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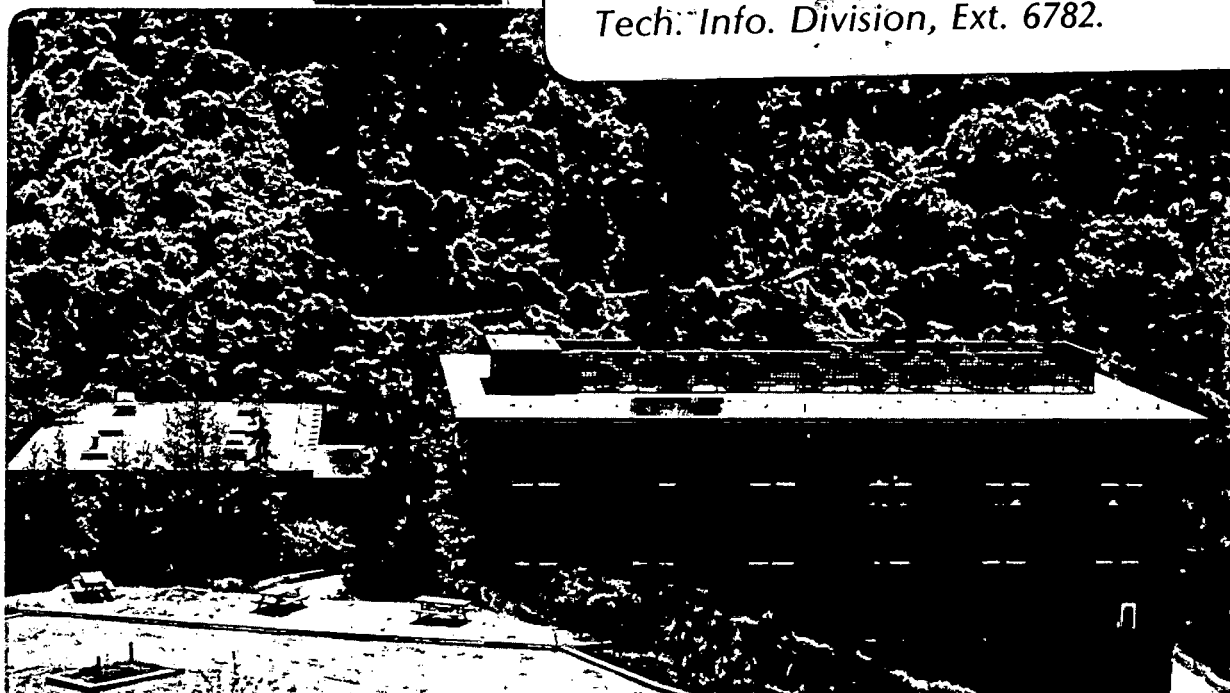
MOLECULAR BEAM STUDIES OF ENERGY TRANSFER
IN SCATTERING FROM CRYSTAL SURFACES

William Leslie Guthrie
(Ph.D. Thesis)

January 1983

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Molecular Beam Studies of Energy Transfer
in Scattering from Crystal Surfaces

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Abstract

The translational energy distributions and angular distributions of D_2O produced from the reaction of incident D_2 and O_2 on a (111) platinum single crystal surface have been measured through the use of a molecular beam-surface scattering apparatus equipped with a time-of-flight spectrometer. The translational energies were measured over the surface temperature range $T_s = 664 \text{ K} - 913 \text{ K}$ and at scattering angles of 7° and 40° from the surface normal. Although the angular distributions can be described by a cosine function, the translational energy distribu-

tions were sub-thermal and deviate from the corresponding Maxwell-Boltzmann distributions. The D_2O translational energy, $\langle E \rangle$, was found to be approximately half the equilibrium value over the temperature range examined, with $\langle E \rangle / 2k$ varying from 280 K to 480 K. These results are discussed in terms of a non-equilibrium desorption model.

A two-photon ionization spectrometer was designed and constructed on a UHV compatible rotary flange which was added to the molecular beam-surface scattering apparatus. The two-photon ionization spectrometer was built to investigate the internal rotational and vibrational energy distributions of NO scattered from Pt(111) surfaces. The rotational energy distributions were measured over the crystal temperature range of $T_s = 400 \text{ K} - 800 \text{ K}$. The probability of vibrational excitation upon scattering was determined over the temperature range of $T_s = 400 \text{ K} - 1200 \text{ K}$. The translational energy distributions and angular distributions were measured using the time-of-flight spectrometer over the crystal temperature range of $400 \text{ K} - 1100 \text{ K}$ and for beam translational energies of 0.046 eV, 0.11 eV and 0.24 eV, so that complete energy exchange information for translation, rotation and vibration is available for this gas-surface system. Significant energy transfer was observed in all three modes. The translational energy of the scattered NO was found to be in equilibrium with the surface for $T_s < 900 \text{ K}$ and for incident beam energies of 0.046 and 0.11 eV. The vibrational and rotational energy distributions were found to deviate from equilibrium distributions. These deviations appear to be due to dynamic effects in the desorption process.

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To my parents.

Chapter 1: Introduction

Despite the complexity inherent in molecular beam apparatuses [1], molecular beam scattering is seeing increased use in studies of both gas-gas and gas-surface interactions. The flexibility in control of the incident gas condition is a powerful advantage which in specialized cases can more than compensate the disadvantages. The incident gas can be prepared with a well defined momentum with a narrow energy spread [2], and with the molecules distributed over a narrow range of internal rotational and vibrational states. Intense pulsed beams can be generated with excellent time resolution [3,4]. Techniques have been developed to prepare beams of molecules, atoms or radicals, and to produce beams with significant specific electronic [5,6] or rotational and vibrational excitation [7,8]. With molecular beam techniques the gas-surface interaction can be studied as a function of surface properties, and of initial gas properties in what approaches state-to-state experiments. This contrasts to the uncontrolled statistical and thermal spread of incident molecular states present in more traditional gas-surface experiments. The second important property of beam experiments is the suppression of gas phase interactions. Collision probabilities are low in the incident beam, so that molecules remain in the prepared state until they are incident on the sample surface. After leaving the surface, the densities are low ($\sim 10^{-8}$ - 10^{-9} torr) so that molecule-molecule interactions are improbable. Therefore the energy and state of the emitted molecules remains unchanged to the the detector. Also the properties of the gas-surface interaction are not masked by diffusion effects or secondary gas-phase reactions of the products.

We have used molecular beam-surface scattering techniques to measure

gas-surface energy transfer in reactive and non-reactive (but strongly interacting) systems. Translational energies were measured using cross-correlation time-of-flight (TOF) techniques. We have adapted and developed a two-photon ionization (TPI) technique for the low densities encountered in molecular beam-surface scattering. The TPI technique has been used to measure the internal rotational and vibrational energy distributions of nitric-oxide scattered from the (111) crystal face of platinum.

Section 2.1 describes the time-of-flight experiment, including a brief description of the apparatus, materials, gases, and sample preparation. Also discussed is the mathematics of the cross-correlation technique, which are presented to facilitate discussion of the data transformation method, spectrometer calibration, chopper design and noise sources. Section 2.2 describes the two-photon ionization experiment. The resonant TPI technique is described and the approximate detection efficiency is calculated. The two-photon ionization technique is compared to the more commonly used laser-induced fluorescence detection scheme. The apparatus is described including the design of the ultra-high vacuum compatible rotary flange, on which the detector was mounted, the ultra-violet laser, and the electronics and data accumulation system.

Chapter 3 describes the experimental results for the angular distributions and translational energy distributions of D_2O produced on the (111) face of platinum from the exothermic reaction of incident D_2 and O_2 . Despite the energy of reaction, the D_2O translational energy is sub-thermal, and these results are discussed in terms of non-equilibrium desorption of the product molecules. Chapter 4 combines the experimental results of two studies of the translational energy and angular distributions, and the internal rotational and vibrational state distributions of

NO scattered from Pt(111) surfaces. This represents the first gas-surface system for which complete measurements have been made of the translational, rotational and vibrational energy before and after surface scattering. Information on all modes allows more assured interpretation of the results. Our data indicate some interesting internal energy transfer effects. The rest of the present chapter will be a discussion of gas-surface energy transfer, and a brief review of experimental and theoretical investigations of the processes involved.

The surface plays several roles in enhancing heterogeneous reactions. First it confines the reactants to two-dimensional motion, which can increase the effective density and interaction rate, while serving as an extremely effective third body. As a third body in the reaction, the surface relaxes momentum and energy conservation requirements relative to the requirements affecting gas-phase reactions. Second the surface can modify the electronic properties of the adsorbate, which can change intermolecular forces and lower reaction activation barriers. Finally the surface serves as a conduit for energy transfer from the bulk so that the solid acts as an efficient thermal bath, providing energy for reactant motion, for overcoming reaction barriers, and for removing the reaction products from the surface. Although energy transfer is not explicit in the first role, it is an important feature. Effective confinement of the reactants at the surface requires a reasonable adsorption probability for molecules incident on the surface, which is dependent on the energy transfer efficiency. An incident gas molecule will remain on the surface if enough of the initial kinetic energy is transferred to the surface to make the total energy less than the free-molecule potential energy. This transfer might occur by direct translational to bulk energy

transfer or by collision induced translational to rotational energy transfer followed by subsequent energy transfer to the bulk.

Despite the role of energy transfer in heterogeneous reactions, and gas-surface interactions in general, there is scarce definite knowledge. Experimental and theoretical studies of gas-surface energy transfer have been difficult. The theoretical problem is one of calculating the forces and dynamics of an infinite particle system, but without the help of the full lattice symmetry properties of bulk solids. Calculations of the dynamics of the motion of complex molecules is in itself difficult, but methods must be found to handle the motion of the substrate as well. There has been some progress in these areas, but unresolved questions include the uncertainty as to the relative importance of energy transfer to the electronic states (electron-hole pairs and plasmons in metals) and the phonons, the appropriateness of single phonon descriptions relative to multiple-phonon descriptions, and the range of validity of classical descriptions.

The theoretical problem breaks down into two parts, a calculation of the energy and forces of the system as a function of atomic coordinates, and a calculation of the dynamics of the system based on those forces. The first task appears to be impossible at this time, with the exception of a few weakly interacting systems [9]. The emphasis seems to have been directed instead to development of empirical models of the gas-surface forces. For example an adaptation of LEPS potentials [10] has been used with reasonable success in calculations of hydrogen dissociation on tungsten and copper [11-13], and in dynamic calculations involving N_2 , NO, Ar and Xe interactions on platinum [14-19] and CO formation on a graphitic overlayer [20]. The determination of the appropriate poten-

tial though is difficult. As Tully has noted, certain aspects of the potential can be determined from available experimental data [21]. For instance thermal desorption and kinetic studies can be used to determine the depth of the attractive part of the potential, vibrational absorption can be used to indicate the shape of the potential near the minimum, LEED and various angle resolved desorption and electron emission spectroscopies can identify the surface position and configuration corresponding to the minimum potential energy, and surface diffusion can indicate the height of the potential barrier between neighboring minima. However this is only a small fraction of the required information, and unfortunately the results of the calculation can be extremely sensitive to the potential used. For instance, dynamic calculations based on what was felt to be a reasonable potential for NO on Pt(111) surfaces showed a 90% probability of NO dissociation [14,15]. But as noted in section 4.2.1 it has been experimentally determined that NO dissociation on Pt(111) is an improbable process.

The calculation of the dynamics of the interaction has seen good progress over the past 15 years and appears to have reached a stage where rough quantitative results can be obtained if an accurate potential is used. Energy transfer is easier to model for inelastic scattering than for trapping-desorption scattering due to the shorter interaction time, and very simple models have agreed well with the experimental data. The hard cube model is essentially a one-dimensional scattering model. In this model it is assumed that the only important forces are those perpendicular to the surface [22-24]. Therefore the tangential component of the momentum is conserved during the collision, but the perpendicular component is altered by an impulsive collision with a surface atom,

approximated by a vibrating cube. The potential used for the collision is an abrupt infinite repulsion (hard wall potential). The energy transfer is treated classically or in a mixed classical-quantum framework [22,25]. A strong advantage of the hard cube model is that the scattering can be calculated in a closed analytical form. A variation of this model involves the introduction of a gradual repulsive potential (soft cube model). Better agreement with experiment has been obtained with three-dimensional lattice models in which the interaction is spread over a few (<30) surface atoms, and tangential energy transfer is allowed [26-28].

Treatment of chemical and trapping-desorption scattering is more difficult. For these scattering mechanisms the interaction times may vary from 10 ps to greater than 1 s, whereas accurate trajectory integration often requires time steps on the order of 10^{-13} s. Therefore explicit calculations of the adsorbate and substrate motion is difficult. If the interaction of interest proceeds rapidly, the substrate motion can often be neglected. A frozen substrate model appears to have yielded good results for dissociative hydrogen adsorption on W [11] and Cu [12] surfaces. If equilibrium of the adsorbate is assumed, the desorption process can be calculated using relatively straightforward classical and quantum mechanical models [29-31].

A very promising approach to handling substrate motion is the generalized Langevin theory [32,14-20]. The calculations are simplified by explicitly integrating the motion of the adsorbate and a small subset of the substrate atoms located around the adsorbate [16]. The "active" substrate atoms exchange energy with the remainder of the solid through a thermal excitation force and dissipative friction term. Tully has indicated a means by which these terms can be made thermodynamically

consistent [16]. These techniques have been used to calculate inelastic and trapping-desorption scattering of Ar, Xe and N₂ on Pt surfaces [14,16-19], and chemical scattering of NO and CO [14,20].

A major unresolved uncertainty is whether transfer to electronic energy of the substrate is important. The models discussed so far have implicitly incorporated the adiabatic Born-Oppenheimer approximation [33] (separation of electronic and ionic coordinates) so that diabatic changes between substrate electronic levels are not included. However there have been recent attempts to incorporate electronic excitation of the substrate [34,35]. It may be important to include these forces since on metals there are readily available surface and bulk plasmon states and a continuum of electron-hole pair excitation states, and there is experimental evidence of diabatic transitions in electron and photon emission during oxygen and halogen adsorption on metals [36-38], and in chemi-ionization of alkali atoms during surface scattering [39,40]. If transfer with electronic excitations of the bulk proves to be important, it will probably only be important for transfer with certain modes of the adsorbate. The relevant bulk transfer mechanism will depend on the energy and coupling mechanism of the particular mode of the molecule.

Vibrational energy - The vibrational energies are often much larger than the cutoff energy of the phonon distribution. For the case of NO scattering from Pt(111), the NO vibrational energy is 0.23 eV whereas the Debye energy of the surface is approximately 0.01 eV. Transfer of energy from phonons to adsorbate vibration would necessarily be multi-phonon and would therefore be a slow process as is indicated by a recent classical calculation [20]. Transfer of energy from electronic states

of the surface is probably the dominant process. Several theories have been developed which calculate the energy transfer between vibrational and electronic levels of the molecule and electronic levels of the solid [41-44]. These theories have had good success in predicting the lifetimes of vibrationally and electronically excited molecules at distances of 10-1000 Angstrom from surfaces [41,45] and showed reasonable agreement to the experimental lifetime of the OH stretch of methoxide on Cu [46] and CO on Cu [47]. The calculation of the adsorbed OH stretch lifetime required the addition of oscillatory charge transfer between the adsorbate and the surface.

Translational energy - There are two different cases to consider, the collision process, and if trapping is involved, the desorption process. Energy transfer in the collision has been adequately described by adiabatic one-dimensional hard-cube models and three-dimensional lattice models [23,24,28], and it does not appear that electronic excitations are important. This is reasonable since the translational to electronic mode coupling should be extremely weak until the atom or molecule is at the surface, and the collision forces produce a very strongly localized distortion of the lattice which can be described classically or as a multi-phonon excitation. This is also the conclusion of a recent quantum model of electron-hole pair generation in inelastic scattering [48]. There is an additional, possibly important collisional transfer channel available to molecules. Translational to rotational mode coupling can cause internal energy transfer [49-51] leading to short-time trapping of the molecule [52-54]. The short-time trapping increases the probability of subsequent rotational and translational to bulk energy transfer, and long-time trapping.

In the adsorbed state the molecule exists in the attractive portion of the potential and the motion is described by the well vibrational levels. At the lower energies, the spacing between levels is probably smaller but of the same rough order as those of the molecular vibrational modes [55], so that bulk electronic energy and phonon energy are probably important in excitation between those levels. At higher energies the levels become continuous so that single phonon transfer will be increasingly important. The energy between levels is probably smaller for the modes associated with tangential motion, and an adiabatic description may be adequate for this motion.

Rotational energy - Rotational energies are generally comparable to phonon energies so it is plausible that rotational energy is excited primarily by phonons.

Experimental studies of gas-surface energy transfer have had to wait for the development of techniques to measure gas energies at low densities. Translational energy transfer was at first inferred from the angular distributions of the scattered or desorbed gas. Velocities of surface products were inferred from the shape of the angular distribution [56-59], rough trapping probabilities were extracted from the diffuse and specular portions of the angular distribution [60,61], and the extent of inelastic energy transfer was inferred from comparisons of the scattered angular distributions to the predictions of hard-cube [39] or 3-D lattice models [28]. There were a few direct time-of-flight measurements in the early 1970's [62-64], but TOF measurements were not made regularly until the latter part of the decade.

Several of the early experiments concentrated on measuring the velocities of surface reaction products which had been identified as

being energetic by angular distribution measurements [56-59]. These studies included measurements of the velocities of H_2 produced on Ni(111) [65], polycrystalline nickel [64,66], Pd(001) and copper [67], and of CO_2 produced on polycrystalline copper [68]. Also studied has been the inelastic scattering of Ar [69], O_2 [70] and N_2 [71] from tungsten, Xe from Pt(111) [72], and He from LiF [73-75]. The inelastic scattering is of interest because of the information that can be gained about the translational to substrate energy transfer. Translational energy transfer is important in the adsorption process. The inelastic scattering of helium can be used to measure the dispersion relation of Rayleigh mode surface phonons [75].

Rotational energy excitation of H_2 and D_2 was observed in inelastic scattering from ionic crystals [49], and vibrational energy of N_2 produced from N atom recombination on iron was measured using an electron excitation technique [76]. There has been a rapid increase of rotational and vibrational measurements in the past two years due to the development of direct laser absorption techniques, using primarily laser-induced fluorescence [50,77-81] and two-photon ionization (section 2.2 and [8]). Systems investigated are NO from Ag(111) [50,77], LiF₂ and CaF₂ [8], graphite [78], Ru(001) [79], and NO covered Pt [80], CO from LiF [81], and HF from LiF [82]. These studies have shown some extremely interesting dynamic effects in rotational and vibrational excitation.

A major problem will be extending these studies to other molecules. NO has been a good molecule to study for several reasons. It interacts with many surfaces without decomposing, it has an electronic level that is excitable with readily available lasers, the rotational levels are well separated and resolvable, the transitions are assigned [83] and the

transition line strengths are known. We have made preliminary measurements that indicate that it may be possible to measure vibrational energies in SO_2 , and rotational and vibrational energies in acetylene, using readily available lasers. In addition the literature indicates that it should be possible to measure internal energies in benzene and possibly As_2 [84]. Extension to other molecules will require development of VUV lasers in the 200nm to 100nm-or-less range. Development of such a laser to measure scattered H_2 internal energies is in progress in Zare's laboratories [85].

Experimental and theoretical developments have been slow, but hopefully both have reached a stage where rapid progress can result. Understanding of the important processes in gas-surface energy transfer will only come from the study of a large number of systems. The studies reported here and the studies mentioned above are only a start in that direction.

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Chapter 2: Experimental

2.1 Time-of-Flight Measurements

2.1.1 Introduction

The requirements of the time-of-flight apparatus vary with the type of study intended. For inelastic scattering of heavier molecules, adsorption and desorption scattering, or reactive scattering, the scattered gases generally have nearly thermal velocity distributions. The velocity distributions are broad and usually featureless, which limits the needed time resolution (5-10%), and the velocities are generally low, on the order of 10^5 cm/sec, which limits the needed path length for a given chopper gate period (chopper speed). The angular distribution of the scattered flux and the time-of-flight distribution at each scattering angle is often important, so the detector should be movable about the sample, which would not be practical if long flight paths were required.

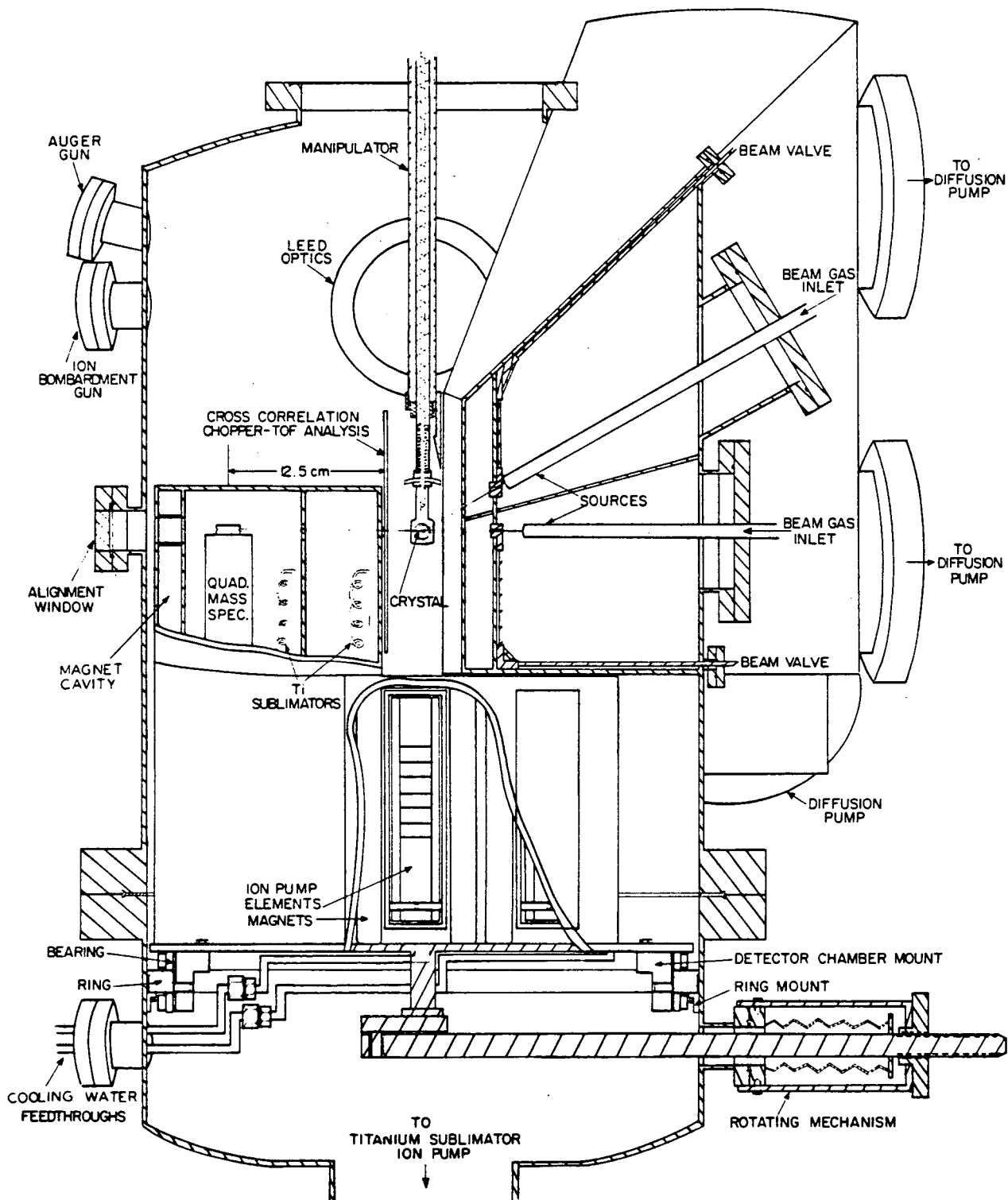
In inelastic, adsorption-desorption, or reactive scattering the detector sensitivity is often the most important consideration. Except for inelastic scattering of weakly interacting gases the angular distributions of the scattered gases are diffuse, and the angle subtended by the detector is small. This angular factor results in only approximately 0.1 % or less of the total flux entering the detector. In reactive scattering, the reaction probability presents additional sensitivity problems. Extremely facile reactions have reaction probabilities in the range of 10^{-1} to 10^{-5} per reactant molecule incident on the surface [1-7]. Industrially important reactions have generally lower reaction probabilities. Although these reactions may have turnover

rates of several to hundreds of product molecules per surface atom per second, at the reaction pressures encountered (atmospheres) these turnover rates correspond to reaction probabilities in the range of 10^{-5} to 10^{-8} per molecule incident on the surface. The introduction of cross correlation time-of-flight techniques to surface scattering has helped to improve the sensitivity of these experiments. In addition, optimization of the beam source intensity and the reduction of the residual background pressure around the detector are critical.

2.1.2 Description of the Apparatus

The design and construction of the apparatus used for these experiments (figure 2.1) was described in detail previously [8,9]. For the experiments reported here the molecular beams originate from two supersonic nozzle expansion sources. Each molecular beam is collimated by a skimmer and two 1 mm apertures in the walls of the differentially pumped source buffer chamber before impinging on the single-crystal sample. The platinum (111) single crystal sample is heated by electron bombardment, and the crystal temperature is determined by a Pt - Pt 10% Rh thermocouple spot-welded to the crystal.

A fraction of the scattered incident or reaction product gas is intercepted by a cross-correlation time-of-flight chopper disk before entering the 0.15 mm opening to the detector chamber. The 12 cm long time-of-flight path crosses the detector buffer chamber and the main detector chamber, and the flux is detected by a quadrupole mass spectrometer (modified UTI 100C). The pumping for the main and detector buffer chambers was hermetically welded into the detector chamber structure and consisted of two 20 liter/sec triode vacuum ion pumps and



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Figure 2.1: Schematic diagram of molecular beam scattering apparatus and time-of-flight spectrometer.

two titanium sublimation pumps. The detector chamber structure was self contained within the main scattering chamber and was mounted by bearings on a metal ring so that the detector was rotatable in angle about the Pt single crystal surface. The detector is currently in the process of rebuilding, which will be described at some future time [10].

The equipment for sample preparation and analysis is contained in the upper portion of the main scattering chamber, Fig. 1. Surface cleaning was achieved primarily through the use of an Ar^+ ion bombardment sputtering gun. Surface structure and order could be determined by the use of Low Energy Electron Diffraction (LEED), and surface elemental composition and cleanliness could be determined by Auger Electron Spectroscopy (AES), using a glancing incidence-angle electron gun and the LEED optics as a retarding-field electron energy analyzer.

2.1.3 Materials

The single crystal (111) oriented platinum sample is a wafer 0.7 cm in diameter and 0.3 mm thick. The sample was spark cut from a single crystal platinum rod (MRC, MARZ grade). The major bulk impurities were palladium, silicon, and calcium. The crystal surface was oriented to within 1° of the (111) direction by Laue x-ray back diffraction and polished by the standard mechanical polishing techniques. The final preparation step was chemical etching in warm dilute aqua regia.

Gases used were NO , He , Xe , O_2 , and D_2 . The NO was purchased from Matheson (99%) with major impurities being NO_2 (0.9%) and N_2O (0.1%). The NO was used without further purification in all but one series of experiments (sec. 4.2.1). The He (99.995 %) and O_2 (99.6%) were supplied by Matheson. The Xe was supplied by Airco (99.995%) and the deuterium was

purchased from Liquid Carbonic and was 99.7% pure in D. These gases were used without further purification.

2.1.4 Molecular Beam Characteristics

The molecular beam sources used were supersonic nozzle expansion sources constructed of 1/4" stainless steel tubes ending in a plate with a 0.08 mm diameter hole. The sources were typically operated at 200 torr backing pressure of the source gas, which was the pressure that produced the maximum beam flux. Scattering from the source chamber background gas gradually attenuated the beam flux with increasing source backing pressure. At these source backing pressures, the pressure in the source chamber was typically 2×10^{-4} torr and the source buffer chamber pressure was in the 10^{-8} torr range.

The beam mean translational energy was measured by time-of-flight techniques. The pure NO beam at a source backing pressure of 200 torr has a mean energy of 0.09 eV. The mean translational energy of the NO beam can be increased or decreased by seeding with He or anti-seeding with Xe respectively [11]. Two standard gas mixtures used were an NO and He mixture in a partial pressure ratio of 1 to 4 (NO/He, 1:4) and an NO and Xe mixture in a partial pressure ratio of 2 to 1 (NO/Xe, 2:1) which had mean kinetic energies of 0.21 and 0.04 eV respectively. The internal energies of supersonic beams are known to be low [11]. The rotational temperature of the incident NO beam was measured to be 45 K (sec. 4.2.3). Measurement of the vibrational cooling, which is known to be less complete, was not possible, but the vibrational temperature was undoubtedly low enough to make the populations of all but the ground vibrational state insignificant.

The translational energy width of the supersonic nozzle beam was found to be $\Delta E/E \approx 0.15$. This is significantly broader than the current state of the art, and is most likely due partly to the construction of the source skimmer which allows the beam shock wave to reform behind the skimmer.

The beam flux from the 1 mm diameter source at a 1 torr backing pressure was calculated previously to be $7.6 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}$ at the surface (0° angle of incidence) [8]. This value is probably inaccurate because it assumes effusive flow from the source, while 1 torr is above the effusive limit of a 1 mm diameter hole. The beam flux for the nozzle source used here can be measured by several techniques. The flux integrated across the cross-sectional area of the beam can be easily measured by using the ideal gas law. All pumps in the main chamber were valved off, and the primary beam source valve was opened. The pressure rise over a given period of time was then recorded. The amount of gas in the chamber, N , is proportional to F , the cross-sectional integral of the flux, and is given by the relation:

$$N = F\Delta t = \Delta PV/kT \quad 2.1$$

for change in pressure ΔP , chamber volume V , and temperature T equal to room temperature. A total pressure rise of 10^{-6} torr occurred in 28 s in a chamber volume of 101 liters which implies an integrated flux of $1.1 \times 10^{14} \text{ s}^{-1}$ for an Ar beam at 200 torr source backing pressure. Assuming a beam diameter of 1.5 mm gives a flux of $6.0 \times 10^{15} \text{ cm}^{-2}\text{s}^{-1}$ at the crystal surface (0° angle of incidence), which is equivalent to a pressure of 2×10^{-5} torr.

A similar value for the flux was obtained by using the detector

mass spectrometer to compare the beam density n of the beam at the desired backing pressure to the density of an effusive beam. The density of an effusive beam can be calculated, and the densities are related to the fluxes f by the mean velocities of the beams $\langle v \rangle$, $f = n\langle v \rangle$.

2.1.5 Sample Cleaning

After the initial mounting in vacuum the principal surface contaminants were found to be Ca and C. The calcium was difficult to remove and appeared to segregate to the surface from the bulk of the crystal. Therefore the near-surface bulk region had to be depleted of Ca through repeated cycles of annealing at 1000 K followed by Ar^+ ion sputtering at an ion energy of 1500 eV.

After the initial cleaning, typical contaminants were Ca, C and occasionally O. The Ca contamination persisted, but at lower levels than found on the new sample. Typical cleaning procedures consisted of 15 minutes of Ar^+ ion bombardment at an ion energy of 1000 eV followed by an additional 15 minutes of sputtering at 600 eV ion energy. The sample was then annealed at ~ 1300 K for 2 minutes. The sputtering and annealing steps were usually sufficient to remove the oxygen and calcium and all or most of the carbon. Residual C contamination was removed by chemical cleaning in an oxygen ambient at a crystal temperature of 650 K. By this procedure the contaminant concentrations could be reduced to below the detectability limit of Auger electron spectroscopy ($\sim 2\%$).

2.1.6 Cross-Correlation Time-of-Flight Technique

The principles of the cross-correlation time-of-flight technique

will be presented in this section to facilitate the discussion of the factors affecting the operation of the time-of-flight spectrometer and the efforts made to improve its performance. The development follows those of papers in the literature [12-16], with the inclusion of some omitted points and the examination of some apparent misinterpretations.

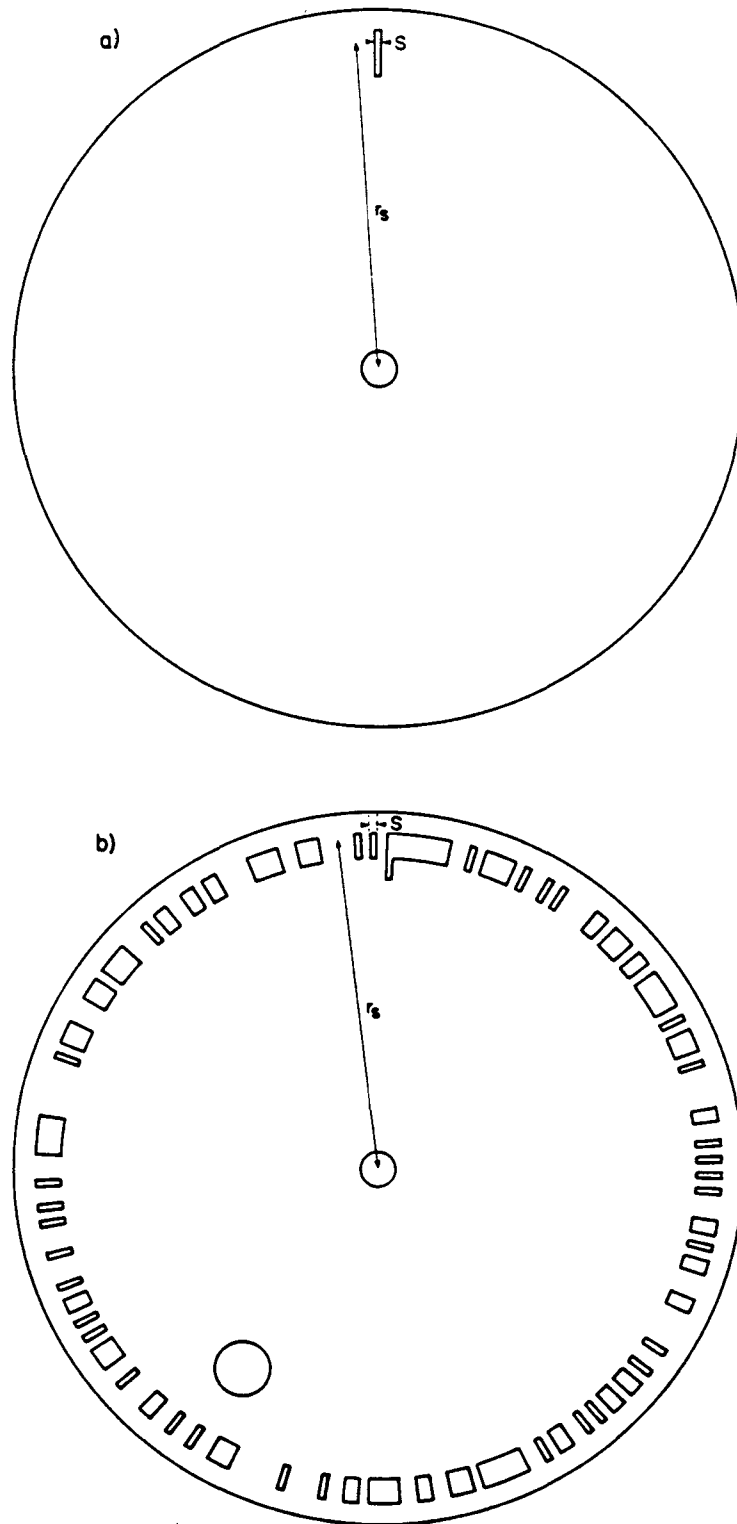
A time-of-flight chopper disk is positioned in front of an aperture at the start of a flight path of length L . The detector, in this case the ionizer of a quadrupole mass spectrometer, is located at the end of the flight path. The chopper is rotated at a frequency F and the chopper teeth periodically interrupt the flow of gas through the aperture. The time τ required for the gas to traverse the flight path is simply related to the gas velocity v by $\tau = L/v$. The unknown velocity and time-of-flight distributions, $f(v)$ and $f(\tau)$, are related by

$$f(\tau) = f(v) \left| dv/d\tau \right| = (L/\tau^2) f(v). \quad 2.2$$

The traditional time-of-flight chopper disk is shown in outline drawing in fig 2.2a. Pulses of molecules pass the aperture at times $t = nT$, for integer n and $T = 1/F$, the period of rotation. The number of molecules $h(t)$ arriving at the detector within interval Δt at time t is given in terms of the unknown time-of-flight distribution $f(\tau)$ by

$$h(t)\Delta t = \int_t^{t+\Delta t} \left(\int_{-\infty}^t f(t-\xi) G(\xi) d\xi \right) dt \approx f(\Delta\tau) D \Delta t \quad 2.3$$

where G is the gating function which describes the transmission probability past the aperture and chopper disk as a function of time, D is the length of time during which the aperture is open, $D/T = S/(2\pi r_g)$, and $\Delta\tau = t - nT$ is the time elapsed since the last opening of the aperture. It should be noted that if $f(t) \neq 0$ for $t > T$, then molecules passing the aperture



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Figure 2.2: Outline drawing of time-of-flight chopper discs a.) Single-slit chopper of radius r_s and slit width S , b.) 255 segment cross-correlation chopper disc of radius r_s and segment width S . The time resolution of the two discs is equal.

during past revolutions of the chopper will arrive at the detector coincident with molecules passing the aperture during the current revolution, so the period of rotation is chosen to be longer than the flight time of the slowest part of the distribution.

The traditional time-of-flight technique is straightforward in that the TOF distribution is given directly by the arrival rate of the gas as a function of time, equation 2.3; but it suffers from a low transmission rate since only the fraction D/T of the molecules that pass the aperture can enter the detector. The other traditional technique, the use of a velocity selector [17], also suffers from a low transmission rate since only the fraction of molecules at the given velocity can enter the detector.

The introduction of the cross-correlation time-of-flight technique to gas scattering [12] substantially improved detector sensitivities. An outline drawing of a typical cross-correlation chopper disk is shown in figure 2.2b. The circumference of the disk is conceptually divided into 255 equal segments each of width $S = 2\pi r_g/255$. The segments are patterned into a pseudo-random sequence of slits and teeth, each an integral multiple of the unit length S . The first segment is extended slightly further toward the center of the disk, and this extended slit produces a time reference pulse as it passes a light emitting diode, photo-diode pair. The off-center hole is used for balancing the distribution of mass.

Figure 2.3a shows a gating function for a hypothetical 31 segment cross-correlation chopper disk. When the gating function is equal to 1 the aperture transmits molecules, when the gating function is 0 the aperture is blocked by the chopper teeth. Figure 2.3b shows the unknown

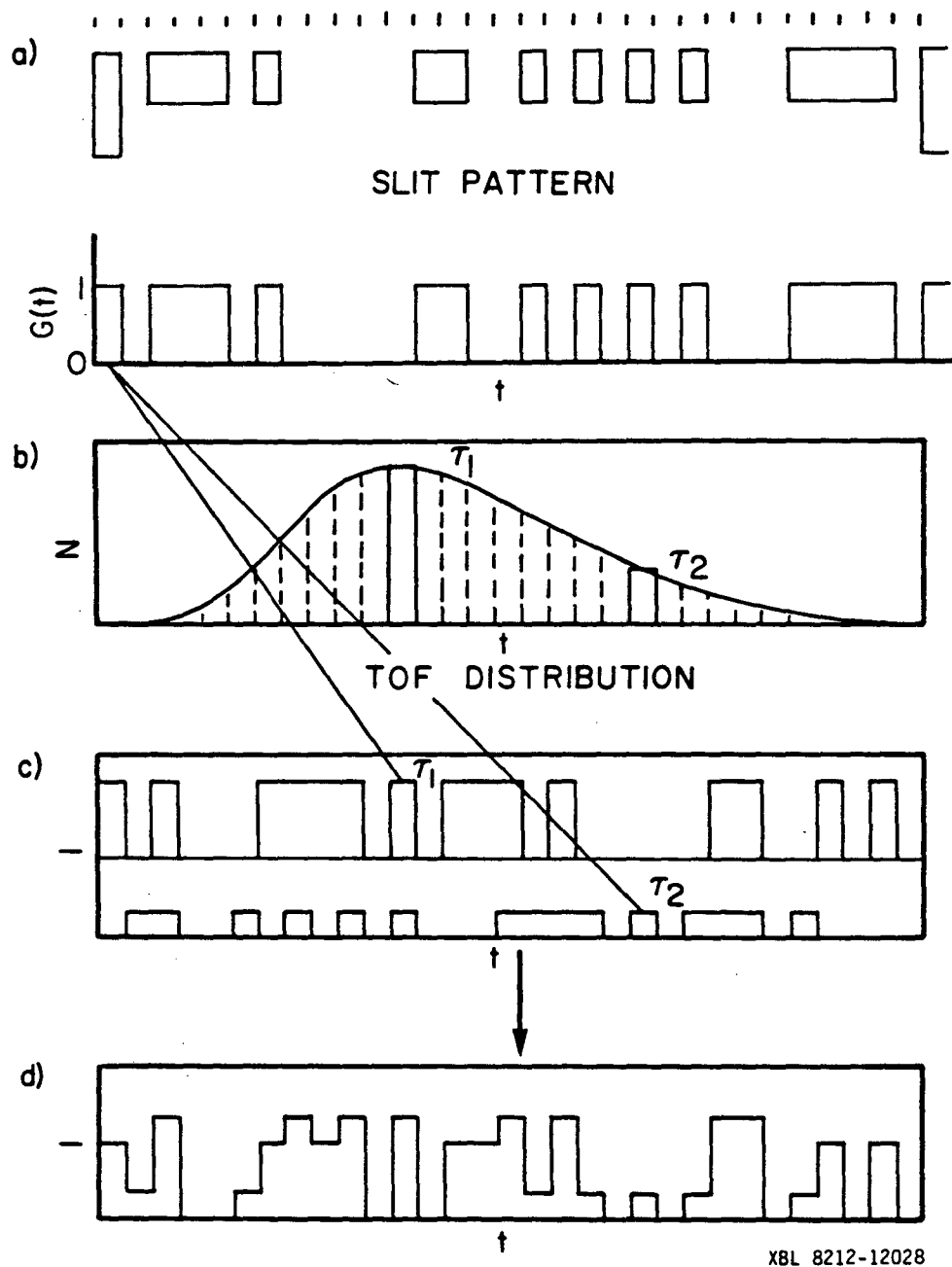


Figure 2.3: Representation of TOF signal a.) 31 segment cross-correlation slit pattern and gating function $G(t)$, b.) Unknown TOF distribution subdivided into velocity groups, c.) Ion current resulting from groups with flight times τ_1 and τ_2 , d.) Sum of currents from c.). Detector current is sum of current from all groups.

