

THE USE OF ANGLE RESOLVED ELECTRON AND PHOTON  
STIMULATED DESORPTION FOR THE DETERMINATION  
OF MOLECULAR STRUCTURE AT SURFACES

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This paper is a brief review of recent data related to the use of angle-resolved electron stimulated desorption and photon stimulated desorption in determining the structures of molecules at surfaces. Examples include a variety of structural assignments based on ESDIAD (electron stimulated desorption ion angular distributions), the observation of short-range local ordering effects induced in adsorbed molecules by surface impurities, and the application of photon stimulated desorption to both ionic and covalent adsorbate systems.

Desorption, Structure, Chemisorption

1. Introduction

Important questions which arise in studies of molecules on surfaces concern the geometric structure of the adsorbed species: at which site is a molecule bonded to the surface, what are the orientations of the bonds between molecule and surface, and what are the bond directions of the ligands in surface molecular complexes? It is now well-established that the electron stimulated desorption ion angular distribution (ESDIAD) method and the angle-resolved photon stimulated desorption (PSD) method using synchrotron radiation are of great use in providing direct information about site location and geometric structure of molecules on surfaces [1-5].

In these methods, electronic excitation of surface molecules by a focused electron beam or a photon beam can result in desorption

of atomic and molecular ions, and neutral species from the surface. The ions desorb in discrete cones of emission in directions determined by the orientation of the bond which is ruptured by the excitation. For example, as illustrated in Fig. 1, ESD or PSD of adsorbed CO bound in a standing-up configuration on a metal surface

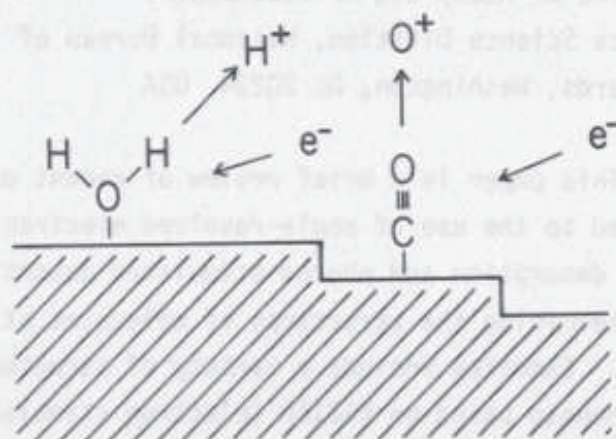


Figure 1. Schematic bonding configurations for adsorbed CO and H<sub>2</sub>O, showing relationship between surface bond angle and ion desorption angle in ESDIAD.

will result in desorption of O<sup>+</sup> in the direction of the surface normal, while ESD/PSD of H<sup>+</sup> from H<sub>2</sub>O adsorbed via the O atom will result in desorption of H<sup>+</sup> in an off-normal direction. Measurements of the patterns of ion desorption provide a direct display of the geometric structure of surface molecules in the adsorbed layer [1-5].

In the present paper, we summarize recent experimental results detailing the utility of ESDIAD and PSD in studies of molecules on surfaces. In particular, we shall emphasize that

- (a) ESDIAD and angle resolved PSD provide direct information about the structure of surface species without complex mathematical analysis, and
- (b) these methods provide information regarding the local bonding geometry of surface species, even in the absence of long range order.
- (c) PSD provides useful information about the physics of the excitation processes which lead to ion desorption, giving insights into radiation damage at surfaces.

