Electron-Stimulated Desorption

It has now been almost 30 years since the 1971 review article entitled *Electron-Stimulated Desorption as a Tool for Studies of Chemisorption: A Review* [1] appeared. At that time, the authors, Theodore Madey and John Yates, were young scientists working together in the Surface Chemistry Section of the Physical Chemistry Division of NBS. Few could have predicted that the subject of this review would multiply and remultiply, until today the electron-stimulated desorption phenomenon and a number of related subjects form a cornerstone of chemistry and physics on surfaces—and that the personal collaboration forged at the time would last for 19 years at NBS, resulting in over 100 joint publications, as well as a deep and lasting friendship.

Surface chemistry is traditionally driven by the thermal excitation of adsorbed species. In areas such as heterogeneous catalysis, thin film deposition by chemical vapor deposition, and corrosion passivation, one often thinks only of thermally-driven surface processes. In the late 1960s, quantitative studies of the thermal desorption of molecules chemisorbed on single crystal surfaces were just beginning. Questions about molecular dissociation and atom recombination processes were being studied on well-defined single crystal surfaces for the first time, both by Yates and Madey at NBS and by other investigators. In this fundamental work simple molecules, such as H_2, CO, N_2, CH_4, and NO, were employed so as not to make the chemistry complex.

The study of desorption processes initiated by electronic excitation instead of thermal excitation represented a departure from conventional research activities at the time and provided a special personal fascination for the authors which has to the present remained strong. The desorption of adsorbed species by nonthermal processes (i.e., electronic activation) became a new focus of the work starting about 1965. As a consequence of their work, Madey and Yates were invited by P.A. Redhead (a pioneer in electron stimulated surface processes, and the editor of the *Journal of Vacuum Science and Technology*) to write a critical review of what was being done worldwide in the area of electron stimulated desorption, a surface phenomenon which had already received the acronym ESD.

It is interesting to note that the title of the review contains the word "Tool." In 1971, many new surface measurement techniques were being devised in the surface physics community and were being transferred to some degree to the surface chemistry, engineering, and materials science communities in the form of exciting and useful new tools for research. The workers at NBS were inclined to think of ESD as a new measurement method for the study of adsorption. The review uncovered more than 100 papers dealing with phenomena related to ESD, extending back to 1918. At the time of the writing of the review, the vast majority of the important papers had been written within the previous 10 years. The most influential work had been done independently by Menzel and Gomer [2, 3] and by Redhead [4] in 1964. The basic electronic excitation mechanism for ESD is now termed the MGR mechanism worldwide in honor of their central contribution.

The 1971 review summarized the experimental methods that had been employed to date for the study of ESD, the theoretical foundation for thinking about the electronic excitation on the surface, and the subsequent desorption process. The authors also included almost all of the particular chemical systems that had been studied by ESD at the time. Since positive ionic fragments are often liberated in ESD, the review contains a number of examples of the use of mass spectrometers and other devices as ion detectors. It also contains criticisms of certain mechanistic ideas which were in the literature, as well as a selection of experimental data that were regarded as being the most reliable (including much of the authors' own data).

In addition to electron-impact induced adsorbate-surface bond breaking (desorption), molecules on surfaces may be chemically converted to other species by electron impact, and the review article illustrated this by including one of the authors' own studies in which adsorbed N_2 molecules were converted to adsorbed N atoms on a tungsten surface, one of the first examples of this phenomenon.

The review was 30 pages long and contained 152 references. It was not possible in a review of that length to do justice to all of this information. In order to summarize the work in these papers, a table was devised to list the principal findings; this table was arranged chronologically and by the adsorbate/adsorbent system and the experimental method. Not surprisingly, work on tungsten and molybdenum surfaces dominated, since during much of the 10 years prior to the review, it was known that atomically clean surfaces of these elements could be prepared through high temperature heating in ultrahigh vacuum. Much of this work was done without the luxury of Auger spectrometers for surface analysis.