TOF distribution $f(\tau)$ to be measured. The TOF distribution can be decomposed into groups of uniform flight time (dashed lines) with two of the groups shown emphasized in the figure (solid lines). The molecules in a given velocity group pass the chopper in bunches according to the gating function and traverse the flight path without spreading in space so that the ion current generated by their arrival at the detector reproduces the gating function $G(t)$, but delayed by the groups flight time τ . This is shown in figure 2.3c for the groups with flight times τ_1 (upper curve) and τ_2 (lower curve). Note that the amplitude of the ion currents are proportional to the magnitude of $f(\tau)$ at τ_1 and τ_2 respectively. The sum of the ion currents from the velocity groups at τ_1 and τ_2 is shown as figure 2.3d. The accumulated ion current is the sum of the currents generated by each velocity group. The magnitude of the TOF distribution at flight time τ can be determined by isolating by cross-correlation that component of the accumulated ion current that is the gating function delayed by time τ , and measuring its amplitude. The advantage of the cross-correlation technique over a single slit chopper is that the transmission rate is higher (50% of the segments are slits) with no loss in time resolution.

More precisely, the molecular arrival rate at the detector can be given by an expression like equation 2.3

$$h(t) = \int_{-\infty}^t f(t-\xi)G(\xi)d\xi + u(t) \quad 2.4$$

where the upper limit of integration can be extended to ∞ since $f(t) = 0$ for $t < 0$. Here $u(t)$ is the background signal rate due to background gases and electrical noise, and $G(\xi)$ is the gating function of the cross-correlation chopper.

The chopper is composed of a sequence of identical slits so the gating function $G(t)$ can be decomposed into a repeated sum of a uniform gating function $g(t)$

$$G(t) = \sum_{i=-\infty}^{\infty} \sum_{j=1}^{255} a_j g(t-t_j-iT) \quad 2.5$$

where t_j is the relative time in each revolution at which the center of segment j passes the aperture, $t_j = jD$ and $0 < t_j < T$, T is the rotational period, and a_j takes the value 1 if segment j is a slit, and takes the value 0 if segment j is a tooth. The uniform gating function has to include the slit gating function g_s and the effects of the finite aperture width, which can be represented by a gating function g_a . The functions g_s and g_a are given by

$$g_s(t) = \begin{cases} 1 & \text{for } |t| < d/2 \\ 0 & |t| > d/2 \end{cases} \quad 2.6a$$

$$g_a(t) = \begin{cases} 1 & \text{for } |t| < a/2 \\ 0 & |t| > a/2 \end{cases} \quad 2.6b$$

where d is the time required for the unit slit to pass a given point of the aperture, and a is the time for a given point on the chopper to pass the aperture. Here one can allow for unit slits narrower than the unit segment, as in a recent chopper described by Comsa et. al. [16]. This means that $d < D = (1/255)T$, where T is the period of chopper rotation. The unit gating function is the convolution of the slit and aperture gating functions

$$g(t) = \int_{-\infty}^{\infty} g_a(\xi)g_s(t-\xi)d\xi/(ad). \quad 2.7$$

Typically the ion counts from ionization of the molecules are accumulated in a multi-channel scaler with 255 channels, one for each unit segment of the cross-correlation sequence, and each channel accumulates data for a time interval of length D, the time for each unit segment to cross the aperture. The signal accumulated in each channel h_k , which will be called the untransformed data, is the integral of $h(t)$ over the channel accumulation time

$$h_k = \int_{t_k-D/2}^{t_k+D/2} h(t)dt = \sum_{i=-\infty}^{\infty} \sum_{j=1}^{255} a_j \int_{t_k-D/2}^{t_k+D/2} \left(\int_{-\infty}^{\infty} g(\xi-t_j-iT)f(t-\xi)d\xi \right) dt + \int_{t_k-D/2}^{t_k+D/2} u(t)dt \quad 2.8$$

where equation 2.5 has been used to substitute for G in the second expression. After several changes of variables the expression for the untransformed data becomes

$$h_k = \sum_{i=-\infty}^{\infty} \sum_{j=1}^{255} a_j \int_{-D/2}^{D/2} \left(\int_{-\infty}^{\infty} g(z-y)f(y+t_k-t_j+iT)dy \right) dz + \int_{t_k-D/2}^{t_k+D/2} u(t)dt. \quad 2.9$$

Integration over z and summing over i gives

$$h_k = \sum_{j=1}^{255} a_j \int_{-\infty}^{\infty} \gamma(y)\bar{f}(t_k-t_j+y)dy + u_k \quad 2.10$$

where $\gamma(t)$, $\bar{f}(t)$, and u_k will be defined below.

Here u_k is simply the value of $u(t)$ averaged over the interval of time during which channel k accumulates data, and $\bar{f}(t)$ is defined as

$$\bar{f}(t) = \sum_{i=-\infty}^{\infty} f(t-iT) \quad 2.11$$

and is a cyclic function with period equal to the rotational period T . As noted above, if $f(t)$ is zero for $t > T$ then $\bar{f}(t)=f(t)$ for $0 \leq t < T$. However if $f(t)$ is non-zero for $t > T$, the tail of the TOF distribution will superimpose on the head of the distribution in the detector, i.e. some of the molecules passing the slits in a given revolution will arrive at the detector at the same time as molecules passing the slits in later revolutions, which is reflected in $\bar{f}(t)$.

Let $\gamma(t)$ be defined as

$$\gamma(t) = \int_{-D/2}^{D/2} g(z-t) dz \quad 2.12$$

where $g(t)$ is the gating function defined above (equation 2.7) as the convolution of the unit slit gating function g_s and the aperture gating function g_a . Then γ can be viewed as a gating function formed by the convolution of g and what can be defined as an electronic gating function g_e , which describes the amount of time each channel accumulates data,

$$\begin{aligned} g_e(t) &= 1 \quad \text{for } |t| < D/2 \\ &= 0 \quad \text{for } |t| > D/2. \end{aligned} \quad 2.13$$

From equation 2.6, g_s extends $d/2$ from the origin, g_a extends $a/2$ from the origin, so that $\gamma(t)$ is centered about $t=0$ and extends only $(D+d+a)/2$ from zero. Therefore the integral in equation 2.10 is a weighted average of the function $\bar{f}$, weighted by the gating function γ , averaged in a narrow interval about time $t_k - t_j$. Defining $\bar{f}_{k-j}$ to be

$$\bar{f}_{k-j} = \int_{-\infty}^{\infty} \gamma(y) \bar{f}(t_k - t_j + y) dy \approx D \bar{f}(t_k - t_j) \quad 2.14$$

gives the final expression for the signal in channel k

$$h_k = \sum_{j=1}^{255} a_j \bar{f}_{k-j} + u_k = \sum_{m=1}^{255} a_{k-m} \bar{f}_m + u_k \quad 2.15$$

where the summation index can be changed since both a_k and $\bar{f}_k$ are cyclic. Equation 2.15 is similar to equation 2.4 where the integral is replaced by the finite sum, a_j takes the place of gating function G, and the TOF distribution function f is replaced by its weighted average.

Willhelmi and Gompf [13] showed that it is convenient to introduce the cyclic cross-correlation matrix A whose elements are the $a_1, A_{k,m} = a_{k-m}$. Then the accumulated untransformed data is given in terms of the unknown TOF distribution by

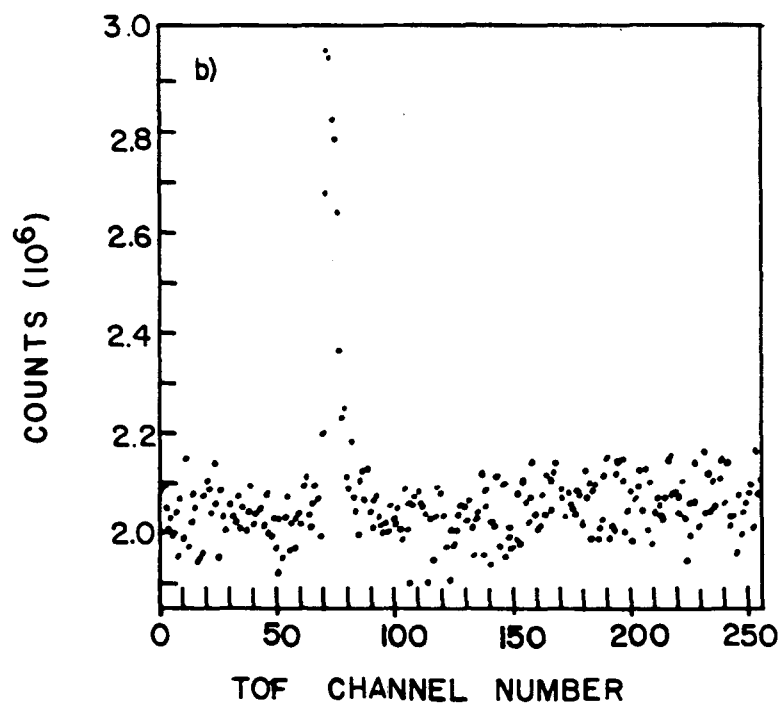
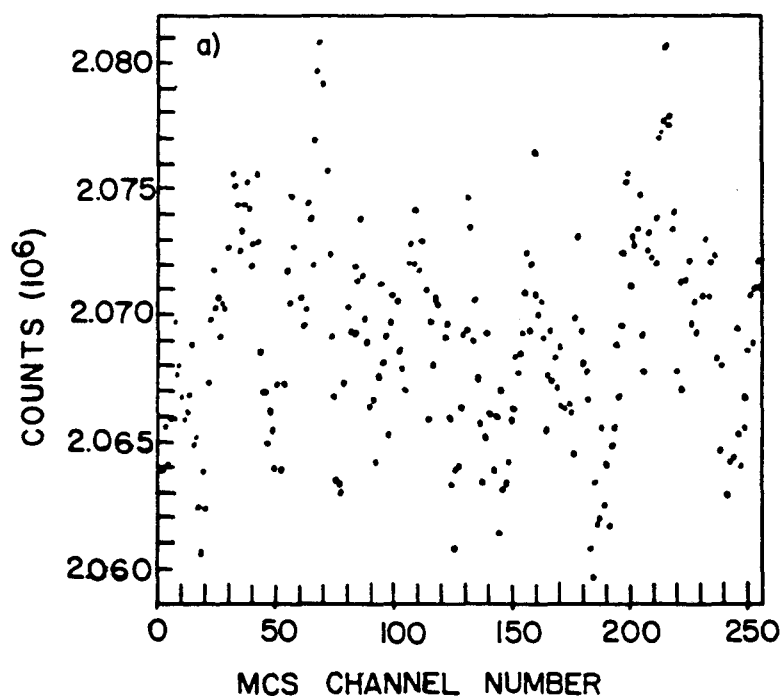
$$\vec{h} = A \vec{\bar{f}} + u. \quad 2.16$$

The time-of-flight distribution is extracted by multiplying the untransformed data by the inverse of A

$$\vec{\bar{f}} = A^{-1} \vec{h} - A^{-1} u \quad 2.17$$

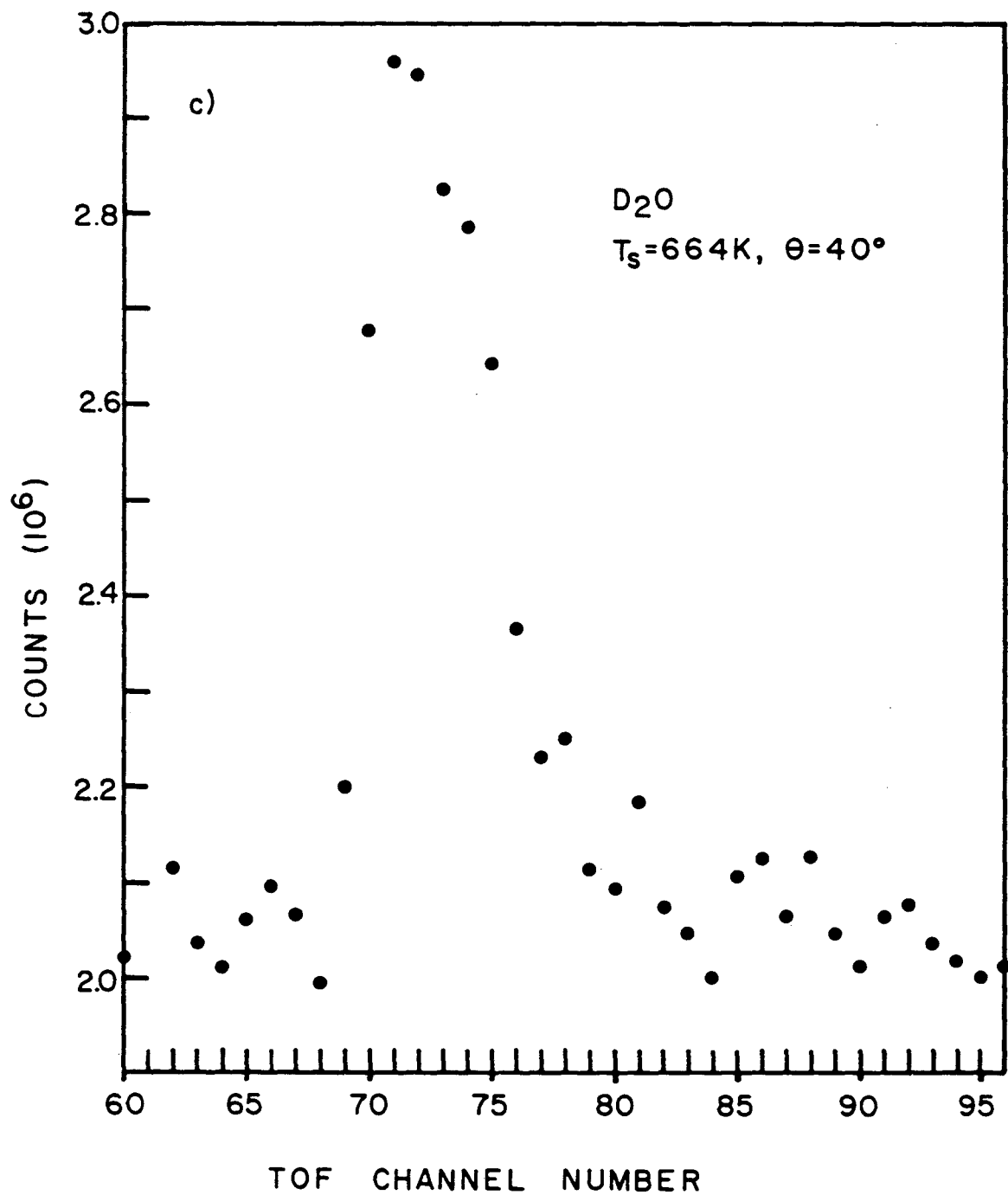
where the background signal u can take two different forms. If the background signal is random, u_k will be constant and independent of k, and will be constant after transformation by A^{-1} , giving rise to a constant background added to the TOF distribution. If the background signal is correlated to the chopper rotation, then the situation is more troublesome. Since a correlated background signal is dependent on the channel k, when it is transformed by A^{-1} it will distort the TOF distribution, as will be discussed below.

A typical example of the untransformed data is shown in figure 2.4a,



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Figure 2.4: Typical TOF data a.) accumulated data for D_2O produced on a Pt(111) surface at $T_g=664$ K b.) TOF spectrum generated by applying cross-correlation matrix to accumulated data.



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Figure 2.4c: Channels 60-96 of TOF distribution. The time resolution is $22 \mu s/\text{channel}$.

which shows the value of h_k as a function of channel number k . The transformed TOF distribution is shown in figure 2.4b. The data shown are for the measurement of the velocity distribution of D_2O from a Pt(111) surface at a sample temperature of $T_s = 664$ K and a channel time $D = 22$ μs . With this time resolution the distribution extends from channels 60-90. This region is shown expanded as figure 2.4c. The signal rate for this experiment is 65 D_2O molecules detected per second against a background signal rate of 7000 ions/s. The data of figure 2.4 took 20 hours of accumulation time.

The error in the distribution σ_f is a function of the total number of counts

$$\sigma_f^2 = n^{-2} \sum_{i=0}^{255} (f_i + u_i) \quad 2.18$$

where n is the number of chopper revolutions during which data are accumulated. In the absence of background signal u , the standard single slit chopper has a better ratio of signal to error f/σ for most channels, but in the presence of background signal the cross-correlation chopper is superior, primarily because of the better transmission rate (50% as compared to 1%), and in fact the data shown in figure 2.4 could not have been collected using the standard TOF technique.

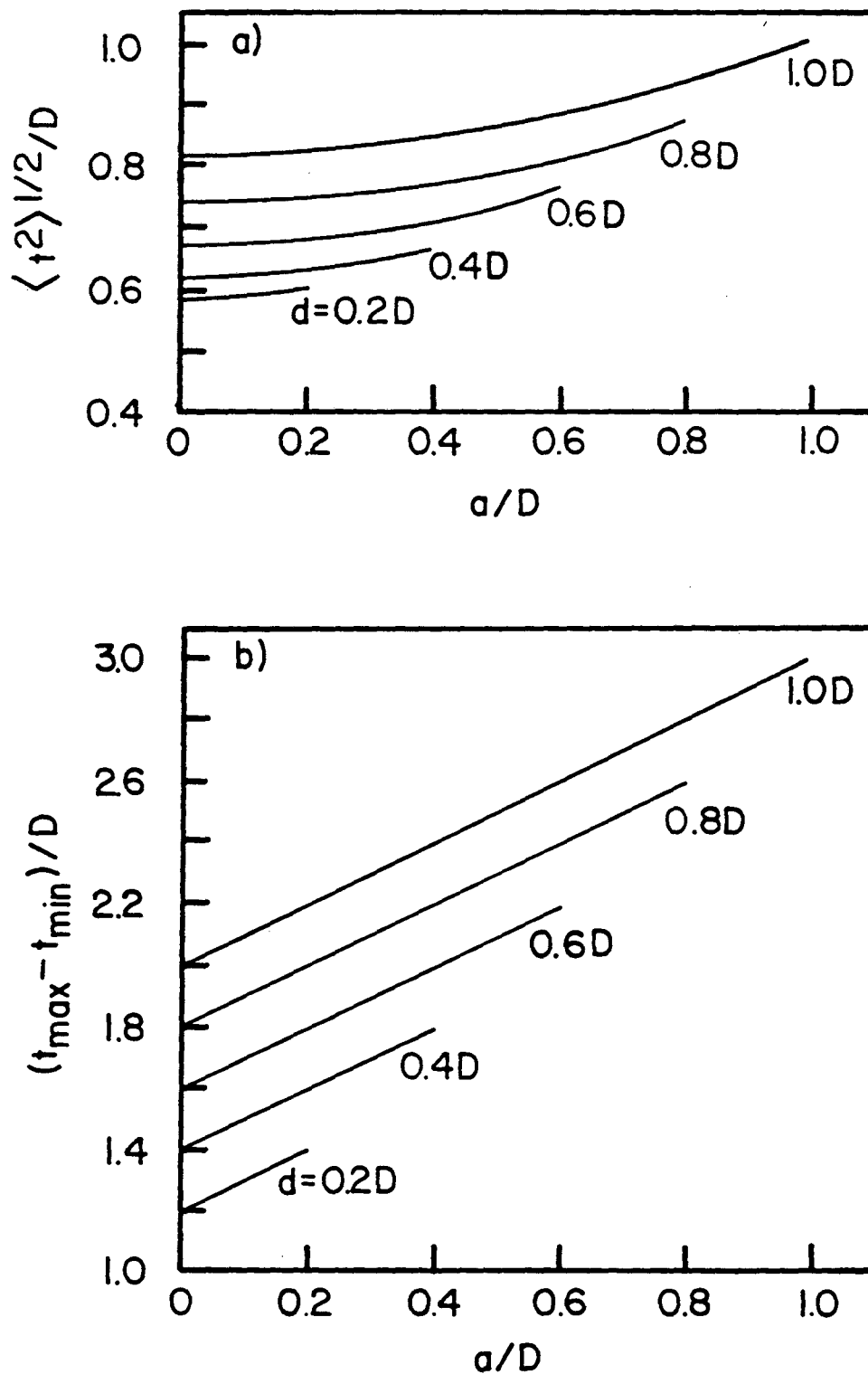
2.1.7 Distribution Broadening

The observed TOF distribution $\bar{f}_k$ is modified somewhat from the true distribution $f(t)$ through broadening by the gating function γ , equation 2.14. The gating function is given by

$$\gamma(t) = \int_{-D/2}^{D/2} \int g_a(\phi) g_s(\xi - t + \phi) d\phi d\xi \quad 2.19$$

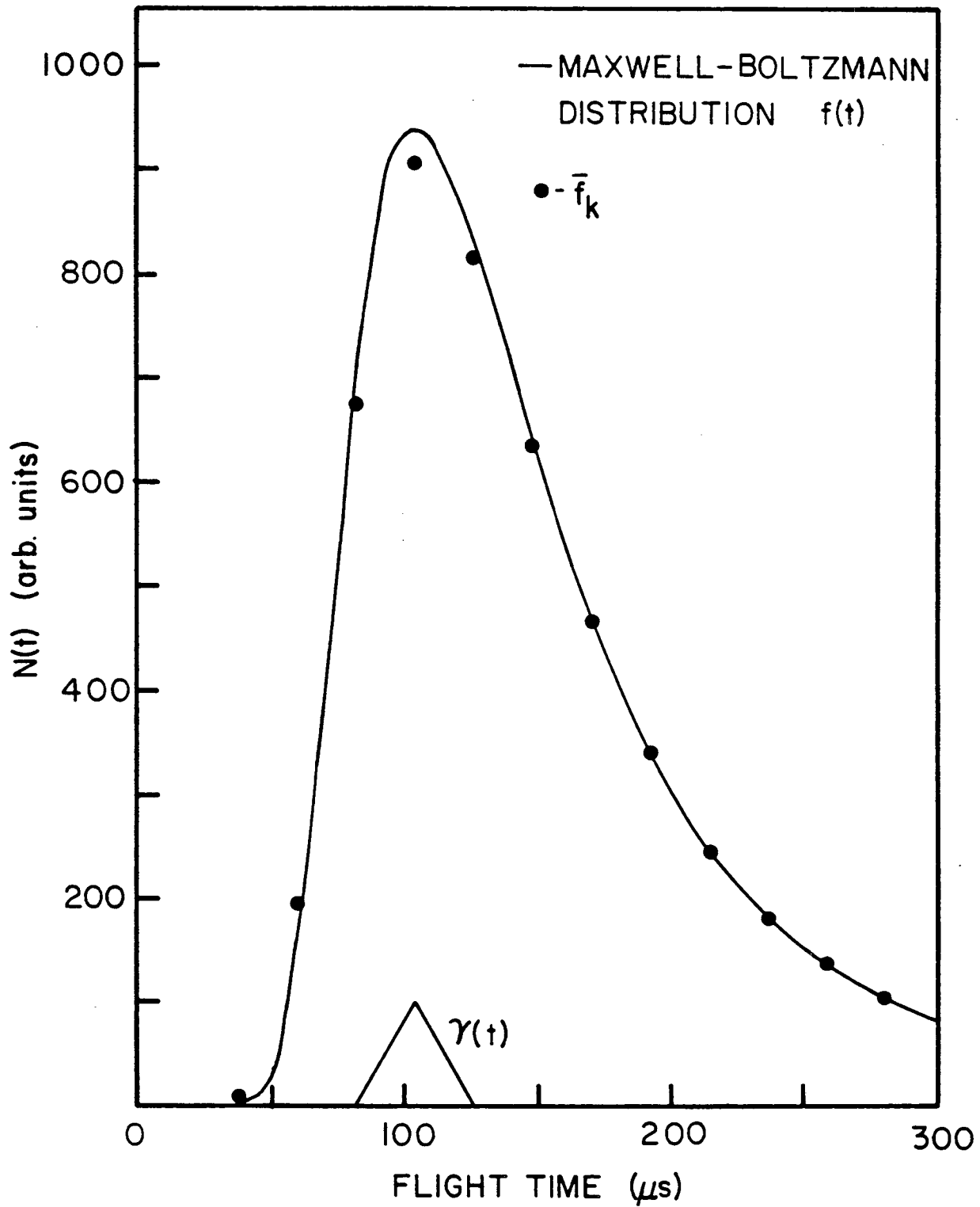
where the aperture gating function g_a and slit gating function g_s are zero for $|t| > a$ and $|t| > d$ respectively. Following the proposal by Comsa et. al. [16] the slit width can be allowed to be smaller than the unit segment width $d < D$, and also let the aperture be smaller than or equal to the slit, $a \leq d$. The gating function $\gamma(t)$ is symmetric about $t=0$ and is equal to zero for $|t| > D+d+a$. $\gamma(t)$ was calculated as a function of d and a , and the average relative width of the gate $(\langle t^2 \rangle)^{1/2}/D$ was calculated and is shown in figure 2.5a. Shown in figure 2.5b is the total extent ($t_{\max}-t_{\min}$) of the gating function γ as a function of d and a . Although γ may extend over as much as three channels, most of the function is weighted around zero as shown in figure 2.5a. In addition the average width of γ does not increase much with increasing ratios of d/D or a/D . The flux into the detector is proportional to d/D and proportional to a^2 for a symmetrical aperture, so the signal will be maximized, with little loss of time resolution, by making $a=d=D$.

The effect of the broadening on a Maxwell-Boltzmann time-of-flight distribution is shown in figure 2.6. The solid curve is a Maxwell-Boltzmann function for a molecular weight of 20, a temperature of 655 K and a flight path length of 10.9 cm. The circles indicate the time-of-flight distribution $\bar{f}_k$ that would be observed given the gating function $\gamma(t)$ shown in the figure and a 22 μ s MCS channel time (180 Hz chopper rotational frequency). These conditions are essentially the conditions used to measure the D_2O velocities. As figure 2.6 shows, the Maxwell-Boltzmann distribution is not greatly affected by the gating function broadening, but if accurate analysis is to be made the broadening has to be considered.



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Figure 2.5: Width of the gating function $\gamma(t)$ as a function of slit width d and aperture width a relative to segment width D , a.) average relative width of γ , $\langle t^2 \rangle^{1/2}/D$, b.) Complete width, $t_{\max} - t_{\min}/D$.



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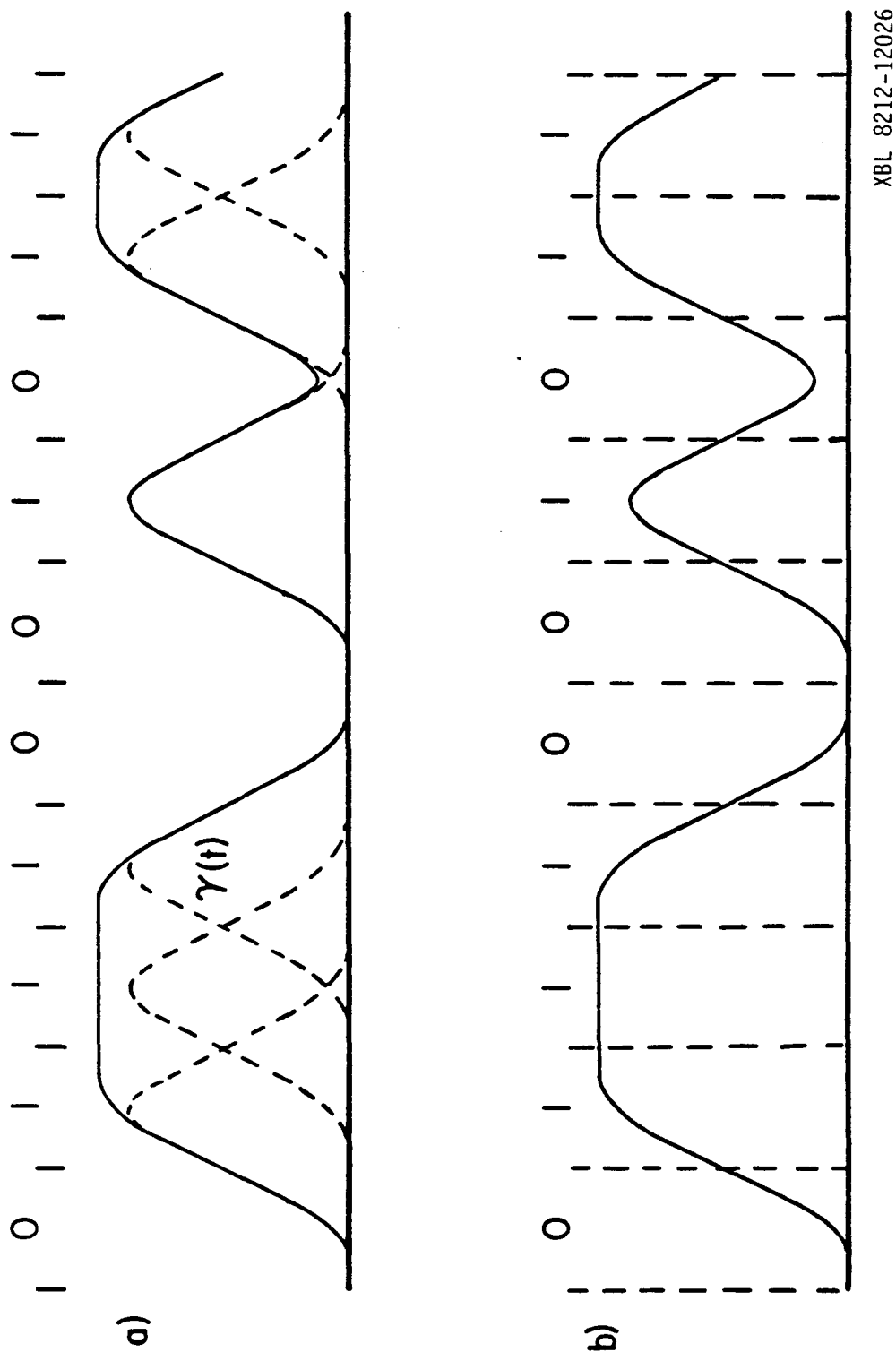
Figure 2.6: Representation of gating function broadening. Maxwell-Boltzmann distribution shown as solid curve. Circles indicate TOF distribution $\bar{f}_k$ that would be observed for the gating function γ shown.

Distribution broadening due to the chopper gating function should not be an overriding concern, since the ultimate time resolution of the TOF spectrometer is determined by the length of the ionization region, which is 5-10% of the path length.

Comsa et. al. recently suggested that the width of the gating function and overlap from neighboring slits will cause different effective gating functions for each slit [16] which will cause errors in the data. They propose that the TOF spectrometer will perform better if the slit width d is decreased until there is no overlap with neighboring segments. This is in contradiction to equation 2.10 which suggests that all slits behave uniformly. Figure 2.6a shows schematically that the gating function of a sequence (0,1,1,1,0,0,1,0,1,1) of slits is composed of a sum of equal unit-slit gating functions γ , but if the gating function of the sequence is arbitrarily decomposed, figure 2.6b and figure 4 of reference [16], then it does appear that the gating functions of the different segments are unequal even though they are identical. Therefore the best performance of the TOF spectrometer can be achieved by making $d=a=D$, which is the condition that gives the maximum transmission of molecules.

2.1.8 Determining the Chopper Transformation Matrix

The theoretical cross-correlation matrix A is given by the slit sequence a_j , $A_{ij} = a_{i-j}$. Using the theoretical matrix to transform the data may result in irregularities in the TOF distribution if the manufacture of the chopper disk is inaccurate [16] i.e. inaccurate slit dimensions or positions. The slit sequence and cross-correlation matrix were determined directly using the experimental arrangement shown



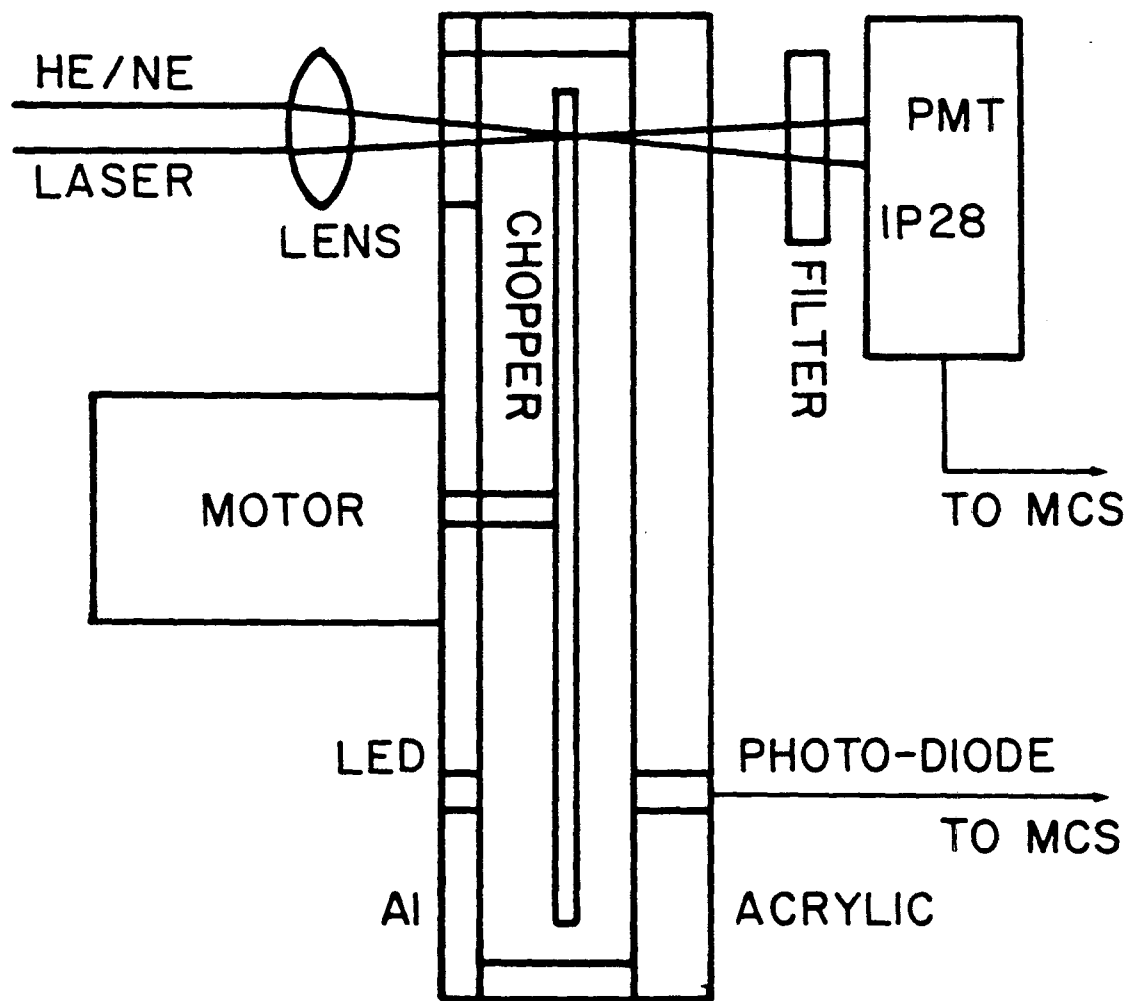
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Figure 2.7: a.) Gating function $G(t)$ constructed of a sequence 0111001011 of the unit gating function $\gamma(t)$. All segments are equivalent. b.) Same sequence decomposed as in figure 4 of [16]. Slit at 3rd segment appears to have different transmission factor than the slit at 7th segment.

schematically in figure 2.8 (the true cross-correlation matrix however, was not used to transform the data in chapters 3 and 4). The photons of the laser beam are measured instead of molecules, the photon flux is attenuated and detected by a photo-multiplier (RCA 1P28). The MCS accumulates the photon pulses from the photo-multiplier, and the LED, photo-diode trigger pair synchronize the chopper motor and MCS. The photon velocity can be taken to be infinite, so the TOF distribution is the delta function $f(t) = \delta(t)$. From equation 2.15, the gating sequence a'_j is then given directly by the untransformed data $a'_j = h_j$, where the a'_j will take values slightly different from 0 and 1 due to the manufacturing imperfections. The cross-correlation matrix is still given by the gating sequence $A_{ij} = a'_{i-j}$, and the inverse transform matrix can be calculated from A. The laser beam is focused on the plane of the chopper disk, minimizing the width of the aperture gating function g_a , to prevent distribution broadening between channels.

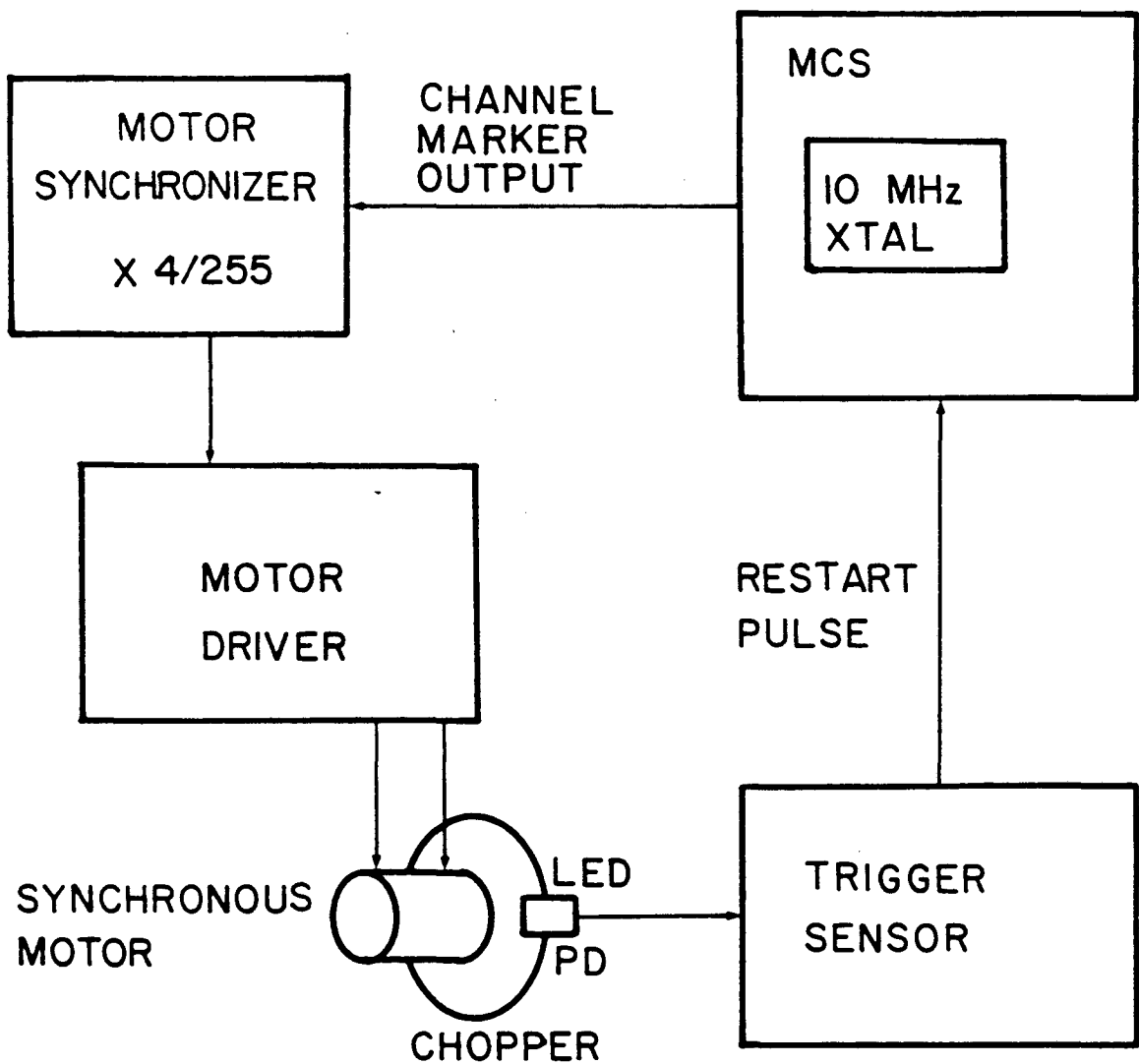
2.1.9 Chopper Synchronization and Phase Jitter

Chopper synchronization with a conventional single slit chopper is not critical as long as the time at which the slit crosses the aperture is known, since the molecular arrival time relative to the slit passage time is unaffected by subsequent changes in rotational speed. Proper operation of the cross-correlation method requires that each slit pass the aperture at its prescribed time, and that synchronization of the multi-channel scaler and chopper disk be maintained. The scheme for chopper synchronization is shown in figure 2.9. The primary time reference is a quartz oscillator in the multi-channel scaler which advances the accumulation channel by one at the end of each interval



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Figure 2.8: Schematic diagram of apparatus for determining true slit sequence.



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Figure 2.9: Schematic diagram of electronics to maintain chopper synchronization. Timing is based on the 10MHz crystal of the multi-channel scaler.

D and outputs a pulse during every channel interval. The chopper is mounted on an A.C. synchronous motor so that the chopper frequency will be synchronized to the motor drive frequency. The motor drive frequency is derived from the MCS channel pulses by a frequency divider multiplier network that produces four pulses for 255 channel pulses (or 510 channel pulses for the double sequence chopper). The four pulses per motor rotation are needed by the input shift register stage of the motor driver to generate the two phase A.C. voltage for the motor. The motor drive electronics match the motor frequency to the MCS channel time, and the trigger pulse from the LED, photo-diode pair restarts the accumulator to synchronize the phase. The motor synchronization circuit was designed specifically for this application, and its circuit schematic is shown in the appendix.

The motor bearings can be expected to stick or slip in a random manner causing erratic rotational motion and phase jitter [16]. The variation in the time of the trigger pulse relative to the motor drive pulses was found to have a time jitter of $\sim 2 \mu\text{s}$ for the lightest chopper (0.005" thick). This phase error is much smaller than the channel time (20 μs) so it appears that the question of rotational sticking for mechanical chopper motor bearings has been overstated.

The rotational momentum of the chopper disk is responsible for the smooth rotation. At a rotational frequency of 200 Hz the rotational momentum is 1.6×10^6 and $6.0 \times 10^6 \text{ gmcm}^2\text{s}^{-1}$ for the 0.005" thick and 0.040" thick disks respectively. The time required for the 0.040" disk to stop after removal of power ($\sim 1500 \text{ s}$) can be used to estimate the average torque resulting from the bearing friction. Assuming that the torque τ is constant, the rotational speed will decrease linearly. From the time

required for the chopper to stop we can estimate that the average torque is $4.0 \times 10^3 \text{ gmcm}^2 \text{ s}^{-2}$.

