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FUNDAMENTAL STUDIES OF THE STRUCTURE AND CHEMISTRY OF SOLID SUR--ETC(U)  
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FUNDAMENTAL STUDIES OF THE  
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SOLID SURFACES

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from hydrazine and ammonia on Ir(111) using high intensity polarized UV radiation has been investigated. The results are consistent with the data from the scattering experiments. AES was used to monitor the absorption of oxygen on Al(111) surfaces and was found to be dependent on both time and oxygen pressure. Further studies will concentrate on the kinetics of aluminum oxidation.

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INTRODUCTION

Work during this contract year has involved substantial effort in equipment development and research in three areas: 1) Hydrazine decomposition on Ir(111); 2) Photoemission of adsorbed species; 3) Oxidation of Al(111). Specifically the work statement for the year is as follows:

- 1) Complete the reactive scattering studies of  $N_2H_4$  from Ir(111)
- 2) Conduct photoemission studies of  $N_2H_4$  on Ir(111)
- 3) Complete photoemission studies of  $NH_3$  on Ir(111)
- 4) Investigate the oxidation of Al(111) in ultrahigh vacuum and in the pressure of water vapor
- 5) Develop suitable in situ cleaning procedures for titanium single crystals.

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## EQUIPMENT DEVELOPMENT

The problems encountered last year in the sensitivity of the mass spectrometer detector used in the reactive scattering system have been solved. A new mass spectrometer, housed within a cryogenically-cooled enclosure with a titanium sublimation pump has been mounted at  $90^\circ$  from the input of the molecular beam to the scattering chamber. This configuration permits scattering studies at a fixed scattering angle for each angle of incidence.

Eventually, the cryogenically-cooled detector will be mounted on our UHV goniometer so that it can be rotated within the UHV chamber and therefore permit selection of the scattering angle as well as the angle of incidence. With its present configuration, however, it has been possible to complete a revealing set of reactive scattering studies of hydrazine from surface temperatures below 200 K up to 1500 K.

The detector is operated in the counting mode and the entire scattering wave-form is input directly to our on-line computer. Data collection-times can be quite long (up to an hour in some cases) and it was necessary to control the crystal temperature on-line to obtain steady-state operation with sufficient precision for such long counting times. This has been accomplished by some in-house software development and the construction of the associated programmable power supplies.

A unique feature of our new detector is that it can be carefully collimated so that only molecules which originate at our test surface may enter the active detection region. This provides a further signal to noise enhancement and also has yielded some direct measurements of surface diffusion of product species in the decomposition of hydrazine.

The design of the new surface spectrometer in which the aluminum oxidation studies were to be accomplished was completed last year. Funds for this chamber are coming from other sources. Figure 1 shows a section through the chamber at the elevation where the various spectroscopic measurements are made. The crystal manipulator will be constructed with a "dog-leg" so that it can be rotated successively to position the crystal at points a, b, or c. At point c, in front of the CMA electron energy analyzer, one can accomplish Auger spectroscopy, ultraviolet photo-emission, x-ray photo-emission, and eventually inelastic ion scattering spectroscopy. It will also be possible to do depth profiling using ion sputtering.

At b, low energy electron diffraction studies can be accomplished. A molecular beam doser will be mounted on port 10 which is directly opposite port 6, through which the mass spectrometer is to be inserted. Thus, the molecular beam doser can be calibrated in situ with the mass spectrometer, and the crystal can then be rotated to face the doser so that a known exposure of even highly reactive gases can be achieved. With the crystal in position a, temperature-programmed desorption can be accomplished directly into the mass spectrometer, and reactive scattering from a nozzle beam which will be inserted at a later date through port 4 can eventually be carried out also.

Front and rear elevations of the chamber showing the location of the necessary ports focusing on points a, b, and c are shown in figures 2 and 3. The double pass CMA and x-ray source for this system have been purchased and tested successfully in other UHV systems. With an additional \$5,000 made available by the Materials Science Center here

at Cornell, it was possible to purchase an analyzer with apertures that permit angle resolved photo-emission measurements at position c.

Some difficulty was encountered in obtaining this custom designed stainless-steel bell-jar in which the bulk of the measurements will be carried out. After careful pre-design, the construction of the chamber was contracted to K.V. Associates, Oakland, California. When delivered it was completely unacceptable in workmanship and returned without payment. The contract was then let to Varian Associates who subsequently delivered a bell-jar with several improperly placed ports. It was returned to be rebuilt and, now in satisfactory condition, is being tested and fitted with Leed, Auger, the UV source, x-ray source, molecular beam doser and cryogenic sample cooling. Provisions for future additions of SIMS, ISS and reactive molecular beam scattering have also been included. It is expected that some of the oxidation studies can be carried out in this system during the next contract year.

This has resulted in a substantial delay in accomplishing even these preliminary measurements of the oxidation of aluminum and the work done to fulfill the work statement was accomplished with another UHV system which had to be pre-empted from another project. This delay is primarily responsible for the no-cost extension which has been requested for this grant.

#### EXPERIMENTAL RESULTS

##### Oxidation of Aluminum (111)

The adsorption of oxygen on Al(111) surfaces has been studied concurrently with the development of the new surface spectrometer in an existing apparatus which is suitable for some of the preliminary measurements. Auger spectroscopy has been used to monitor surface

compositions and these have been correlated with the observed LEED patterns.

Auger spectra are singularly useful in the Al/O<sub>2</sub> system because there is a 13 eV "chemical" shift in the LVV transition in metallic aluminum compared to that in Al<sub>2</sub>O<sub>3</sub>. Thus oxygen which is simply chemisorbed can be distinguished from the development of a surface oxide by observing simultaneously the O<sub>KLL</sub> (512eV), the metallic Al<sub>LVV</sub> (67eV), and the Al<sub>LVV</sub><sup>3+</sup> (54eV) transition. Examples of both spectra are seen in figure 4.

The results of one of these experiments is illustrated in the figure 5, where the square symbols represent O<sub>512</sub> and the triangular Al<sub>54</sub><sup>3+</sup>. No surface oxidation is evident until exposures of ca. 270 Langmuirs. Curve a is calculated by assuming that oxygen uptake occurs initially only by chemisorption, which can be represented by:

$$\frac{dN_O}{dt} = (0.012) \left(1 - \frac{N_O}{N_{Al}}\right) \frac{P_{O_2}}{(2\pi m_{O_2} kT)^{1/2}}$$

where:

- N<sub>O</sub> = surface concentration of oxygen
- N = surface concentration of aluminum
- P<sub>O<sub>2</sub></sub> = oxygen pressure
- m<sub>O<sub>2</sub></sub> = oxygen molecular mass
- t = time
- T = temperature

Curve b is the uptake data reported by Flodström (1). The Flodström data and ours diverge from the simple adsorptive uptake at about the exposure at which the surface oxide (Al<sub>54</sub><sup>3+</sup>, the triangle) is initiated.