Since 1971, well over 1000 papers on ESD have been published. Both Yates and Madey have published additional review articles in the field [5-8], and in 1991 65 reviews of ESD existed in the literature [6]. The acronym ESD, while still employed, has been replaced somewhat by the more encompassing acronym DIET (Desorption Induced by Electronic Transitions). An international meeting on this topic is held every two and a half years; the eighth meeting, organized in 1999 at Rutgers University by Ted Madey, attracted 80 attendees. The acronym DIET includes electronic excitation by photons as well as electrons, and in recent years photodesorption has become a dominant area in which both authors are working at their separate universities.

The writing of the review article was carried out on two continents. John Yates was working in Britain at the time, and many mailings of manuscript and figures were done in both directions to meet deadlines. One of the critical mailings from Britain was lost (and never found) as a result of the use of the Armed Forces mailing system because of a mail strike in Britain. The authors were caught off guard after publishing the 1971 review, since they were soon notified that it had become a Science Citation Classic by Citation Indices. They later remarked to Paul Redhead, "If we had thought we were writing a Classic, we would have written it in Latin."

One of the most exciting developments emanating from this collaboration had to do with the discovery of the ESDIAD (electron stimulated desorption ion angular distribution) phenomenon in 1974. Here the positive ion desorption products were found to be ejected in sharp beams whose direction was closely related to the direction of the chemical bond being ruptured in the electronic excitation process [9]. Fig. 1 shows the early ESDIAD apparatus and the three authors of the first paper, as well as photographic images of the ion angular distributions obtained.

Both Yates and Madey have left NBS for the academic world, and many honors have come to them, leading to professional recognition not only for the collaborative work done at NBS, but also for more recent work done independently at the University of Pittsburgh and at Rutgers University. The early work at NBS was centrally important to their professional development and to many of the rich opportunities they experienced since leaving government service. Indeed, the period from 1963 to the 1980s was generally one of extraordinary freedom in research at NBS in the field of surface science. Other NBS staff members who were their colleagues or friends and who numbered among the founders of the field include E. W. Plummer, J. W. Gadzuk, R. D. Young, C. J. Powell, A. Melmed, R. Klein, and M. D. Scheer. The research benefited from the support of the Administration at NBS during this time, both at the Director's level (A. Astin, L. Branscomb, R. Roberts, E. Ambler) and at intermediate levels (M. B. Wallenstein, J. D. Hoffman, J. McNesby, M. D. Scheer, and R. Klein). Without excellent scientific colleagues and visionary administrators, NBS would not be historically recognized for its important role in establishing, and continuously nurturing to this day, the exciting and technologically important field of surface science.

It is appropriate to complete this account by citing recent articles from each of the authors' laboratories which are connected conceptually to the ESD phenomenon. In the first example, a photochemical dissociation process, involving an oriented O_2 molecule chemisorbed with its O-O axis parallel to the step-edge sites of a Pt single crystal, is found to preferentially eject an O atom toward a neighboring CO molecule to produce CO_2 which then desorbs [10]. This selectivity measured for target CO molecules on the step sites compared to CO molecules located on the terrace sites is termed surface aligned photochemistry (SAP), and is schematically illustrated in Fig. 2. This is the first observation of SAP involving molecular alignment on a stepped single crystal template.

The second example addresses an issue that has long puzzled planetary astronomers: what is the origin of the copious atomic sodium vapor in the rarefied atmosphere of the planet Mercury, and of our Moon? An image of this effect is shown in Fig. 3. A detailed DIET study of a model system (sodium atoms and ions adsorbed on SiO_2 surfaces, simulating moonrocks) identified the likely scenario: when ultraviolet light from the sun strikes the lunar surface, it excites the surface electronically and causes desorption of sodium atoms [11]. Electrons in the solar wind can also cause ESD of sodium from the lunar surface, but the more plentiful solar photons are the main culprits.

In conclusion, ESD and other DIET processes today impact a host of scientific issues, including structure and dynamics of adsorbed molecules, quantum state-resolved desorption, dynamics of charge transfer, and surface photochemistry. DIET processes also provide insights into the science and technology of radiation damage, which affects quantitative surface analysis using electron and photon beams, partial pressure measurements, stability of x-ray optics, electron- and photon-beam lithography, and molecular synthesis in interstellar space. ESD and DIET continue to be scientifically exciting, growing fields!