2.1.10 Calibration

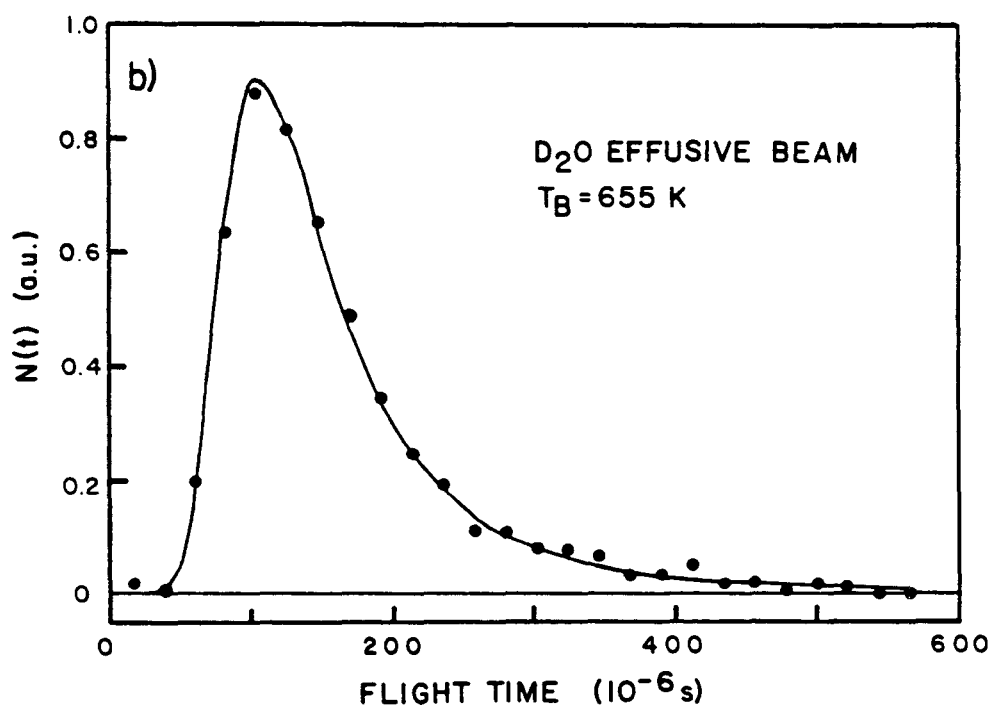
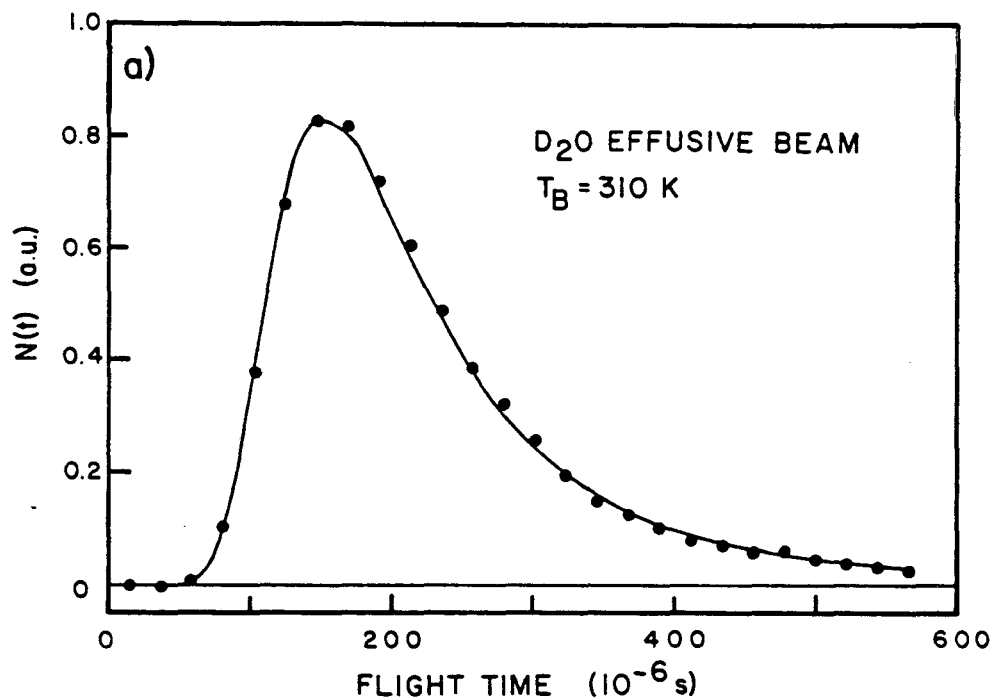
Initially, or after any work on the motor or chopper, the spectrometer must be calibrated to determine the two unknown quantities, the exact flight path length and the relative phase (number of channels offset) between the entrance aperture and the position of the zero-channel trigger detector.

The spectrometer is calibrated by measuring the TOF distributions of gases from an effusive source, using gases of different molecular weight or at different temperatures. The effusive distributions are simultaneously fitted in a computer to Maxwell-Boltzmann functions by a minimization of squares fitting routine which adjusts the path length and zero time as parameters. The program which was developed integrates the Maxwell-Boltzmann function by the gating function to calculate the relative number of counts expected in each channel, and accounts for time delays due to ion transit through the mass filter [32].

The results of a typical calibration are shown in figure 2.10. The data for the TOF distribution of effusive D_2O beams for temperatures of 310 K and 655 K are shown in figures 2.10a and b respectively. The expected Maxwell-Boltzmann distributions corresponding to the best fit of the parameters, which are 10.9 cm of path length and 63.9 channels of zero-time offset, are shown as the solid curves.

2.1.11 Coherent and Semi-Coherent Background Signals

Two types of coherent background signal were observed. The most



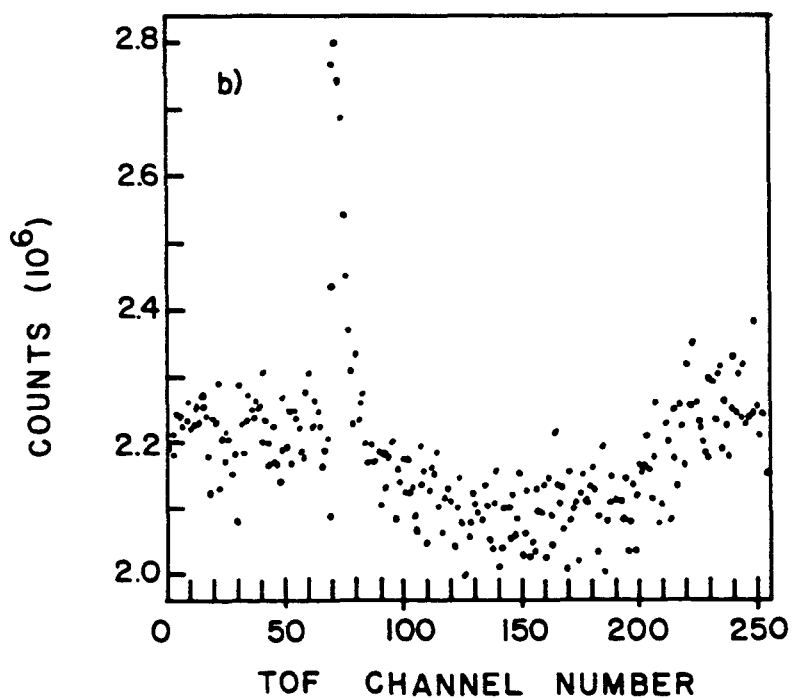
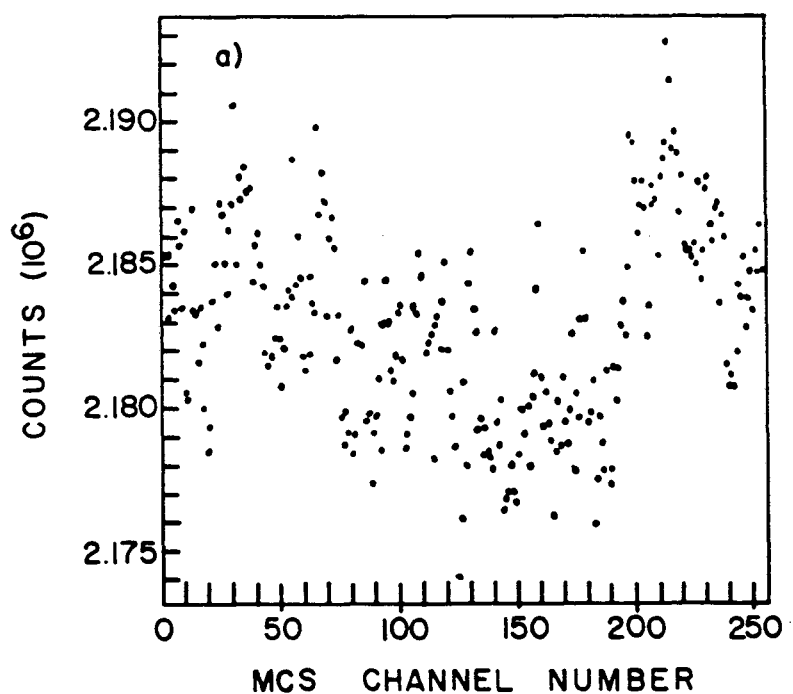
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Figure 2.10: Typical data used for TOF calibration. Circles are data for D_2O from an effusive source at source temperature a.) 310 K and b.) 655 K. Solid curve is the expected Maxwell-Boltzmann distribution.

prevalent was found to be due to transients on the A.C. power line caused by switching high current equipment in the building. This background was not strictly coherent in that it could occur at any phase relative to the chopper rotation, however a single switching transient could produce several thousand spurious counts in only one or two channels of the multi-channel scaler, so that the noise is not averaged over all channels. The effect on the time-of-flight distributions was to cause severe fluctuations in the distribution from channel to channel, i.e. a "non-smooth" distribution, where the scatter could be many times greater than that due to statistical error. The switching noise was reduced by better chamber grounding and by attempts to eliminate ground loops in the electrical lines. The transients were recently eliminated by replacing the ion multiplier (Galileo 4700) with a higher gain multiplier (Galileo 4800) which allowed better discrimination against the transient pulses.

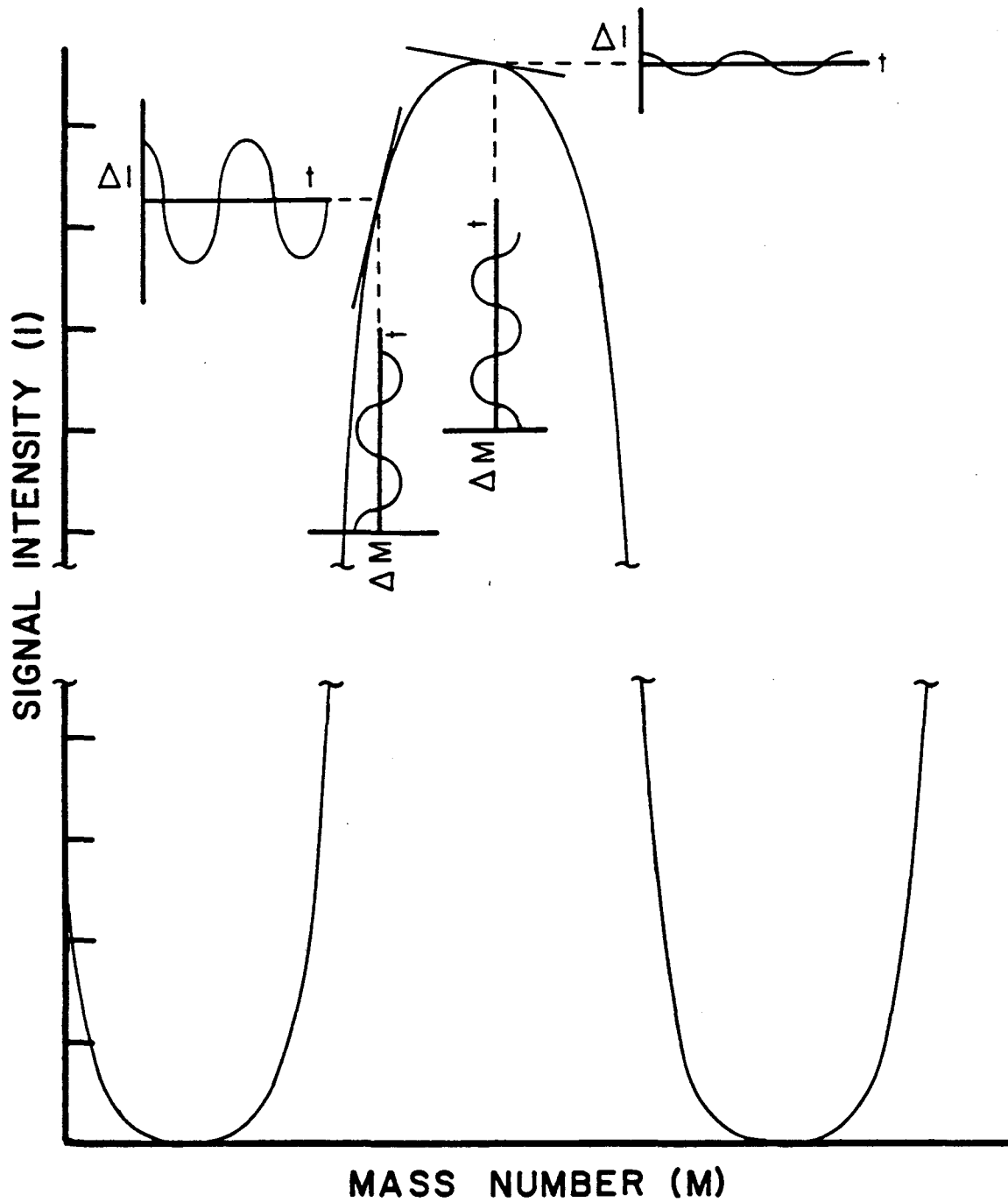
A source of coherent noise that produced a sinusoidal variation in the background count rate of the accumulated untransformed data was often found in data where the signal count rate to background count rate was low, figure 2.11a. These fluctuations were coherent with the chopper rotation and appeared to be due to vibrations of the chamber caused by motor and chopper imbalance. The vibrations couple to the mass spectrometer producing synchronized changes in the transmission efficiency of the mass filter. The resulting distortion in the TOF distribution is shown in figure 2.11b. The untransformed and TOF distributions shown in figures 2.11a and b should be compared to the distributions shown in figure 2.4.

It has been observed before that motion of a mass spectrometer or



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Figure 2.11: TOF data in the presence of coherent noise. a.) accumulated data, b.) TOF distribution transformed from a.). Compare to figure 2.4.



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Figure 2.11c: Representation of hypothesized noise mechanism. The transmission of the background gas is changed as the vibrations change the tuning point of the mass spectrometer.

its associated quadrupole radio-frequency lines can change the mass tuning by changing the capacitance of the r.f. lines and filter rods. Changes in tuning were observed during motion of the detector for measurements of the scattering intensity as a function of scattering angle. The same effect could produce a sinusoidal coherent noise signal by the process outlined schematically in figure 2.11c where capacitance changes cause sinusoidal variations in the tuned mass, causing the variations in transmission efficiencies of the steady background signal. As indicated in the figure the magnitude of the coherent variations should be larger if the mass spectrometer is tuned slightly off the maximum of the mass peak, which was the observed trend.

2.1.12 Vacuum Interlocking

The apparatus was vacuum interlocked to prevent serious damage to the system from vacuum failures in any of the interconnected chambers. In case of vacuum failure, the apparatus is protected by closing the associated right angle valves to the source chambers, or vacuum gate valves to the buffer chambers or main chamber. The interlock controller described in the appendix responds to low liquid nitrogen levels in the LN traps, and problem conditions with the diffusion pump cooling water flow, temperature, or foreline pressure. A signal representing the latter conditions was available as an output from the diffusion pump interlock power controller. For convenience the circuitry of the main and buffer source chambers were combined so that a vacuum problem in either pumping system causes isolation of both chambers of a given source.

Valve control is achieved by supplying power to air control solenoids on the pneumatically actuated valves. The main source chamber right

angle valves were equipped with pneumatic actuators, but the source buffer chamber gate valves (K.V. Co. GV68H) had to be converted from hand actuation to pneumatic actuation. The main chamber gate valve was equipped with a mechanical motor drive for emergency closures which allows manual operation under normal conditions. The valve actuators for all the valves are connected so that the valves will close during power failures.

2.2 Two-Photon Ionization Measurements of Internal Energy Distributions

2.2.1 Introduction

For interactions of noble gases with surfaces the extent and nature of energy exchange is completely known through measurement of the atomic velocity of the scattered gas. In polyatomic molecules the rotational and vibrational modes are available for energy transfer and may be important factors in the gas-surface dynamics. The experimental questions of interest include the relative importance in the adsorption process of translational energy transfer to internal modes versus translational energy transfer to the phonons of the solid, the rates of internal excitation (or deexcitation) of the adsorbed molecule, and the extent of coupling of the internal modes to the desorption process.

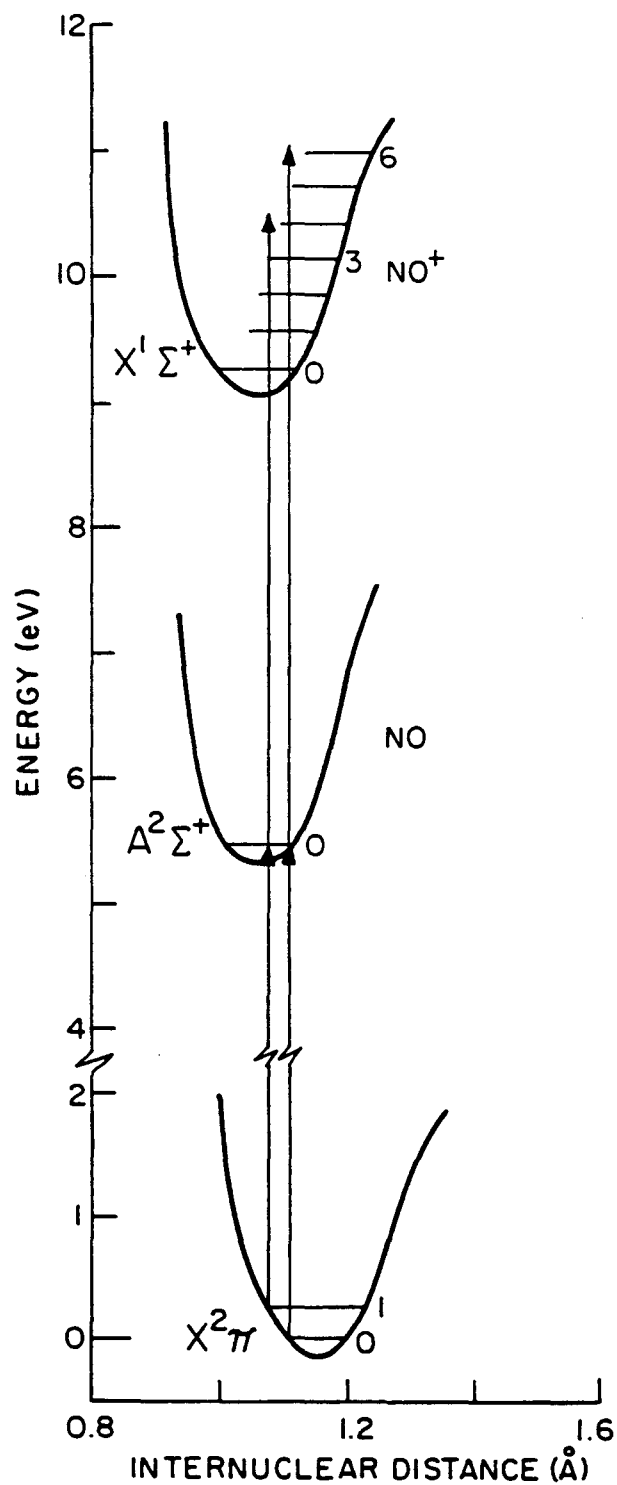
Initial measurements of internal energy transfer were made by indirect means [18]. Direct measurements can be made through optical absorption using vibrational [19] or electronic [20] transitions of the molecule under investigation. We have developed an apparatus to use two-photon ionization as a means of probing the internal energies of

gases emitted from surfaces. The following sections describe the two-photon ionization (TPI) technique and compare it to the laser-induced fluorescence (LIF) technique, the design and construction of the apparatus, and the experimental techniques.

2.2.2 Two-Photon Ionization and Laser-Induced Fluorescence

The detection scheme that we have used is two-photon ionization, both photons being of the same energy and resonant with an allowed single-photon electronic transition. The electronic levels of NO are shown schematically in figure 2.13. The number of molecules in any rotational and vibrational level of the ground electronic $X^2\Pi^+$ state can be determined by tuning the laser to an allowed transition from that level to the first excited electronic state, $A^2\Sigma^+$, and measuring the amount of absorption. The absorption can be observed by allowing the excited molecules to decay back to the ground electronic state and observing the fluorescence, or by using a high laser intensity to further excite the molecule to an ionized state while observing the number of ions produced.

Laser induced fluorescence has been used successfully in several labs to study the inelastic transfer of translational energy to rotational energy in NO scattering from Ag(111) [20,21], the rotational energy distributions of NO from Pt(111) and graphite covered platinum [22], pyrolytic graphite [23], and Ru(001) [24]. Ours is the first use of two-photon ionization for these studies. Being a two-photon absorption process, TPI is inherently less efficient than laser induced fluorescence. But as will be shown below, when using the LIF technique the laser intensity has to be limited to avoid non-linear saturation effects, whereas



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Figure 2.12: Representation of NO electronic levels. The molecules are distributed among the rovibronic levels of the $X^2\Pi$ state. The laser is tuned to allowed transitions to the $A^2\Sigma^+$ state. Absorption of a second photon will cause a transition to an NO^+ ionic state.

commercial lasers are intense enough to give nearly the same excitation efficiency with the TPI process. The difference then is the collection efficiency, which is higher for two-photon ionization and can make TPI the superior detection scheme. Experimental difficulties encountered in LIF when the fluorescence lifetimes are too short or too long are another reason for preferring two-photon ionization.

The three electronic levels of interest and the important transition processes, stimulated absorption, stimulated emission, fluorescence, and ionization, are shown schematically in figure 2.13. The rate equations for the change in populations under the laser irradiation can be written as follows

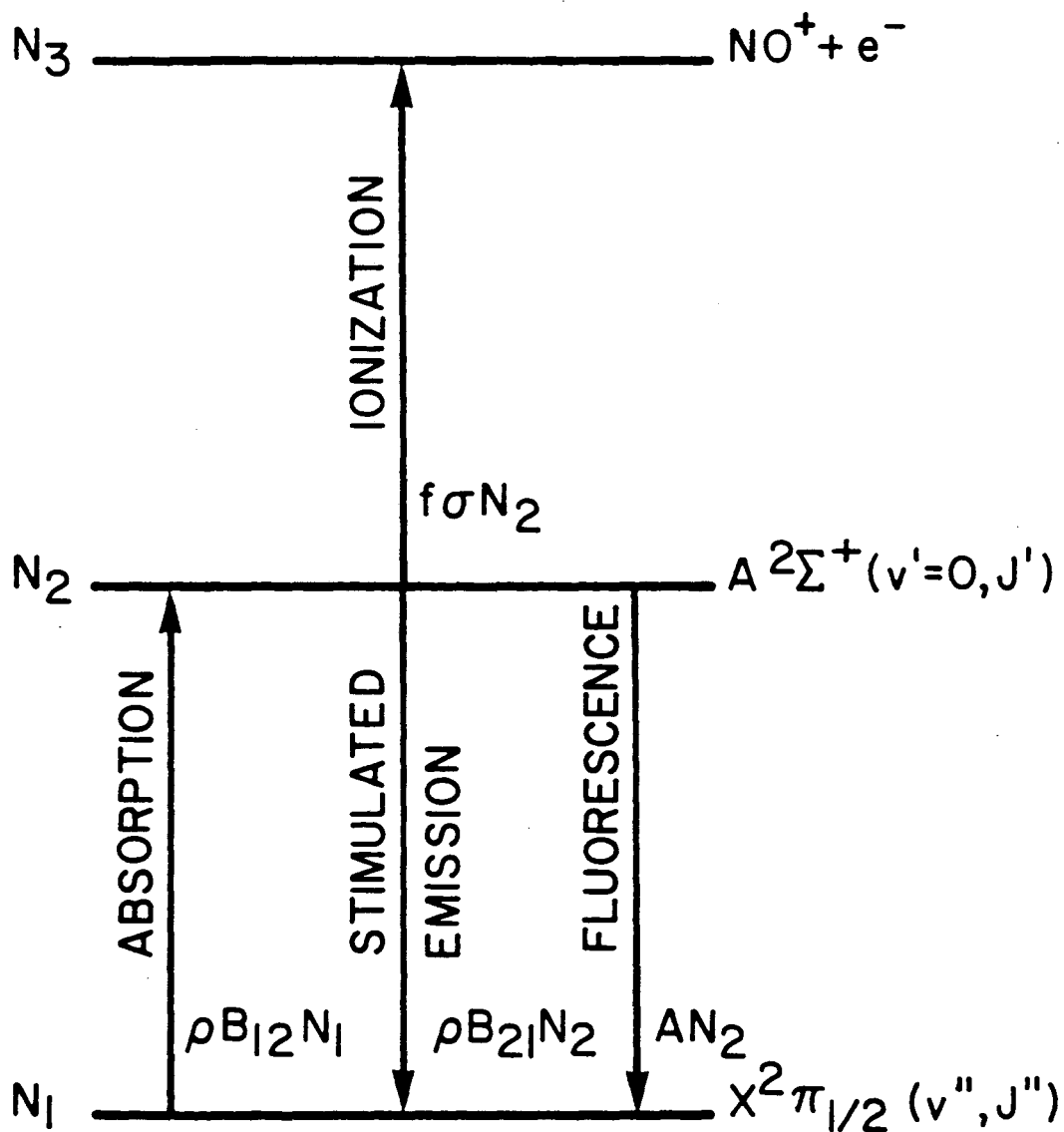
$$dN_1/dt = -\rho(\nu)B_{12}N_1 + \rho(\nu)B_{21}N_2 + A_{21}N_2 \quad 2.20a$$

$$dN_2/dt = \rho(\nu)B_{12}N_1 - \rho(\nu)B_{21}N_2 - A_{21}N_2 - f\sigma N_2 \quad 2.20b$$

$$dN_3/dt = I/q = f\sigma N_2 \quad 2.20c$$

where the populations, N_i , are described in the figure, I is the signal current, $\rho(\nu)$ is the laser energy density at the transition frequency, given in units of Joules cm^{-3}s , f is the total photon flux, σ is the ionization cross section from the excited $A^2\Sigma^+$ electronic state, and A and B are the Einstein coefficients for fluorescence and stimulated absorption and emission. Generally, simple rate equations are not valid at high laser intensities, but for two-photon interactions the equations are valid for very intense laser intensities [25] as long as other states are not made accessible through non-linear processes. These requirements are satisfied for our NO experimental conditions.

The laser energy was in the range of 200 - 800 μJ with a spectral width of 1.5 cm^{-1} , the laser pulse had a duration of 10 ns and was



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Figure 2.13: Diagram of rates of absorption, stimulated emission, and fluorescence between the $X^2\Pi$ and $A^2\Sigma^+$ states, and rate of ionization from the upper $A^2\Sigma^+$ state. N_1 , N_2 and N_3 are the number of molecules in the ground $X^2\Pi_{1/2}$, $A^2\Sigma^+$, and ionized state respectively.

focused to a cross-sectional area of 10^{-3} cm^2 . The fluorescence rate for NO is $A_{21} = 5.0 \times 10^6 \text{ s}^{-1}$. The coefficient for stimulated absorption can be calculated from A_{21} to give $B_{12} = 2.44 \times 10^{26} \text{ cm}^3 \text{ j}^{-1} \text{ s}^{-2}$. The degeneracies of the X and A levels will depend on rotational number and rotational branch, but are nearly equal, so $B_{21} \approx B_{12} = B$. The cross section for ionization is $7.0 \times 10^{-19} \text{ cm}^2$ [26] at 266 nm, and it will be assumed that the ionization cross-section does not change drastically at 230 nm.

The excitation rates are then $A_{21} = 5.0 \times 10^6 \text{ s}^{-1}$, $f\sigma = 79.0 \text{ E}(\mu\text{j}) / A(\text{cm}^2) \text{ s}^{-1}$ and $B\rho = 2.55 \times 10^7 \text{ E}(\mu\text{j}) / A(\text{cm}^2) \text{ s}^{-1}$ where E is the laser pulse energy in μJoules and A is the cross-sectional area in cm^2 . The stimulated absorption and emission rates are a few orders of magnitude larger than the ionization and fluorescence rates so that the rate equations can be simplified to

$$dN_1/dt = -\beta(N_1 - N_2) \quad 2.21a$$

$$dN_2/dt = \beta(N_1 - N_2) - \gamma N_2 \quad 2.21b$$

$$dN_3/dt = \gamma N_2 \quad 2.21c$$

where $\beta = \rho B$ and $\gamma = f\sigma$, with the initial conditions $N_2(0) = N_3(0) = 0$ and $N_1(0) = N_0$.

Equations 2.21 can be solved by the standard approach substituting in equations 2.21a and b

$$N_1^{(i)} = N_{10}^{(i)} \exp(-\lambda_1 t) \quad 2.22a$$

$$N_2^{(i)} = N_{20}^{(i)} \exp(-\lambda_1 t) \quad 2.22b$$

and solving for the decay rates λ_1 for the two solutions i, with the $N_{10}^{(i)}$ and $N_{20}^{(i)}$ determined by the initial conditions. The total number of molecules ionized can be solved by integrating the ionization rate

$$N_3 = \int_0^T \gamma N_2(t) dt \quad 2.23$$

once $N_2(t)$ is known. The rates will have to be calculated at each point along the beam since the cross-sectional area increases away from the focus. However since β is on the order of 10^{12} s^{-1} at the focus and $\beta \gg \gamma$ the molecules quickly reach saturation, $N_1 = N_2 = N_0/2$. The ions produced can be approximated by

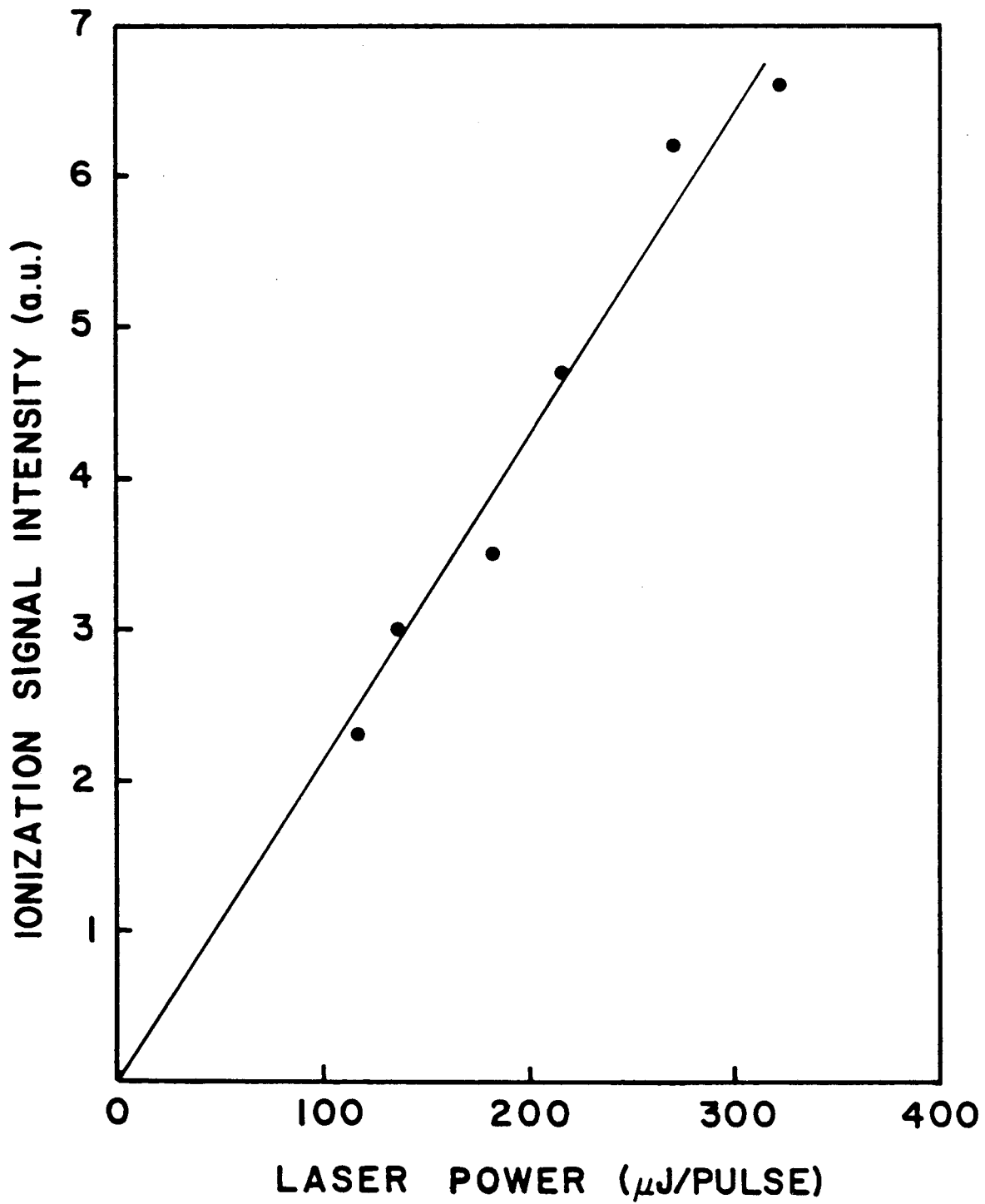
$$N_2 \approx N_0 \gamma T / 2 \quad 2.24$$

where T is the duration of the laser pulse. For the current experimental conditions the NO ionization efficiency is $\sim 7\%$ at the laser focus.

If the intensity is high enough to saturate the first transition, equation 2.24 shows that the signal intensity should be linear in the laser intensity, which is what was observed experimentally as shown in figure 2.14.

The ionization rate decreases at points along the laser beam away from the focus as the inverse of the cross-sectional area. At the same time the number of molecules within the beam increases as the cross-sectional area so the number of ions produced per unit length of laser path is constant. This may have affected the angular distributions, see chapter 4.

In comparing the TPI and LIF techniques it is important to note that when using the laser-induced fluorescence technique the laser intensity is kept low to limit the population of the $A^2\Sigma^+$ state. If the population of the upper state goes above approximately 15% of the total molecules, the stimulated emission becomes significant and the signal is no longer linear with laser power. Rather than limit the



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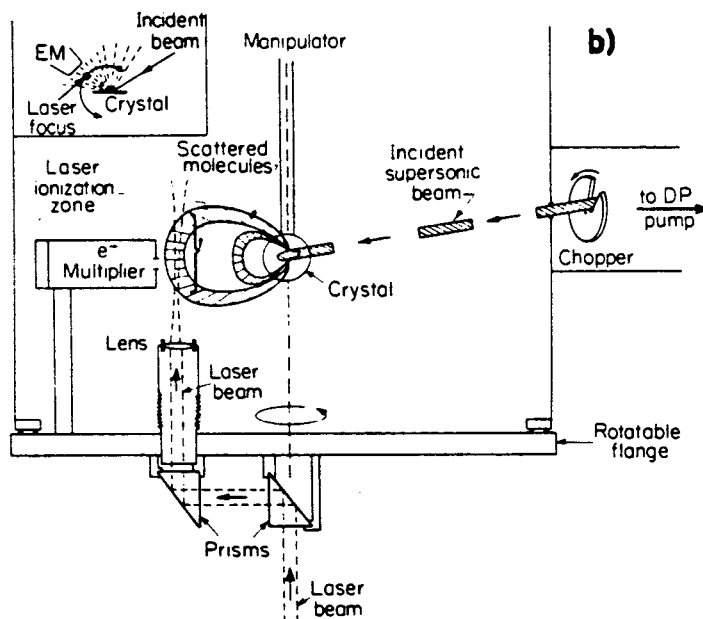
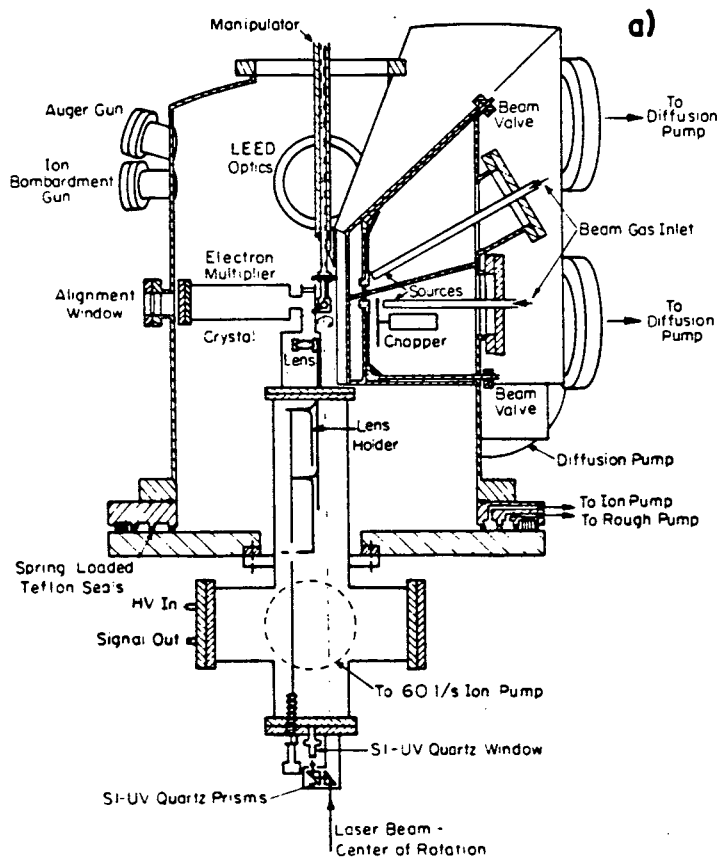
Figure 2.14: TPI signal amplitude as a function of laser intensity.

Measured at $\lambda=2268$ A.

laser power, the laser beam can be diverged to decrease the intensity but excite molecules over a larger volume. However, diverging the beam creates poor angular resolution, and for this reason the volumes of excitation will be approximately equal when using the LIF technique and TPI technique. Therefore the excitation efficiencies are comparable. The factors affecting the relative detection efficiencies of the two techniques are listed in table 2.1. Two important factors are the collection efficiency for the particles, and the quantum efficiency of the particle detectors. A small electric field can extract 100% of the ions, but the fluorescence is isotropic, and only approximately 30% of the light can be collected with reasonable size optics. In addition U.V. photo-multipliers are a factor of 7 less efficient than ion multipliers. The overall effect is that the total efficiency can be approximately 10 times greater using the two-photon ionization technique.

2.2.3 Apparatus

The molecular beam scattering apparatus configured for internal energy distribution measurements is shown schematically in figure 2.15. The time-of-flight detector and the end wire seal flange were replaced by the TPI detector and a UHV compatible rotary flange. The laser beam is aligned along the center axis of the main chamber which also corresponds to the axis of rotation of the detector and rotary flange. The laser beam is deflected 2.5 cm from the center axis by two quartz prisms and enters the detector through a UV quartz window. The laser is focused to an uneven spot of $\sim 8 \times 10^{-4} \text{ cm}^2$ cross-sectional area (figure 2.16) by a 12.5 cm focal length quartz lens. The lens was adjusted so that the focal point was in the plane defined by the crystal normal and



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Figure 2.15: a.) Schematic diagram of molecular beam scattering apparatus and two-photon ionization spectrometer. b.) Representation of detector operation.

Figure 2.16: Profile of laser beam focus. Micrograph shows the pattern of vaporization of a gold foil placed at the focus.

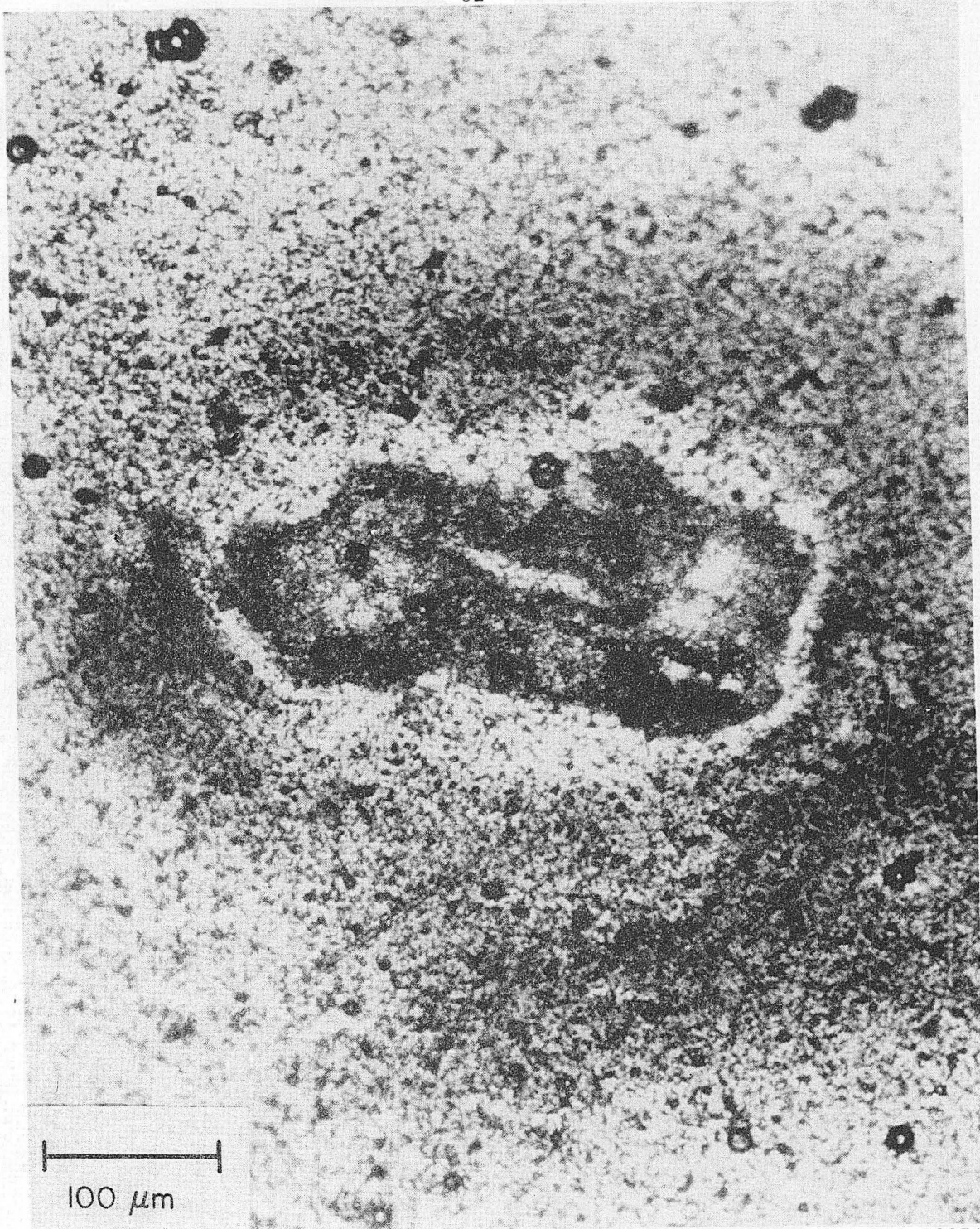


Fig. 2.16

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Table 2.1

	Two-photon ionization	Laser-induced fluorescence
Excitation efficiency	~0.07	~0.15
Collection efficiency	1.00	~0.30
Detector quantum efficiency	Cu-Be electron multiplier - 0.70	UV sensitive, solar blind photo-multiplier - 0.10
Excitation volume	1.00	Assumed the same
Discrimination against laser light	good	poor

the incident beam and located at a radius of 2.5 cm from the crystal surface. With this geometry the angular resolution is 1° in the direction of detector rotation ("in plane" direction) but possibly an order of magnitude poorer in the direction along the beam ("out of plane" direction).