The data depicted in the figure were obtained at O<sub>2</sub> partial pressures of 2 x 10<sup>-8</sup> Torr. At higher partial pressures the onset of oxidation occurs at lower exposures. For example at 2 x 10<sup>-7</sup> Torr oxidation begins

at only 100 Langmuirs exposure. Thus the initiation of oxidation depends on both time and oxygen pressure. More work is planned to examine these kinetics, but it will best be carried out in the new system where the resolution and sensitivity of the Auger spectrometer are enhanced.

We have also found methods (2) for producing thick layers (several thousand Å) of  $\gamma$ -alumina by wet oxidation in boiling water. Depending on the temperature, either  $\gamma$ -alumina or Böhmite are formed. Since  $\gamma$ -alumina may be formed by thermal treatment of Böhmite either high or low oxidations can be used to produce these "thick"  $\gamma$ -alumina layers. The  $\gamma$ -alumina or Böhmite can be verified by x-ray diffraction outside our vacuum system. Measurement of the Auger spectra of such systems and the adsorption of the aforementioned basic gases should provide the necessary "fingerprint" information to identify the  $\gamma$ -alumina as it is nucleated during the early stages of wet oxidation.

As the conditions for formation of these defect or "transition" aluminas are identified in the low resolution system, they will be studied in more detail in the high resolution system under construction, and perhaps using synchrotron radiation at the national laboratory for synchrotron radiation at Steughton, Wisconsin.

#### The Decomposition of Hydrazine

The decomposition of hydrazine has been studied in Ir(111) from temperatures below 200K up to 1500 K, using the super-sonic molecular beam scattering system (figure 6). Results using a d.c. (unmodulated) beam are seen in figure 7. Hydrazine begins to decompose at ca. 200 K producing  $\text{NH}_3$ ,  $\text{N}_2$  and  $\text{H}_2$ . Between 200 K and 600 K ammonia is a primary product via



The detector in these experiments was positioned at  $45^\circ$  with respect to the crystal normal and the hydrazine beam was incident at  $-45^\circ$ . At this emission angle there is a temperature interval 200 K to 320 K in which there is essentially no nitrogen produced in direct conflict with the decomposition stoichiometry.

It has been found that the nitrogen emission in this temperature regime has an extremely strong angular dependence. In figure 8 several angle resolved temperature programmed desorption spectra for nitrogen emission from hydrazine on Ir(111) are depicted. The 290 K peak is strongly directed normal to the surface. Normally directed emission from desorption has been reported earlier (3) but this is the first time it has been observed for a surface decomposition. No previous observations have been directed so strongly. The half-width (FWHM) of the  $N_2$  flux for the data depicted in figure 8 is only  $6.5^\circ$ . This is a very significant observation, since it suggests how one can in such cases obtain some rudimentary information about the morphology of the potential energy surface associated with the kinetically active surface species (4). With this normally directed  $N_2$  emission, it is not surprising that there is a "window" in the nitrogen emission recorded at  $45^\circ$  emission as depicted in figure 7.

Decomposition data for reactive scattering of a hydrazine beam modulated (the wave-form is a square-wave) at 25 Hz is shown in figure 9 for surface temperatures from 200 K to 1500 K. The most striking feature of these results is the structure in the temperature dependence of the  $NH_3$  evolution rates compared to those for the continuous d.c. beam, figure 7. The amplitudes for the reactively scattered wave-forms in this region are only 5-10% of those for the unmodulated beam. Thus 90-95% of the

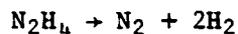
ammonia is produced by a kinetically simple route which is so slow that it is demodulated out of the signal at 25 Hz. There is a fast branch which is more complicated kinetically, but which has a low branching ratio.

By careful analysis of the frequency spectra of these time-correlated experiments it is possible to delineate the details of these surface mechanisms and often to measure the rate coefficients of individual elementary reactions at the surface (5). In doing this we have pioneered a new technique (6) in which the Fourier transform of the entire wave-form is utilized (7) instead of just the fundamental mode which "lock-in" detection yields (5). We have found some wave forms, for example, which have statistically significant amplitudes up to the 29th Fourier coefficient. This is surprising, but also extremely useful. Practically it means that we can obtain in a single experiment the same information that would require 15 separate experiments using the lock-in method.

There is an additional advantage to the Fourier transform method. The pulse shape used for the incident beam (square wave) has only odd components in its Fourier spectrum. Therefore the scattered wave will have large amplitudes only in its odd components. If the surface reactions are linear in surface concentrations, in fact, all of the even Fourier components will have zero amplitude. A non-linear surface reaction will produce even components and we have shown (8) that their frequency spectra contain the same detailed kinetic information about the non-linear steps as the odd components contain.

Using these transform techniques it has been possible to deduce much about the detailed mechanism of the hydrazine decomposition reaction as shown in figure 10. Below 200 K hydrazine is reversibly adsorbed but at

200 K the decompositions begin via two main parallel routes. The slow route produces over 90% of the  $\text{NH}_3$  at 200 K and passes through adsorbed  $\text{NH}_3$  as an intermediate. The fast branch (100-1000 times faster than the slow branch) passes through two intermediates, designated  $\text{N}_2\text{H}_4$  and  $\text{N}_2\text{Hy}$ , whose structure and composition are not yet known. At 320 K  $\text{N}_2\text{Hy}$  decomposes to  $\text{N}_2$  and quenches the secondary branch via  $k_6$ . At 400 K  $k_7$  becomes larger than  $k_6$  opening up the direct channel from  $\text{N}_2\text{H}_4$  to gas phase  $\text{NH}_3$ . At 500 K  $\text{N}_2\text{H}_4$  decomposes to  $\text{N}_2$  quenching the  $k_7$  channel to gas phase ammonia. Above 600 K even the adsorbed  $\text{NH}_3$  species decomposes to gaseous  $\text{N}_2$  and only the overall reaction:



occurs.

To date, only the  $\text{NH}_3$  scattering has been analyzed. Though the experiments have been completed the analysis of the nitrogen wave-forms has yet to be done. In principle, it should be possible to determine all of the rate coefficients depicted in figure 10, but in practice it may be necessary to obtain data at a few other chopping frequencies to accomplish this. Further, analysis of the  $\text{NH}_3$  wave-forms, analysis of the  $\text{N}_2$  emission and the identification and completion of the key experiments which may be necessary to define the magnitudes and temperature dependence of all the rate coefficients in the decomposition mechanism are planned for the next contract year.

#### Photoemission Studies

The photoemission from  $\text{N}_2\text{H}_4$  and  $\text{NH}_3$  on iridium (111) has been investigated using the high intensity, polarized ultraviolet radiation which is available at the National Synchrotron Laboratory at Stoughton Wisconsin. Photoemission from  $\text{N}_2\text{H}_4$  adsorbed at liquid  $\text{N}_2$  temperatures

shows that it is adsorbed at liquid  $N_2$  temperatures having emission bands at energies comparable to those expected from gas phase molecular orbital calculations. Above 200 K the photoemission from adsorbed hydrazine is more complicated, but appears qualitatively like the superposition of hydrazine and ammonia. All these observations are consistent with the mechanism deduced from the scattering.

