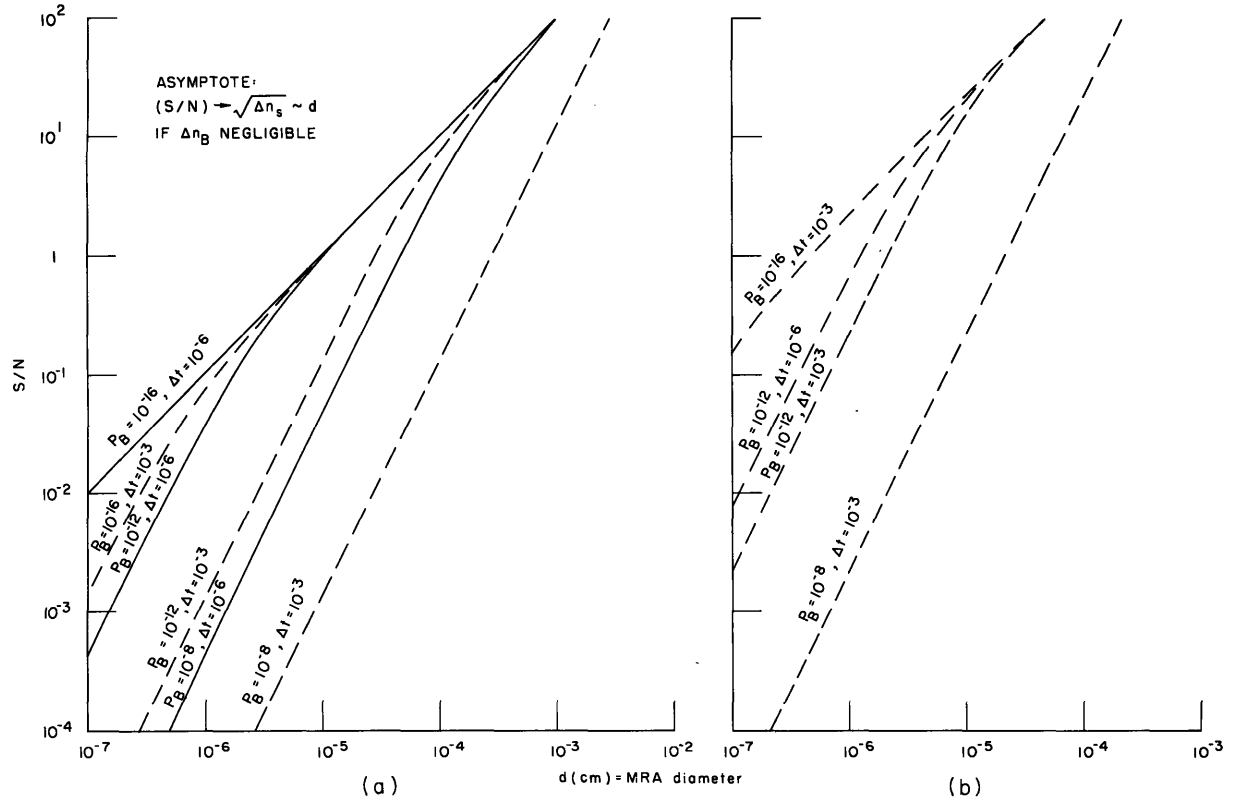


Fig. I-3. Maximum signal-to-noise (S/N) vs resolution for SDMM where

only shot noise is considered. Thus  $S/N = Ad^2 / \sqrt{Ad^2 + Bp_B \Delta t}$ , where  $A = f \sigma_o \epsilon (\Omega/\pi)$  and  $B = 3.5 \times 10^{22}) \epsilon A_{UI} / \sqrt{MT}$ .

(a)  $\epsilon = 10^{-3}$ ,  $\Omega/\pi = 10^{-1}$ ,  $f = 10^{-1}$ ,  $A_{UI} = 10^{-1} \text{ cm}^2$ , which are readily obtainable values.

(b)  $\epsilon = 10^{-2}$ ,  $\Omega/\pi = 5 \times 10^{-1}$ ,  $f = 1$ ,  $A_{UI} = 10^{-1} \text{ cm}^2$ .

a beam on-time of  $\Delta t_{\text{thermal}} \approx 10^{-6}$  s is adequate for approximately complete thermal desorption of the water for the case of  $d = 10^{-6}$  cm and  $J \approx 10^2 \text{ A-cm}^{-2}$ .<sup>5</sup> Even if  $\Delta t = 10^{-6}$  s for the heat pulse, the relatively slow thermal molecules may require an extra  $10^{-4}$  to  $10^{-3}$  s to reach the UI, so that the effective  $\Delta t$  is  $10^{-4}$  to  $10^{-3}$  s. Since  $S/N = 5$



## (I. MOLECULE MICROSCOPY)

corresponds to a picture with 5 shades of gray, which we use for illustration to be a picture of minimum quality, it is apparent that with the assumed parameters (surface coverage, ionizer efficiency, and solid angle) and for pictures made with a single stain-desorption cycle, the best initial resolution is  $d \approx 6 \times 10^{-4}$  cm.

Helpful conversations with many members of our group are gratefully acknowledged, particularly with J. G. King; and also with H. F. Dylla, B. R. Silver and D. G. Lysy for discussions concerning ESD damage and for checking calculations.

### References

1. J. C. Weaver and J. G. King, Proc. Natl. Acad. Sci. U. S. 70, 2781 (1973).
2. T. E. Madey and J. T. Yates, Jr., J. Vac. Sci. Technol. 8, 525 (1971).
3. A. V. Crewe, D. N. Eggenberger, J. Wall, and L. M. Welter, Rev. Sci. Instr. 39, 576 (1968).
4. M. Isaacson, D. Johnson, and A. V. Crewe, Rad. Research 55, 205 (1973); and L. Reimer, Proc. Thirty-first Annual EMSA Meeting, 1973, p. 476.
5. A typical radiation dosage for thermal desorption is  $\sim 10^{-4}$  coulomb-cm<sup>-2</sup>, so that  $N_D \approx 10^3$  could be tolerated if  $\sigma^* \approx 10^{-1}$  coulomb-cm<sup>-2</sup> holds. This estimate comes from an unpublished heat-pulse calculation by M. G. R. Thomson and J. C. Weaver; see also D. G. Payan and J. C. Weaver, Quarterly Progress Report No. 104, Research Laboratory of Electronics, M. I. T., January 15, 1972, pp. 35-39.
6. Extranuclear Laboratories, Inc., Pittsburgh, Pennsylvania.