The ion signal detector is a 20-stage electron multiplier (Hamamatsu Cu-Be R-595) operated at bias voltages in the range of 2000-3500 V. The detector assembly, electron multiplier and laser beam rotate about the sample with the motion of the rotary flange to allow measurements of rotational and vibrational energies at each scattering angle, as shown schematically in figure 2.15b.

As constructed and as shown in figure 2.15a the region around the excitation area was differentially pumped by a 60 liter/s ion pump to reduce the background NO pressure and signal. However it was found that stray laser light on neighboring metal and quartz surfaces of the differential chamber produced large background ion currents that masked the NO TPI signal. To rectify the problem the differential pumping had to be abandoned and the materials near the laser focus removed. Without differential pumping the background NO contributes up to 10% of the detected signal. It was however observed that the surface ion production process was partially thermal in nature, and can be suppressed by cooling of the surfaces involved with liquid nitrogen. The addition of liquid nitrogen cooling to a differential detector would be a worthwhile future modification, and the cooling would further reduce background gas pressures.

The nitric oxide beam originates from the supersonic nozzle described in section 2.1.4, to which a low frequency incident beam chopper

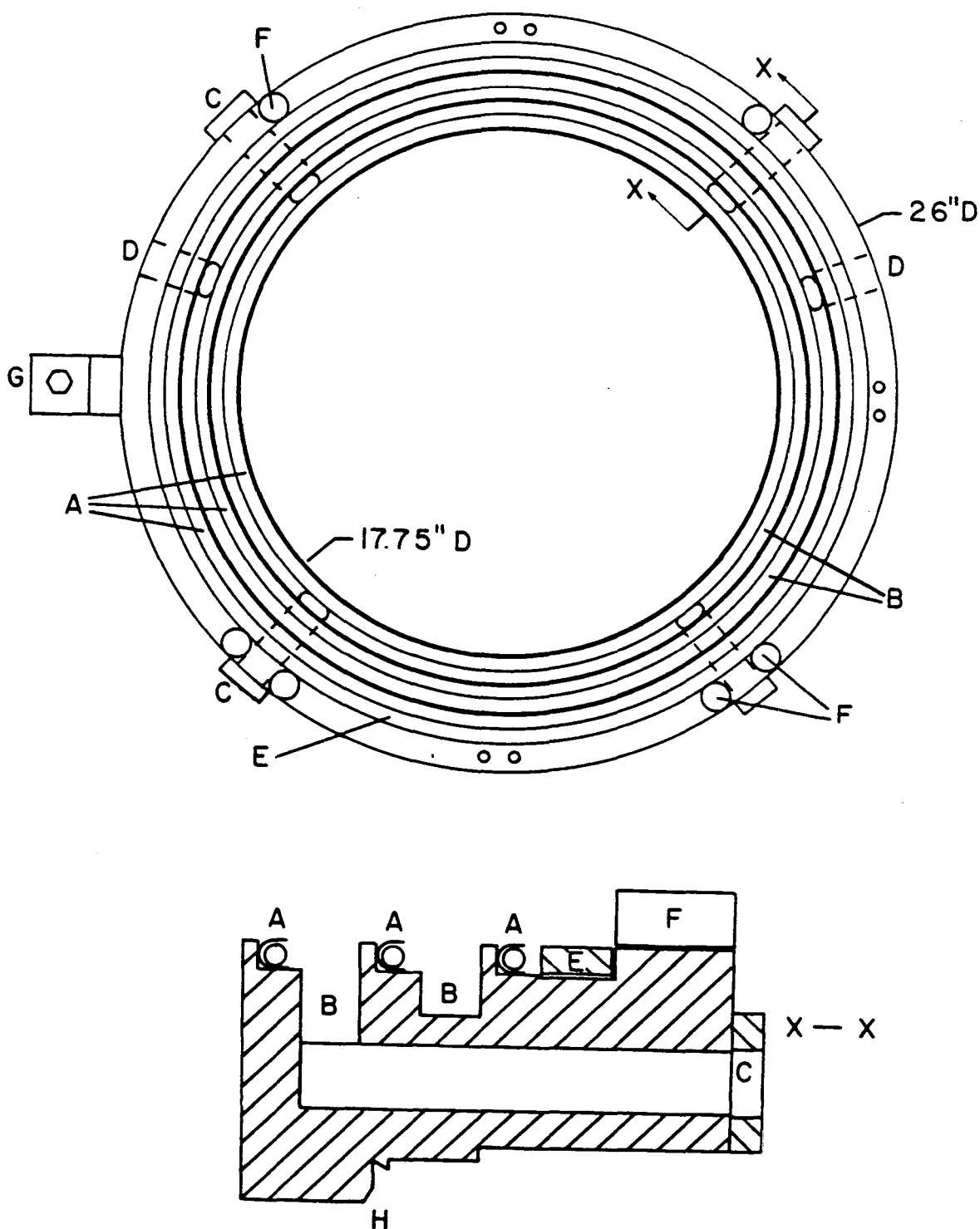
was added. The chopper rotates at 10 Hz to synchronize the NO beam pulses to the laser repetition rate, and generates molecular beam pulses that are 5 ms in duration. Limiting the beam flux to those times immediately around the time of sampling by the laser reduces the rate of surface contamination caused by the molecular beam and reduces the NO background pressure in the scattering chamber. The background pressure was 5×10^{-10} torr with the NO beam on and 2×10^{-10} torr with the NO beam off.

The equipment for surface analysis and preparation located in the upper portion of the scattering chamber were described above, section 2.1.2, as were the materials and surface preparation techniques (sections 2.1.3 and 2.1.5).

2.2.4 UHV Compatible Rotary Flange

A drawing of the fixed seal surface of the UHV compatible rotary flange is shown as figure 2.17. The face seal flange is a modification of a differentially pumped cylindrical seal rotary flange described in the literature [27]. The fixed section of the flange has the seal surfaces and differential pumping channels machined in one surface and a male Perkin-Elmer 18" (ID) wire seal flange [28] machined into the opposing face to seal to the pre-existing female flange on the main scattering chamber. The three concentric seals are spring loaded Teflon of 18", 20" and 22" ID (Fluorocarbon Mechanical Seal Division AR314E18000, AR314E20000, AR314E22000). The channels between seals are pumped by an 18 scfm mechanical pump (outer channel) and an 8 liter/sec ion pump (inner channel).

The seals require approximately 5.3×10^6 dynes load per cm of seal



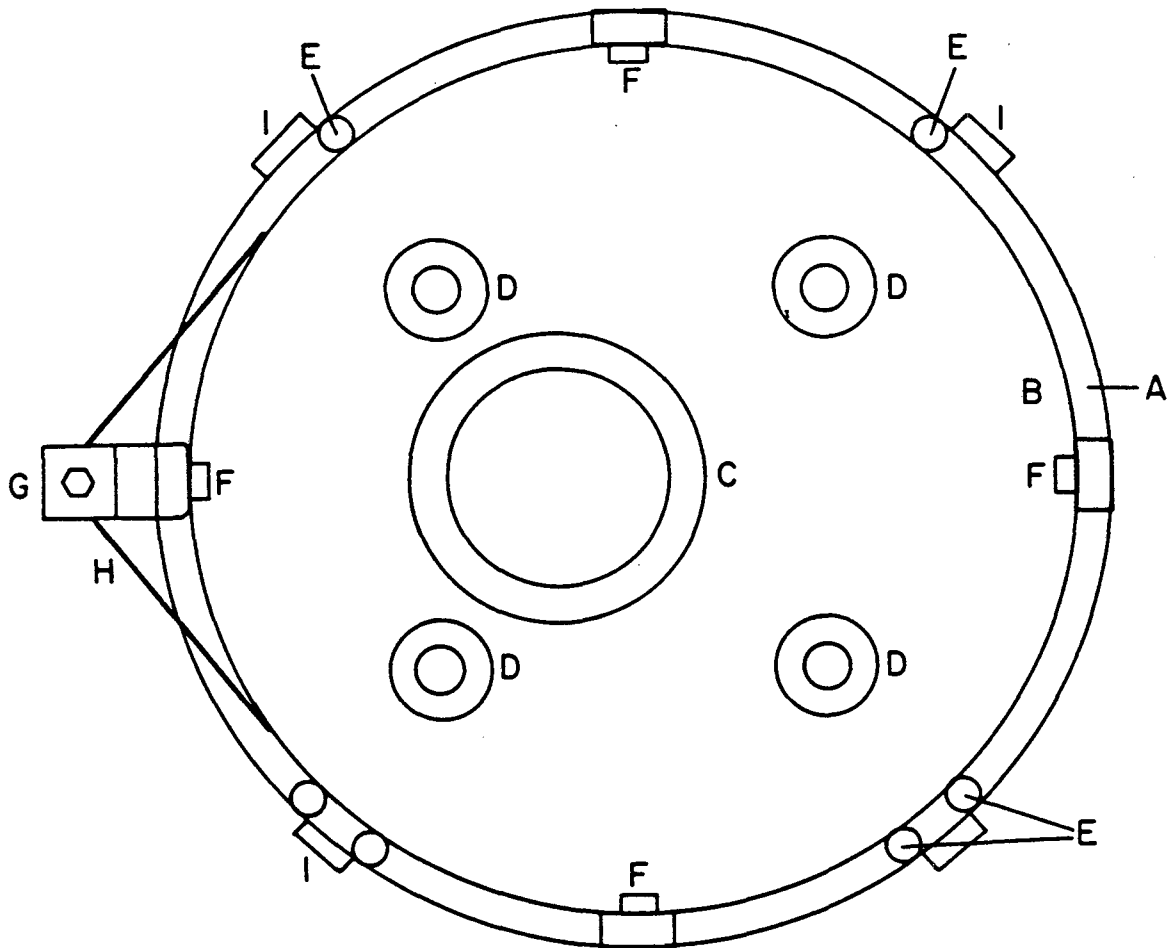
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Figure 2.17: Drawing of fixed section of the rotary seal flange. A- Teflon seals B- Pumping channels C- Ion-pump ports D- Mechanical-pump ports E- Thrust bearing F- Locating cam bearings G- Chain drive H- Ultek wire-seal flange face [28].

circumference to reach optimum sealing, which means that the seals will support 2.5×10^9 dynes of the total load. The atmospheric load on the flange is approximately 2.5×10^9 dynes (based on a 55.9 cm diameter area under vacuum) so the flange bearings will be required to take very little of the total thrust load. For this reason a simple 24" OD metal washer thrust bearing made of heat hardened stainless steel (17-4 P.H.) was chosen as the main bearing. Six 1" diameter cam bearings are placed around the circumference of the rotatable section to contain lateral motion, figure 2.17. These bearings are somewhat moveable to allow adjustment of the center of rotation of the rotary flange. Four additional cam bearings shown in figure 2.18 are positioned on the back face of the rotatable section to prevent it falling off in case of vacuum loss.

The rotatable section is a stainless steel plate 2" by 24" O.D., figure 2.18. The surface which mates to the spring loaded seals is machined to approximately 10 μ m R.M.S. finish. An 8" flange for mounting the detector is positioned 5.1 cm from the center of the section. In addition there are four 2.75" flanges placed symmetrically, as shown in figure 2.18. The 2" thick rotatable section will deflect less than 5×10^{-2} mm under vacuum as calculated using standard formulas [29]. The flange can be rotated by hand using the chain drive sprocket and chain bolted to the rotatable section.

Using the published Teflon-seal permeation rate of 8.8×10^{-9} liter/sec per cm of seal circumference [27] and standard formulas for channel conductance one can calculate that the highest pressure in the mechanical pumped channel should be 10^{-3} torr, so that the pressure will be limited by the 10^{-2} torr base pressure of the mechanical pump. Likewise the highest pressure in the ion pumped channel should be 10^{-9} torr, so that



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Figure 2.18: Rotary flange. A- Seal flange, figure 2.17 B- Rotating section C- Detector flange D- 2 3/4" flanges E- Locating cam bearings F- Retaining cam bearings G- Chain drive H- Chain I- Ion-pump ports.

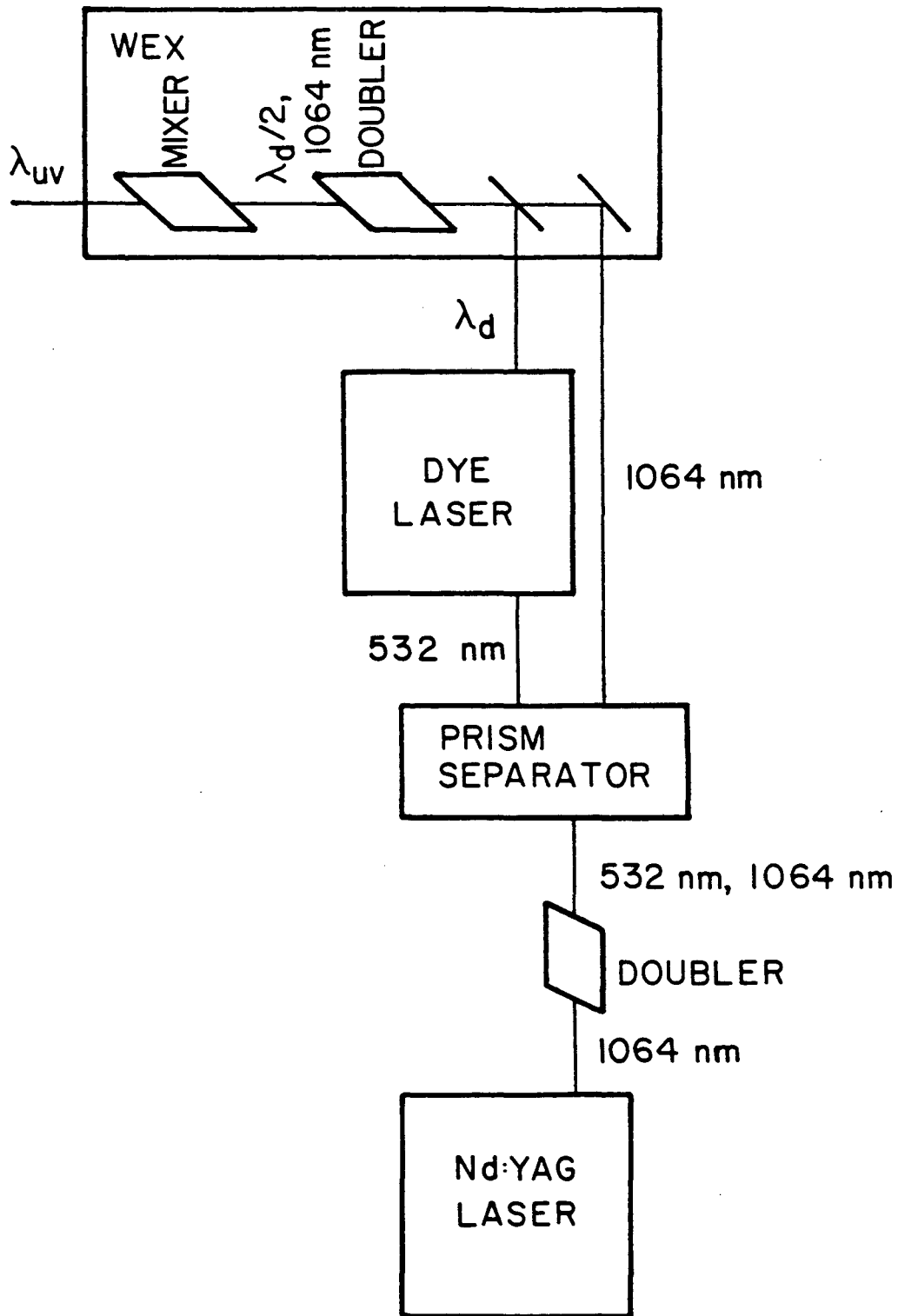
the pressure will be limited by the 10^{-7} to 10^{-8} torr base pressure of the ion pump. The load on the main chamber from leakage through the final seal should be negligible. With the flange stationary the main chamber base pressure is 2×10^{-10} torr, and rises by $\sim 3 \times 10^{-11}$ torr when the flange is being rotated.

2.2.5 Pulsed Ultra-Violet Laser

The commercial Quanta-Ray pulsed ultra-violet laser system [30] is shown in schematic outline in figure 2.19. The output of the neodymium YAG laser (DCR A-1) is passed through a KDP doubling crystal producing ~ 200 mJ of energy at 532 nm. A prism separator directs the 532 nm light into the dye laser (TDL-1) to excite the dye cells. The dye laser output and remaining 1064 nm fundamental of the Nd:YAG enter a set of mixing and doubling crystals (WEX-1) which are tuned to successively double the dye laser frequency and mix the doubled light with the 1064 nm light. The doubled dye laser light has an energy of 20 mJ/pulse, and the mixing produces 0.7 to 1 mJ/pulse of energy at the output UV wavelength. The dye laser wavelength was varied to produce the tunable UV radiation near 225 nm and 236 nm required to excite the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{1/2}(v''=0)$ and $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{1/2}(v''=1)$ NO transitions.

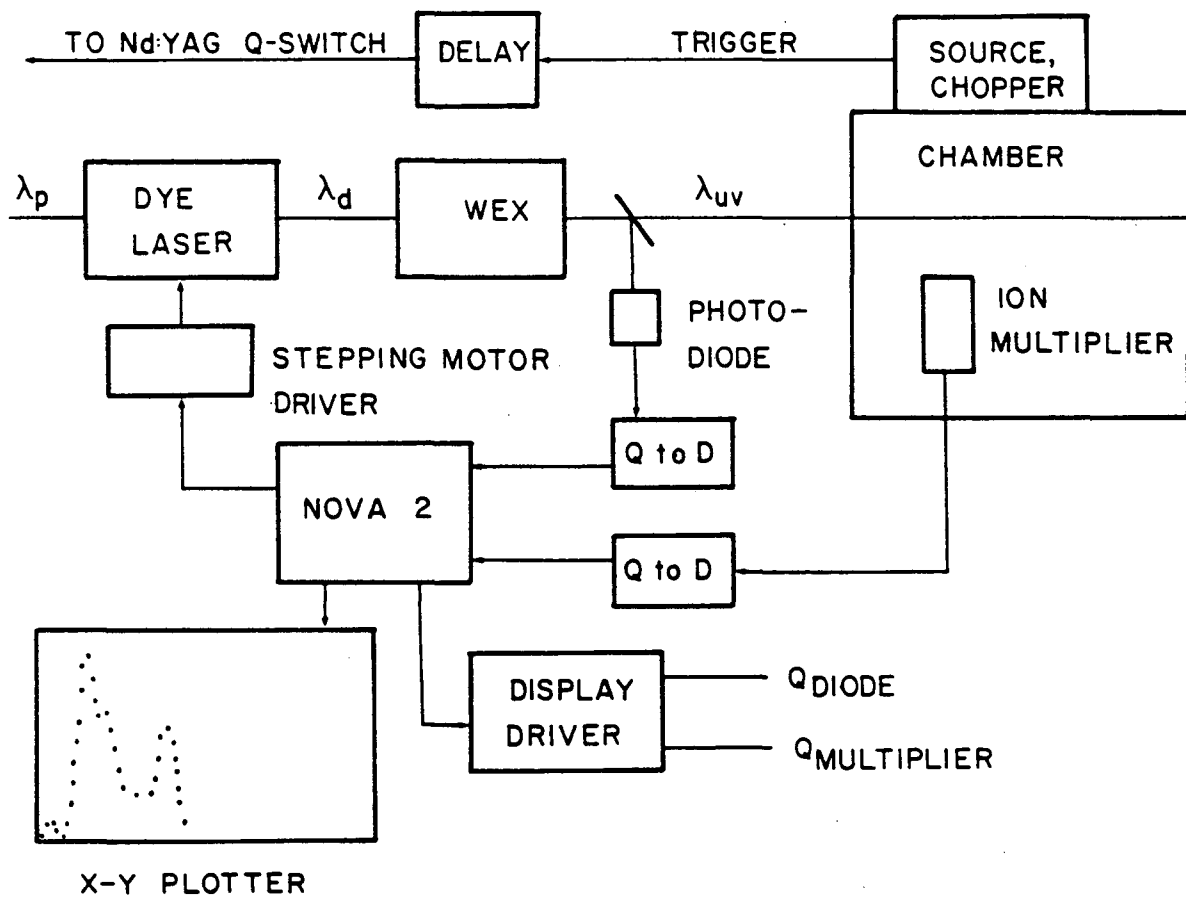
Dispersion in the WEX separating prism caused a deflection of 0.14° in the UV beam direction for every 1 nm of wavelength tuning. This may cause severe experimental problems, so a mechanical system was developed to rotate the Pelin-Broca prism in the WEX to compensate for the deflection.

2.2.6 Electronics and Data Accumulation



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Figure 2.19: Diagram of ultra-violet laser system.



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Figure 2.20: Diagram of data accumulation system.

The arrangement and interconnection of the control and data accumulation electronics are shown in figure 2.20. To measure the UV laser intensity a fraction of the UV light was reflected from a quartz window into a cell containing sodium-salicylate solution. The fluorescence from the solution created current in a visible-light sensitive photodiode (EG&G SGD100). The current from the photodiode was digitized in a gated charge-to-digital converter (LeCroy, model 2248) and transferred to a NOVA 2 minicomputer.

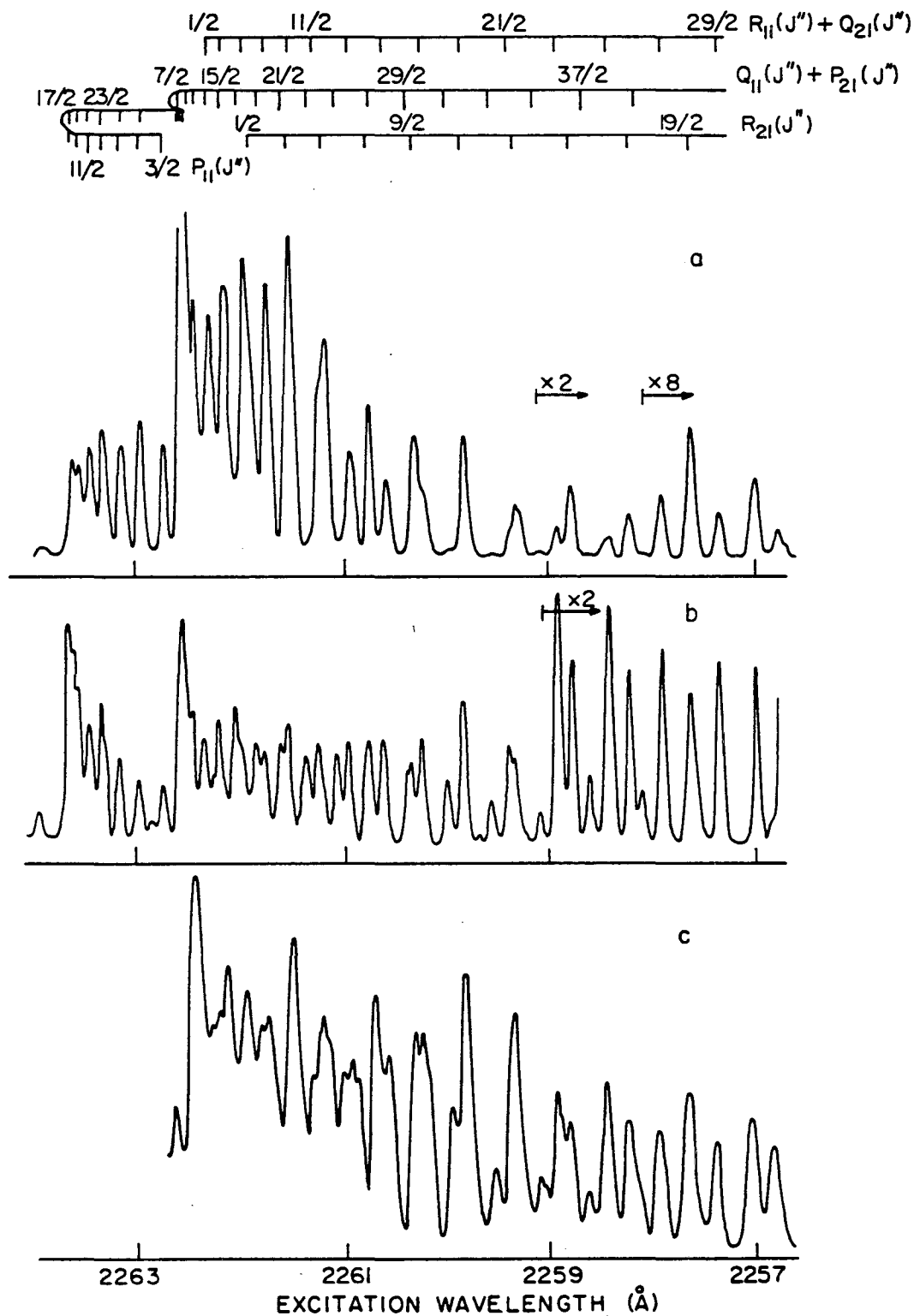
The current output from the ion-multiplier consisted of a pulse caused by scattered UV laser light incident on the multiplier, followed after 1 μ sec by a pulse of current from the ions arrival at the multiplier. A second charge-to-digital converter was gated to extract the ion current. The gating signals were derived from the Q-switch output signal of the Nd:YAG pump laser.

Signal processing was performed by the minicomputer. A program was written (see appendix for listing) that operated in two modes, a spectrum sweep and accumulation mode, and a boxcar-integrator emulation mode. The minicomputer was programmed to normalize each ion pulse by the laser intensity raised to any predetermined value. The normalized ion current, unnormalized ion current, and laser intensity were numerically averaged for 20-200 laser pulses, and voltages proportional to the average ion current and laser intensity were output through a display driver for monitoring the experiment.

In the spectrum sweep and accumulation mode the minicomputer controls the laser wavelength through a stepping motor driver connected to the dye laser grating motor. The computer advances the grating and plots the normalized ion intensity versus UV wavelength on an X-Y

plotter. In the boxcar-integrator emulation mode the normalized ion current is output to some monitoring device, and the laser is controlled separately.

Typical rotational spectra are shown in figures 2.21. Figure 2.21a is the spectrum of the incident beam, figure 2.21b is a spectrum of room temperature gas phase NO at a pressure of 5×10^{-8} torr, and figure 2.21c is a typical spectrum of NO molecules scattered from the Pt(111) crystal at a surface temperature $T_s = 580$ K. The spectra are at a laser wavelength of ~ 226 nm corresponding to the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{1/2}(v''=0)$ electronic transition. The assignment of the rotational lines is shown at the top of figure 2.21a and is based on values from the literature [31].



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Figure 2.21: Two-photon ionization spectra. The assignment represents a one photon rovibronic absorption of the $A(v''=0) \leftarrow X(v''=0)$ transition. a.) Incident supersonic beam, b.) Room temperature ambient NO gas, 5×10^{-8} torr, c.) NO molecules scattered from a Pt(111) surface at 580 K.

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 31. R. Engleman, Jr, P.E. Rouse, H.M. Peek and V.D. Baiamonte, "Beta and Gamma Band Systems of Nitric Oxide", Los Alamos Scientific Laboratory, Report LA-4364 (1969).

32. This program is available in the Somorjai group's PSS library MOLBEM and is stored as subset ZECAL.

Chapter 3: Spatial and Translational Energy Distributions of Product D₂O from a (111) Platinum Surface

3.1 Introduction

The translational energy and spatial distributions of surface reaction products can provide information of the desorption process, or the dynamics of the final bond formation step. Often the spatial and translational energy distributions are related, and hence provide the same information. Good examples of this relationship are the velocities and angular distributions of H₂ produced from the recombination of H_(a) + H_(a) on Ni(111) [1], polycrystalline nickel [2,3], Pd(100) and Cu [4], and of CO₂ produced from the reaction of CO + O₂ on polycrystalline platinum [5]. In these systems the product-surface potential energy contains a parallel barrier in the exit channel. This barrier accelerates the product molecules towards the surface normal resulting in peaked angular distributions [6-8]. It was proposed that the peaked angular distributions would be accompanied by energetic desorption velocity distributions, which were confirmed by time-of-flight (TOF) measurements.

In these systems the velocities are determined by the potential energy seen by the products, and the velocity distributions indicate that the desorption times are too short to allow transfer of the translational energy to the solid. These studies were initiated because of the peaked angular distributions, and to date these are the only reactions studied and the only type of dynamics investigated.

In more general exothermic systems, a question of greater interest will be the amount of the reaction energy transferred into translational energy. This transfer is in turn related to the time elapsed from any

exoergic bond formation steps to the desorption. Another important effect may be the rate of thermal energy transfer from the surface to the adsorbate relative to the rate of desorption.

The amount of the exoergicity appearing as translational energy will depend critically on the time development of the reaction. If much of the chemical energy is released in a concerted step combining bond formation with the desorption, or in a product formation step quickly followed by desorption, the excess energy may not transfer to the surface and may effectively channel into product translation. However, if the reaction proceeds slowly and much or all of the energy is released in early adsorption or intermediate formation steps then the chemical energy can effectively dissipate to the surface and the velocity distributions will be determined solely by the desorption process. The latter case is generally thought to be characterized by cosine function angular distributions and equilibrium Maxwell-Boltzmann velocity distributions.

The formation of D_2O is strongly exoergic, but the product angular distribution from Pt(111) surfaces is known to be well described by a cosine function [9], implying equilibrium translational energy distributions. This makes the D_2O reaction a good system for testing these concepts. In addition there are numerous studies concerning the interactions of the reactants and product with platinum surfaces, and investigations of the mechanisms and intermediate products of the reaction. This information will substantially aid the interpretation of the translational energy data.

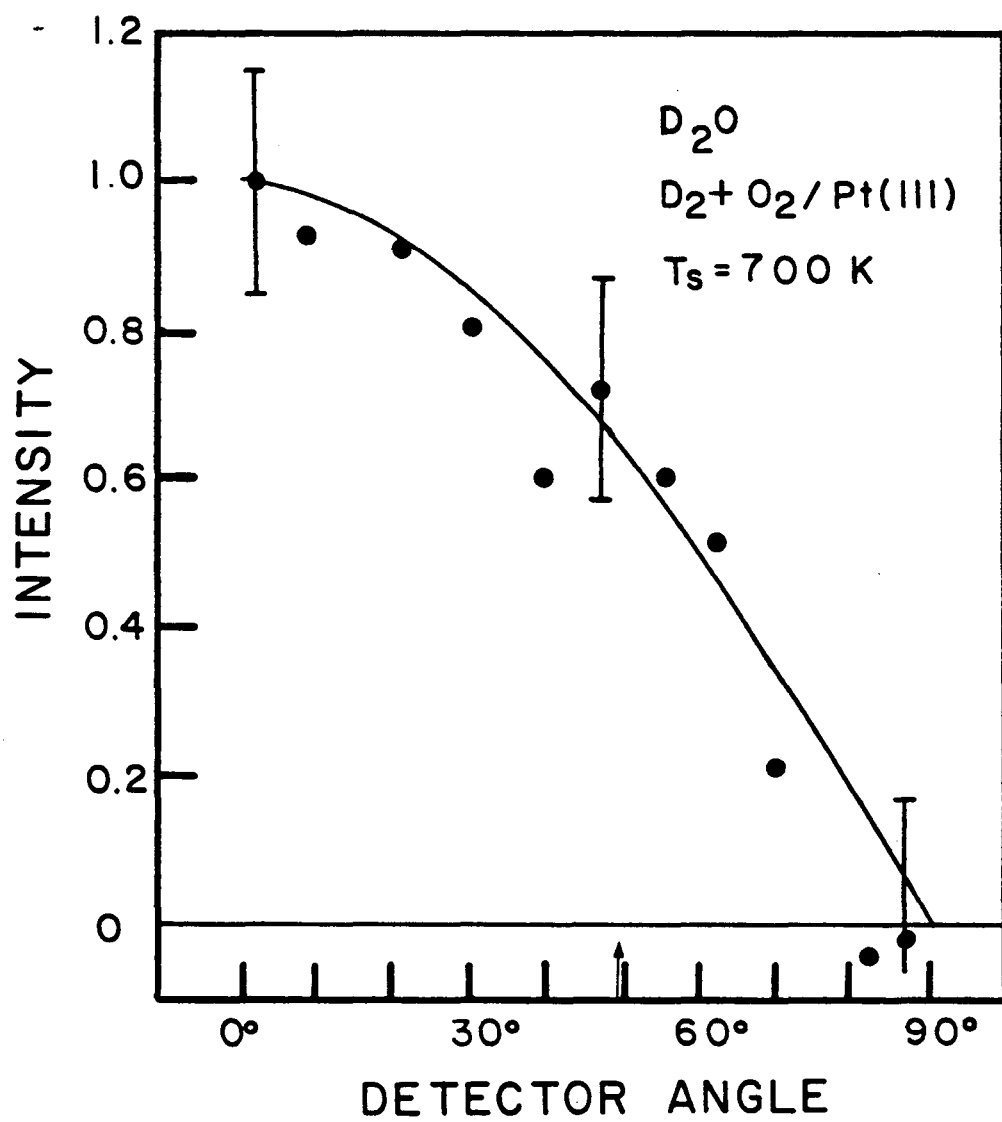
3.2 Results

For the D_2O product angular distribution measurements the reactants

originated from the two separate beam sources. The oxygen molecular beam was generated in the secondary beam source chamber (closest to the manipulator end, figure 2.1) and the deuterium atomic or molecular beam originated from a microwave discharge source [10] or molecular source in the primary beam source chamber (closest to the detector end, figure 2.1). The deuterium beam was modulated by a 150 Hz tuning fork chopper (Bulova L40C) to differentiate reaction product D_2O from background D_2O . The angle of incidence was 49° and the detector was rotated through forward scattering angles from the surface normal to parallel to the surface.

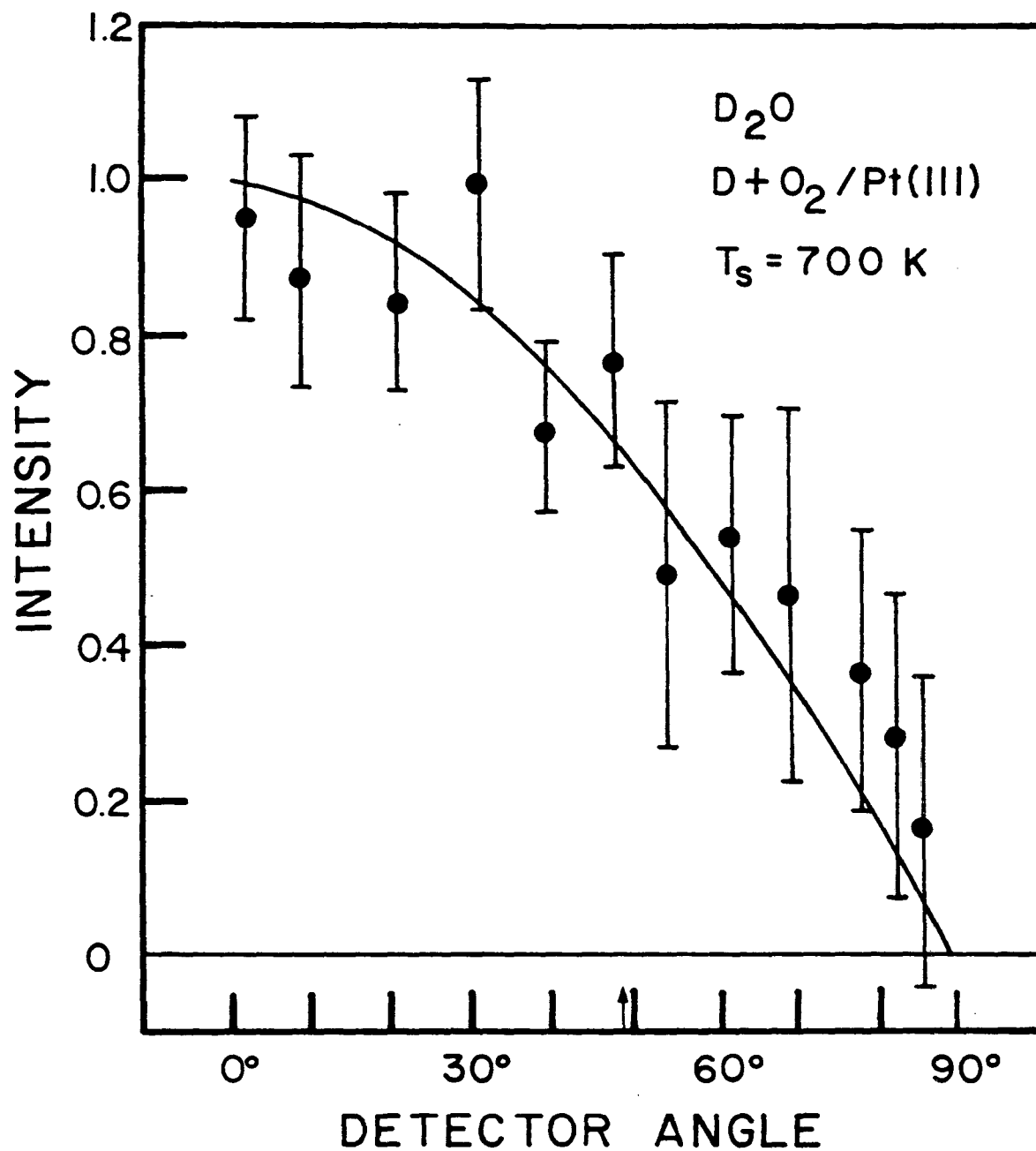
The D_2O product angular distribution for incident D_2 and O_2 , as a function of scattering angle from the surface normal, is shown in figure 3.1. The surface temperature was 700 K. Figure 3.2 shows the product D_2O angular distribution from the reaction of $D + O_2$ at the same temperature. Within the limits resulting from the rather large statistical errors, the angular distributions are independent of the nature of the deuterium reactant, either atomic or molecular. As discussed below this may indicate that the molecular deuterium dissociates upon adsorption on the platinum surface and that the deuterium reacts as an adsorbed atomic species. Shown with the measured angular distributions as the solid curve is a cosine function of the scattering angle. Both number density angular distributions can be seen to be well approximated by a cosine function. By conventional interpretations this would imply equilibrium of the gas and solid and the resulting Maxwell-Boltzmann velocity distribution [11,12].

The calibration of the time-of-flight spectrometer with effusive D_2O beams was discussed earlier (section 2.1.10), and the comparison of the



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Figure 3.1: Product D_2O angular distribution. Incident D_2 and O_2 beams, $T_s=700\text{ K}$. Solid curve is cosine function.



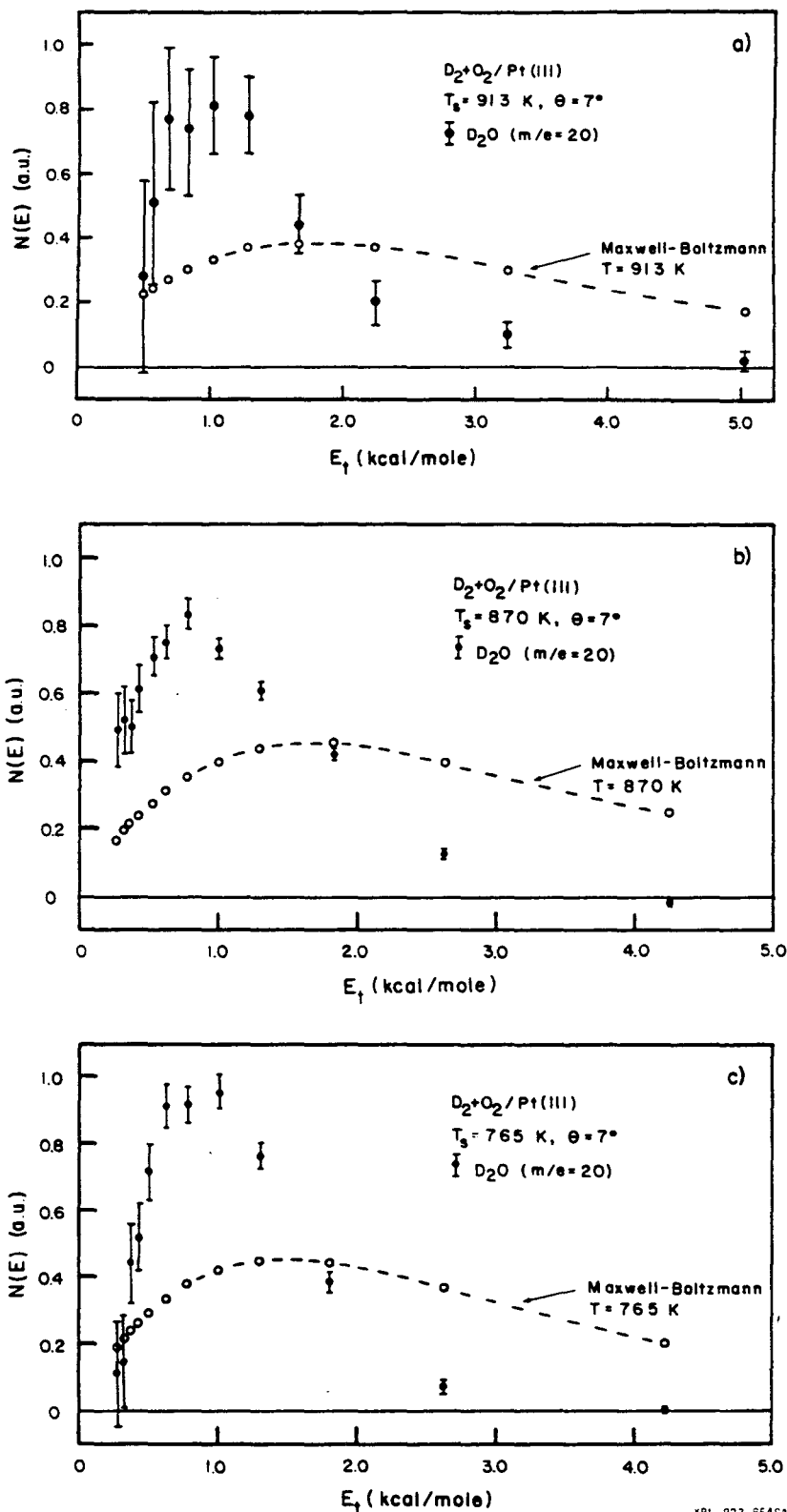
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Figure 3.2: Product D_2O angular distribution. Incident D atom and O_2 molecular beam, $T_s=700 \text{ K}$. Solid curve is cosine function.

effusive distributions to the expected Maxwell-Boltzmann function at the source temperature is shown in figures 2.10a and b. The agreement can be seen to be quite good, which indicates accurate operation of the TOF spectrometer.