More detailed studies have been accomplished with adsorbed  $NH_3$ . Concentration on this species has been dictated by its central role in the main channel of the decomposition reaction. There are three molecular orbitals for  $NH_3$ . Two, the nitrogen lone-pair,  $3A_1$  and the  $2A_1$ , are primarily of S-character from the nitrogen. One, the 1E, is a  $\pi$ -like N-H bonding orbital. Each of these orbitals has been identified by energy and orbital symmetry in the photoemission studies. The  $2A_1$  is essentially unperturbed by adsorption. The 1E are stabilized slightly (ca. 0.2eV) but the  $3A_1$ , lone pair, orbital is lowered 1.5 eV and donates its lone-pair strongly to the surface as evidenced by the large change in the work function which accompanies adsorption (9).

Angle resolved photoemission from the 1E orbital has resulted in identification of the specific binding site (10) as shown in figure 11. Here the angle resolved intensity is shown super-imposed upon the binding site at the surface. The three large lobes are initial state modulations which indicate the position of the hydrogen atoms via the angular dependence of the N-H molecular orbital. The shorter lobes are substrate scattering features which must have the symmetry of the substrate. It is the two minor lobes separated by  $40^\circ$  which identify the adsorption site via their alignment with the next nearest neighbor substrate atoms. The binding site is a  $t_{2g}$  vacancy and would be the next lattice site occupied

if the bulk structure were to propagate past the surface. In the next contract year constant initial state (CIS) studies of the photoemission will be undertaken to determine the  $\text{NH}_3$  to Ir distance perpendicular to the surface.

#### Cleaning Procedures for Titanium Crystals

A titanium crystal(001) (i.e. basal plane in the hexagonal system) has been oriented and prepared strain-free. Because of the delay in the receipt of our main chamber for the new surface spectrometer it has not been possible to begin the in situ studies of the titanium cleaning procedures.

#### SUMMARY

All of the first four items in the work statement have been accomplished. In the case of the decomposition of hydrazine and the photoemission studies of adsorbed  $\text{NH}_3$  the results have suggested important additional work which should be completed. This work is detailed in the proposal for the subsequent contract year. The fifth item was not accomplished because of time limitations.

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8. Sawin, H. and R.P. Merrill, "Non-linear Surface Reactions in the Fourier Analysis of Reactive Scattering", in preparation.
9. Purtell, R.J., R.P. Merrill, C.W. Seabury and T.N. Rhodin, "Photoemission Studies of NH<sub>3</sub> Adsorbed on Ir(111)", to be submitted to Surface Sci.

PAPERS RESULTING FROM CONTRACT SUPPORT - CURRENT YEAR

A. Papers Published

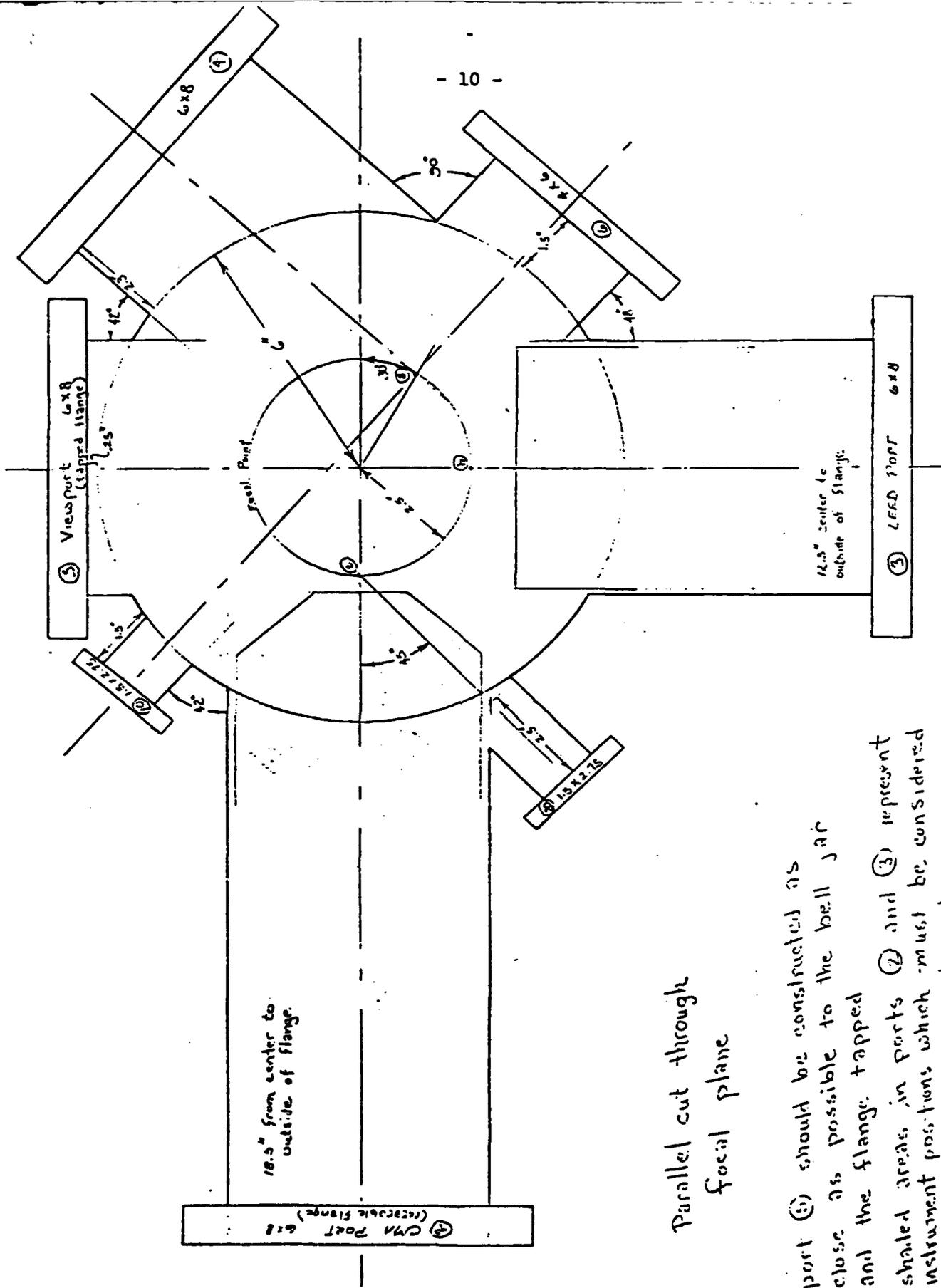
1. Merrill, R.P. and W.H. Weinberg, "Reply to Comments on the CFSO BEBO Approach", J. Catalysis, 51, 296 (1978).
2. Dion, D.R., J.A. Barker and R.P. Merrill "Double Rainbow Features in Classical Scattering from Solid Surfaces - Ne on Ag(111)" Chem. Phys. Lett. 57, 298 (1978).
3. Seabury, C.W., T.N. Rhodin, R.J. Purtell and R.P. Merrill, "Chemisorption and Reaction of NH<sub>3</sub> on Ni(111)" Surface Sci. xx, xxx (1979).