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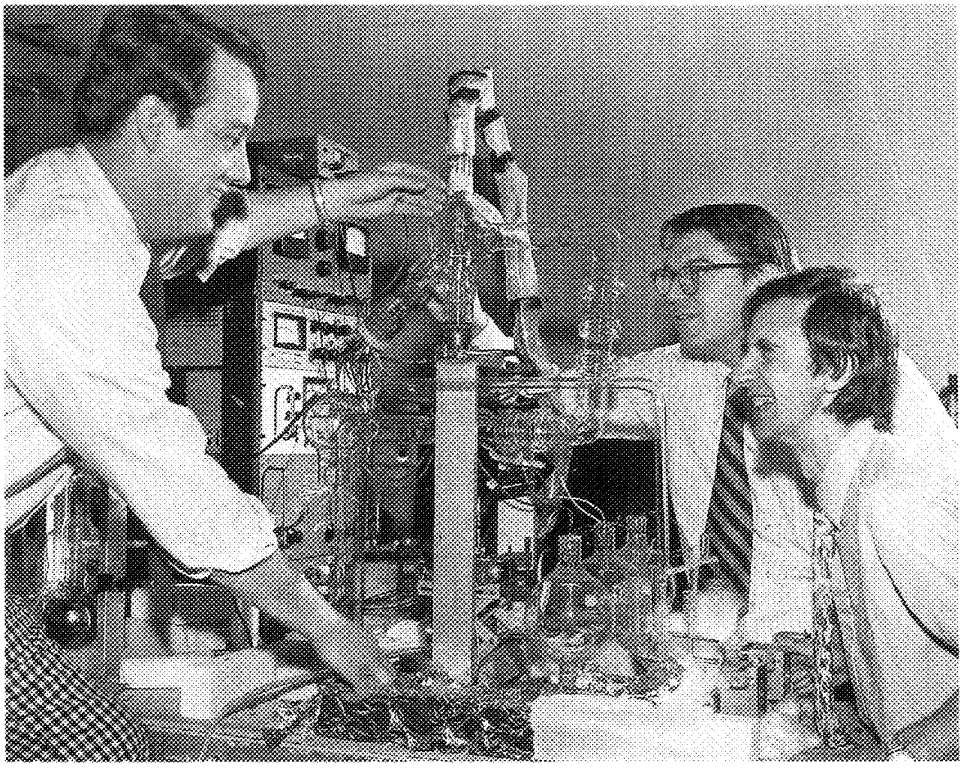

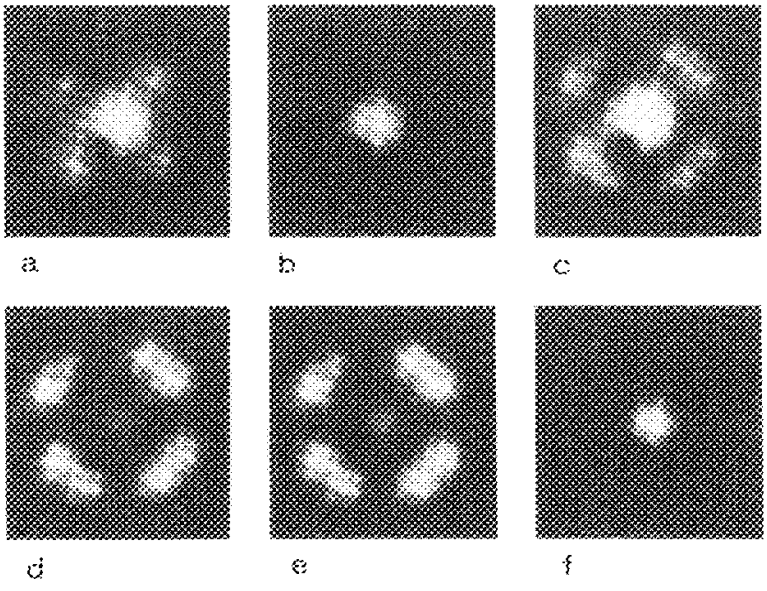

Fig. 1. (a) 1974 photograph of the first NBS ESDIAD system, a hybrid of glass and metal. From left to right, T. E. Madey, J. T. Yates, Jr., and J. J. Czyzewski. Madey's left hand is pointing to the ESDIAD tube; the ESDIAD patterns were photographed from below (from [9]).