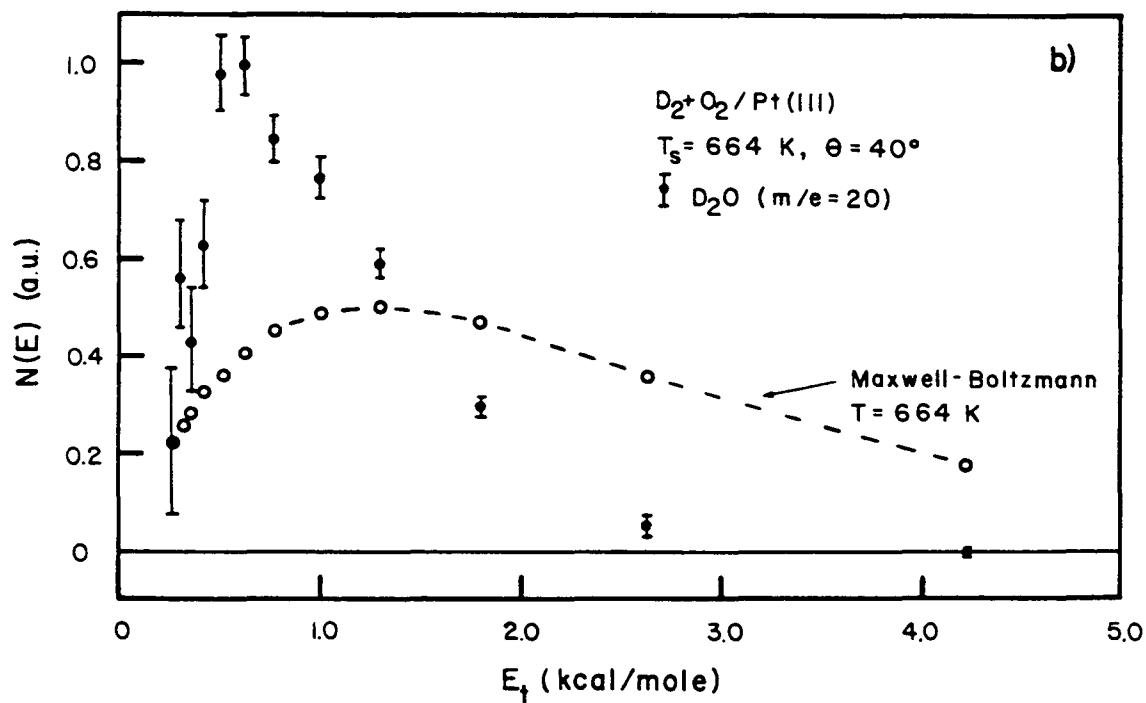
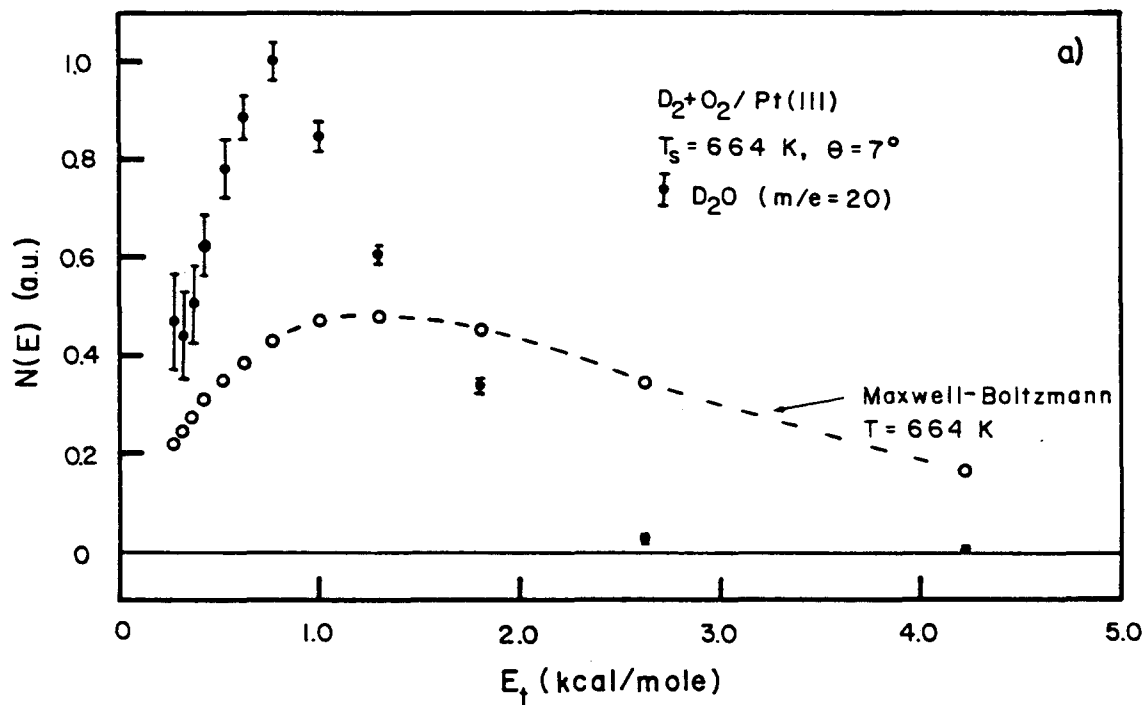
The time-of-flight distributions transformed to energy distributions are shown in figures 3.3 and 3.4. The mass spectrometer ionizer is density sensitive, hence the collected time-of-flight distributions are number density distributions $P_d(t)$, and are related to the flux distributions $P_f(t)$ by the velocity, $P_f(t) = vP_d(t)$. The transformation to an energy distribution is made by multiplication by the Jacobian, $P(E) \propto t^3 P_f(t) \propto t^2 P_d(t)$.

Figures 3.3a, b and c show the data for the translational energy distributions observed at an angle of 7° from the surface normal at surface temperatures of 913 K, 870 K and 765 K respectively. Figures 3.4a and b show two translational energy distributions for a sample temperature of 664 K taken at angles of 7° and 40° respectively. The striking feature of these distributions is that they are all roughly similar, are strongly peaked at lower translational energy, and fall rapidly to zero with increasing translational energy. There is only a slight increase in the relative number of molecules in the high translational energy tail of the distributions with increasing sample temperature. For comparison the number of counts that would result from a gas with a Maxwell-Boltzmann distribution at the respective sample temperatures is indicated in figures 3.3 and 3.4 as the open circles connected by dashed lines. The Maxwell-Boltzmann distributions have been normalized to the number of counts in the measured translational distributions. The Maxwell-Boltzmann distribution for a gas from a surface is $P_f(v) \propto$



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Figure 3.3: D_2O translational energy distributions for a.) $T_s = 913 \text{ K}$, $\theta = 7^\circ$ b.) $T_s = 870 \text{ K}$, $\theta = 7^\circ$ c.) $T_s = 765 \text{ K}$, $\theta = 7^\circ$. Open circles represent corresponding Maxwell-Boltzmann distributions.



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Figure 3.4: D_2O translational energy distributions for a.) $T_s=664 \text{ K}, \theta=7^\circ$
 b.) $T_s=664 \text{ K}, \theta=40^\circ$. Open circles represent the corresponding Maxwell-Boltzmann distributions.

$v^3 \exp(-mv^2/2kT)$ with a cosine angular distribution, which gives $P(E) \propto \exp(-E/kT)$ for velocity v , translational energy E and temperature T . The microscopic origin of the factors in the Maxwell-Boltzmann distribution will be discussed below for the desorption process.

Table 3.1 shows the important parameters of the energy distributions, the mean energies in terms of equivalent temperatures $\langle E \rangle / 2k$, with the statistical errors, and the relative widths of the velocity distributions $\langle v^2 - \langle v \rangle^2 \rangle / \langle v \rangle^2$. Table 3.1 shows that the mean energies are one half or less of the energies expected for equilibrium with the surface, and that the relative widths are significantly smaller than the value for a Maxwell-Boltzmann distribution, 0.132.

These quantities were calculated from the TOF density distributions $P_d(t)$ by using the distribution moments

$$M_1 = \sum_{j=0}^N (v_j)^1 P_d(t_j) \quad 3.1$$

for i th moment M_i , velocity v_j , and for the flight time and velocity of the j th channel $t_j = L/v_j$. The total flux is M_0 , the mean energy is $\langle E \rangle = M_2/M_0$, and the distribution width is $\langle \Delta v^2 \rangle / \langle v \rangle^2 = [(M_3/M_0) - 1]$.

Figure 3.5 shows the average translational energy of the distributions plotted relative to $2k$ times the surface temperature T_s , which is the average translational energy expected for a Maxwell-Boltzmann distribution at T_s . For equilibrium between gas and surface, the points should lie along a line with unity slope.

The experimental conditions for the TOF distribution measurements were the O_2 and D_2 beams originating from the two 0.08 mm supersonic expansion nozzle beam sources (sec 2.1.4) operated at backing pressures of 200 torr. The O_2 and D_2 beams originated from the secondary

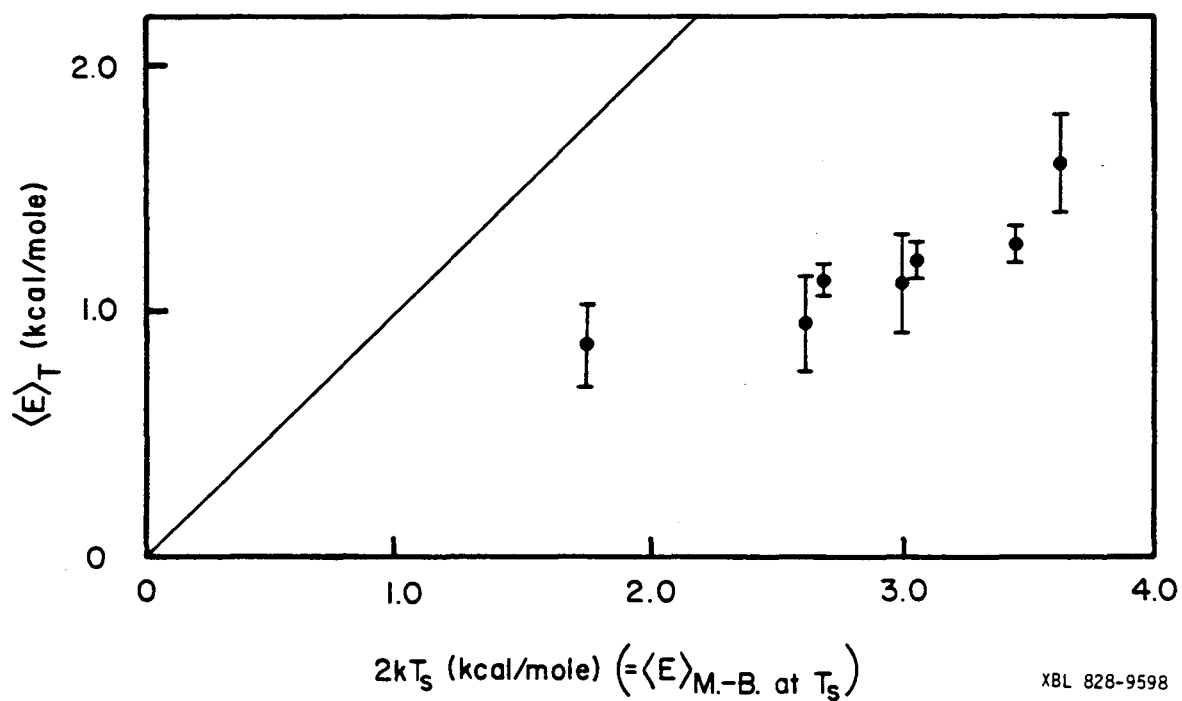


Figure 3.5: Mean energy of D_2O produced on Pt(111) surface as a function of $2kT_s$. Solid line indicates the mean energy that would result for equilibrium between the surface and the product D_2O .

Table 3.1

Temperature, Angle	Translational Energy $\langle E \rangle / 2k$	Distribution Width $\langle v^2 - \langle v \rangle^2 \rangle / \langle v \rangle^2$
664 K, 7°	283 K $\pm$ 11 K	0.065 $\pm$ 0.013
664 K, 40°	277 K $\pm$ 11 K	0.067 $\pm$ 0.013
765 K, 7°	305 K $\pm$ 12 K	0.065 $\pm$ 0.013
870 K, 7°	321 K $\pm$ 11 K	0.071 $\pm$ 0.013
913 K, 7°	400 K $\pm$ 53 K	0.101 $\pm$ 0.028
913 K, 47°	470 K $\pm$ 53 K	0.101 $\pm$ 0.029

and primary beam source chambers respectively. The incident angle of the beams was 49° . The composition of the Pt(111) surface was checked regularly by Auger electron spectroscopy. There was generally an oxygen coverage of 10-20% of a monolayer (based on a calibration by Gland [13]), and the coverage was essentially independent of temperature. It appears that this oxygen must be some form of strongly bound and relatively inactive oxide since chemisorbed-oxygen coverages should be lower at the higher temperatures [14].

The D_2O signal count rates were typically 30-80 ions/s against a background count rate at $m/e = 20$ of 7000 ions/s. With the low count rates, it took approximately 20 hours of real data accumulation time to achieve reasonable statistical errors for each TOF distribution, and two to three times that in actual experimental time. The pronouncedly slow velocity distributions combined with the low data rates caused concern that the distributions might be seriously affected by spurious signal sources. Several blank experiments were performed to test for spurious sources. First the contribution to the distribution of inelastically scattered background gases from the main scattering chamber was examined. Various gases with $m/e = 20$, including D_2O produced from D_2 and O_2 on chamber walls, various filaments and in the ion pumps, might affect the distribution. Experiments in which both beam gases entered the main scattering chamber but only one was allowed to strike the platinum surface were performed. No distribution was observed, indicating that the background gases do not seriously affect the measurements. Since the resolution of the mass spectrometer was decreased to increase the data rate, it was expected that O_2 scattered from the surface might contribute to the distribution through incomplete filtering of the

O^+ fragment ($m/e = 16$). With the O_2 beam incident on the surface but no D_2 , no distribution was observed after 3 hours (mass spectrometer tuned to $m/e = 20$). Indirect measurements set an upper limit to the contribution of incomplete filtering. With an intense beam of O_2 directed into the detector the ratio of O_2 counts at $m/e = 32$ to the number of incompletely filtered O^+ counts at $m/e = 20$ was determined to be 8.5×10^{-4} . Measurement of the number of O_2 counts ($m/e = 32$) present under experimental conditions indicated that the O^+ fragment contributes approximately 1.0 count/s to the distributions, which is a tolerable level.

The relative D_2O production rates at the five temperatures examined in this study are shown in figure 3.6a. The increase in production to approximately 900 K is primarily due to the increasing formation rate. Above 900 K the rate falls again, which is most likely due to lower concentrations of chemisorbed oxygen at temperatures above 900 K. It has been observed that the Pt(111) surface coverage of chemisorbed oxygen declines at temperatures between 850 K and 900 K [14].

Figure 3.6b shows the D_2O production rate as a function of the O_2 source backing pressure. The D_2O production rate is strongly dependent on the O_2 source stagnation pressure (O_2 flux) but nearly independent of the H_2 source stagnation pressure. The dissociative adsorption probability for H_2 incident on Pt(111) surfaces has been determined to be approximately 0.10 [15-17]. The probability reported for dissociative adsorption of O_2 on Pt(111) surfaces has varied [13,18-22], but appears to depend critically on background CO pressure and surface oxygen coverage, and appears to fall exponentially with decreasing surface defect density [13,18-20]. Given the change in reaction rate with changes in the incident beam intensities, it appears that the D_2O formation

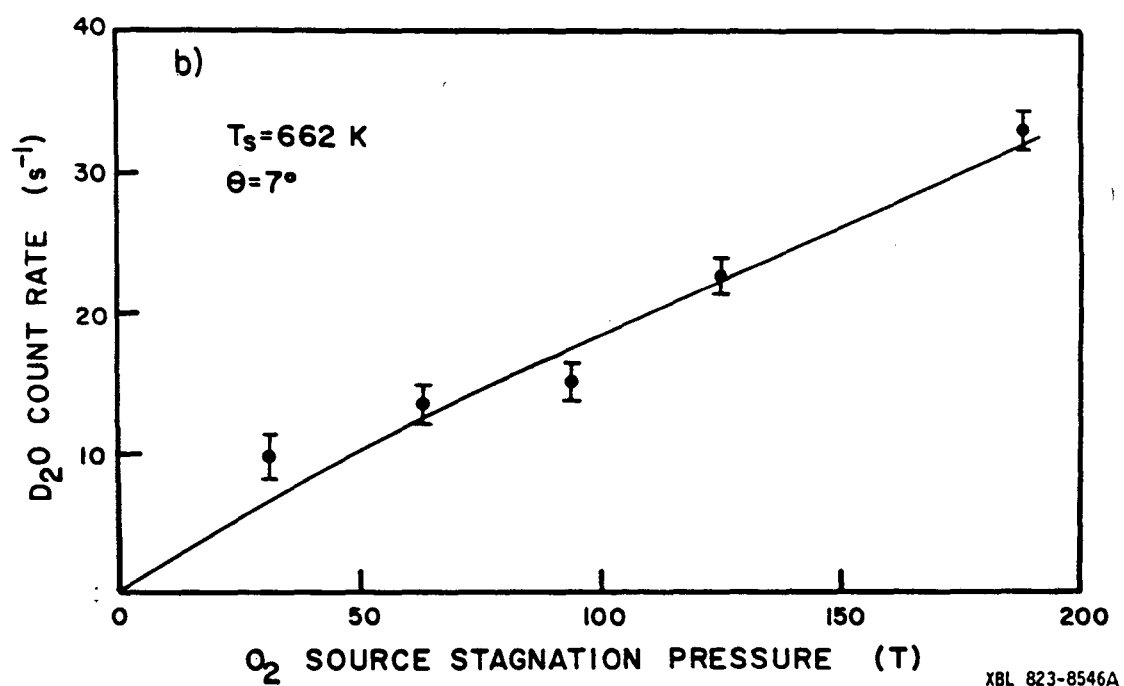
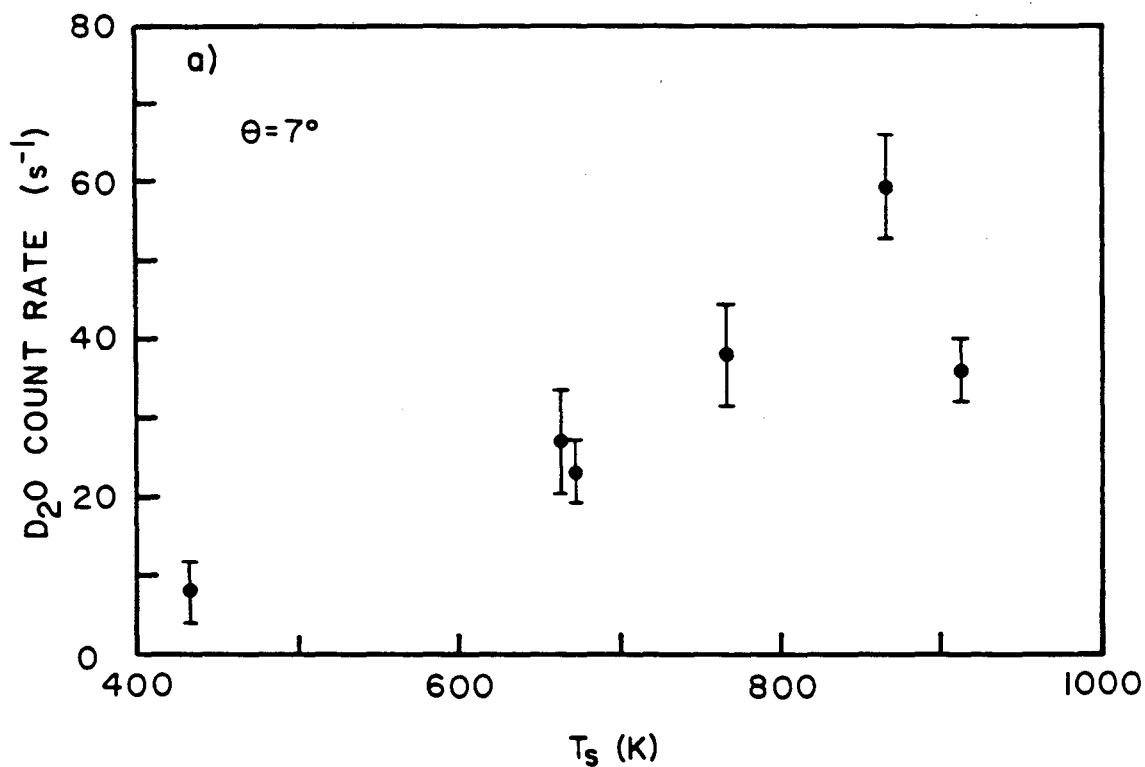


Figure 3.6: D₂O production rate on the Pt(111) surface a.) as a function of sample temperature, b.) as a function of O₂ source stagnation pressure.

reaction is limited by the oxygen arrival rate. This also implies that the oxygen coverage observed by AES must be due to an inactive oxide form.

3.3 Discussion

The present results are the first to show reaction products that have consistently lower translational energies than the equilibrium value (corresponding to the surface temperature). The D_2 velocities from single crystal Ni(111) surfaces had shown mean energies both higher and lower than the equilibrium values, depending on the angle of desorption of the D_2 molecules [1]. Other studies have shown consistently energetic velocities for H_2 produced by H atom recombination and desorption on polycrystalline Ni, Pd and Cu [2-4] and for CO_2 produced from the oxidation of CO on Pt [5].

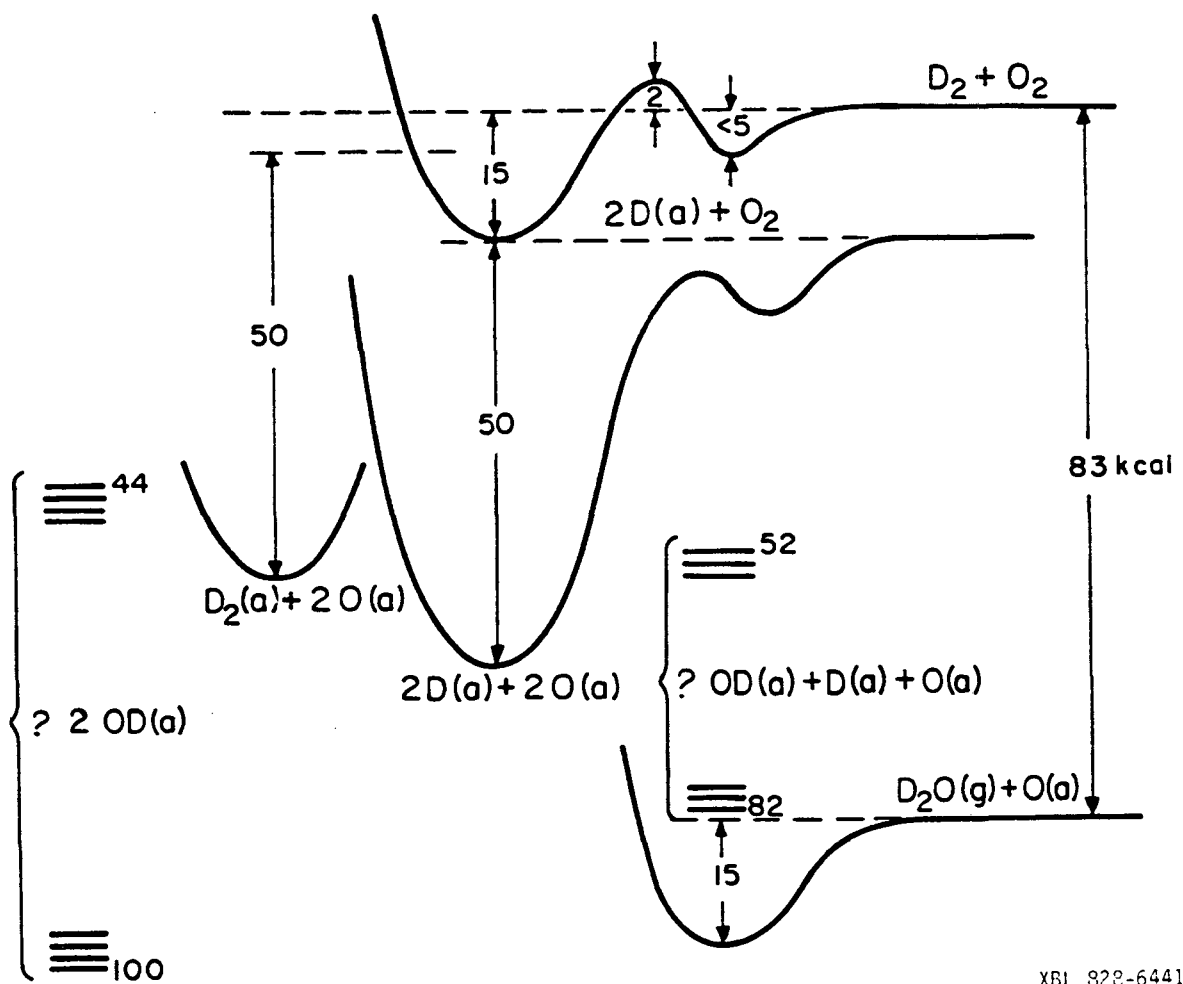
The cosine angular distributions for product D_2O should imply equilibrium velocity distributions [11,12]. However a clear conclusion from the translational energy data (figures 3.3 and 3.4) is that the D_2O translational energies are not in equilibrium with the surface. These sub-thermal translational energies clearly indicate that none of the chemical exothermicity of the reaction is channeled to product velocity. It will be shown that this fact coupled with energy values from the literature will very nearly identify the D_2O reaction mechanism. The sub-thermal distributions, however, have to be explained in terms of dynamic effects in the desorption process.

The overall reaction $D_2(g) + O_2(g) \rightarrow D_2O(g) + O(a)$ is exothermic by 83 kcal/mole. The question of the disposal of this energy will depend critically on the time development of the reaction and the mechanisms of

water formation. In determining the likely energy flow it is important to know the energy levels of the deuterium and oxygen reactants (and to determine the likely state of the reactants) and the energy levels of any likely intermediates. Water formation has been well studied on platinum and there is extensive literature on the reactant energies. A reaction energy level diagram based on the literature is shown as figure 3.7. It has been observed that H_2 and O_2 dissociatively adsorb on Pt(111) surfaces liberating 15 kcal/mole [16,17,23] and 50 kcal/mole [13,14] respectively. A weaker dissociative state of hydrogen may exist with an adsorption energy of 5 kcal/mole [17]. In addition to the dissociative adsorption, oxygen has been observed to adsorb molecularly in a weakly bound state with a heat of adsorption of 8 kcal/mole [13,14]. There is indirect evidence too of a molecular hydrogen state [16] which would have to have a heat of adsorption of much less than 5 kcal/mole.

From the energy level diagram it can be seen that the adsorption process liberates a sizeable fraction of the available energy, liberating 10 kcal/mole if the reactants adsorb molecularly and 65 kcal/mole if they adsorb dissociatively. However, the surface temperature is high enough to overcome the energy barriers to dissociation, and given the large energy difference between the molecular and atomic states, it is almost certain that all the surface oxygen and deuterium will be dissociated.

A reaction through a three atom collision $D(a)+D(a)+O(a) \rightarrow D_2O(a)$ is ballistically improbable, and the molecular reactions $D_2(a)+O_2(a) \rightarrow D_2O(a)+O(a)$ and $D_2(a)+O(a) \rightarrow D_2O(a)$ are energetically improbable as just discussed. If D_2O formed directly from the atoms $2D(a)+O(a)$ large amounts of energy would be released. The three atom collision would release approximately 20 kcal/mole, which would probably be observ-



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Figure 3.7: Energy levels of reactants, intermediates and product. D binding energy from [22], O binding energy from [13,14], OD binding energy from [24,25], gas phase bond energies from [36].

able in the translational energy distributions. So it appears that the reaction must liberate additional energy through the formation of some intermediate such as OD.

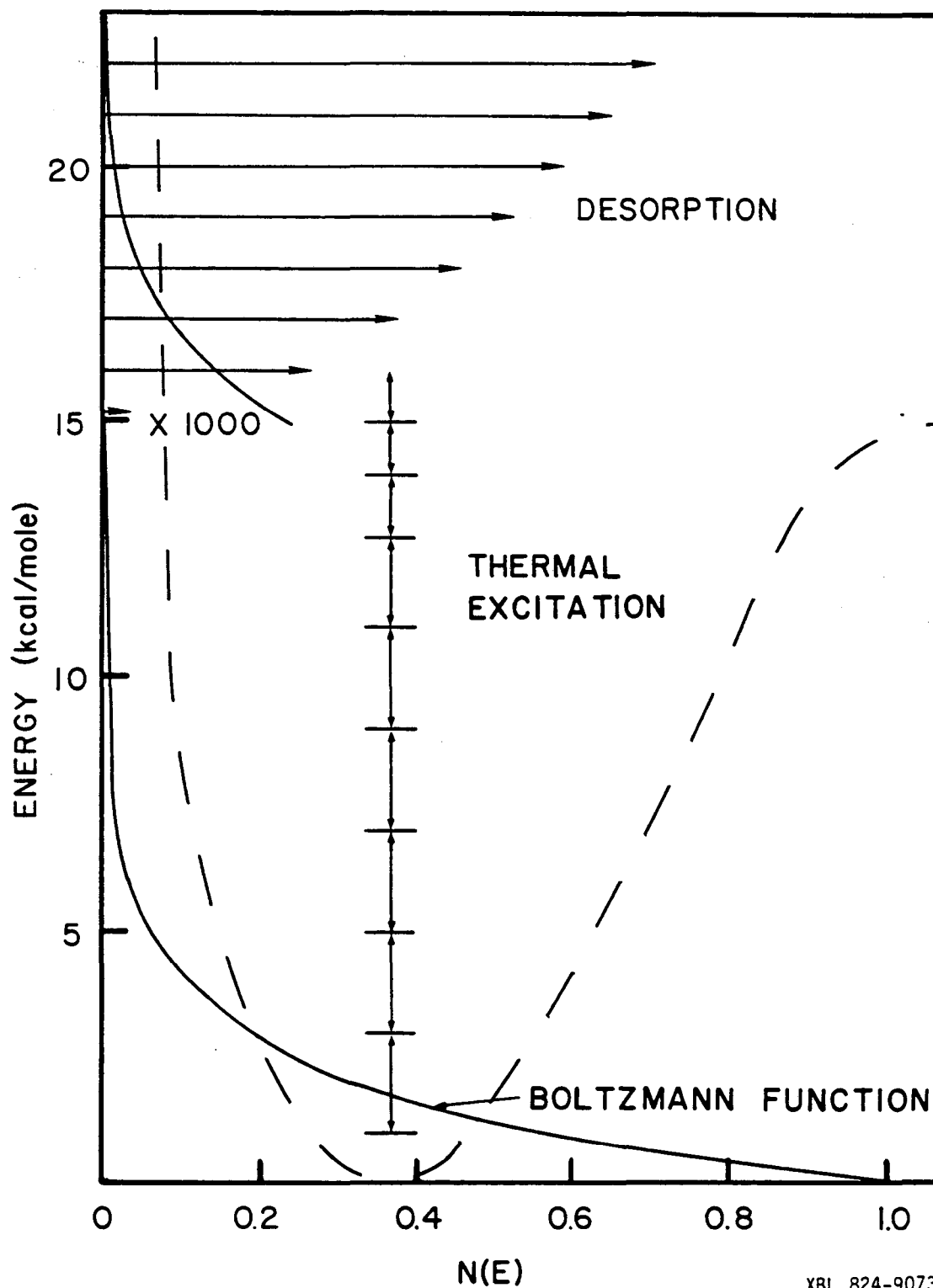
Recently OH has been observed on Pt(111) surfaces, produced from the coadsorption of O₂ and H₂ at 100 K and from the coadsorption of O₂ and H₂O at 100 K with subsequent heating to 150 K [24], and OH has also been observed as a side desorption product of the water formation reaction on polycrystalline Pt [25]. The apparent activation energy for OH production in that experiment was 31 kcal/mole. With OD formation as an intermediate step, the energy available to the D₂O product will depend on the value of the OD energy, which is not accurately known. If the OD heat of adsorption equals the the apparent production energy of 31 kcal/mole [25], the energy levels involving surface OD radicals would be the upper limits indicated in figure 3.7. The heat of adsorption must in fact be much larger since these levels make OH groups energetically unfavorable relative to the atomic constituents. The formation of OH groups from adsorbed H₂O and atomic oxygen indicates that two OD groups must be lower in energy than D₂O(a)+O(a) as shown by the lower limit of the energy level for the OD states in figure 3.7. There should be an activation barrier between the two states, but the step $2OD(a) \rightarrow D_2O(a)+O(a)$ must be endothermic [24].

The literature has helped to identify mechanisms by which the exothermicity of the reaction $D_2+O_2 \rightarrow D_2O$ can be dissipated early in the surface interaction, the energy is probably released in the adsorption of the reactants and in the formation of surface OD species. In addition there is sufficient time for this energy to transfer to the crystal, the water reaction has been observed to take 63μs at 850 K to 1 s at

600 K to complete [9]. An endothermic last step, however, can not account for the slow velocity distributions. Since the reaction times are long the intermediates will reach thermal equilibrium with the surface, and the D₂O velocities should at least reflect the random thermal motion of the OD_(a) intermediate. We propose that subsequent to formation, the D₂O remains on the surface for at least several vibrational periods, allowing the molecules to exchange energy with the surface and to reach a steady state, but non-equilibrium, energy distribution.

The factors affecting the velocities of desorbing gases are the energy distribution of the molecules on the surface, any energy dependence to the rate of desorption, the effect of any repulsive forces on the molecules, and the density of available states in momentum space. In equilibrium, the energy distribution of the adsorbed molecules is assumed to be a Boltzmann distribution $\exp(-E/kT)$, the desorption rate is proportional to the z component of velocity, $v \cos(\theta)$, and the density of states in momentum space is proportional to v^2 [27]. With no repulsive forces this results in the Maxwell-Boltzmann velocity and spatial distribution $P(v, \theta) = v^3 \cos(\theta) \exp(-mv^2/2kT)$. Figure 3.8 is a schematic representation of the proposed model. The solid curve is a Boltzmann distribution for an equilibrium temperature of 900 K. The Boltzmann distribution is drawn relative to a representation of the 15 kcal/mole deep [26] Pt-D₂O potential energy well (dashed line). As shown, most of the ensemble will lie below the edge of the potential well. Approximating the density of states by that for a three dimensional harmonic oscillator one can find that approximately 99% of the initial ensemble is below the edge of the well.

Desorption is possible for all molecules with energies greater than



XBL 824-9073

Figure 3.8: Diagrammatic representation of D_2O desorption. The solid curve is the equilibrium population of energy levels $\exp(-E/R \ 900 \text{ K})$ for energy E , and is drawn relative to the 15 Kcal/mole Pt- D_2O well depth (dashed line). The appearance into the gas phase is proportional to v_z [27].

the well energy. The desorption will deplete molecules from this part of the distribution. As indicated in figure 3.8, the desorption probability is proportional to v_z [27], which means that depletion of the distribution is greatest in the high energy tail. Molecules make transitions between the energy states through energy transfer from the surface. If the thermal excitation rate is fast compared to the desorption rate the equilibrium distribution of energies is maintained and the gas will have a Maxwell-Boltzmann velocity distribution [27-29]. However for weakly bound molecules or at high temperatures the desorption rate can be greater than the excitation rate with a resulting perturbation of the kinetic energy distribution away from equilibrium [30]. In the non-equilibrium desorption process the molecular velocities reflect the shift of the surface energy distribution to lower energies [28,29,31].

There have been several theoretical studies of various aspects of non-equilibrium desorption [28-34], and the observed translational energy distributions agree reasonably well with the behaviour predicted by theory. The average translational energy has been predicted to increase linearly with temperature at low surface temperatures T_s . At some transition temperature the translational energy should start to deviate from the equilibrium value and eventually reach an asymptotic value at higher T_s [29].

There is disagreement in the temperature calculated for the transition from equilibrium desorption behaviour to non-equilibrium desorption behaviour, but the values lie near 0.02 to $0.01 E_a/k$ [32-34], where E_a is the desorption activation energy. However strong non-equilibrium effects were predicted for argon and xenon desorption from Pt(111) for $T < 0.01 E_a/k$ [29]. We have observed strong non-equilibrium effects at

$T_s=500$ K. Using the reported D_2O desorption energy of 15 kcal/mole [26] gives $T_s = 0.006E_a/k$ which is in the same range as, but lower than, the temperatures predicted for observing non-equilibrium desorption.

Since the reaction rate falls rapidly with decreasing temperature there is insufficient signal to measure the translational energy at temperatures below 500 K. It is likely that we do not observe the transition to equilibrated desorption simply because it occurs at too low a temperature. Extrapolation of the observed mean translational energies to the line indicating equilibrium behaviour suggests that the transition occurs at approximately 200 K (figure 3.5)

The average translational energy (figure 3.5) increases only slowly with T_s , as predicted by the theoretical studies, with the exception of the highest temperature point ($T_s=913$ K). This increase in energy is not large relative to the statistical error, but within the non-equilibrium desorption model could indicate an increase in desorption energy due to changing surface conditions. For instance the surface coverage of chemisorbed oxygen should decrease around 900 K [14], and if the loss of oxygen increases the D_2O binding energy, then the translational energy would increase slightly at that temperature.

Within the model for non-equilibrium desorption the angular distributions and translational energies provide an indication of the degree of coupling between the parallel (x-y) and perpendicular (z) modes of motion of the adsorbate. With weak energy transfer between the x-y motion and z motion, the desorption process perturbs only the distribution of z energies, and the x-y motion remains more nearly equilibrated [28]. This would lead to angular distributions broader than cosine distributions, and translational energy distributions dependent on desorption

angle. The translational energy is the sum of the energies in the z direction and x-y direction so there will be increasing translational energy with increasing desorption angle. If there is rapid energy transfer between z motion and x-y motion, the energy for motion in all directions will be equally perturbed from equilibrium. Then the result will be cosine angular distributions and angle independent, but sub-thermal, translational energies. An angular distribution only slightly broader than a cosine distribution was calculated for Ar and Xe desorption from Pt(111), but translational energies as a function of desorption angle were not calculated [29]. D₂O is more structurally complex and more strongly bound to Pt than Ar or Xe, so the efficient energy transfer between translational modes, as evidenced by the cosine angular distribution and angular independence of translational energy, is expected.

The thermal excitation rate of D₂O on platinum can be estimated from the desorption rate based on the idea that non-equilibrium desorption results from desorption rates that are fast relative to thermal excitation rates. At the lowest temperature examined, 500 K, strong deviations from equilibrium were observed. The desorption rate can be estimated at this temperature assuming Arrhenius kinetics for desorption. Assuming a preexponential of 10^{13} and using the 15 kcal/mole desorption energy determined by Fisher and Gland [26] gives a desorption rate of approximately 10^7 s^{-1} . A rough assumption would be that the thermal excitation rate should be less than 10^7 s^{-1} . It seems implausible that the thermal excitation rates could be this low. For instance the vibrational excitation rates that have been inferred for NO adsorbed on platinum (next section) are higher. If the desorption energy measured by Fisher and Gland is in error by as much as 5 kcal/mole then the desorption

rate increases to 10^9 s^{-1} (surface residence times of 10^{-9} s) which is a higher but still seemingly unreasonable thermal excitation rate. This approach, however, is probably misleading. It is probably more appropriate to consider the time during which the adsorbate has energy greater than the gas phase potential energy, rather than the total surface residence time. Unfortunately, these times require accurate modeling to calculate.

The nature of the excitation is also relevant. If it is possible within a single event to transfer energies that are large compared to the expected spread in thermal energies, then the thermal excitation times should be on the order of a few vibrational periods. On the other extreme, with only small incremental energy transfer, the excitation process resembles more a random walk or diffusion process, and low excitation rates become more reasonable. The thermal diffusion extreme is probably more appropriate to adsorbates on platinum at these temperatures.