B. Papers Submitted for Publication

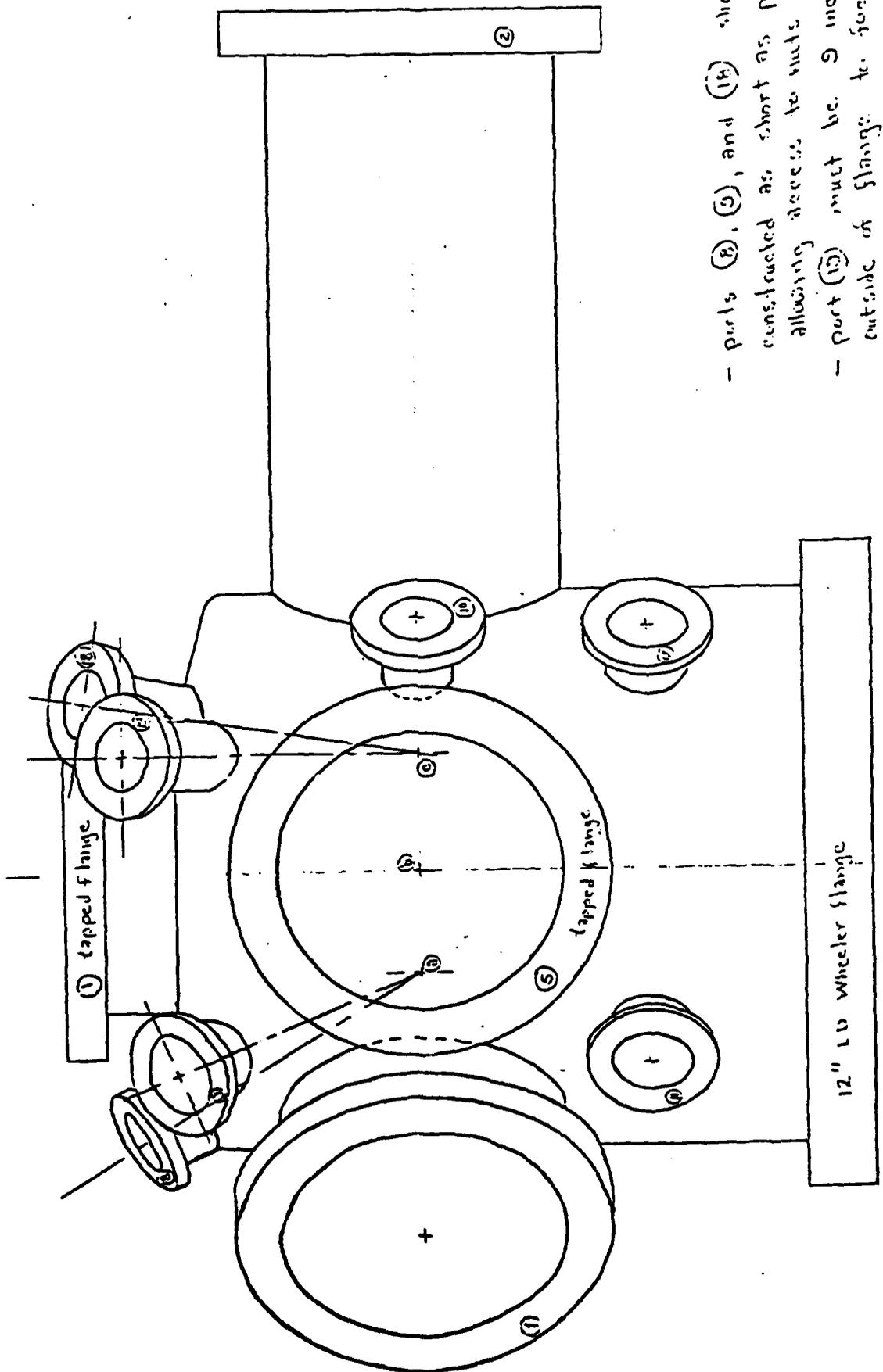
1. Monroe, D.R. and R.P. Merrill "Adsorption of Oxygen on Pt(111) and Its Reactivity to H<sub>2</sub> and CO" Submitted to Journal of Catalysis.
2. Komiyama, M., and R.P. Merrill "Concentration Profiles in the Impregnation of Porous Catalysts: Ni on  $\gamma$  Alumina" Accepted for publication in the Journal of Catalysis.
3. Purtell, R.J., R.P. Merrill, C.W. Seabury and T.N. Rhodin, "Molecular Adsorbate Structure from Angular Resolved Photoemission: Ammonia on Iridium(111)" Submitted to Phys. Rev. Lett.

C. Papers in Preparation

1. Angle Resolved Temperature Programmed Surface Decomposition: Molecular Nitrogen from Hydrazine Decomposition on Iridium(111).
2. The Reactive Scattering of Hydrazine from Ir(111).
3. Classical Surface Scattering Calculation: Rainbow Patterns and Energy Exchange.
4. Fourier Analysis of the Complete Scattering Wave Form in Reactive Molecular Beam Scattering.
5. Identification of Non-Linear Reactions in Reative Surface Scattering Using Fourier Transforms.
6. Photoemission Studies of Ammonia Adsorbed on Iridium(111).
7. A Molecular Beam Doser for Calibrated Adsorption Studies at UHV.



- port ⑥ should be constructed as close as possible to the bell jar and the flange, tapped
- shaded areas in parts ② and ③ represent instrument positions which must be considered in discussing subsequent parts



- parts ⑧, ⑨, and ⑩ should be constructed as short as possible, allowing access to nuts and bolt
- part ⑫ must be 9 inches from outside of flange to focal point

Figure 2 Surface Spectrometer: Front Elevation.