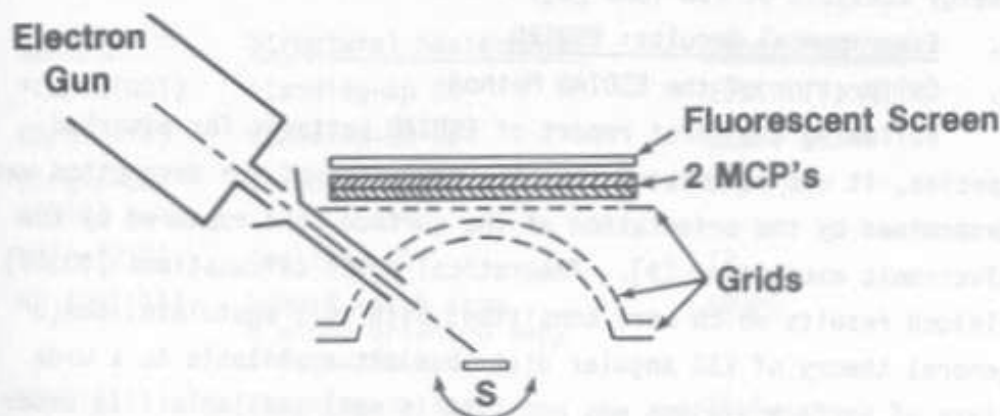


Several reviews of ESDIAD have appeared recently [1-5], and the fundamentals of the method and experimental procedures are described extensively therein. The present paper is a shortened, updated version of References [4] and [5], and the reader is referred to those papers for more details. The physical principles of ESD and PSD are treated comprehensively in a recent volume [3].

The plan of this paper is as follows: Section 2 contains a brief discussion of experimental procedures, and the application of ESDIAD to specific molecular systems is described in Section 3. Examples include a variety of structural assignments based on ESDIAD, and the observation of short-range local ordering effects induced in adsorbed molecules by surface impurities. The emphasis will be on the structure of adsorbed molecules rather than atoms. Section 4 is a brief discussion of a major perturbation on ion trajectories due to the image potential, and the utility of PSD for determining the mechanisms of ion desorption processes is given in Section 5.

## 2. Experimental Procedures

An extensive discussion of experimental methods of ESD and PSD is given in [3,4] and will not be considered in detail here. Briefly, two types of detection schemes have been employed for most of the published ESDIAD studies: an area detector with visual display [Fig. 2] and a scanning ion detector, used by Niehus [2].



**Figure 2.** Schematic of NBS ESDIAD apparatus. ESDIAD patterns are displayed using the grid-microchannel plate-fluorescent screen detector array [1,4,5].

In the display-type apparatus originally developed at NBS [1,4,5] and shown in Fig. 2, a focused electron beam bombards a single crystal sample. The ion beams which desorb via ESD pass through a hemispherical grid and impinge on the front surface of a double microchannel plate (MCP) assembly. The output electron signal from the MCP assembly is accelerated to a fluorescent screen where it is displayed visually (the ESDIAD pattern) and photographed. By changing potentials, the elastic low energy electron diffraction (LEED) pattern from the sample can be studied. Mass identification of ESD ions is accomplished using a quadrupole mass spectrometer, which is also used as a detector in thermal desorption studies of the adsorbed layer.

PSD studies are performed using a source of synchrotron radiation which provides a continuously tuneable photon flux in the energy range  $20 \text{ eV} < h\nu \lesssim 100 \text{ eV}$ . In PSD of ions, the low signal levels and high background signals from scattered light cause special problems for angle-resolved measurements. An ellipsoidal mirror analyzer, a display-type instrument designed by Eastman and colleagues, has been used successfully for angle resolved PSD studies [6,7]; however, most PSD measurements reported to date do not include angle resolved measurements. At the NBS synchrotron light source, SURF-II, a double pass cylindrical mirror analyzer (CMA) is used for mass and energy analysis of PSD ions [8].

### 3. Experimental Results: ESDIAD

#### A. Calibration of the ESDIAD Method

Following the first report of ESDIAD patterns for adsorbed species, it was postulated that the direction of ion desorption was determined by the orientation of the surface bond ruptured by the electronic excitation [9]. Theoretical model calculations [10,11] yielded results which were consistent with this postulate, but a general theory of ESD angular distributions applicable to a wide class of surface systems was not (and is not) available. In order to test the postulate, the NBS group adopted an empirical approach, viz., to apply the ESDIAD method to adsorbate-substrate systems whose surface geometries have already been predicted or determined based on other structure-sensitive surface probes.

Table 1 summarizes and lists molecular adsorbates which have been studied in various laboratories using ESDIAD (see [4] for original



references). The table indicates those molecules which have been used to "calibrate" the ESDIAD method, i.e., molecules for which a structural identification has been made using methods such as high resolution electron energy loss spectroscopy (EELS), reflection-absorption infrared spectroscopy (IR), ultraviolet photoemission spectroscopy (UPS) and angle resolved UPS (ARUPS), or low energy electron diffraction (LEED).