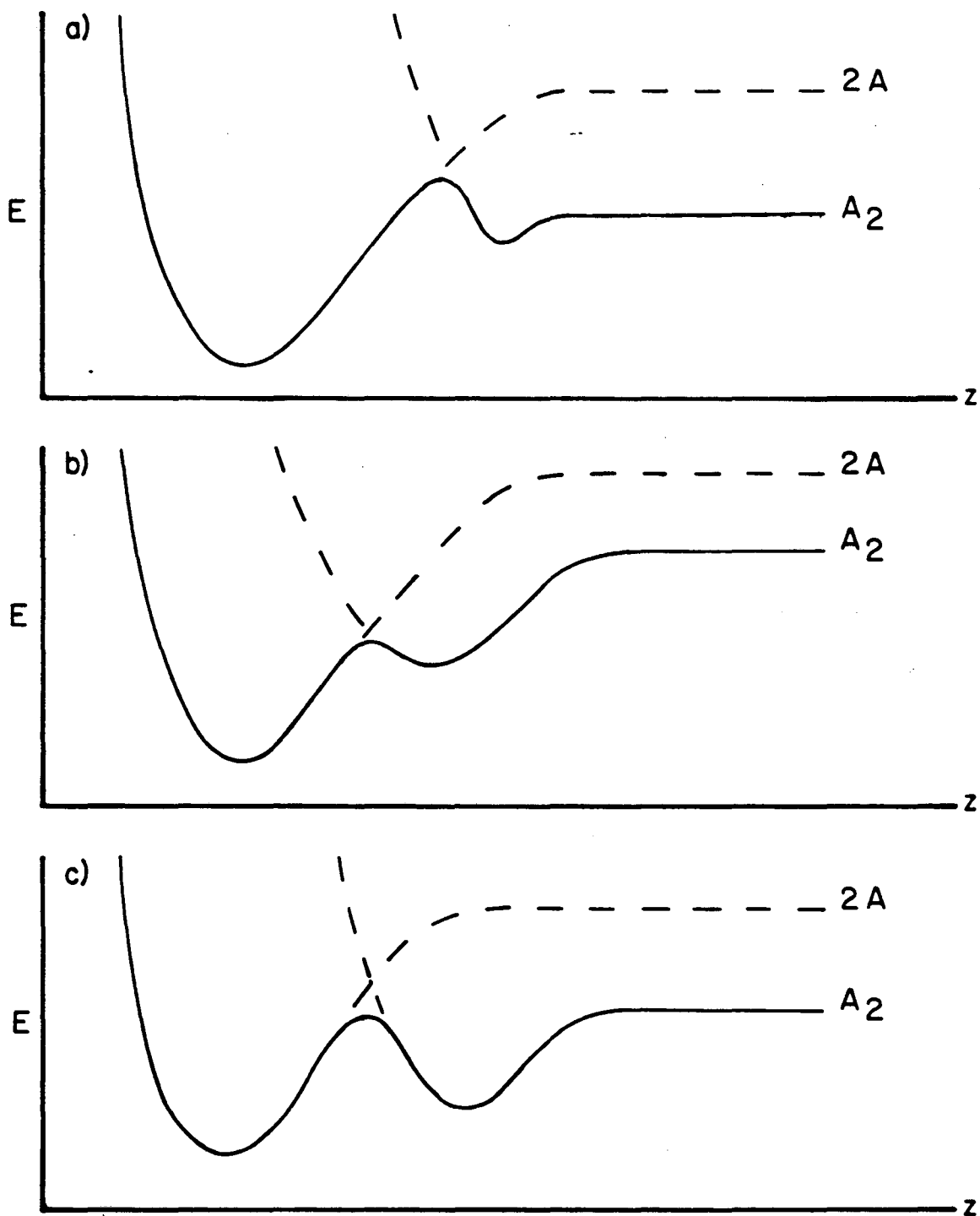
It is interesting that all the translational energy distributions, figures 3.3 and 3.4, fall to nearly zero value near a translational energy of 85 meV. This energy corresponds to roughly six times the Debye phonon limit for platinum and indicates that many phonons can be transferred during the time in which the molecule is above the edge of the energy well.

Assuming a desorption step independent of any bond formation steps, the data agrees well with theoretical predictions of non-equilibrium desorption behaviour. But one should also consider the implications of concerted bond formation and desorption mechanisms. Dynamic effects that could produce cold translational energies have not been proposed or discussed in the literature, but some general considerations can be discussed.

An important question is the potential energy of the product immediately upon formation, relative to its potential energy far from the surface. For these discussions it is simpler to consider the potential energies that might be encountered in a simple recombination of a diatomic molecule. Representations of different potential energy surfaces are shown as figures 3.9a, b and c. If the potential energy of the newly formed product is positive, as shown as the crossing of the atomic and molecular curves of figure 3.9a, the sum of random thermal energy and potential energy will lead to energetic translational energies as discussed previously for H atom recombination and CO₂ formation [1-8]. When the potential energy is negative, figure 3.9b, the thermal energy is insufficient for immediate desorption, so that the desorption occurs through energy transfer from the surface, and becomes independent of the bond formation. Only for potential energies near zero, figure 3.9c, is it possible to expect non-energetic, concerted desorption processes.

There will also be potential energy variations as a function of the separation of the two reactants. It is quite possible for this coordinate to have an activation barrier that will release potential energy into product vibration. A transfer of interatomic potential energy to vibrational energy was observed in N₂ produced on polycrystalline iron [35]. Since a concerted formation and desorption implies little interaction between the product and surface, any excess vibrational energy should be observable in the gas phase, so that if a reaction product showed sub-thermal translational energies but vibrational excitation, it would be a clear indication of concerted desorption.

As discussed previously, energetic velocities of products in other studies indicate that energy transfer in desorption is minimal. However



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Figure 3.9: Representation of potential energy surface for recombination for cases where the potential energy of the point of recombination (point of crossing of atomic and molecular potentials) is a.) positive b.) negative c.) approximately zero.

in those systems the potential which accelerates the molecules also directs them away from the surface. Thermal or sub-thermal translational energies require that there be no directional potential, and we must assume that random thermal motion will result in half of the newly formed molecules being directed towards the surface. These molecules will likely exchange energy with the surface so that the observed distribution should be more energetic than the nascent distribution.

Factors affecting the velocities of molecules under this type of model will be the thermal energy of the reactants (OD and D) and momentum conservation, any forces exerted by the surface during the formation, the density of states in momentum space, and any energy dependence in the formation rate.

The difference in desorption rates of concerted mechanisms compared to independent desorption processes may produce an interesting effect. When the desorption process controls the rate of gas appearance the surface exit rate is v_z , which becomes an important term in the expression for the velocity distributions [27]. In a concerted desorption the rate of appearance depends on the rate of reaction, which should not necessarily depend on the z component of velocity, since that is not the reaction coordinate. One might estimate the velocity distribution in that case. Assuming that the final reaction step is $OD_{(a)} + D_{(a)} \rightarrow D_2O_{(a)}$, most of the mass is in the OD fragment. The energy of the product will be determined by the OD energy, which might be assumed to be Boltzmann. Without the v_z desorption dependent term the translational energies would be approximately $v^2 \exp(-mv^2/2kT)$, which is shifted to lower energies than the Maxwell-Boltzmann distribution. The mean energy of this distribution is 1.5 kT, i.e. 75% of the Maxwell-Boltzmann value. However, the

cosine angular distribution observed in equilibrium desorption is a direct result of the v_z dependence to the desorption rate, and it is not clear that a cosine angular distribution could result without that dependence.

There are enough factors affecting the velocities resulting from concerted reaction desorption steps to make the idea of sub-thermal velocity distributions seem plausible. This is an area that could benefit from precise theoretical consideration.

The D_2O translational energy distributions (figures 3.3 and 3.4) and angular distributions (figure 3.1 and 3.2) demonstrate that a cosine angular distribution can result even if thermal equilibrium is not attained. The common association of a cosine angular distribution with equilibrium between the gas and the surface is not always correct. The angular distribution will have a cosine angular dependence if the molecular velocities are isotropic and if the rate of appearance in the gas phase is dependent on the normal component of velocity. If these conditions are met a cosine angular distribution will result regardless of the molecular energy distribution. Thus it is clear that angular distributions are insufficient for determining energy exchange.

3.4 Conclusion

The D_2O product angular and velocity distributions have been measured in the temperature range $T_g = 500 \text{ K} - 913 \text{ K}$. In this temperature range mean translational energies equal to less than half of the equilibrium values were found in translational energy distributions that showed strong high energy deviations from equilibrium distributions. These results can be adequately explained within the framework of a non-

equilibrium desorption model, however the non-equilibrium effects appear to be stronger than theoretically predicted. Within this model the cosine angular distributions and desorption angle independence of the translational energy distributions imply efficient coupling between perpendicular and parallel modes of motion of adsorbed D_2O . The approximate cutoff energy of the translational energy distributions indicates that several phonons can be transferred during the time in which the molecule is above the edge of the energy well.

Several factors of concerted bond formation and desorption processes which could lead to sub-thermal distributions have been proposed and discussed. It is conceivable that such a process might explain the D_2O angular and velocity distributions, but more work is needed along these lines.

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Chapter 4: Translational, Rotational and Vibrational Energy Distributions of Nitric Oxide Scattered from the (111) Crystal Face of Platinum

4.1 Introduction

Energy transfer between gas molecules and the surface region of a solid is a critical process in dissipating the translational energy necessary for adsorption to occur; and to supply the thermal energy for surface diffusion of the adsorbate, for decomposition, for overcoming the barriers in activated bond formation and for product desorption. The motivation for studying gas-surface energy transfer is the importance of these processes in surface reactions. We have studied the energy transfer to nitric oxide through measurements of the translational, rotational and vibrational energies of NO scattered from the (111) crystal face of platinum as a function of incident translational energy and surface temperature.

Historically, energy transfer was at first inferred from angular distributions. With the development of UHV compatible time-of-flight (TOF) spectrometers the translational energies of surface scattered gases could be measured directly. Primarily, the inelastic scattering found in weakly interacting systems has been studied [1-4], including the inelastic energy transfer of N₂ on W[1], O₂ from clean and oxidized W [2], Ar on W [3] and Xe on Pt [4]. Internal energy measurements have been made possible by the introduction of laser induced fluorescence (LIF) techniques [5], bolometric infrared absorption techniques [6], and two-photon ionization (TPI) techniques (section 2.2). Systems investigated include the inelastic scattering of NO from Ag(111) [7-9], NO from LiF and

CaF₂ [10], NO from graphite [11], HF from LiF [6], and CO from LiF [12]. The rotational energy was determined for the more strongly interacting systems of NO from NO covered platinum [5] and NO desorbed from Ru(001) [13]. The rotational modes may be particularly important in enhancing the adsorption process. The translational to rotational energy transfer [8,14,15] might cause the molecules to be temporarily bound [16-18], which would enhance further transfer from translational and rotational energy to the surface.

The effect of incident rotational or vibrational energy on the adsorption probability can be inferred from the internal energies of scattered gases by applying microreversibility and detailed balancing arguments [19]. State selective adsorption is one of the simplest examples of processes that may be important in laser-induced, surface-enhanced state selective chemistry. The rates of molecular deexcitation near a surface is of equal importance to laser-enhanced surface reactions and can also be investigated by the techniques described in this chapter.

The study reported in this chapter is the first for which the angular distribution, rotational energy, vibrational energy, and translational energy have been measured for scattering in a single gas-surface system, and one of only a few studies of translational energy transfer in strongly interacting systems. We have found that data on the effect of scattering on the energy of all modes is important in interpreting the deviations from equilibrium energy distribution in a given mode, and in understanding the important surface processes involved.

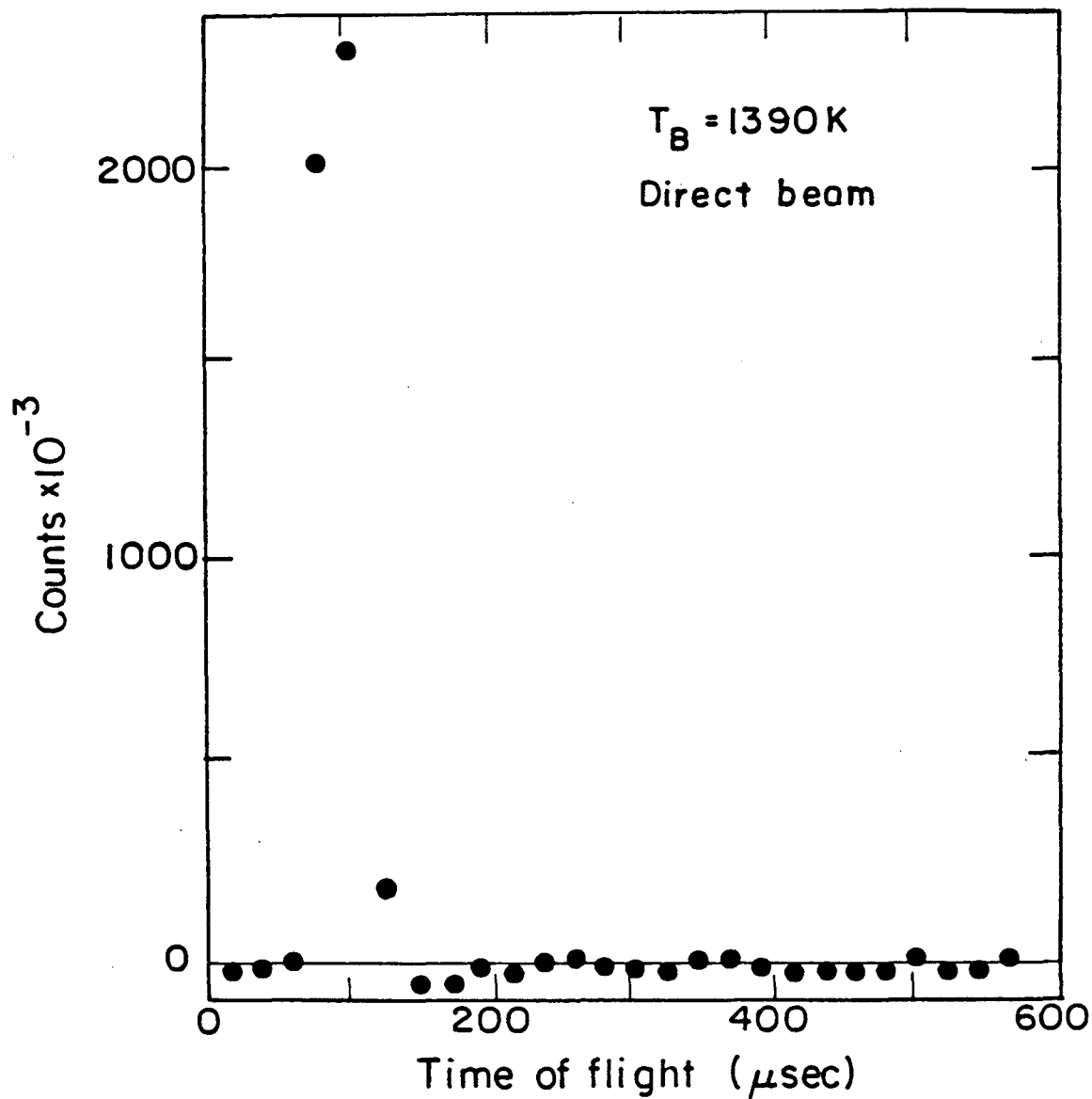
Finally the rotational and vibrational state selectivity of TPI or LIF suggests some potentially powerful and useful techniques for extracting additional information in surface scattering experiments.

4.2 Results

4.2.1 Velocity Distributions

For the NO time-of-flight measurements the TOF cross-correlation chopper was operated at 20 $\mu\text{sec/channel}$ (196 Hz rotational frequency). The incident NO originated from the primary beam source so that the detector could rotate in the plane of scattering (the plane defined by the incident beam and the vector normal to the surface). The angle of the incident beam relative to the surface normal was 51° . The nozzle expansion source (section 2.1.4) was operated at a source stagnation pressure of 200 torr and was seeded in He (partial pressure $\text{He/NO}=4/1$), operated as a pure NO beam or anti-seeded in Xe (partial pressure $\text{Xe/NO}=1/2$) to give equivalent translational temperatures ($\langle\text{K.E.}\rangle/2k$) of 1390 K (0.24 eV), 615 K (0.11 eV) and 265 K (0.046 eV) respectively from the room temperature nozzle. The TOF distribution of the incident He-seeded NO beam is shown in figure 4.1. When an incident beam is referred to as having a translational temperature T it will mean that the mean kinetic energy is $\langle\text{K.E.}\rangle=2kT$. The characteristics of the incident beam are described in greater detail in section 2.1.4, the sample preparation and gases are discussed in sections 2.1.3 and 2.1.5, and the analytical equipment in section 2.1.2.

The calibration of the TOF spectrometer was described in section 2.1.10. The spectrometer was calibrated against a large number of effusive NO direct beam distributions. A typical effusive distribution taken for calibration is shown as figure 4.2. The solid curve is the expected Maxwell-Boltzmann distribution for the nitric oxide mass and source temperature (300 K). The Maxwell-Boltzmann distribution has been broadened by the known electronic and mechanical gating widths. As can



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Figure 4.1: Time-of-flight distribution of the 0.24 eV (1390 K) incident beam. Beam source stagnation pressure was 200 torr (partial pressure ratio He/NO = 4/1).

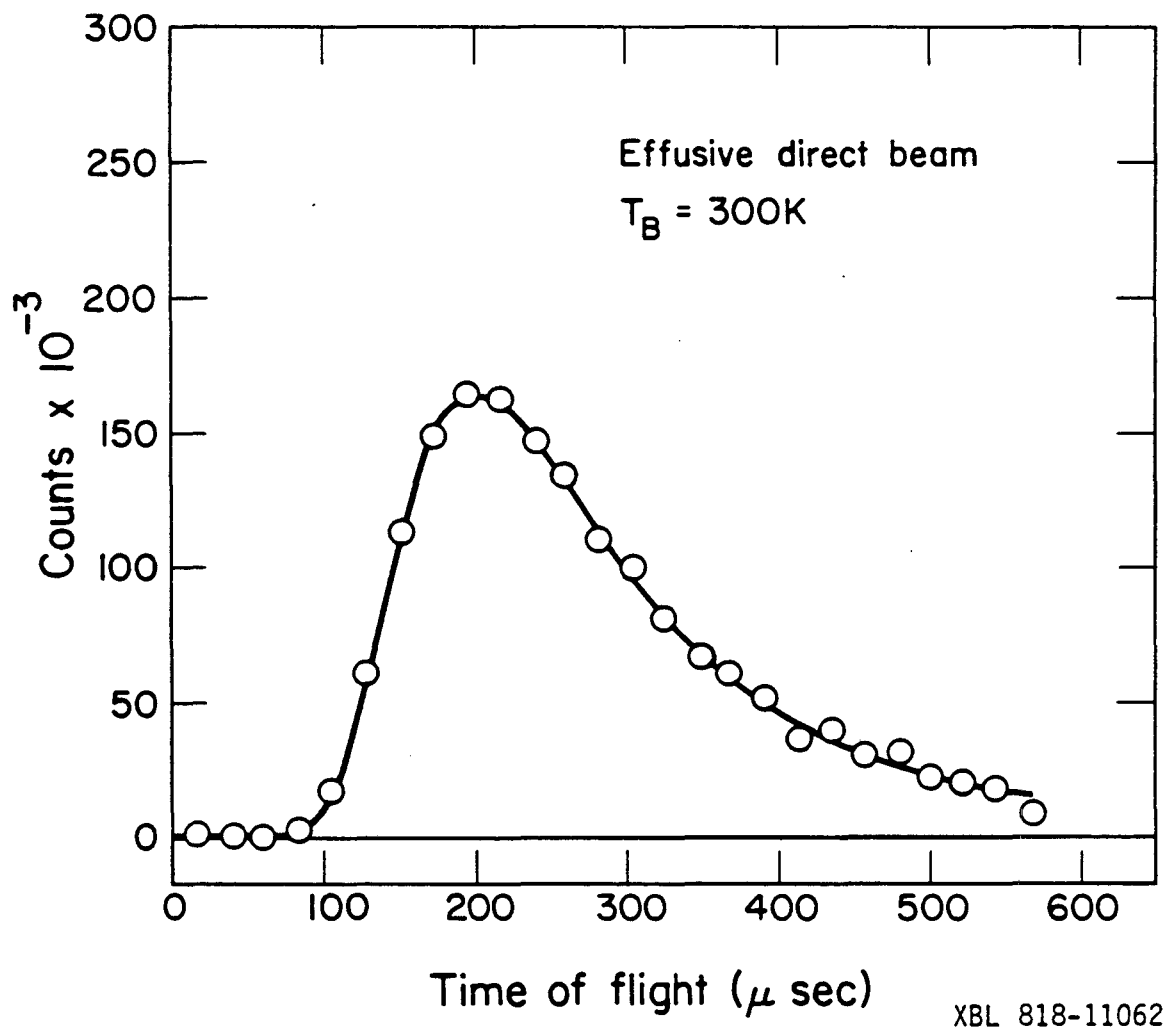
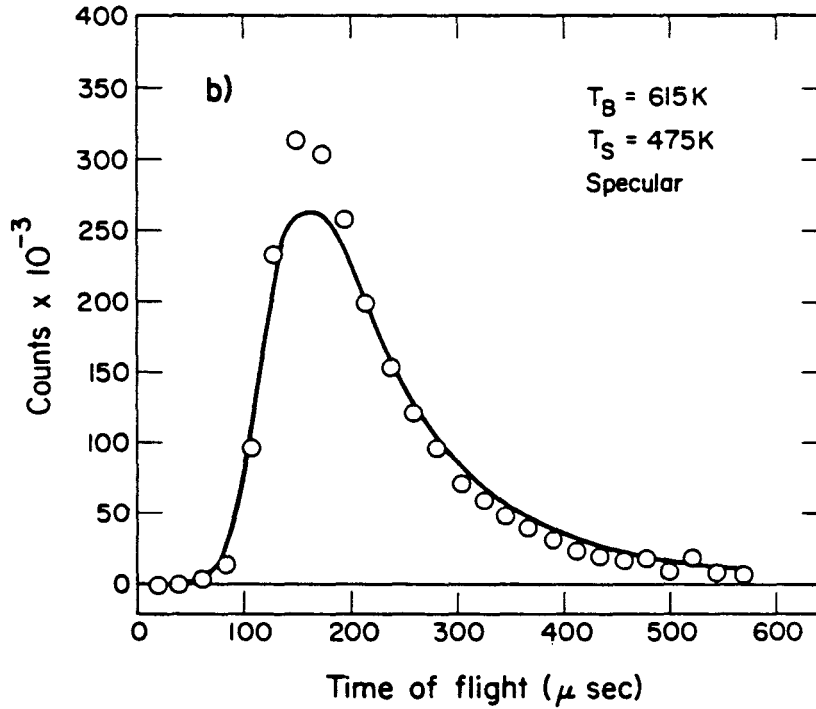
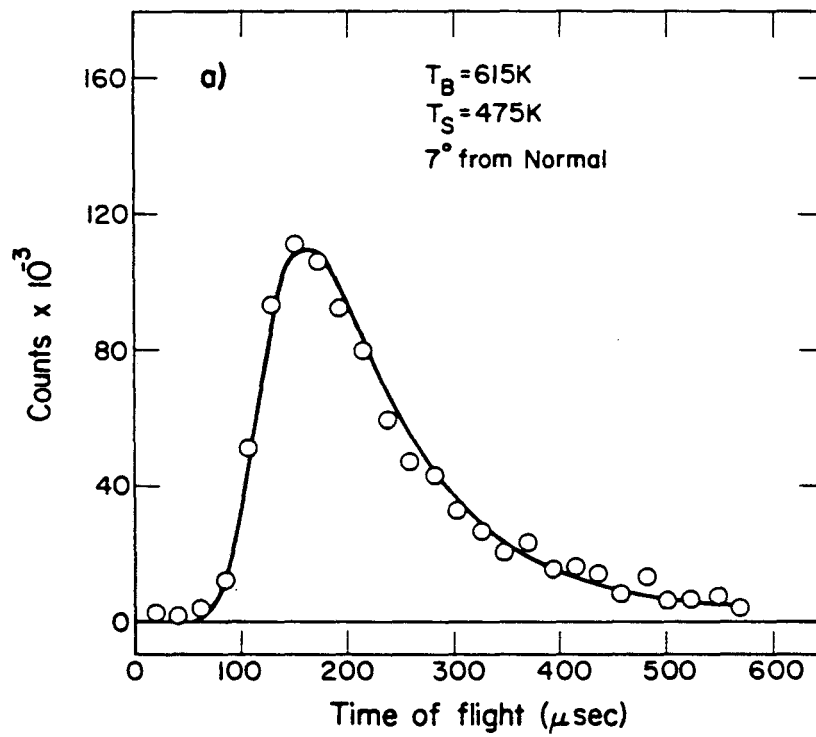


Figure 4.2: TOF distribution of NO from an effusive source at 300 K. The solid curve is a Maxwell-Boltzmann distribution. The comparison of the distributions indicates the results of the spectrometer calibration.

be seen, there is excellent agreement between the broadened Maxwell-Boltzmann distribution and the observed effusive distribution. The TOF spectrometer conditions extracted from the calibration were 11.4 cm path length and 63.8 zero-channel time, which agrees with what was expected from the mechanical dimensions.

Typical TOF distributions for NO scattered from the (111) crystal face of platinum are shown in figures 4.3 and 4.4. Figures 4.3a and b compare the TOF distributions observed near the surface normal (7°) and at the specular angle (51°) respectively for the same surface temperature (475 K) and incident beam translational energy (615 K). The Maxwell-Boltzmann distribution (solid line) has been broadened by the chopper and electronic gating functions, and normalized by the number of data counts in each distribution. As will be discussed the velocity distributions are expected to be more nearly equilibrated for molecules scattered into angles near the surface normal than for those scattered into the specular angle, and this is visually evident in figures 4.3a and b. The distribution for scattering near the normal (figure 4.2a) matches the equilibrium Boltzmann distribution. Figures 4.4a and b show two distributions at a higher incident beam energy, $T_B=1390$ K. Figure 4.4a shows the TOF distribution observed for NO scattered from Pt(111) at a temperature of 475 K for molecules scattered at 7° from the surface normal. The difference in conditions for the data of figures 4.3a and 4.4a is the higher incident beam energy of figure 4.4a. It can be seen that the TOF distribution, figure 4.4a, deviates somewhat from the equilibrium Maxwell-Boltzmann distribution. Figure 4.4b is a TOF distribution of the molecules scattered to the specular angle (51°) from a surface at 1110 K. At $T_S=1110$ K the specularly scattered molecules have a TOF distribution that is



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Figure 4.3: TOF distributions for $T_B=615$ K, $T_S=475$ K. a.) $\theta=7^\circ$, b.) $\theta=51^\circ$. The solid curves are the Maxwell-Boltzmann distributions at the crystal temperature.

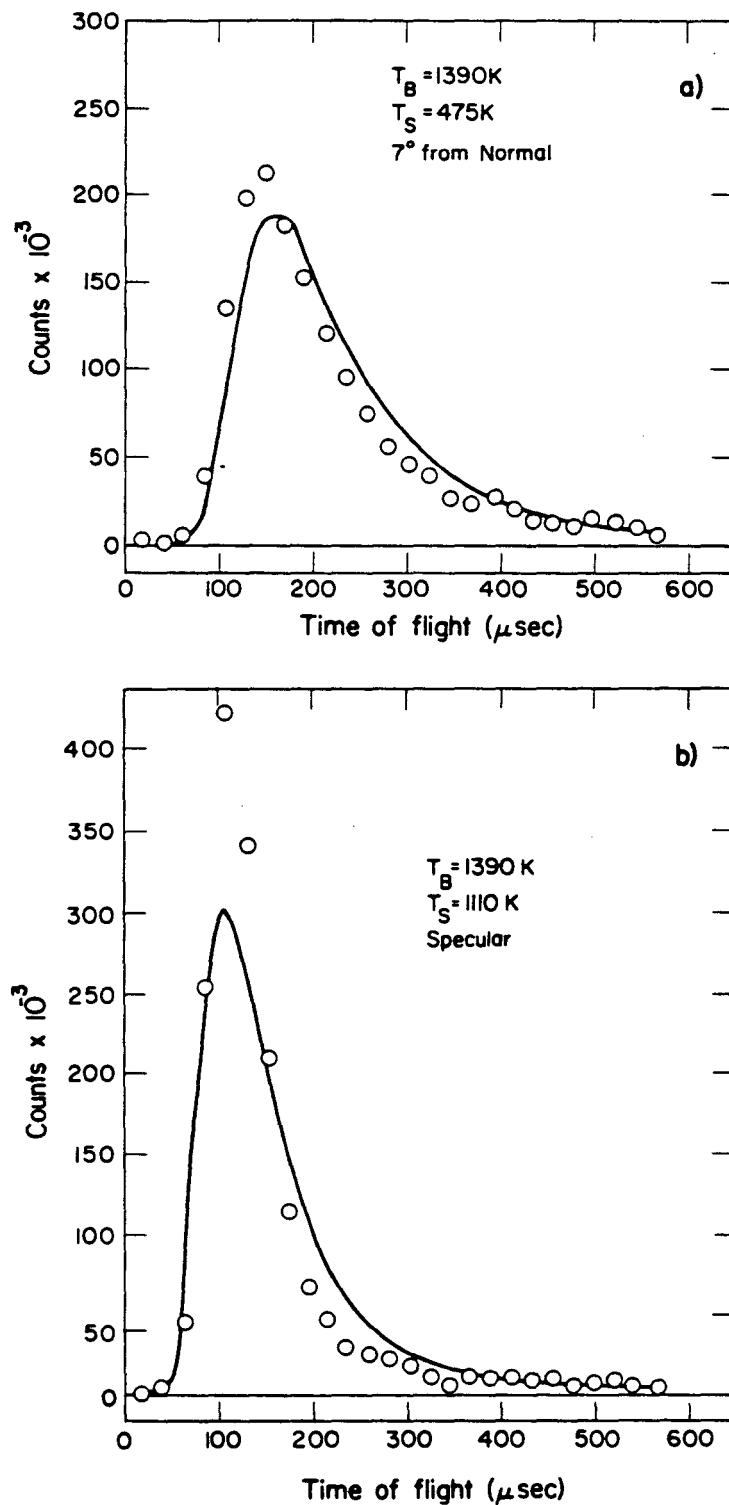
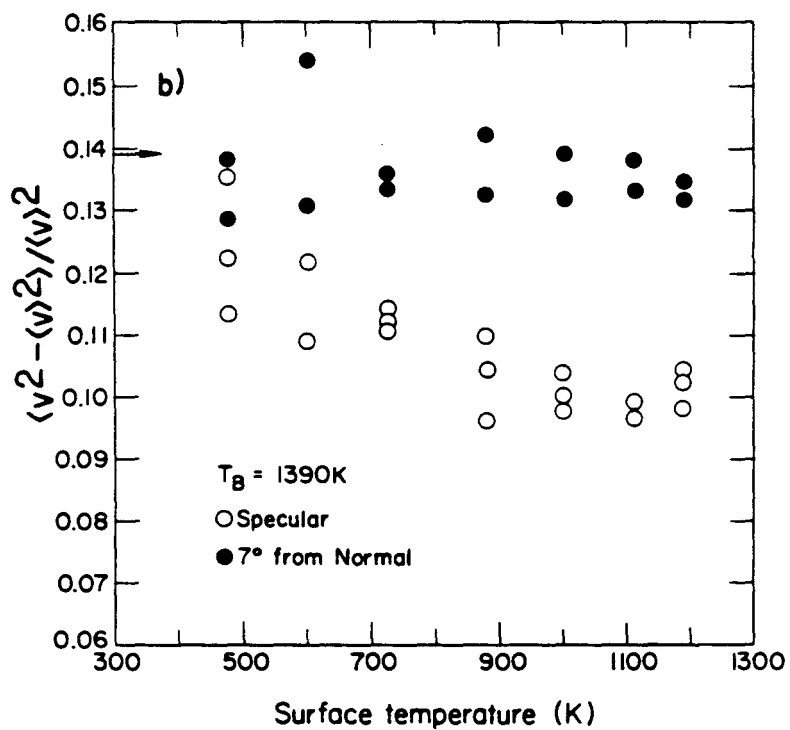
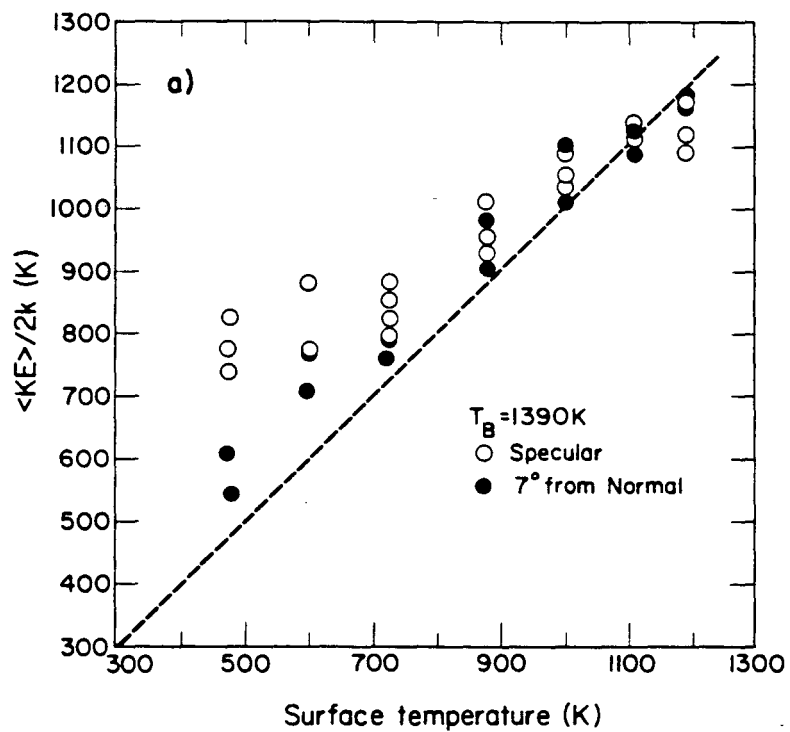


Figure 4.4: TOF distributions for $T_B=1390 K$ a.) $T_S=475 K$, $\theta=7^\circ$, b.) $T_S=1110 K$, $\theta=51^\circ$. The solid curves are the Maxwell-Boltzmann distributions at the crystal temperature.

far from equilibrium. It should be noted that the distribution is significantly broader than the incident beam distribution, figure 4.1, but peaks at only a somewhat lower velocity.

As in the case of the D₂O TOF distributions, the NO distributions have been summarized by calculating the mean kinetic energy $\langle K.E. \rangle$ in terms of an equivalent temperature $\langle K.E. \rangle / 2k$ and the relative distribution width $\langle v^2 - \langle v \rangle^2 \rangle / \langle v \rangle^2 = \langle \Delta v^2 \rangle / \langle v \rangle^2$. The mean kinetic energy and distribution width were calculated from the moments M_1 of the density TOF distributions as described in section 3.2.

Figure 4.5a shows the data for the mean energy of the NO flux scattered from the Pt(111) surface as a function of crystal temperature and as measured at two detector angles. The solid circles are the data for molecules scattered near the surface normal, the open circles are the data for molecules scattered to the specular angle (51°). The incident beam kinetic energy is 1390 K. The dotted line indicates the mean energy expected from a gas in equilibrium with the surface. Figure 4.5a shows that the mean energy of the specularly scattered molecules is greater than or equal to the mean energy of molecules scattered near the surface normal, and the energies of both distributions approach the equilibrium energy with increasing T_g . The relative width $\langle \Delta v^2 \rangle / \langle v \rangle^2$ of these distributions is plotted as figure 4.5b. The arrow on the left axis indicates the distribution width expected for molecules in equilibrium with the surface. Experimental broadening of the distributions makes the expected equilibrium width slightly larger than the theoretical value for a Maxwell-Boltzmann distribution, 0.132. Again the full circles are for scattering near the surface normal, the open circles for scattering at the specular angle. The distribution widths are greater for the molecules scattered near the



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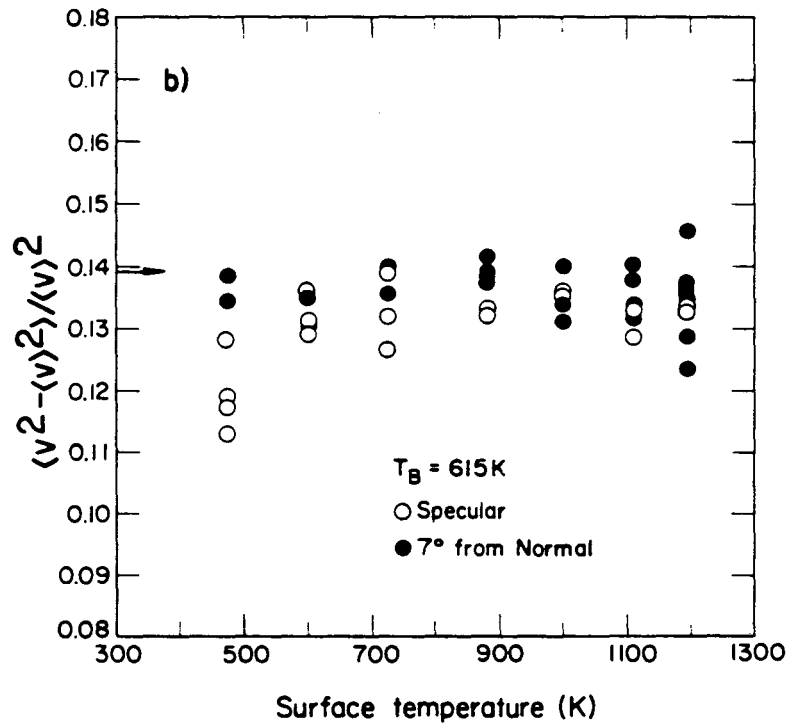
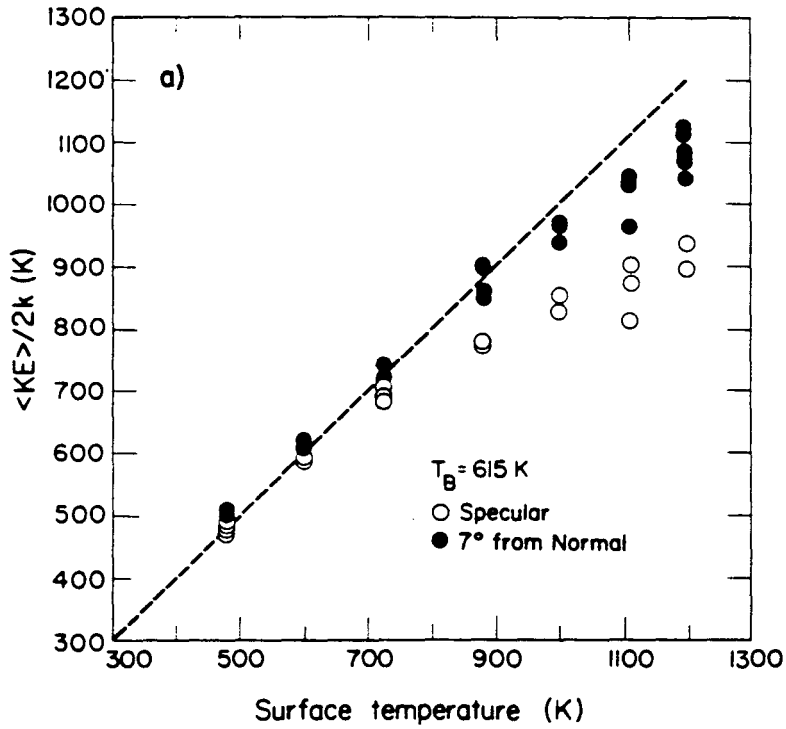
Figure 4.5: $T_B = 1390 K$ a.) Correlation of $\langle KE \rangle / 2k$ of the scattered beam with respect to surface temperature b.) correlation of $\langle \Delta v^2 \rangle / \langle v \rangle^2$.

normal than for those specularly scattered.

In interpreting the distributions through these parameters, it is necessary to consider the mean energy and the distribution width together since the mean energy may accidentally equal the equilibrium value due to the incident beam energy and or surface temperature; and the different scattering mechanisms present may make the widths of the distributions artificially large, as will be discussed below. Accommodation of the gas with the surface requires that both parameters have the equilibrium value.

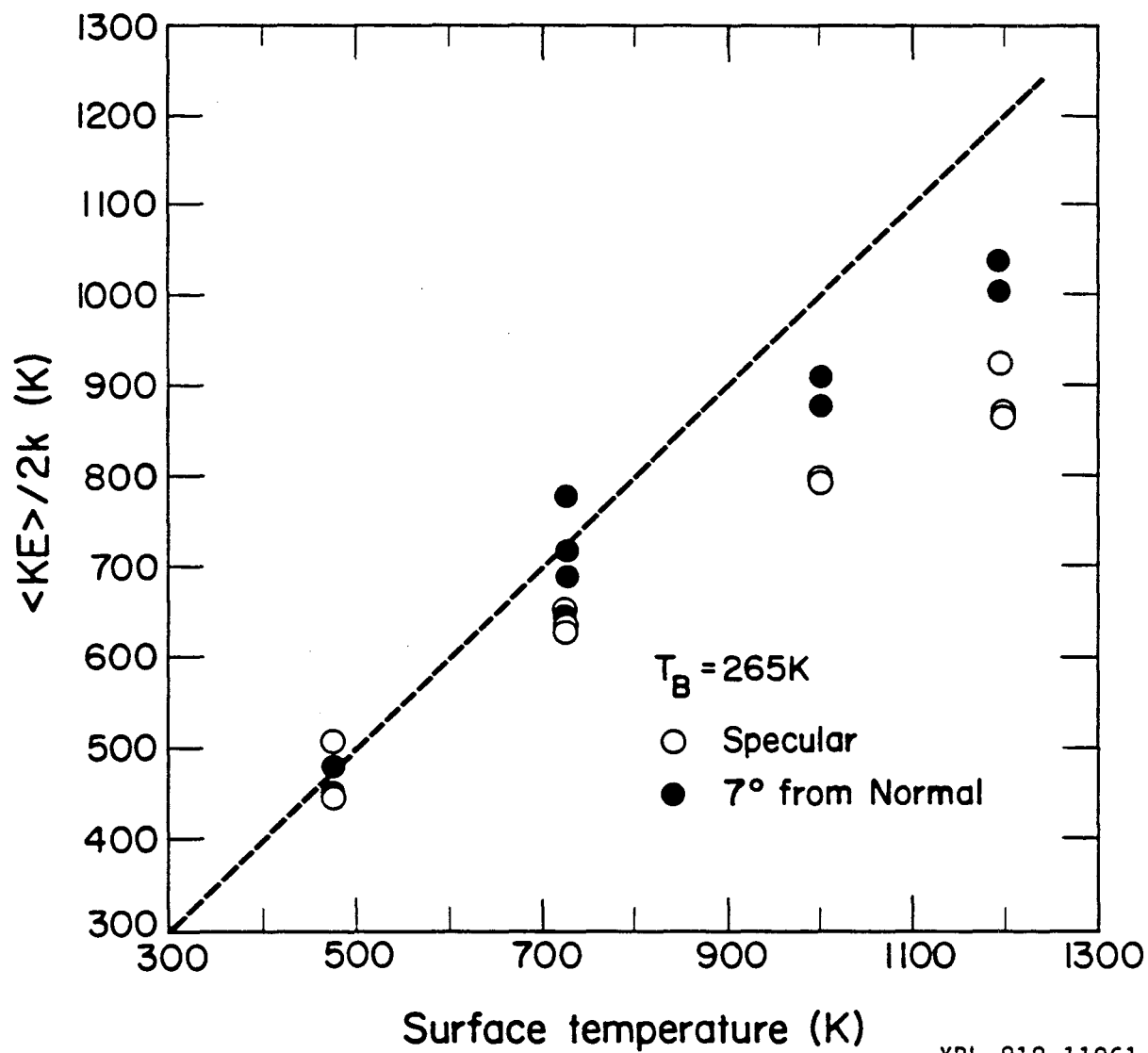
Figures 4.6a and b show data for the mean energy and relative distribution width of the scattered NO, but for a lower incident beam energy, $T_B=615$ K. It can be seen that the mean kinetic energy is equal to the equilibrium energy for temperatures below approximately 800 K, figure 4.6a. At higher temperatures the mean energy deviates from equilibrium to lower energy, but the molecules scattered at 7° remain more nearly accommodated than the molecules scattered at 51° . The distribution width, figure 4.6b is approximately equal to the equilibrium value, particularly for the molecules scattered at 7° . The distributions of the specularly scattered molecules are slightly narrower at lower temperatures than Maxwell-Boltzmann distributions. The difference in distribution width as a function of scattering angle is visually evident in figure 4.3a and b. The data shows accommodation of the gas to the surface at temperatures up to approximately 900 K. Deviations from equilibrium increase with temperature above 900 K.