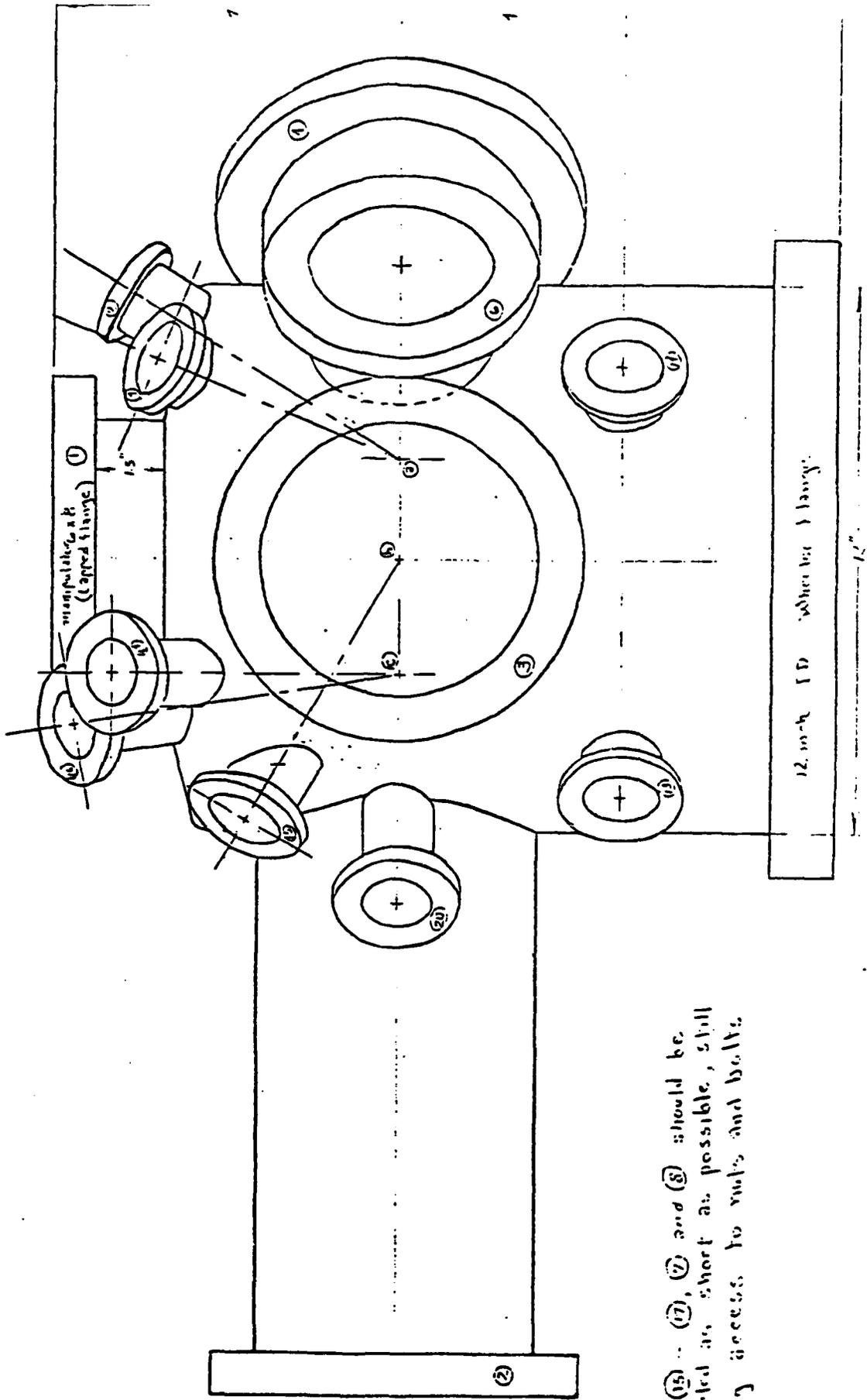


Figure 7 Surface Spectrometer: Rear Elevation.