In each case listed in Table I, the ESDIAD results are consistent with the other techniques. E.g., for standing-up CO on Ru(001), Ni(111) and W(110), the molecule is bound via the carbon atom to the metal surface with its molecular axis perpendicular to the surface; ESD  $O^+$  (and  $CO^+$ ) ions desorb in the direction perpendicular to the surface. For the bridge-bonded CO structure identified on Pd(210) using IR, the molecular axis is inclined from the perpendicular to the macroscopic surface, and ESD  $O^+$  emission occurs in the predicted off-normal direction. A "halo" of  $H^+$  ion emission is seen for ESD of  $NH_3$  on Ni(111), consistent with the ARUPS identification of ammonia bonded to Ni via the N atom with the H atoms oriented away from the surface. Similar consistency is found for each of the other cases listed in Table I.

TABLE I. Structural assignments of adsorbed molecules based on ESDIAD measurements: These structures have been identified using various sensitive methods as well as ESDIAD.

| System               | Structural Assignments                                      | Other Methods         |
|----------------------|---|-----------------------|
| *CO/Ru(001)          | standing-up CO  | EELS, IR, ARUPS       |
| CO/Ni(111)           | standing-up CO  | EELS, ARUPS           |
| virgin-CO/<br>W(110) | standing-up CO  | UPS                   |
| CO/Pd(210)           | inclined CO   | IR                    |
| $NH_3$ /Ni(111)      | bonded via N atom,<br>H atoms oriented away<br>from surface | ARUPS                 |
| NO/Ni(111)           | standing-up and<br>inclined NO                              | EELS                  |
| $H_2O$ /Ru(001)      | coverage and temperature<br>dependent structures            | EELS                  |
| $C_6H_{12}$ /Ru(001) | "chair" form of $C_6H_{12}$<br>parallel to surface          | EELS                  |
| $WO_3$ (111)         | inclined W-O  | LEED; crystallography |

\*Also verified using Angle Resolved PSD

TABLE II. Other surface structures identified using ESDIAD.

| <u>System</u>                                   | <u>Structures</u>                   |
|---|-------------------------------------|
| CO/Ni(111)                                      |                                     |
| virgin-CO/stepped W(110)                        |                                     |
| $\alpha$ -CO on W(110)                          | standing-up CO and "inclined"       |
| CO/W(100), (111)                                | CO both observed under different    |
| CO/Mo(001)                                      | conditions of temperature and       |
|   | coverage.                           |
| NH <sub>3</sub> /Ru(001)                        |                                     |
| NH <sub>3</sub> and H <sub>2</sub> O on oxygen- | similar to NH <sub>3</sub> /Ni(111) |
| dosed Ni(111), Al(111)                          | azimuthal ordering                  |

Table II contains a list of other adsorbed molecules for which structural assignments have been made using ESDIAD. In many cases, the structures were not previously suspected (e.g., inclined CO on Ni(111), Mo(100) or W(100); oxygen-stabilized ordering of NH<sub>3</sub> and H<sub>2</sub>O on Ni(111) - see below, Section 3.B) but none are inconsistent with experimental results.

It appears from the evidence in Table I that for all molecular systems where we have a priori knowledge of the surface structure, the ion desorption angle observed in ESDIAD is related to the surface bond angle. In particular, it is found that the expected azimuthal angle of the surface bond is preserved in ESDIAD, but the polar angle is increased for the ion trajectory, due largely to image charge effects [1]. To date, no exceptions have been found.

#### B. Short-range Local Ordering in Absence of Long-range Order

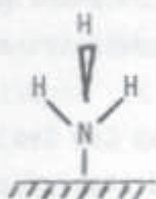
In a particularly interesting application of the ESDIAD method, it has been found that traces of preadsorbed oxygen on a metal surface will induce a high degree of azimuthal order in adsorbed molecules which are disordered azimuthally on the clean surface [13].



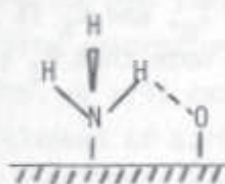
Figure 3: Schematic ESDIAD patterns for NH<sub>3</sub> on Ru(001).