The incident beam energy for the data shown in figure 4.7 is 265 K. The mean energy of the scattered molecules shows the same trend as a function of T_g as the mean energy observed for $T_B=615$ K, figure 4.6a. The scattered molecules have the equilibrium mean energy for crystal



XBL 8212-12168

Figure 4.6: $T_B = 615$ K a.) Correlation of $\langle KE \rangle / 2k$ of the scattered beam with respect to surface temperature b.) correlation of $\langle \Delta v^2 \rangle / \langle v \rangle^2$.



XBL 818-11061

Figure 4.7: Correlation of $\langle KE \rangle / 2k$ of the scattered beam with respect to the surface temperature. $T_b = 265 \text{ K}$.

temperatures below approximately 800 K. Above 800 K there is even less accommodation visible for the 265 K incident beam energy data than for the 615 K incident beam energy data. The value for the distribution width for this data is inconclusive due to larger statistical errors and is not shown. The statistical errors are larger because of the lower intensity of the Xe seeded NO beam.

The Pt sample used had minor problems from Ca contamination, and these problems were increased by the NO scattering experiments. It appears that the presence of NO on the Pt surface enhanced the surface segregation of Ca from the bulk of the platinum sample, particularly at the higher temperatures. Ca surface segregation was a consideration in the results reported here, and the experimental times had to be limited to decrease any possible effects. Initially clean Pt surfaces, as determined by Auger electron spectroscopy, would typically have 0.1 to 0.05 monolayer coverage of oxygen and calcium after 30 minutes of data collection at crystal temperatures of 1000 K or greater.

The correlation of the Ca and O coverage suggests that Ca segregation is due to the presence of oxygen supplied by the beam. It may be that the oxygen contamination results from impurities such as NO₂ or N₂O present in the NO gas [20]. To check this possibility we further purified the commercially available NO (Matheson 99.0%) by distillation from a bulb in an LN₂/n-pentane slush at 113K into a bulb in an LN₂ trap. The purified NO was determined to be 99.98% pure by gas chromatography. However, the rate of contamination of the Pt sample was unchanged using either the distilled or undistilled NO as the incident beam gas. It appears that a small amount of NO (<1%) dissociates on the Pt(111)

surface during scattering, and is the source of the surface oxygen.

Since at higher temperatures it was only possible to limit the extent of surface contamination, experiments were performed to examine the effect of Ca and O submonolayer coverages on the TOF distributions. Distributions were accumulated of NO scattered from the Pt(111) surface with pre-experimental coverages of Ca and O varying from 0.0 to approximately 0.5 monolayers. The TOF distributions were found to be independent of the surface coverage. Thus the energy transfer does not appear to be affected by the presence of small to considerable concentrations of these atoms.

4.2.2 Angular Distributions

The angular density distributions of NO scattered from the Pt(111) surface are shown in figures 4.8a, b and c for an incident beam energy of 1390 K. The crystal temperature was 475 K, 725 K and 1195 K respectively. For this data the He seeded NO beam originated in the primary beam source so that the detector moves in the plane of scattering and will detect any specular flux that might be present. The specular scattering angle is indicated by the arrow on the lower axis of the figures. The incident beam was modulated by the 150 Hz tuning fork chopper (Bulova L40C) to differentiate the scattered flux from background signal.

The angular distribution from the crystal at 475 K is broad and diffuse, and nearly matches a cosine function. At $T_s=725$ K, figure 4.8b, the angular distribution has become broader than a cosine function, and there is an indication from 40° to 65° of a specular peak in the distribution. The angular distribution of NO scattered from the surface at 1195 K, figure 4.8c, exhibits contributions of a broad diffuse distribu-

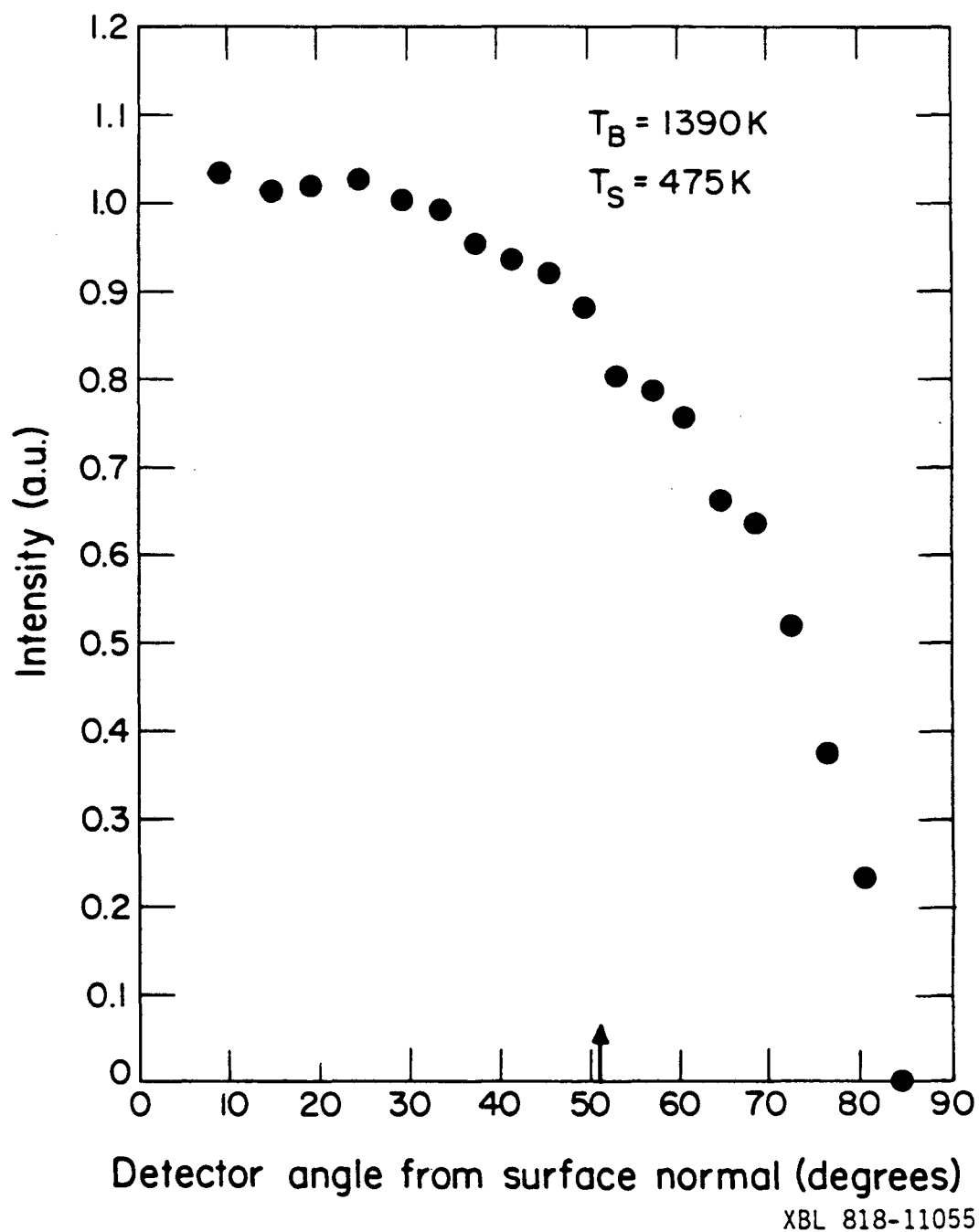
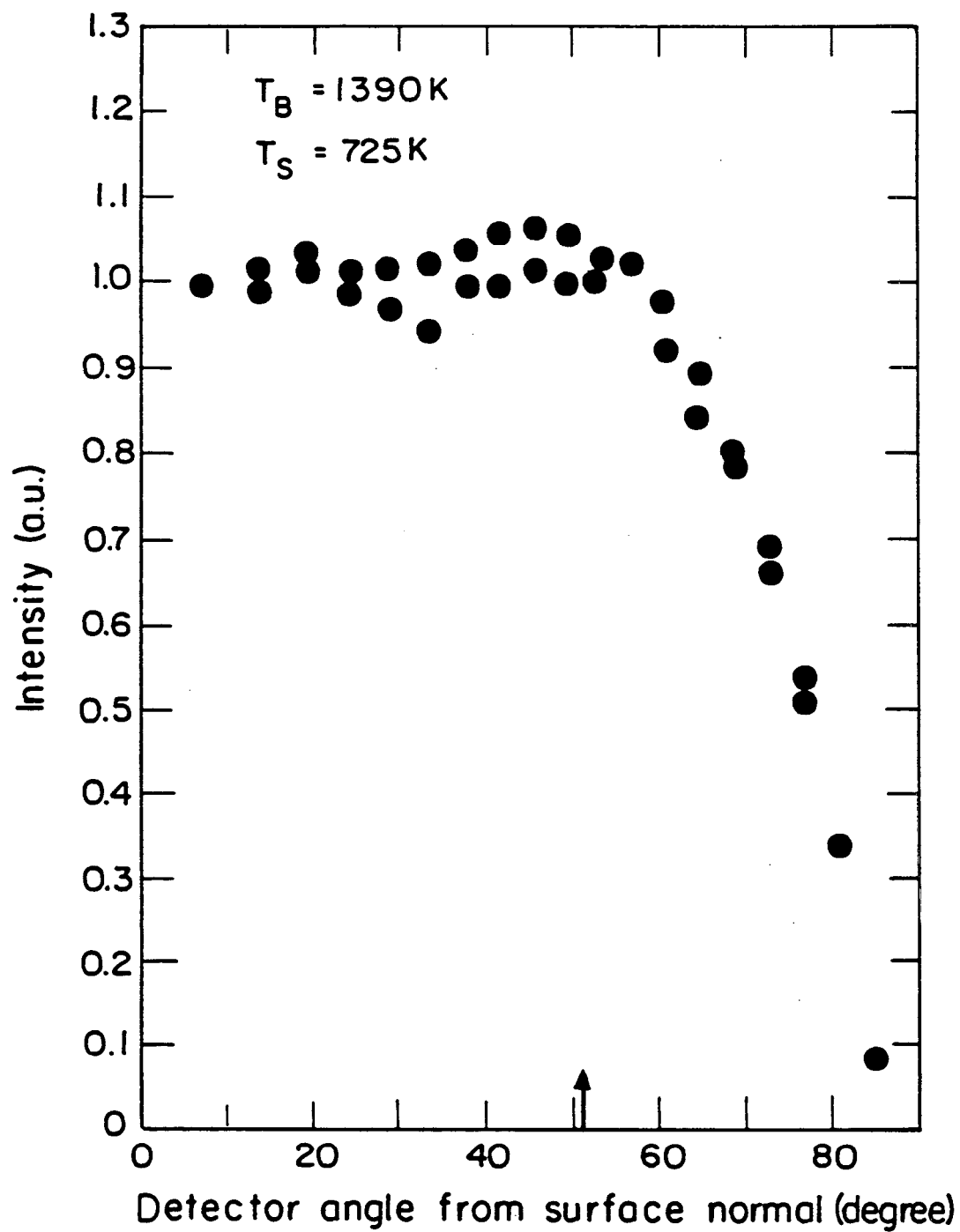


Figure 4.8a: Angular distribution of NO scattered from the Pt(111) surface.

The arrow indicates the specular angle. $T_B=1390\text{ K}$, $T_S=475\text{ K}$.



XBL 819-6598

Figure 4.8b: $T_B=1390\text{ K}$, $T_S=725\text{ K}$.

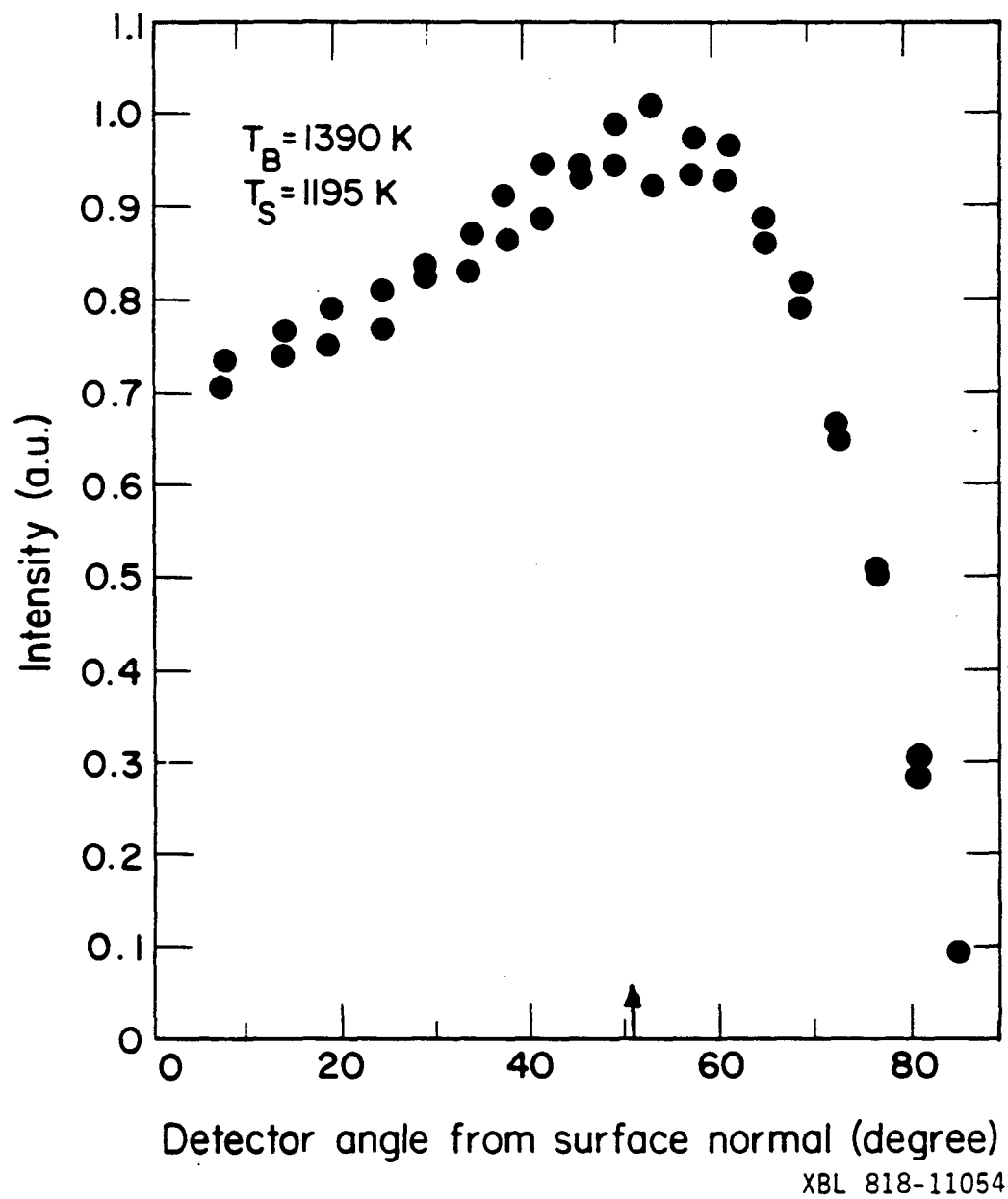


Figure 4.8c: $T_B=1390 \text{ K}$, $T_S=1195 \text{ K}$.

tion with an additional pronounced specular contribution. The specular feature can be seen to be broad in angle.

The angular data observed for an incident beam energy of 615 K is shown in figures 4.9a, b and c for crystal temperatures of 475 K, 725 K and 1195 K respectively. The angular data for an incident beam energy of 265 K is shown in figures 4.10a and b for crystal temperatures of 725 K and 1195 K respectively. The general trends observed are that the degree of specularity increases with increasing surface temperature, figures 4.8a, b and c, and with increasing incident beam energy, figures 4.10a, 4.9b and 4.8b. When the specular feature is absent the angular distribution of the scattered molecules can be approximated by a cosine function.

The changes in angular distribution could be due to changes in scattering behaviour, or to changes in surface roughness, since cosine angular distributions have been observed for He elastically scattered from roughened tungsten surfaces [2]. To separate the effect on the angular distribution of the gas-surface interaction from the effect of simple surface roughness we simultaneously measured the angular distribution of He scattered from the NO covered surface. The simultaneous angular distributions were done for the scattering of the He seeded NO beam since the helium angular distribution could be obtained by tuning the mass spectrometer from $m/e=30$ to $m/e=4$. Figure 4.11a shows the angular distribution of He scattered from a clean Pt(111) surface at a temperature of 880 K. The distribution peaks at the specular angle and is approximately 2° wide (FWHM), which is only slightly broader than the angular resolution of the detector. Figure 4.11b shows the angular distribution of He co-scattered with NO at a surface temperature of 725 K. The width of the angular distribution from the NO covered

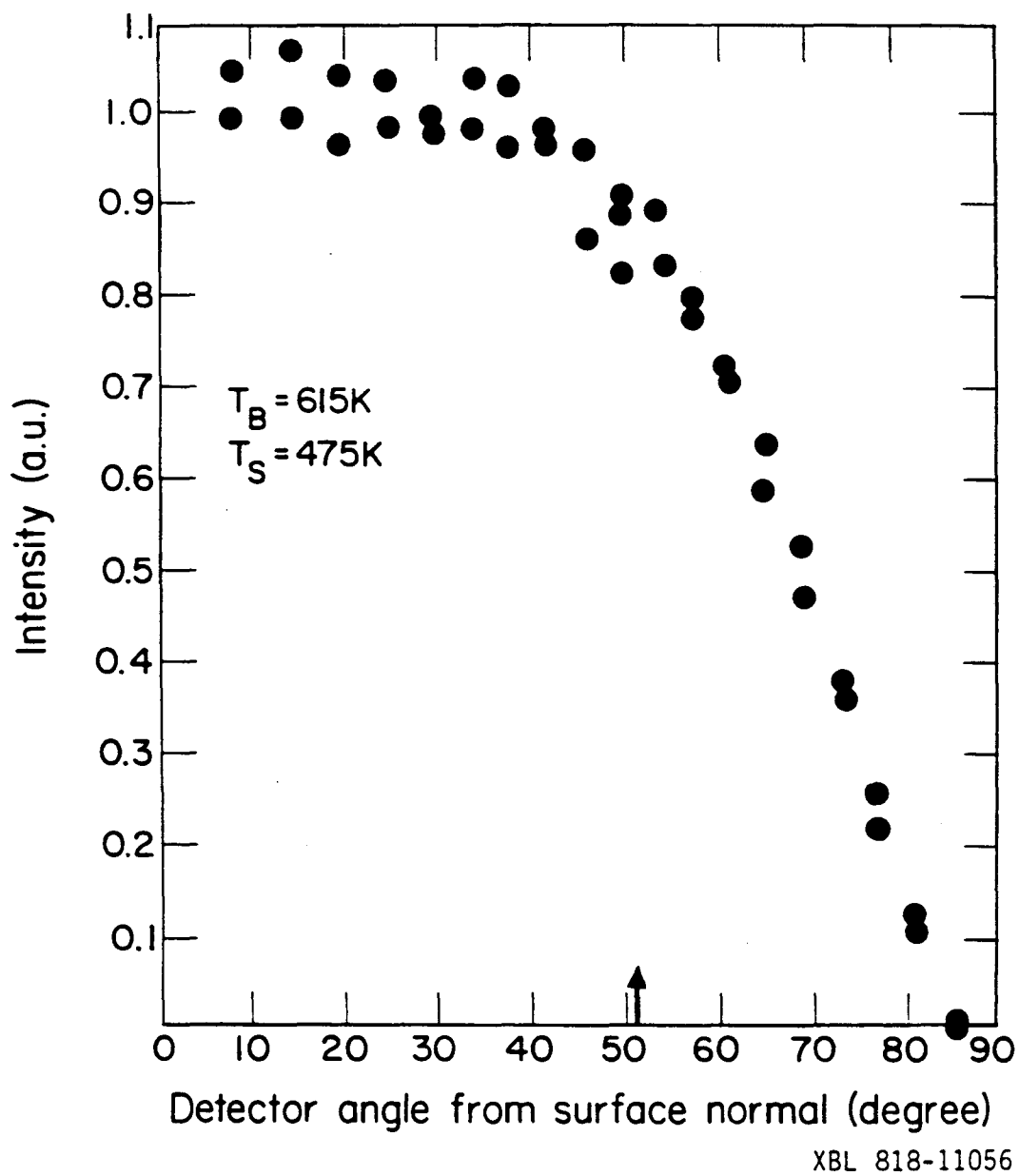


Figure 4.9a: Angular distribution of NO scattered from the Pt(111) surface.

The arrow indicates the specular angle. $T_B=615$ K, $T_S=475$ K.

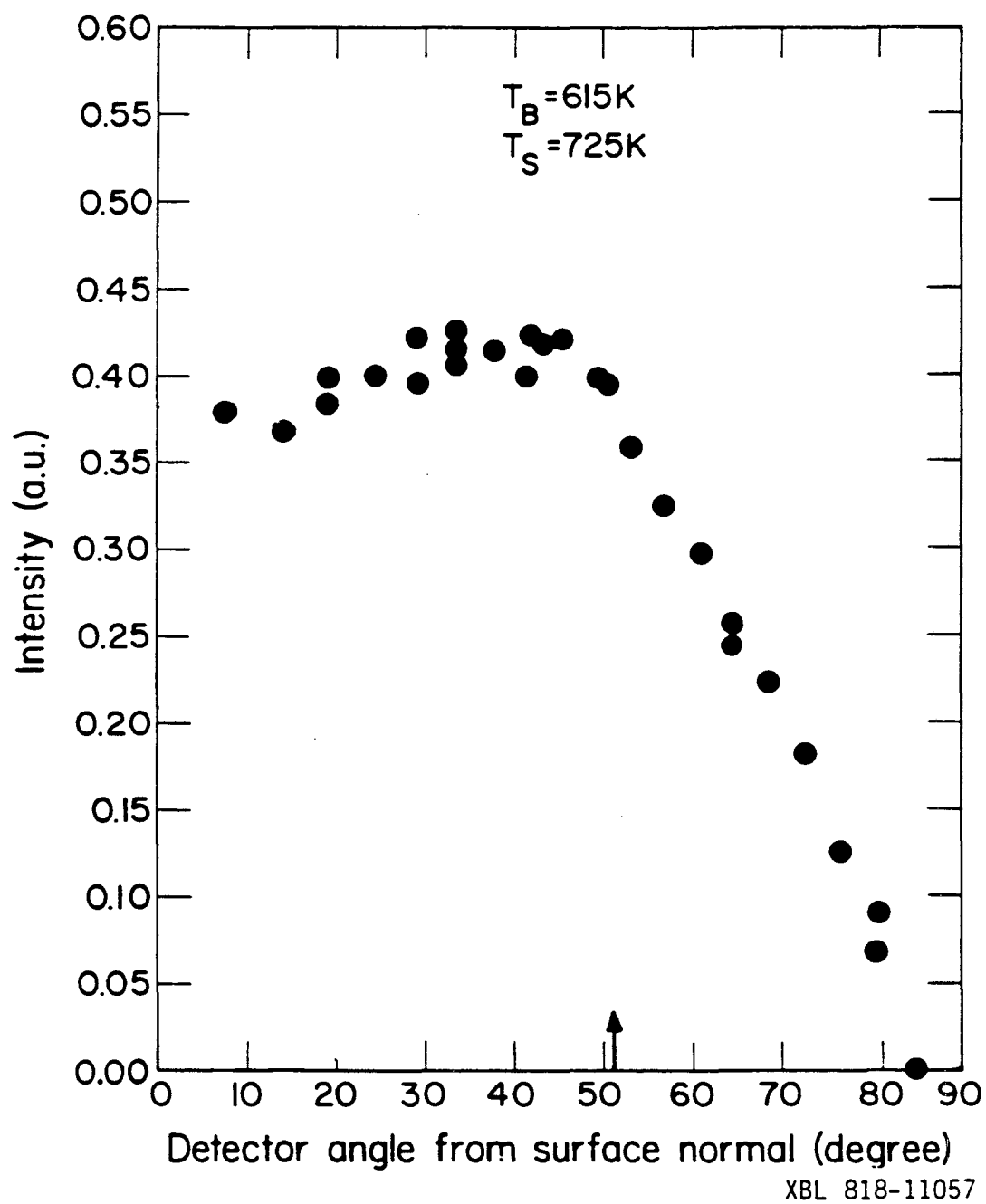


Figure 4.9b: $T_B=615$ K, $T_S=725$ K.

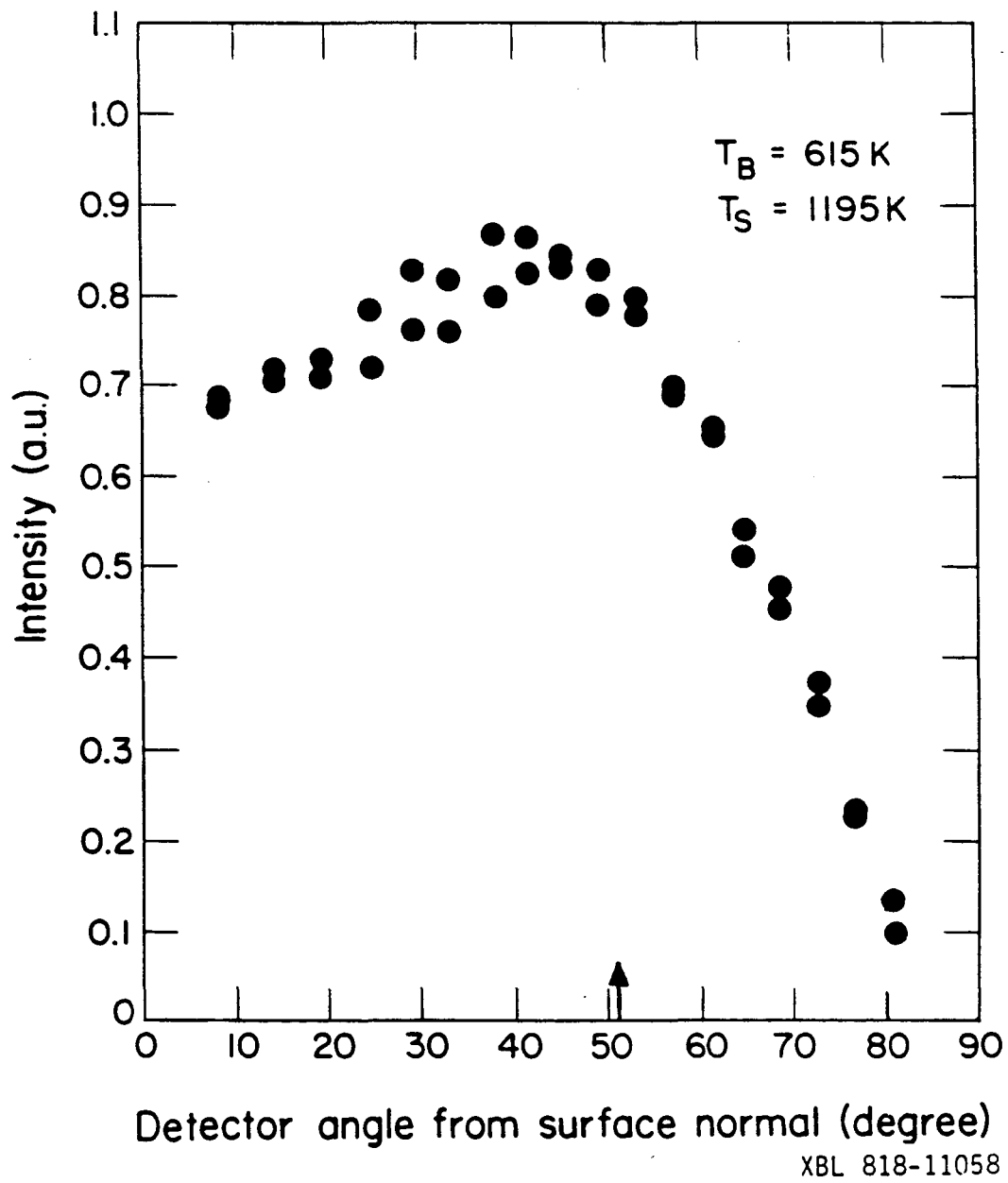


Figure 4.9c: $T_B=615 \text{ K}$, $T_S=1195 \text{ K}$.

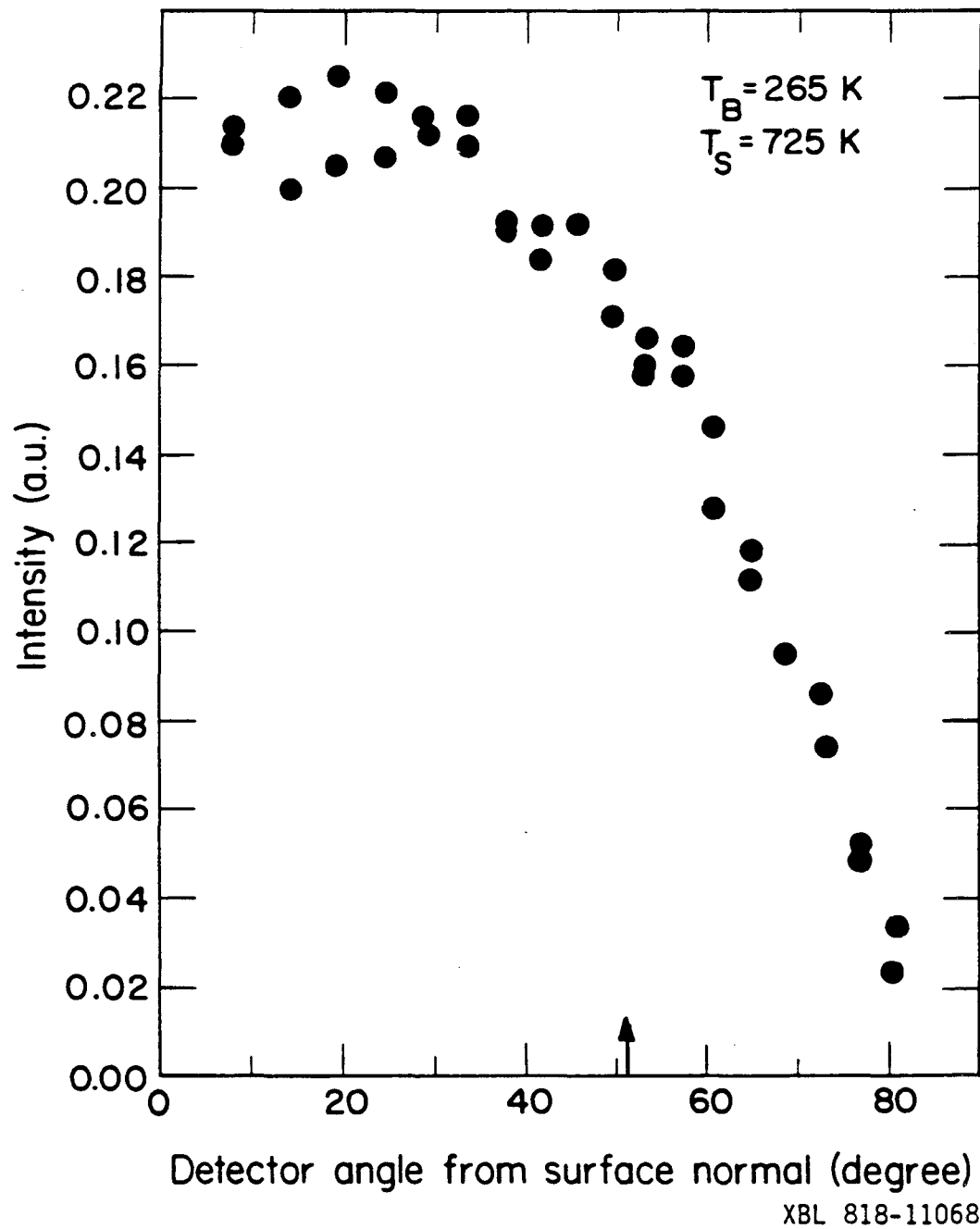


Figure 4.10a: Angular distribution of NO scattered from the Pt(111) surface.

The arrow indicates the specular angle. $T_B=265 \text{ K}$, $T_S=725 \text{ K}$.

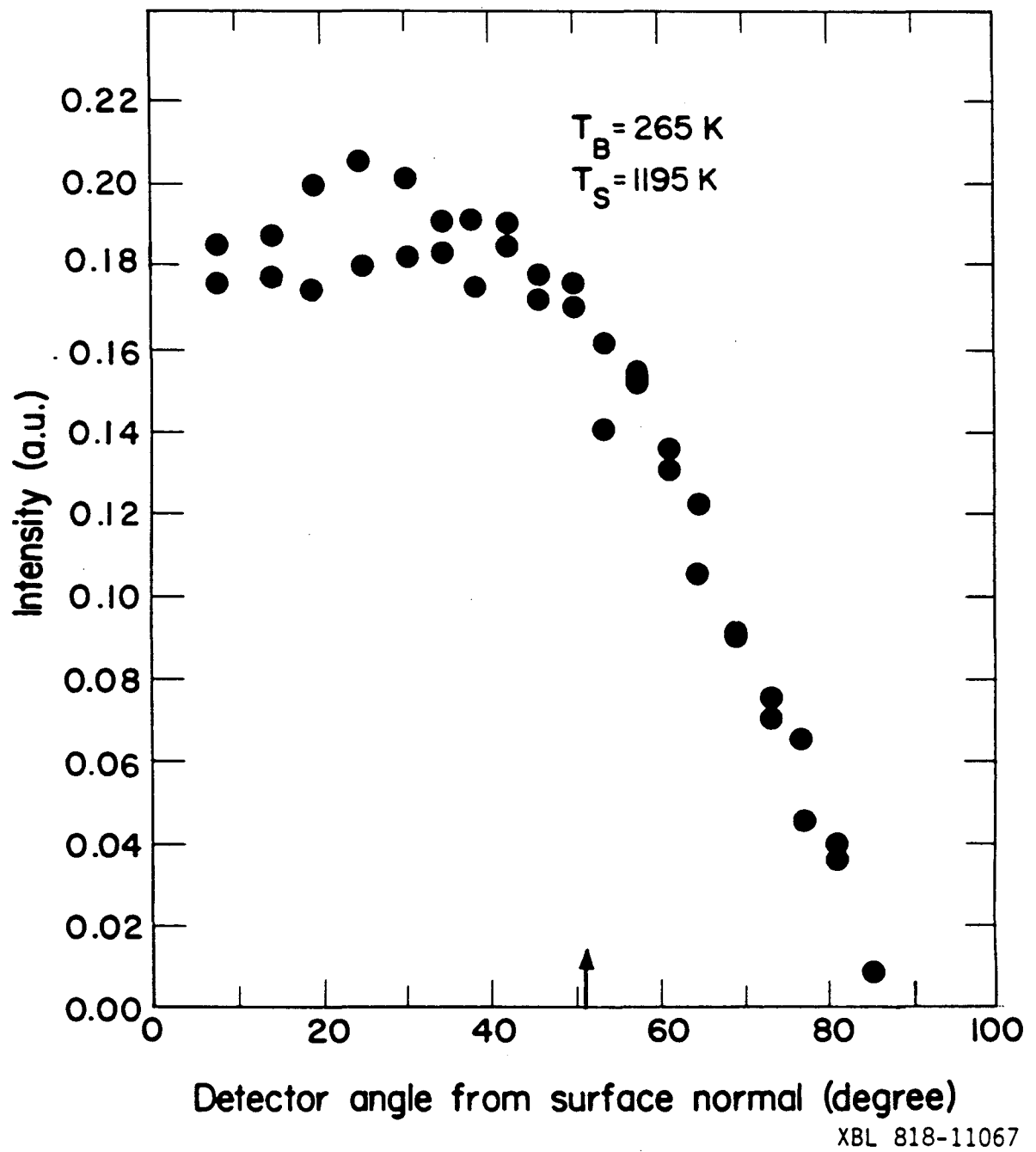
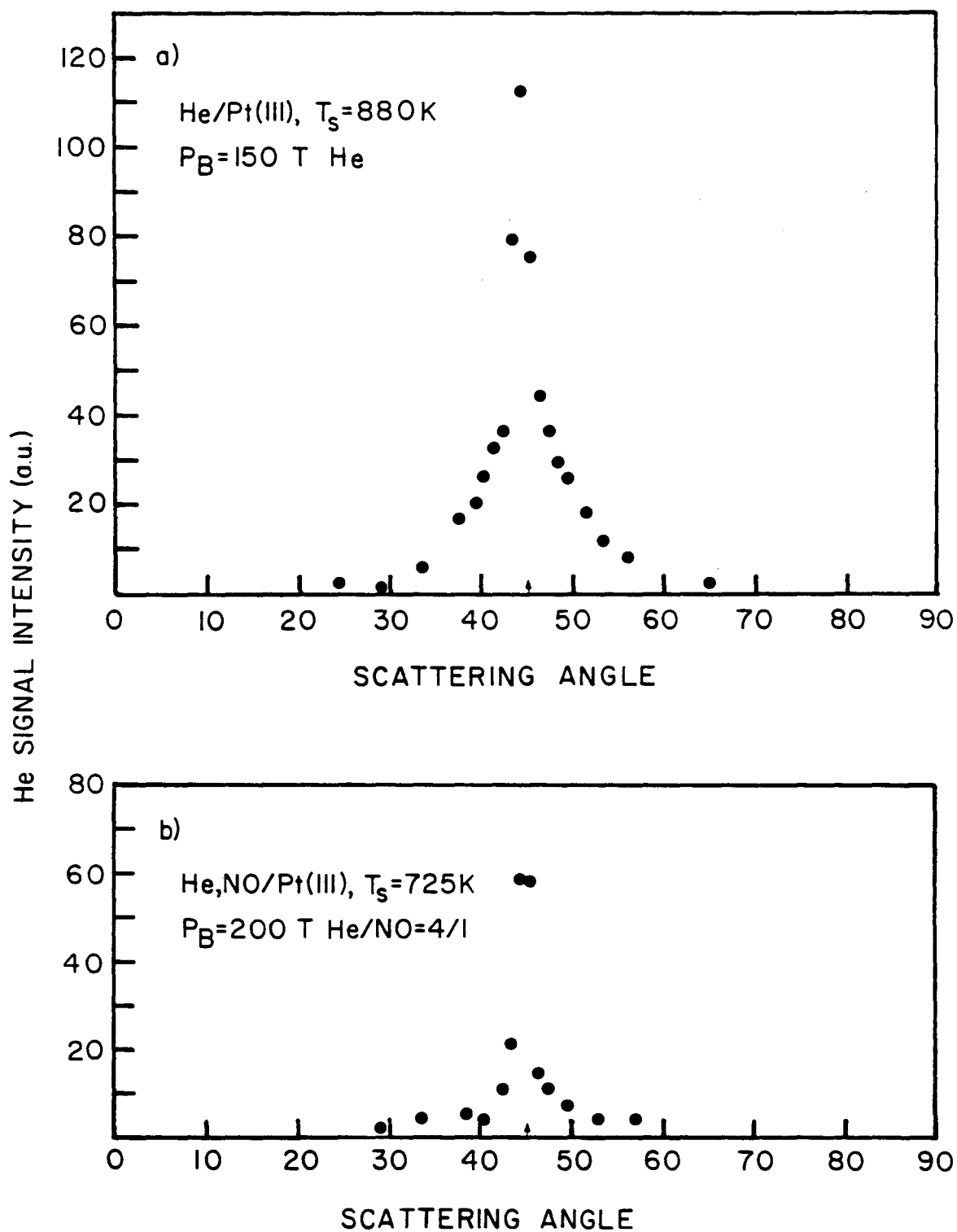


Figure 4.10b: $T_B=265 \text{ K}$, $T_S=1195 \text{ K}$.

surface is essentially equal to the width from the clean surface, however the intensity of the peak is lower due to a slight increase in surface roughness. The scales of the vertical axis of figure 4.11a and b are the same, but the flux incident on the surface will be somewhat lower for the data shown in figure 4.11b, so that the intensities can be only roughly compared. Angular distributions as a function of crystal temperature were measured for the co-scattered helium, and the maximum intensity of those angular distributions is plotted as a function of temperature in figure 4.12. The degree of surface roughness decreases with temperature to 880 K then increases again with increasing crystal temperature. This is probably caused by decreasing NO surface coverage with increasing temperature, but above 880 K the change in coverage is probably compensated by increasing thermal roughness from platinum atom motion.