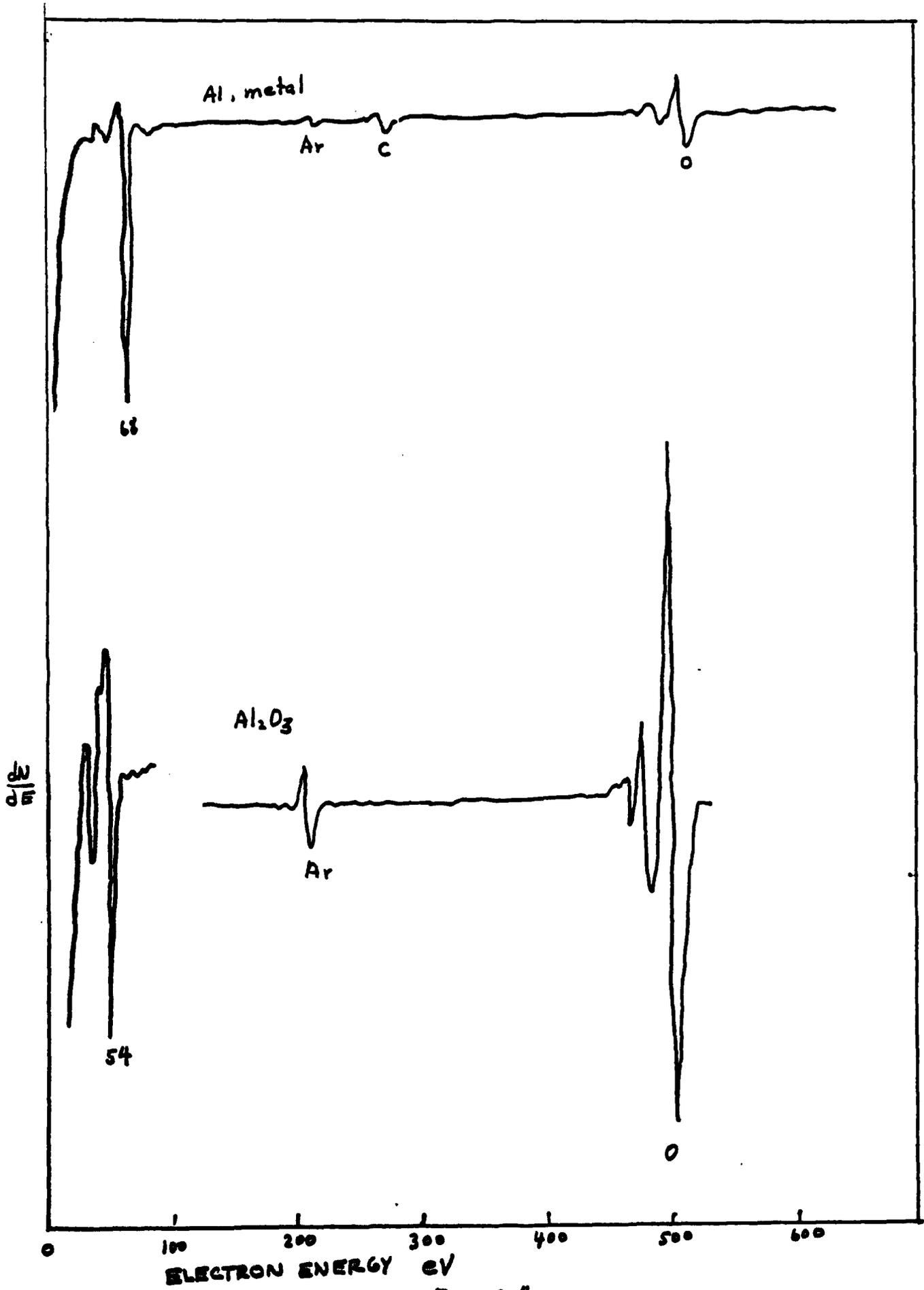
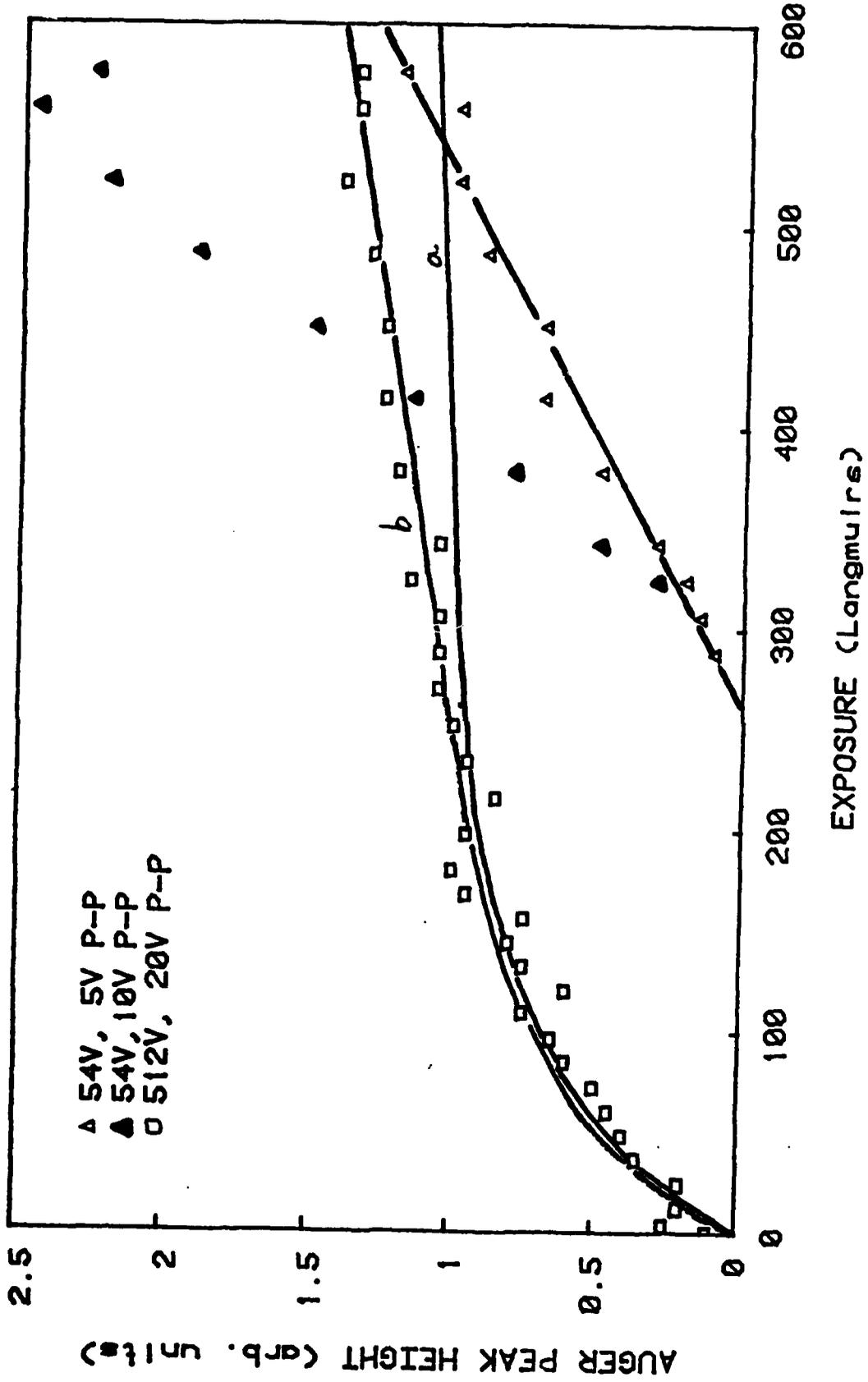
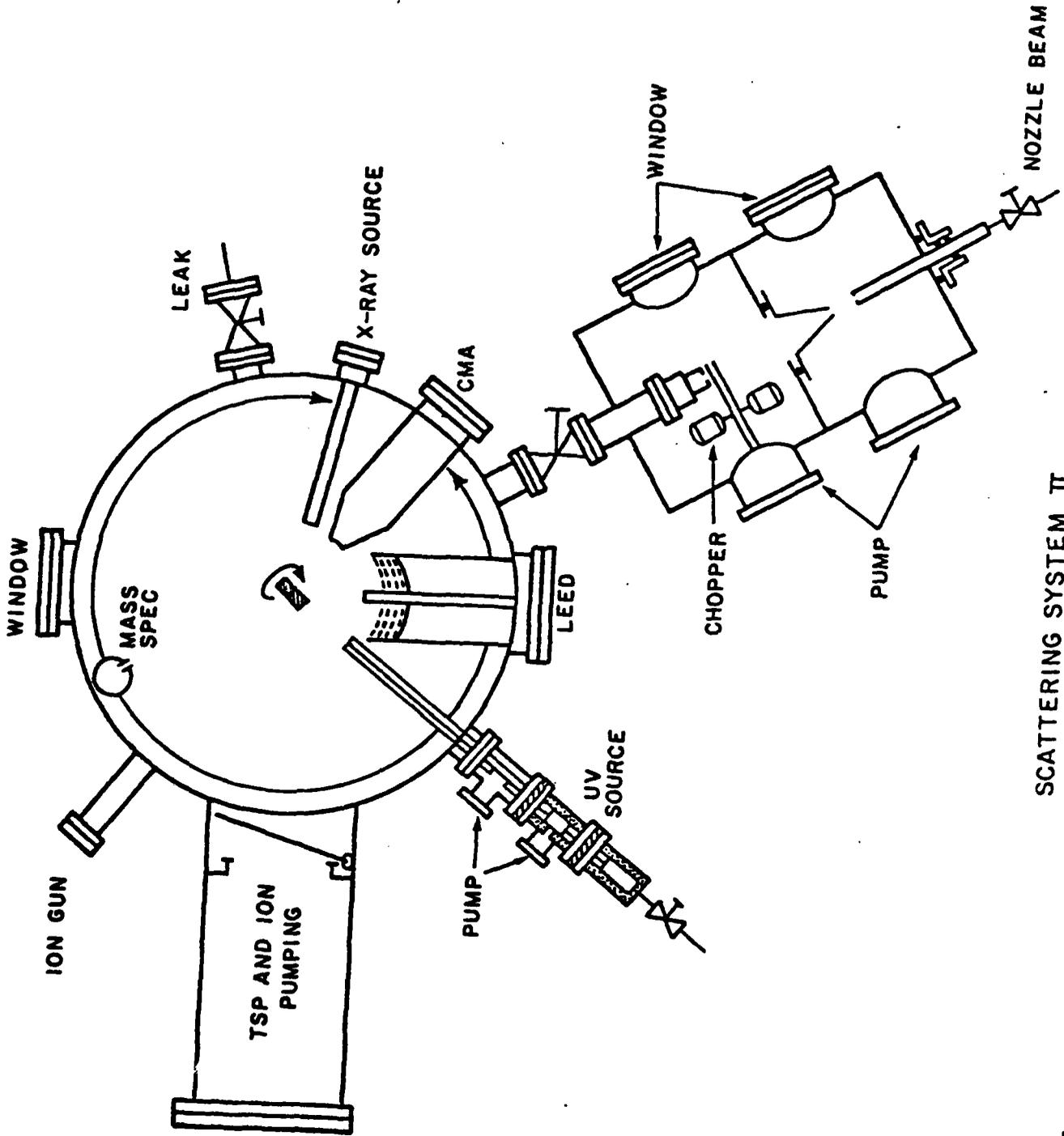