(b) ESD Ion Angular Distribution (ESDIAD) patterns for desorption of oxygen ions (O^+) from W(100). This sequence shows the effect of heat treatment on ESD patterns for oxygen on W(100).

Temperatures corresponding to each pattern are (a) <400, (b) 630, (c) 705, (d) 795, (e) 865 and (f) 930 K (from [9]).

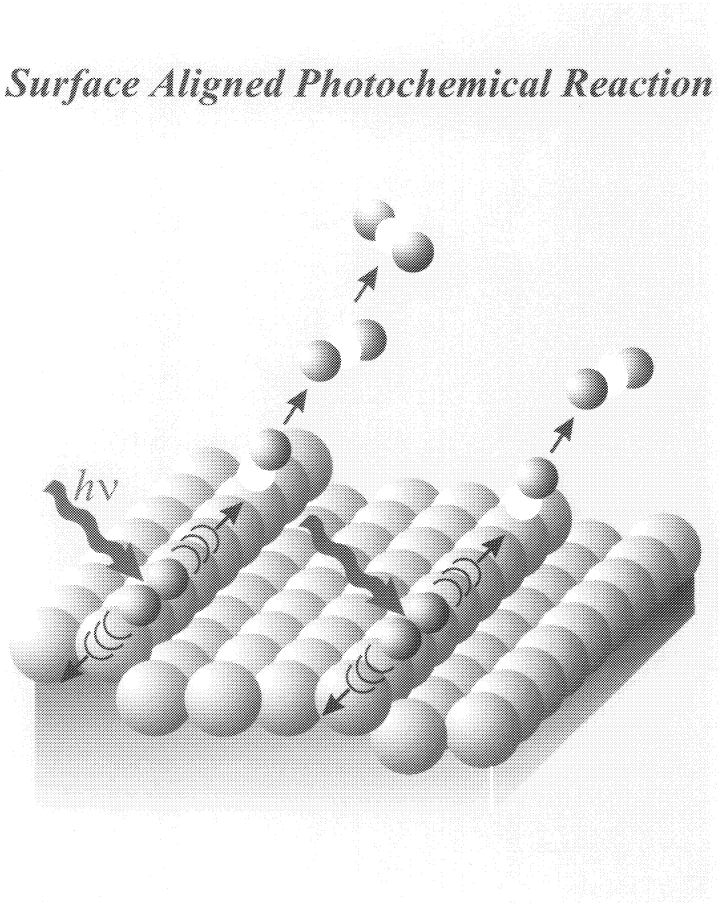

Fig. 2. Surface Aligned Photochemistry—The most probable reaction process is illustrated for the photoexcitation of adsorbed O_2 on a step site on a Pt single crystal and leading to reaction with step-bound CO molecules to produce CO_2 [10].

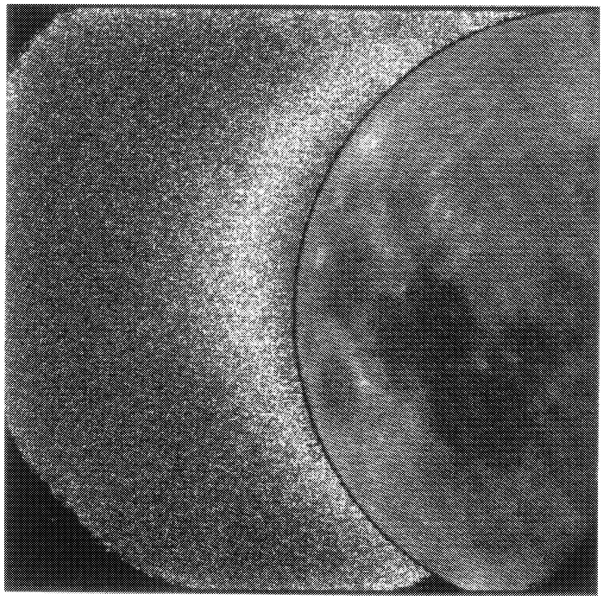

Fig. 3. Image of lunar sodium atmosphere due to DIET from the lunar surface [11,12].

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