Figure 3 schematically illustrates the ESDIAD patterns for  $\text{NH}_3$  on Ni(111) and Ru(001) surfaces, on which  $\text{NH}_3$  is bonded via the N atom as follows



The "halo" ESDIAD pattern (3a,b) is generated by  $\text{H}^+$  ions desorbing from an array of adsorbed  $\text{NH}_3$  molecules which has random azimuthal orientation of the H ligands on the clean surface. In the presence of a fractional monolayer of O, the  $\text{H}^+$  ESDIAD pattern develops discrete beams due to a local azimuthal ordering of  $\text{NH}_3$  induced by adsorbed oxygen. Fig. 3c is a schematic of the pattern characteristic of  $\text{NH}_3 + \text{O}$  on Ru(001), which is postulated to arise from a hydrogen-bonding interaction between  $\text{NH}_3$  and O [13]:



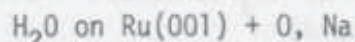
Similar azimuthal ordering effects have been seen for  $\text{H}_2\text{O}$  and  $\text{NH}_3$  on various surfaces of Ni, Al, and Ru. More recent studies of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  on other substrates show that both electropositive and electronegative additives (e.g. O, Na) can induce locally-ordered molecular rearrangements in the adsorbed molecules [14,15].

In certain cases where  $\text{H}_2\text{O}$  forms ordered hydrogen-bonded overlayers in registry with the substrate [14], the additive can induce disorder in the layer.

Systems in which the additive induces short range order which is either absent or different on the clean surface include:

- $\text{NH}_3$  on Ru(001) + O, Na
- $\text{NH}_3$  on Ni(111) + O
- $\text{NH}_3$  on Al(111) + O
- $\text{H}_2\text{O}$  on Ni(111) + O
- $\text{H}_2\text{O}$  on Ru(001) + Na

Under certain conditions of coverage, both long range order and short range order in the overlayer are destroyed for



It appears that both geometrical and electronic factors are involved in the effect of surface additives on local ordering of adsorbed molecules.

#### 4. Influence of Image Potential on Ion Trajectories

Several authors have discussed the influence of the image potential on ion trajectories [1,16]: the image potential causes an increase in the polar angle for ion desorption. Clinton's [16] calculations indicate that an ion desorbing with an initial angle  $\alpha_i$  with respect to the surface normal will arrive at the detector with an apparent desorption angle  $\alpha_o$  given by

$$\cos \alpha_o = \cos \alpha_i \left[ \frac{1 + V_I / [(E_K - V_I) \cos^2 \alpha_i]}{1 + V_I / (E_K - V_I)} \right]^{1/2} \quad (1)$$

In this expression,  $V_I$  is the screened image potential at the initial ion-surface separation  $Z_o$ , and  $E_K$  is the final, measured kinetic energy of the ion. We note that  $V_I$  is a negative quantity, so that

$$|V_I / (E_K - V_I)| \leq 1 \text{ and } \alpha_o \geq \alpha_i.$$

In order for equation (1) to have a real physical solution, the following relationship must be satisfied:

$$\left| \frac{V_I}{(E_K - V_I) \cos^2 \alpha_i} \right| \leq 1 \quad (2)$$

This means that there will be a cut-off angle for ion desorption defined by the value of  $\alpha_i$  for which  $\alpha_o = 90^\circ$ . For values of  $\alpha_i$  greater than the cutoff angle, the ions will follow low trajectories and be recaptured by the surface. The possibility of beam-damage induced by bombardment of surface species by low energy ESD ions is very likely.

As discussed previously [1], it appears that the major final-state perturbation of ion trajectories is in the polar direction. In general, for a perfectly planar surface or for desorption along an azimuth of symmetry, the perturbation of the azimuthal angle



should be minimal.