FIGURE 4

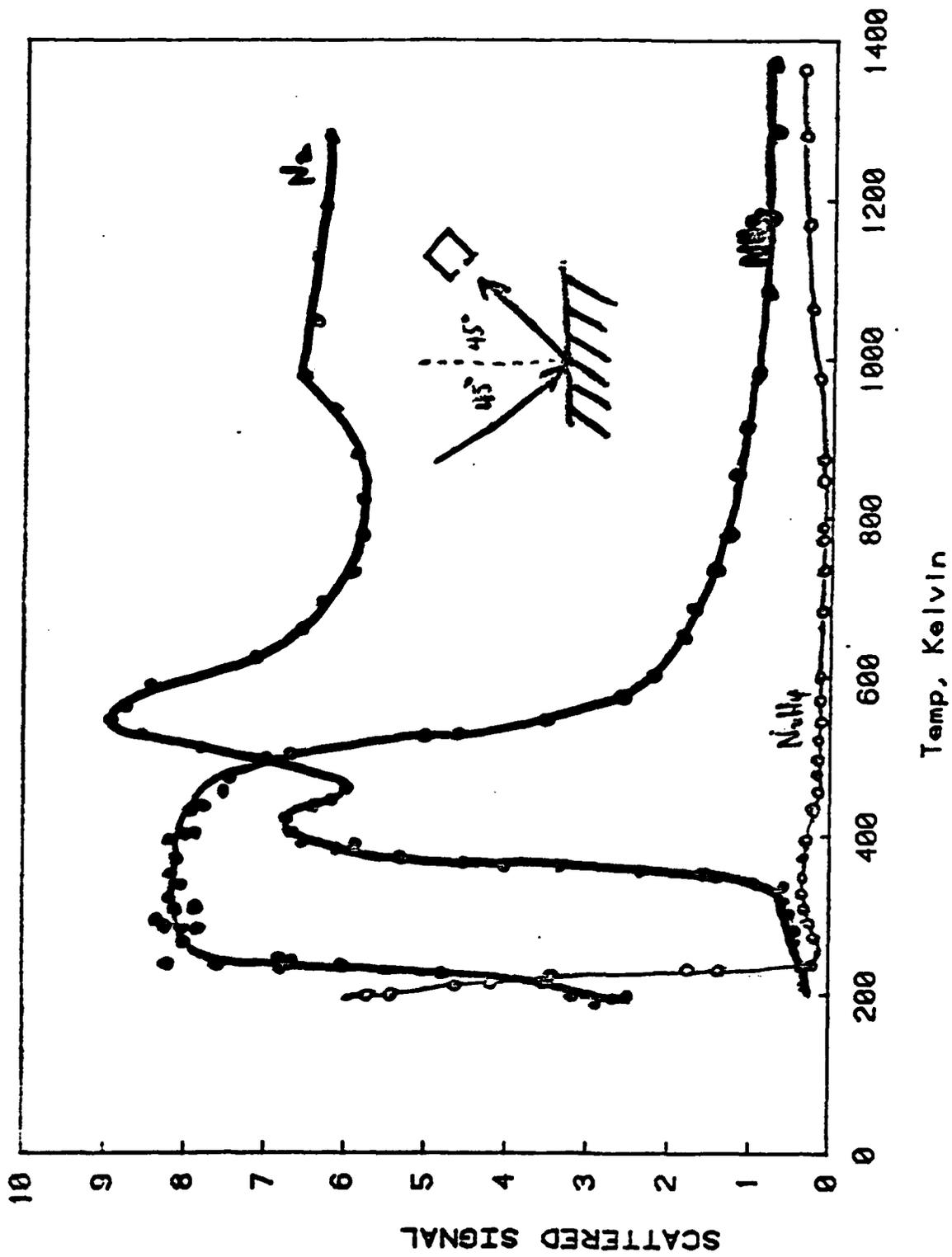
# AIC(111) OXYGEN EXPOSURE





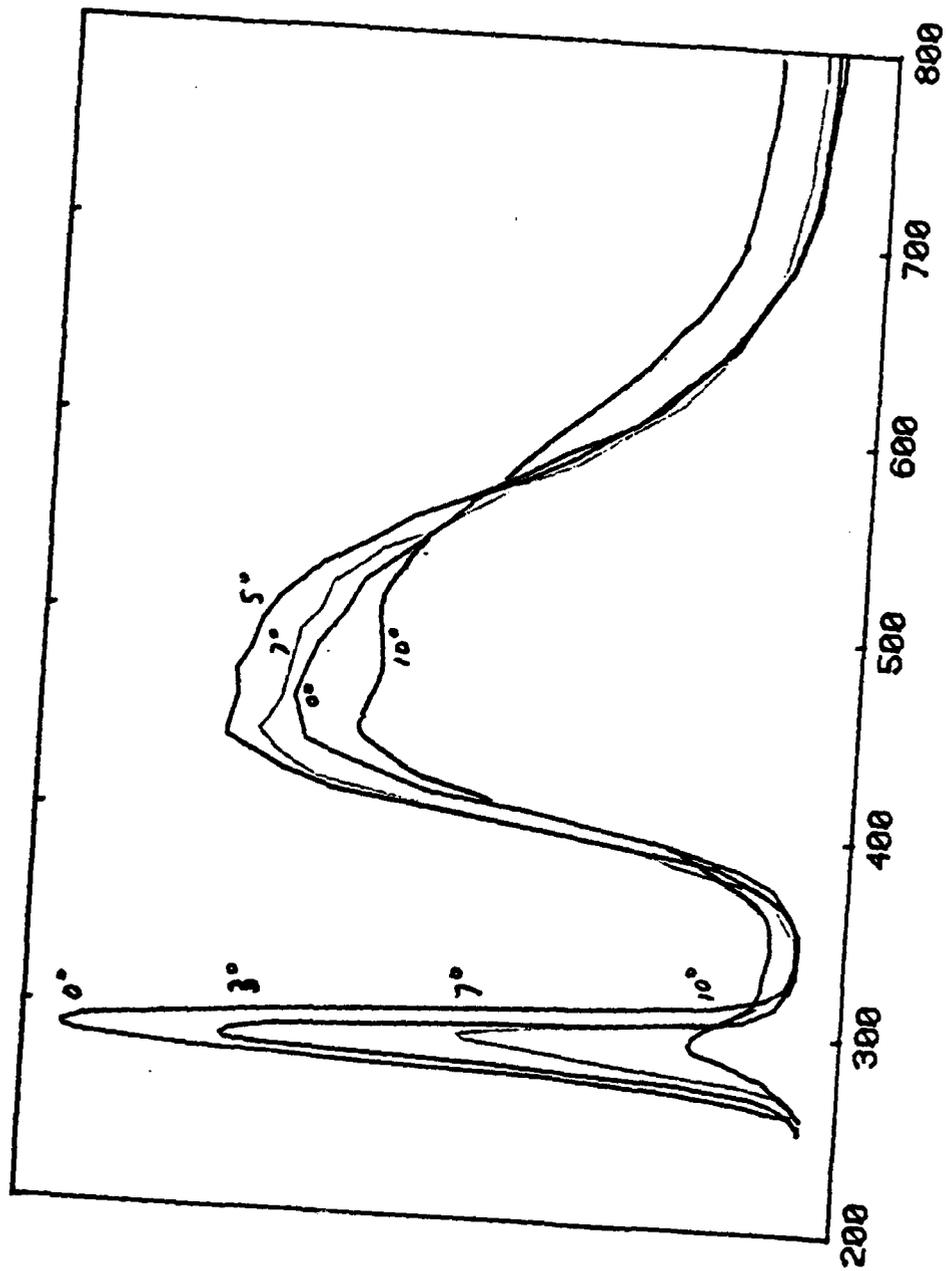
SCATTERING SYSTEM II

FIGURE 6



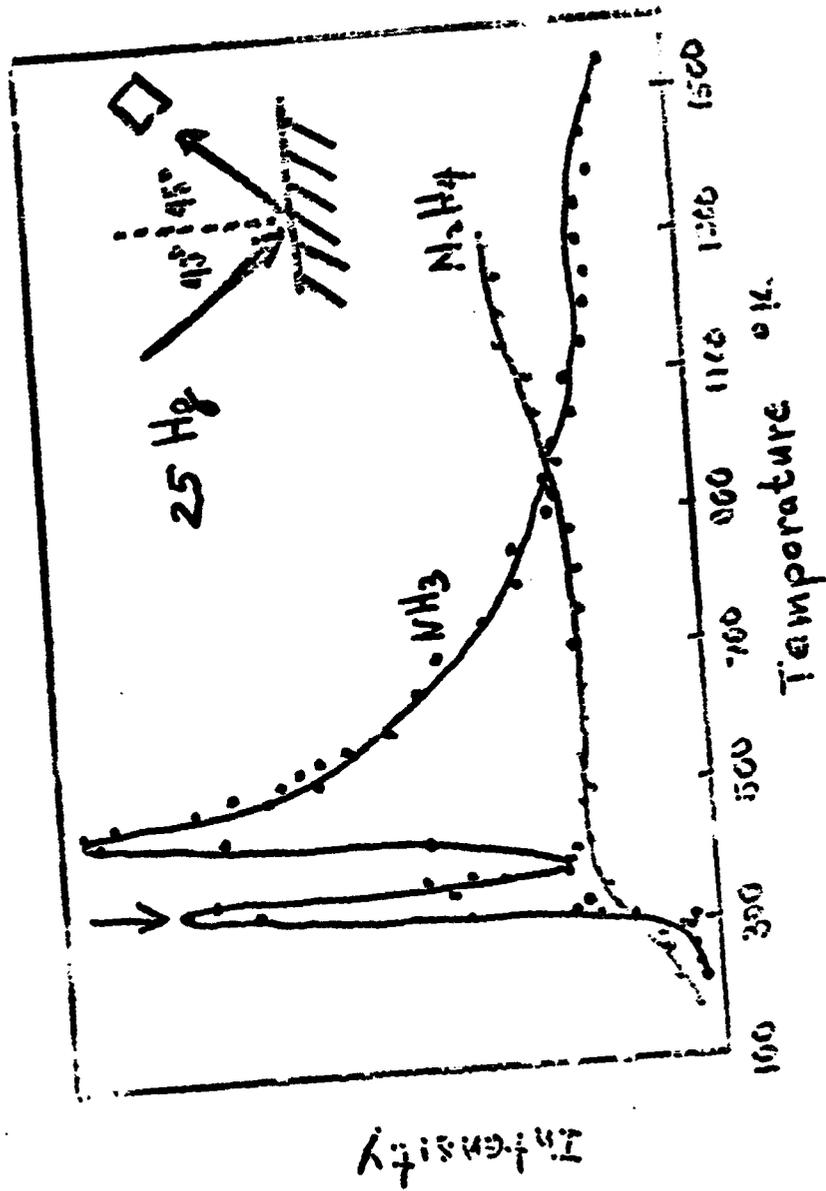