## 5. Mechanisms of ESD/PSD Processes

A number of different initial electronic excitations have been identified as contributing to ESD and PSD of ions and neutrals from surfaces, including valence electron excitations, and both shallow and deep core hole excitations. It appears on the basis of evidence to date that ESD and PSD are initiated by the same elementary excitations, and that differences which occur in spectral yield curves (ion yield vs. energy of  $e^-$ ,  $h\nu$ ) reflect differences in the physics of the excitation process for electrons and photons. The different spectral dependences of ion desorption yields are described in detail by Knotek [17] and depend on a variety of factors (energy dependence of initial excitation cross section, accessibility of final states, and definition of energy deposition). In general, PSD ion yields rise sharply at threshold to a peak, and fall off at higher energy as  $1/E^n$ , where  $2 < n < 3$ . ESD ion yields rise more slowly at threshold and reach broad peaks at 3-4 times the threshold energy. Hence, the relatively sharp PSD ion yields are generally more useful for isolating and identifying desorption mechanisms than are ESD yields. In the following paragraphs, we will explore ESD/PSD desorption mechanisms for two different classes of surface species: ionically-bonded surface atoms, and covalently-bonded surface molecules.

### (a) Ionic systems

Ion desorption from maximal valency, ionically-bonded surfaces is believed to proceed via an Auger decay mechanism proposed by Knotek and Feibelman (K-F) [18]. Maximal valency means that the cation is ionized down to the noble gas configuration (e.g.,  $K^+$ ,  $Ca^{2+}$ ,  $Ti^{4+}$ , etc. in  $K_2O$ ,  $CaO$ ,  $TiO_2$ , etc.), and that the highest occupied level is its highest core level, of binding energy  $\sim 20$  eV. There is always some degree of covalency, but to a first approximation, the valence electrons have little density at the cation. In the K-F mechanism as applied to  $TiO_2$ , for example, ion desorption can be initiated by the production of a vacancy in the highest occupied core level, Ti 3p. The vacancy is filled by an interatomic Auger process involving an electron from the  $O^{2-}$ , and the release of two additional Auger electrons from the  $O^{2-}$  can leave the oxygen positively charged. The Coulomb potential for  $O^+$  in the presence of  $Ti^{4+}$  is repulsive, and the  $O^+$  will desorb from the surface.

An adsorbate system to which the K-F mechanism appears applicable is the adsorption of oxygen on Ti(001), where a variety of evidence indicates that surface  $\text{TiO}_2$  is formed [8]. Fig. 4 shows the PSD  $\text{O}^+$  ion yield vs. photon energy, and compares it with the secondary electron yield from Ti, which is proportional to the Ti 3p ionization probability [8]. The similarity of the onsets and energy dependences of the  $\text{O}^+$  ion yield and Ti 3p core hole excitation leads to the conclusion that ion desorption is initiated by the production of a Ti 3p core hole in accordance with the K-F model. The differences in detail of the two curves of Fig. 4 may indicate additional excitation mechanisms as well. Similar evidence for the K-F process in ion desorption has been observed for W(111) [7], as well as a number of ionic solids.

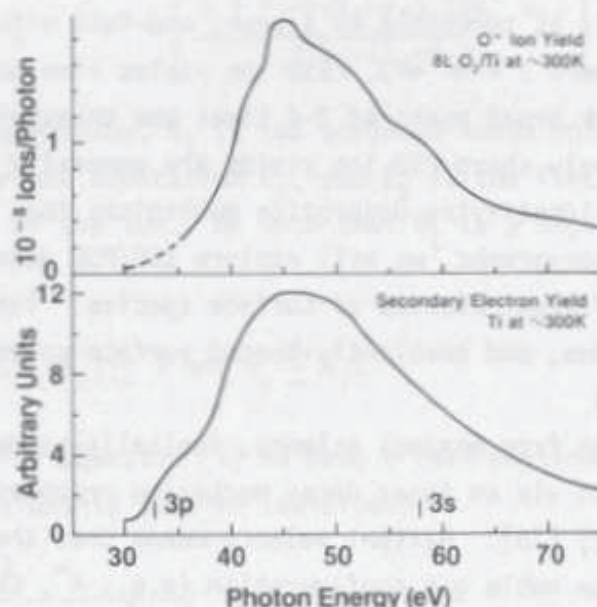


Figure 4: PSD  $\text{O}^+$  yield vs. photon energy for oxygen adsorbed on Ti(0001); comparison with secondary electron yield [8].

#### (b) Covalent systems

The mechanisms for ion desorption from covalently-bonded systems are less characterized. The first ESD mechanism, proposed by Menzel, Gomer and Redhead [19,20], suggested a Franck-Condon type transition to a repulsive final state from which desorption or de-excitation (and possible-recapture) could occur. The exact nature of the repulsive final states is only now being elucidated by theorists. In a number of cases, the most promising candidates are two-hole states in valence



orbitals, in which the holes remain localized on the surface molecule for a sufficiently long period of time ( $\sim 10^{-14}$  s) that bond rupture can occur and an ion can be ejected [21].

To illustrate PSD of a covalently-bonded adsorbate, CO on Ru(001) was studied [22]. CO is bonded in molecular form to Ru, via the carbon end of the molecule. The PSD  $O^+$  ion yield as a function of photon energy (solid curve) is compared with the probability of Ru core level production (dashed curve) in Fig. 5. There is little correlation between the onsets or structure in the two curves, indicating that Ru core levels are not involved in the ion desorption process in this energy range. Ramaker has recently proposed that the 41 eV peak in Fig. 5 is due to a  $5\sigma^{-2} 6\sigma^2$  excitation, and that the 50 eV peak is due to ionization of the CO  $3\sigma$  state, which then undergoes heavy mixing with 2hle (two hole-one electron) states in the adsorbed molecule [21].

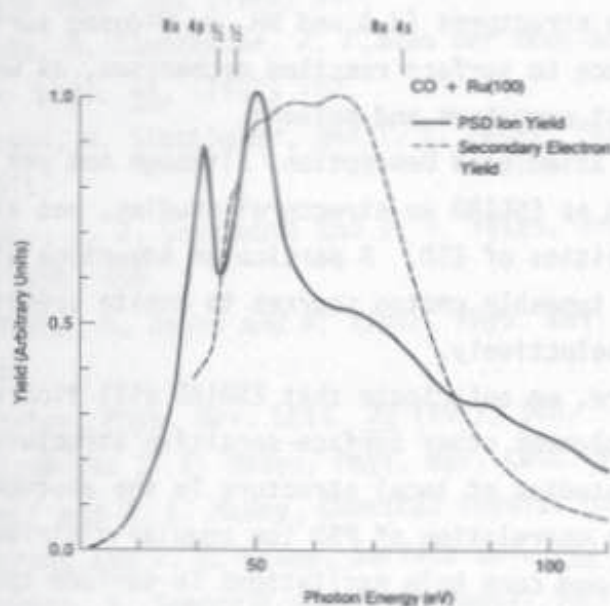


Figure 5: PSD from CO/Ru(0001).

Menzel and colleagues [23] show that excitation of deep core levels (O1s, N1s, Cls) can also lead to desorption of ions from covalently-bonded adsorbates. Adsorbate core hole ionization is quickly followed by Auger decay which ends in multiply valence-ionized adsorbate states. Certain "multiple-hole" states will lead to dissociation and desorption of ions.

## 6. Summary

We summarize the structural information obtainable using ESDIAD and PSD as follows:

- 1) ESDIAD provides direct evidence for the structures of surfaces molecules and molecular complexes, and in certain cases (e.g., oxides) can provide structural information about the substrate surface.
- 2) ESDIAD is particularly sensitive to the orientation of hydrogen ligands in adsorbed molecules. In general, electron scattering from surface H is sufficiently weak that LEED is not very useful.
- 3) ESDIAD is sensitive to the local bonding geometry of molecules on surfaces even in the absence of long-range translational order.
- 4) The identification using ESDIAD of impurity-stabilized surface structures ( $H_2O$  and  $NH_3$  on O-dosed surfaces) is of relevance to surface reaction mechanisms, as well as to catalyst promoters and poisons.
- 5) Photon Stimulated Desorption, although not yet as extensively applied as ESDIAD in structural studies, has all of the capabilities of ESD. A particular advantage of PSD is the use of tuneable photon sources to excite specific surface bonds selectively.

In the future, we anticipate that ESDIAD will find wide use as a technique to complement other surface-sensitive structural probes, particularly in studies of local structure in the absence of long range order. The correlation of PSD ion angular distributions with specific valence and core hole excitations in surface species should be particularly fruitful, especially for complex systems (mixed oxides, coadsorption systems, catalytic systems). The combination of angle-resolved PSD with SEXAFS (surface x-ray absorption fine structure) will provide an opportunity to measure both bond orientation and bond length. Finally, the angle resolved desorption of neutrals (including metastables) and negative ions will provide new insights into both structure and mechanisms of excitation.

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