DC REACTIVE SCATTERING OF HYDRAZINE FROM Ir(111)

Figure 7



NITROGEN DECOMPOSITION FROM HYDRAZINE ON Ir(111)

Figure 8



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Figure 9



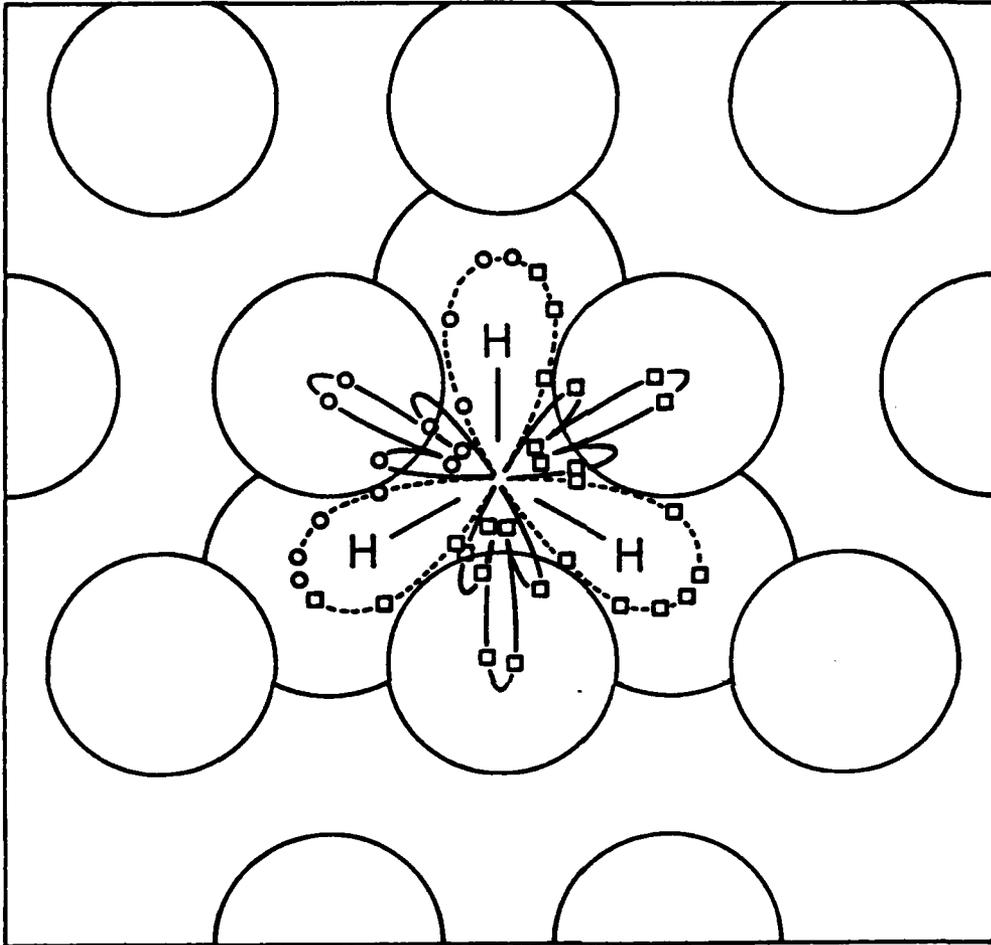


Figure 11