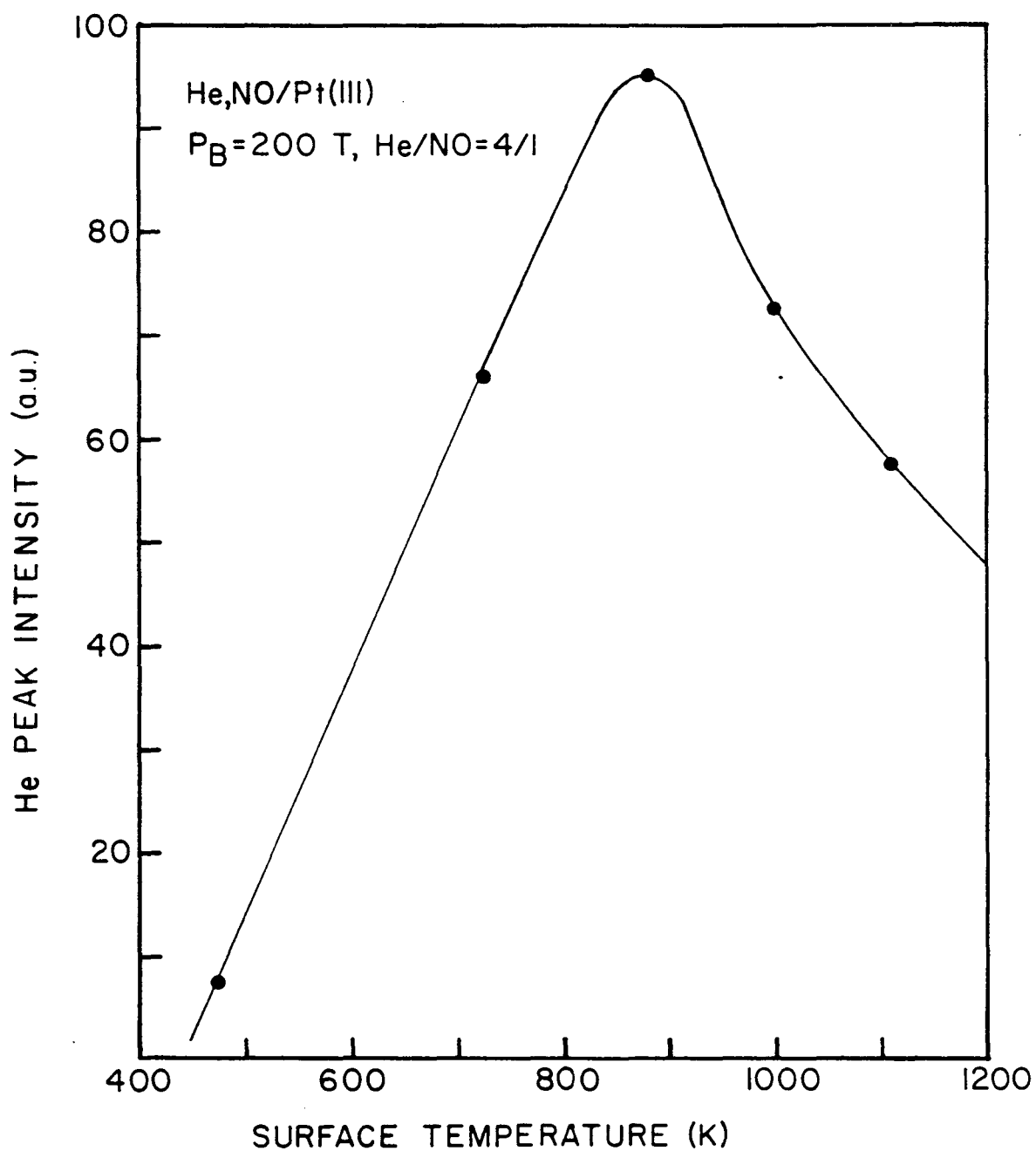
4.2.3 Rotational Energy Distributions

The two-photon ionization technique, which was used to measure the distribution of energy in internal states, and the apparatus were described in section 2.2. The rotational distributions reported here were all measured for the ground vibrational state $v''=0$. The UV laser was tuned across the resonant absorption lines of the transition $A^2\Sigma^+(v'=0, j')$ $\leftarrow X^2\Pi_{1/2}(v''=0, j'')$ at 226 nm. The transitions from the $\Pi_{3/2}$ state were examined as well, but were not used in the analysis. Typical NO ionization spectra for the $\Pi_{1/2}$ transition are shown again as figure 4.13. Figure 4.13a is the ionization spectra of the NO molecules of the incident supersonic beam, which have a rotational temperature of 45 K. Figure



XBL 8212-12092

Figure 4.11: Angular distributions of He scattered from the Pt(111) surface. a.) Clean Pt surface at $T_s = 880$ K. b.) NO covered surface (He co-scattered with NO) $T_s = 725$ K.



XBL 8212-12093

Figure 4.12: Intensity of the peak of the He angular scattering data as a function of crystal temperature. He co-scattered with NO from the Pt(111) surface.

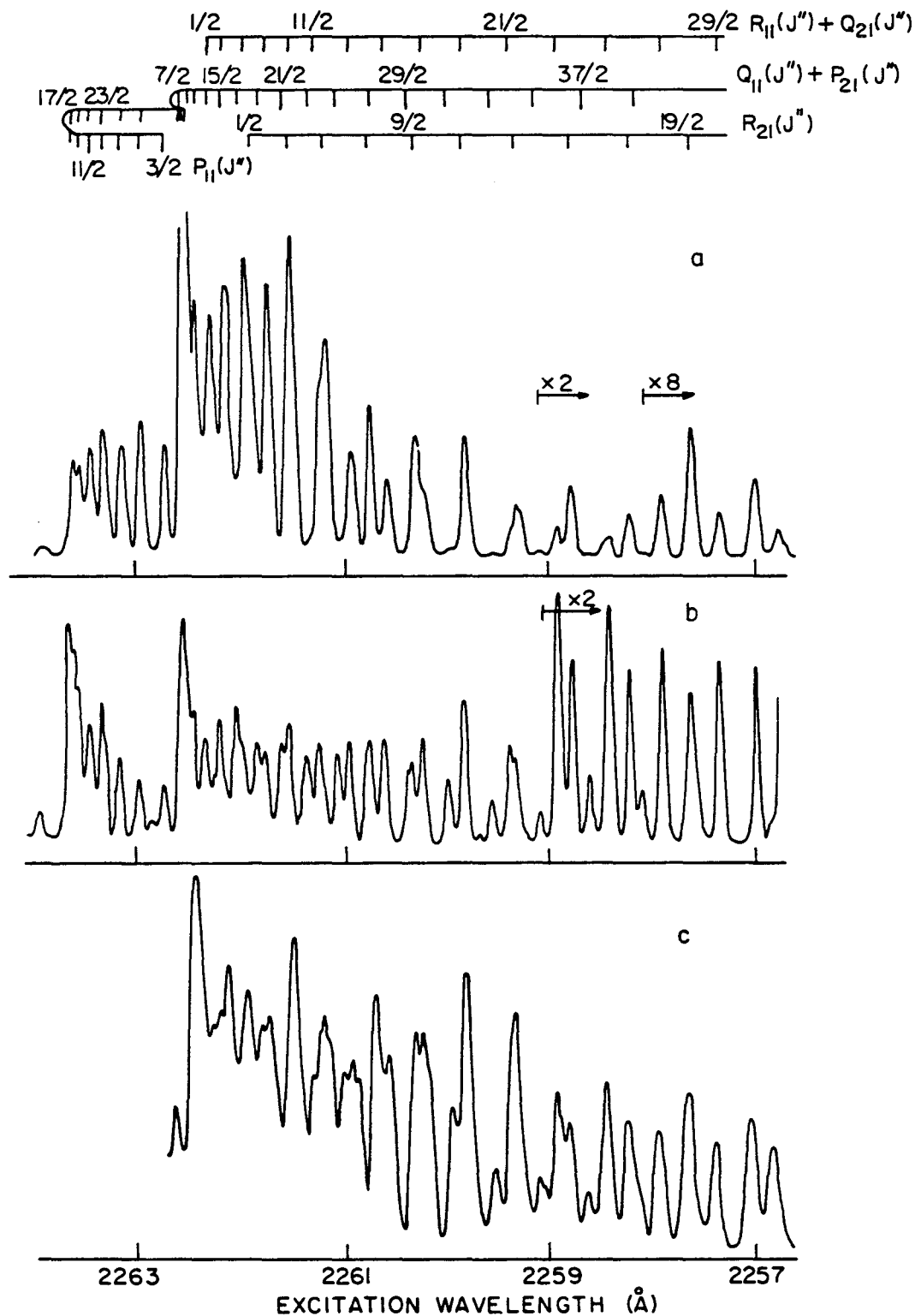
4.13b is the ionization spectra of room temperature NO gas at a pressure of 5×10^{-8} torr and figure 4.13c is the ionization spectra of NO molecules scattered from the Pt(111) surface at a temperature of 580 K. The initial rotational level j'' is assigned at the top of figure 4.13, based on values in the literature [21].

In the analysis, the intensity of each rotational line is measured and plotted as a function of rotational energy. In extracting a rotational temperature we are essentially describing the distribution by assuming a rotational energy distribution function (Boltzmann function) and fitting it to the experimental distribution to extract the parameter (temperature) that best describes the experimental results. Therefore the rotational temperature is not a temperature in the strict definition, but simply a parameter that describes the distribution. Such a description is valid as long as the rotational levels are in equilibrium with themselves, i.e. agree with a Boltzmann distribution. This was the case for most of the data, however the rotational distributions for scattering at surface temperatures higher than 800 K could not be described by a single rotational temperature (see Table 4.1).

Assuming a Boltzmann distribution for the rotational energy, the expression for the rotational line intensities N_j'' is

$$N_j'' = g_j'' S_j'' \exp(-E_j''/kT_R) \quad 4.1$$

where g_j'' is the rotational degeneracy, $g_j'' = 2j'' + 1$, S_j'' is the rotational line strength and E_j'' is the rotational energy. The rotational line strength is a correction factor that accounts for rotational dependencies in the excitation efficiency. If the resonant transition rate is slow relative to the ionization rate then the Honl-London factors are the



XBL 823-5393

Figure 4.13: Two-photon ionization spectra. a.) Incident supersonic NO beam. b.) Room temperature ambient NO gas, 5×10^{-8} torr. c.) NO molecules scattered from a Pt(111) surface at 580 K.

appropriate line strength factors for equation 4.1. However the calculation for the excitation rates, section 2.2.2, indicate that the resonant transition rate is orders of magnitude greater than the ionization rate, so that the resonant transition will be saturated. In saturation the relative excitation efficiency will be directly proportional to the relative number of molecules in saturation in the upper electronic state, which will depend on the ratio of the degeneracies of the excited and initial states, $(2j'+1)/(2j''+1)$. This factor is equal to one in the Q branch, and is essentially unity for the rotational levels used in the P and R branches, since we cannot resolve and did not use the transitions from the lower rotational levels. Here it is assumed that the ionization rate is independent of the rotational level of the excited Σ state. In addition to the calculation, there is sufficient experimental evidence of saturation. Saturation of the resonant transition has been observed in other laboratories [52] at much lower power densities than those here, and the assumption of saturation yielded the most consistent analysis of ambient room temperature NO rotational distributions, figure 4.13b. Using $S_j''=1$ (equation 4.2) in the analysis of the room temperature distribution yielded a rotational temperature of 290 ± 20 K. However using Honl-London factors gave a rotational temperature significantly less than room temperature 230 ± 20 K. In addition we see power induced broadening of the absorption lines which we attribute to saturation broadening. The spectral resolution decreases from 1.5 cm^{-1} at $25 \text{ } \mu\text{J/pulse}$, which is approximately the laser resolution, to 2.0 cm^{-1} at $150 \text{ } \mu\text{J/pulse}$ and above.

Using unity rotational line strength in equation 4.1, taking the logarithm and rearranging the terms gives

$$\ln(N_j''/(2j''+1)) = E_j''/kT_R + C \quad 4.2$$

where C is a proportionality constant. The rotational temperature can be directly extracted from the slope of a plot of the logarithm of the normalized line intensities versus the rotational energy. Such a plot for two typical rotational energy distributions is shown in figure 4.14. The figure shows the data for the rotational distributions observed for NO scattered from the Pt(111) surface at a temperature of 580 K. The NO beam was incident on the crystal at an angle of 62° and had a translational energy of 0.1 eV ($T_P=615$ K). The solid circles are the data observed for molecules scattered in the direction of the surface normal, the open circles are the data for molecules scattered at the specular angle (62°). As indicated in figure 4.14 the rotational temperature of the scattered NO is 400 ± 40 K and 480 ± 45 K for the molecules scattered at 0° and 62° respectively. The angular dependence to the rotational temperature was greater than the experimental error and was reproducible. Since the higher rotational temperature was found for molecules scattered into the specular direction, it was assumed that the rotational temperature at specular would depend on the translational energy of the incident beam. However doubling the incident translational energy to 0.24 eV (by He seeding) gave the same rotational temperature for the specularly scattered molecules (465 ± 45 K).

The rotational distributions are summarized in table 4.1 along with the experimental conditions. Table 4.1 shows that the rotational temperature is a weak function of crystal temperature and that the rotational distribution is in general not in equilibrium with the surface. The dependence of rotational temperature on scattering angle, and lack of dependence on incident translational energy is also indicated in the

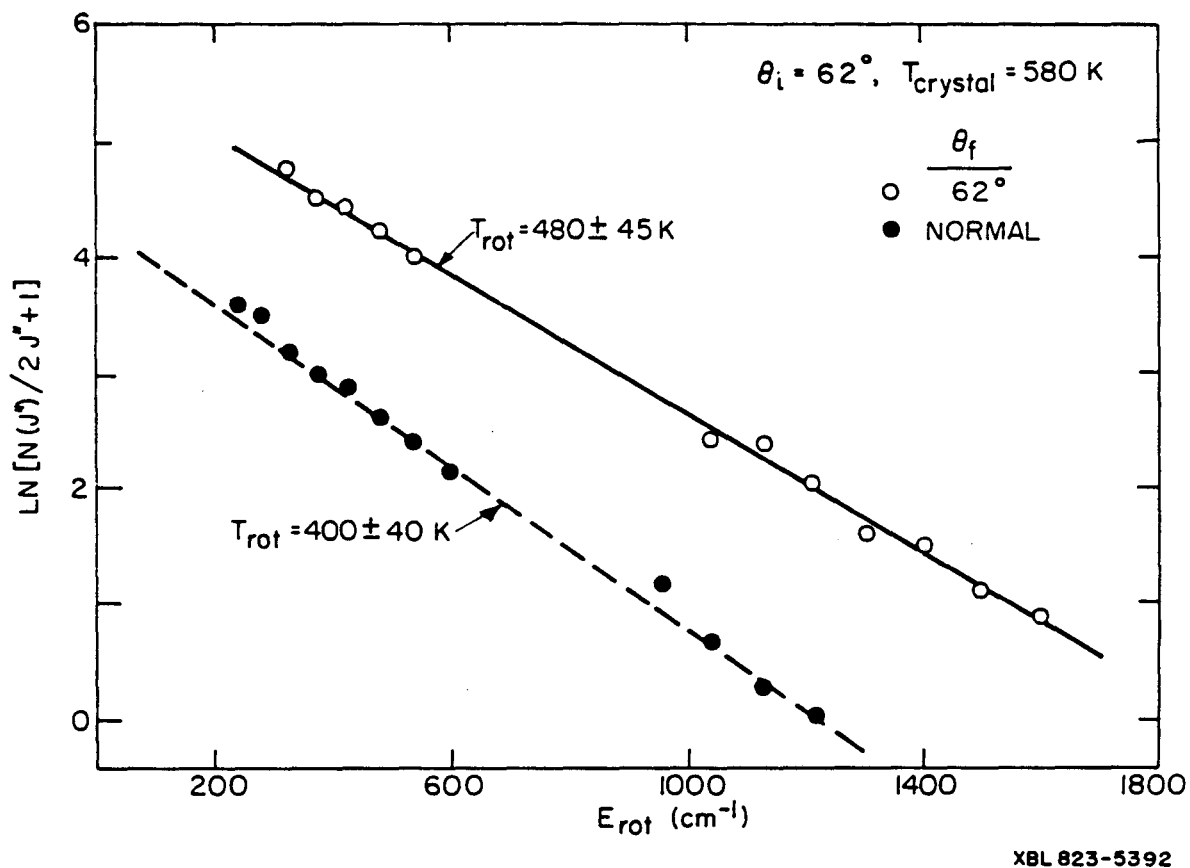


Figure 4.14: Rotational distribution analysis. $\text{LN}[N_j/(2j+1)]$ versus rotational energy. Data are for $T_s=580 \text{ K}$. Open circles are data observed for molecules scattered at 62° , closed circles for molecules scattered at 0° .

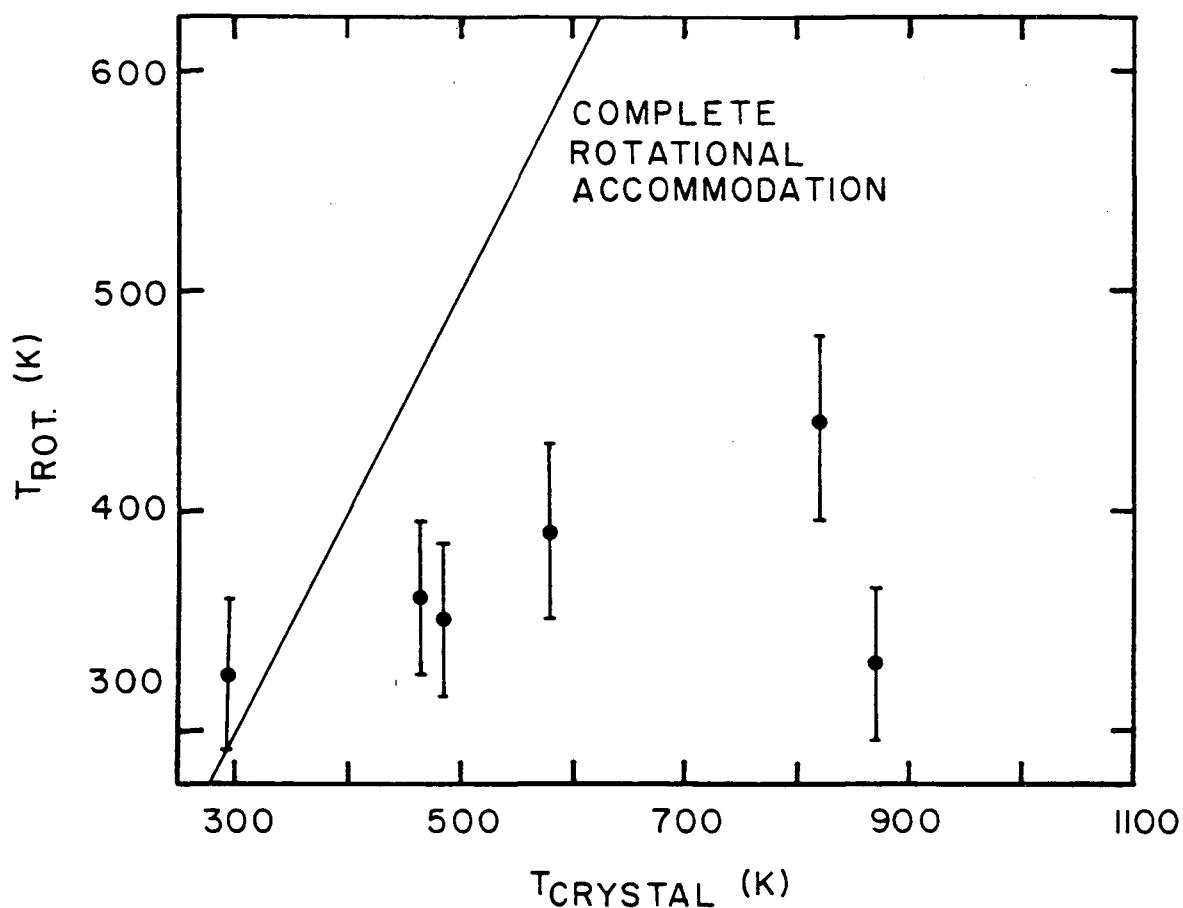
Table 4.1: Rotational Temperature (T_{rot}) at Various Crystal Temperatures

T_{crystal} (K)	T_{rot} (K)	Comments
295	325 ± 30	scattering from an overlayer of NO
465	360 ± 35	detector at normal to the surface
485	350 ± 35	detector at normal to the surface
580	390 ± 45	detector at normal to the surface
580	470 ± 45	detector at the specular angle (62°)
580	465 ± 45	He/NO 4:1 seeded beam, detector at specular angle
820	440 ± 45	detector at normal to the surface
870, $j'' < 18 \frac{1}{2}$	330 ± 35	detector at normal to the surface
870, $j'' > 23 \frac{1}{2}$	580 ± 60	detector at normal to the surface

data for a surface temperature of 580 K. Finally the distribution observed for a surface temperature of 870 K could not be described by one rotational temperature, indicating that the rotational states were not in equilibrium with themselves. The data for the rotational temperature of the NO molecules scattered into the direction of the surface normal is plotted as a function of crystal temperature in figure 4.15. The high temperature point at 870 K is the rotational temperature for the low j'' states of the distribution and is somewhat misleading since that distribution can not be adequately described by a rotational temperature. The solid line indicates the rotational temperature for rotational accommodation with the surface.

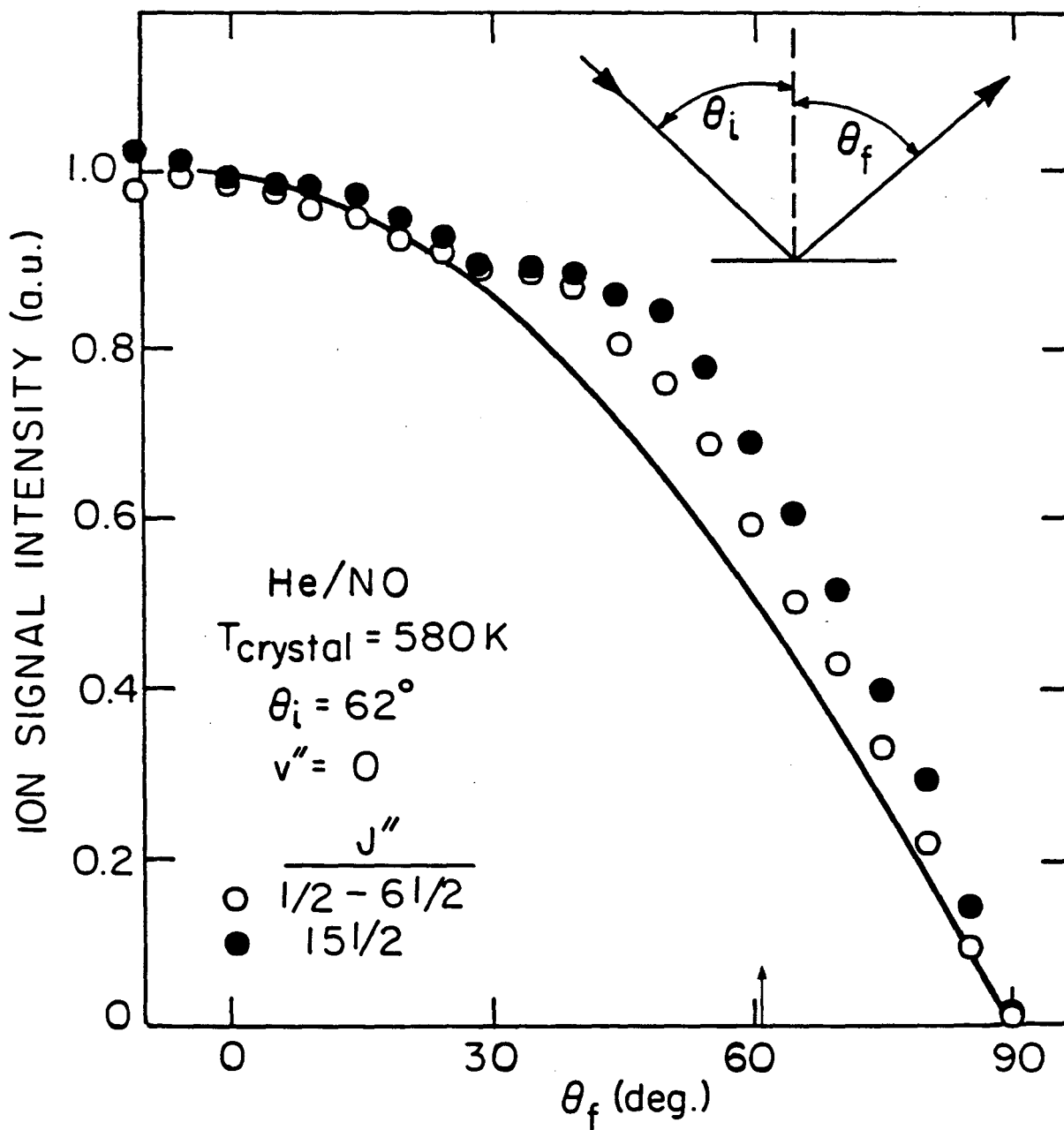
The angular distributions of NO molecules in two different final rotational states are shown in figure 4.16. The temperature of the Pt(111) crystal was 580 K, the angle of the incident beam was 62° as indicated on the lower axis of the figure, and the incident beam translational energy was 615 K. The open circles are the data for scattered molecules in the band head of the $Q_{11}+P_{21}$ branch at 226.26 nm. This band head contains rotational states $j''=1/2$ to $6\ 1/2$. The filled circles are the angular distribution for scattered molecules in the $j''=15\ 1/2$ state measured at the $15\ 1/2$ line of the R_{11} branch (226.08 nm). The angular distributions are dominated by a diffuse cosine distribution with slight increases in flux near the specular angle. The specular enhancement is more pronounced in the angular distribution of molecules in the $15\ 1/2$ rotational level, which is consistent with the different rotational temperatures observed at the normal and specular scattering angles,

Table 4.1



XBL 8212-12095

Figure 4.15: Rotational temperature as a function of crystal temperature observed for molecules scattered at 0° . The solid line indicates the rotational temperature corresponding to equilibration at the crystal temperature.



XBL 827-6042

Figure 4.16: Angular distribution of NO molecules scattered from the Pt(111) surface. Open circles are the angular distribution of molecules in the $j''=1/2 - 6 1/2$ rotational states, $v''=0$. Solid circles are the angular distribution observed for molecules in the $j''=15 1/2$ state, $v''=0$. $T_s=580 \text{ K}$, the beam energy is 0.11 eV (615 K).

4.2.4 Vibrational Energy Distributions

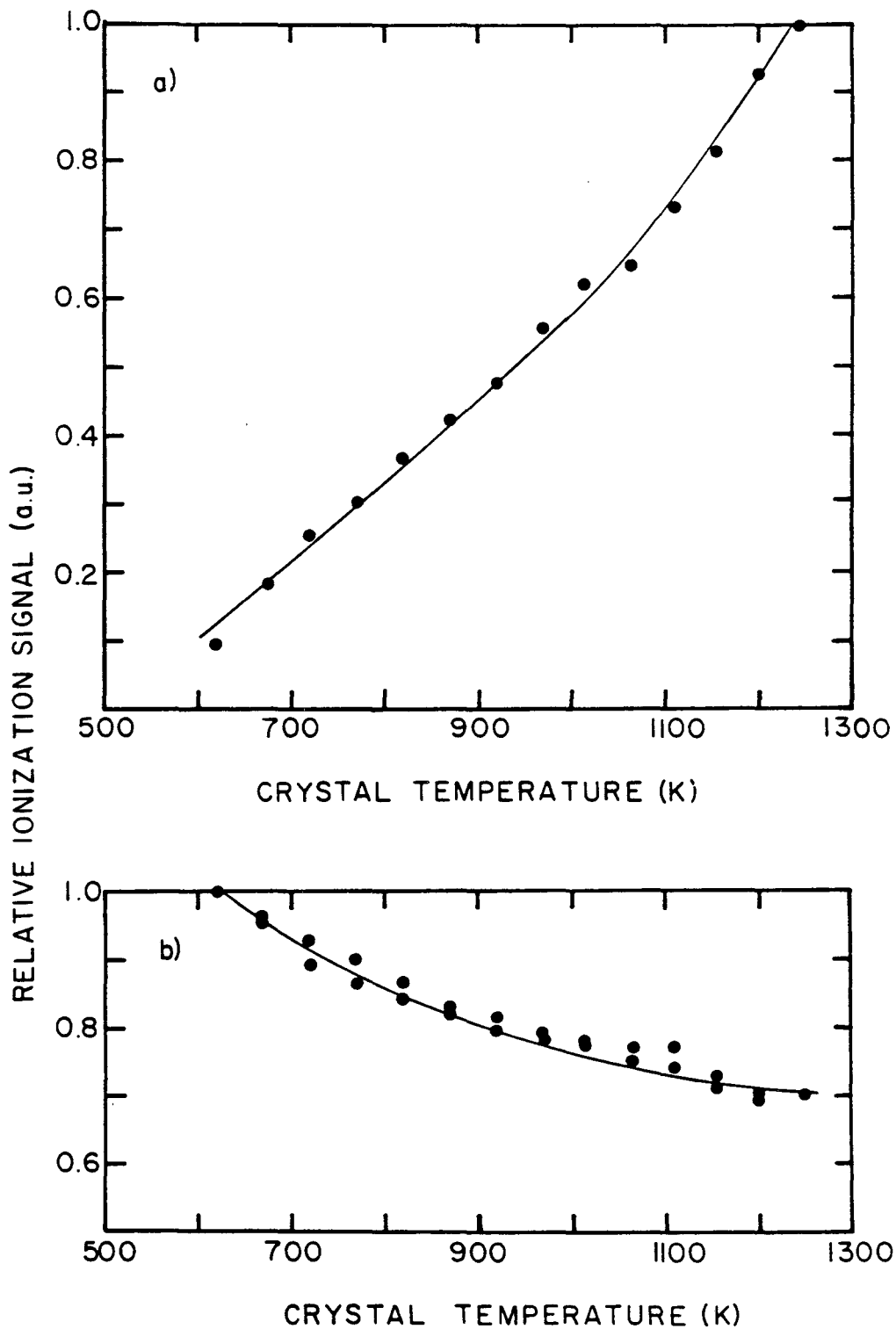
The population of molecules in the vibrationally excited $v''=1$ state was measured through the $A^2\Sigma^+(v''=0) \leftarrow X^2\Pi_{1/2}(v''=1)$ transition at ~ 236 nm. The $\Sigma(v''=1) \leftarrow \Pi(v''=1)$ transition could also be used for this purpose, but the absorption lines in that transition overlap the high j'' states of the $\Sigma(v'=0) \leftarrow \Pi(v''=0)$ transition, whereas the $\Sigma(v'=0) \leftarrow \Pi(v''=1)$ transition is free of interference from other vibrational manifolds.

Ideally one should measure the intensity of each rotational line in the $v''=1$ manifold and sum the intensities of the lines to calculate the number of molecules in the $v''=1$ vibrational state, but this approach is impractical given the low intensities of the $v''=1$ absorption lines. Instead the population measurements were based on the intensity of the $Q_{11}+P_{21}$ band head. This approximation is justified since the band heads are usually relatively insensitive to rotational temperature [22]. Also we have determined above that the rotational distribution is not very dependent on crystal temperature in the $v''=0$ manifold, and a rough measurement of the rotational temperature in the $v''=1$ manifold indicated that the rotational temperatures were similar for the two vibrational states.

In measuring the ratio of scattered molecules in the first excited vibrational state to those in the ground vibrational state, the incident angle of the NO beam was 62° with a translational energy of 0.11 eV ($T_B=615$ K). The scattered molecules were observed at the angle of the surface normal. The relative number of scattered molecules in the $v''=1$ vibrational state was measured as a function of crystal temperature by

tuning the laser to the peak of the $Q_{11}+P_{21}$ band head ($v''=1$) and recording the signal intensity as the crystal temperature was varied. The data for the relative population of the first excited vibrational state is shown in figure 4.17a. The dye laser dye was changed and the UV laser tuned to the peak of the $Q_{11}+P_{21}$ band head ($v''=0$). The relative number of molecules in the ground vibrational state as a function of crystal temperature is shown in figure 4.17b. The decline in the number of ground state molecules with increasing temperature is partly due to excitation to the first vibrational state and to excitation to higher rotational levels of the ground vibrational state. However the biggest factor will be the change in the angular distribution of the scattered molecules (figure 4.9).

The ratio of the curves for the relative populations of ground state and vibrationally excited molecules gives the vibrational population ratio of the scattered molecules as a function of temperature, to within a multiplicative constant. An exact ratio can not be determined directly since different detector sensitivities were used to measure the two states, and there will be different, and unknown, excitation efficiencies for the two transitions. However an exact measurement of the population ratio at one temperature is all that is needed to scale the data over the entire temperature range. We devised the technique described below to measure the population ratio at four crystal temperatures, $T_g=620, 820, 990$ and 1155 K. The data for the relative ratio were fit to these points to determine the exact population ratio over the temperature range of $400-1200$ K, shown in figure 4.18. The crosses are the data for the ratio of the population of the $v''=0$ state and $v''=1$ state. The circles are the relative number of molecules in the $v''=0$ state, i.e. the same data



XBL 8212-12094

Figure 4.17: Relative number of molecules observed in the $v''=1$ and $v''=0$ vibrational states as a function of crystal temperature. a.) $v''=1$, b.) $v''=0$.

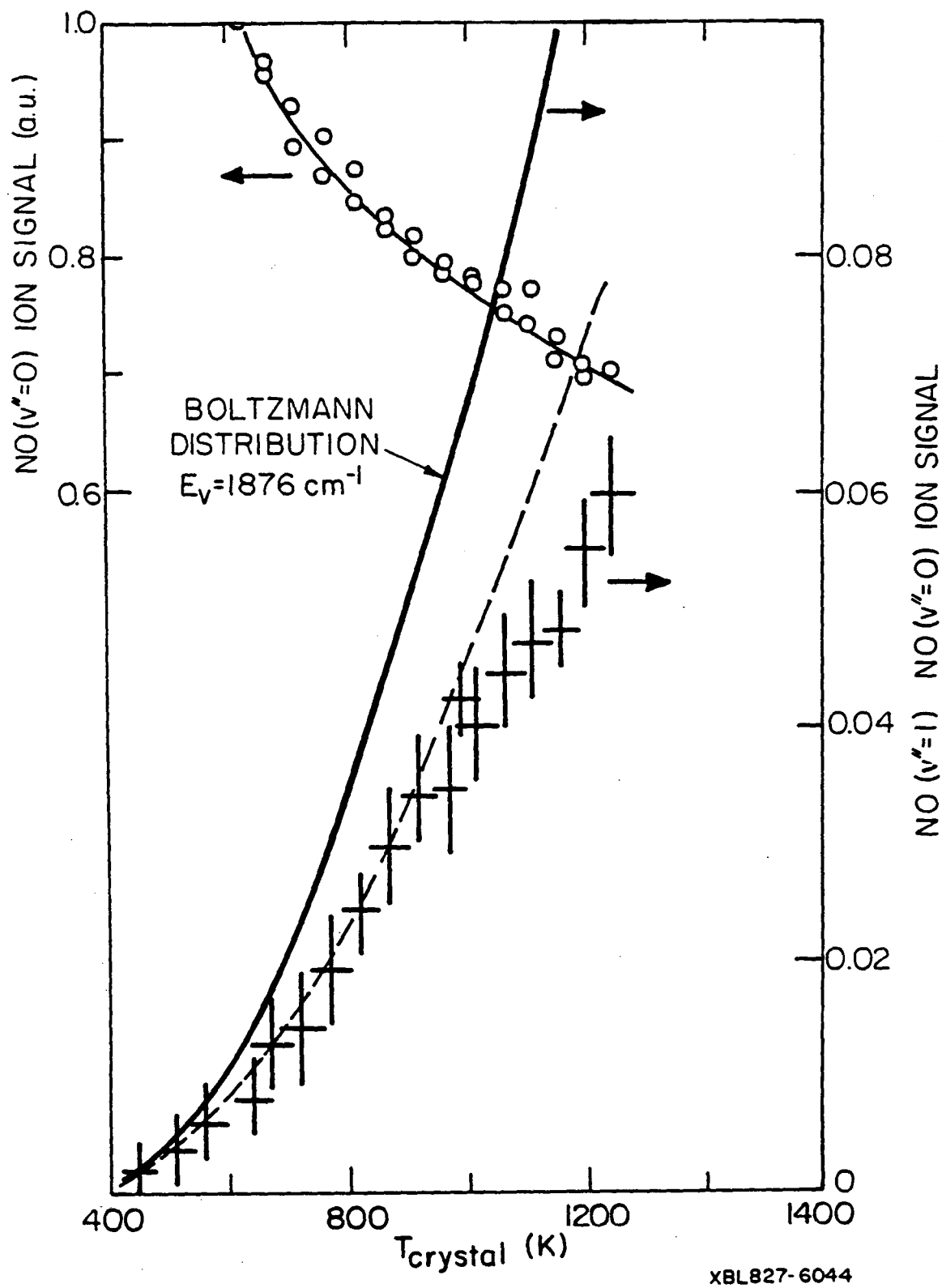
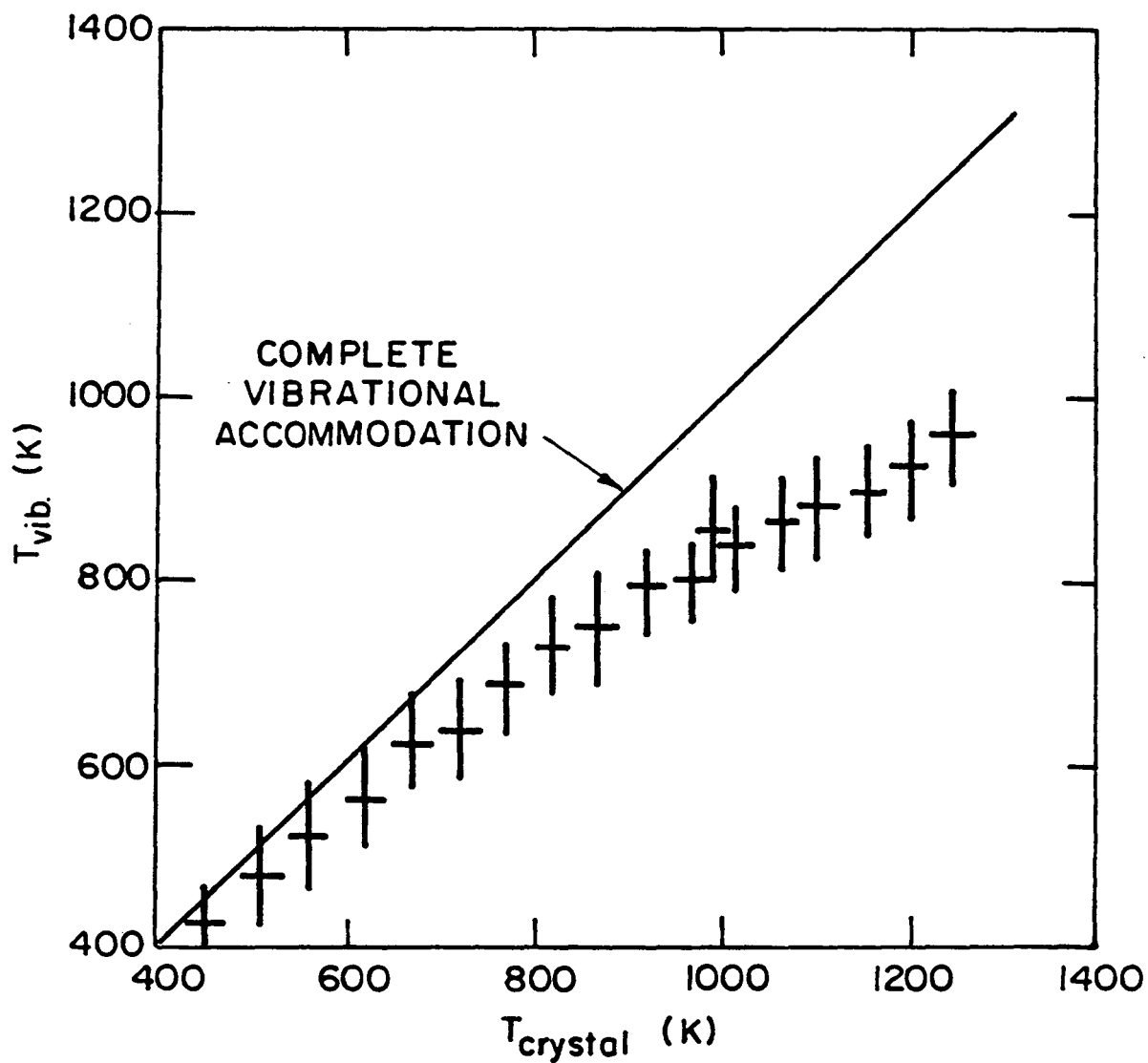


Figure 4.18: Vibrational population ratio $\text{NO}(v''=1)/\text{NO}(v''=0)$ as a function of T_g (crosses). Solid curve is a Boltzmann function of T_g . Dashed curve is an empirical fit, $0.67\exp(-1876\text{cm}^{-1}/kT)$, to the low temperature data.

as presented in figure 4.17b. The solid curve is a Boltzmann distribution, $\exp(-E_v/kT_g)$ where we have used the NO gas phase value for the vibrational energy, $E_v=1876 \text{ cm}^{-1}$. The data points would lie along the solid curve if the vibrational levels were in equilibrium at the crystal temperature. The dotted curve is an empirical fit to the lower portion of the data using the function $A\exp(-E/kT_g)$. The best fit is obtained for $A=0.67$ and $E=1876 \text{ cm}^{-1}$. This empirical fit shows that over the temperature range 400-900 K the vibrational population ratio deviates from the equilibrium Boltzmann ratio by a constant multiplicative constant. At crystal temperatures above 1000 K the vibrational excitation efficiency drops and the vibrational population ratio deviates from this empirical curve.

The data is plotted in a different fashion in figure 4.19 to indicate the vibrational temperature of the scattered gas as a function of crystal temperature, where the vibrational temperature is defined to be the equilibrium temperature that would be required to give the observed population ratio $\text{NO}(v''=1)/\text{NO}(v''=0)$. It can be seen that the vibrational temperature of the scattered NO molecules approximately equals the crystal temperature to 800 K, with increasing deviation at higher crystal temperatures.

The technique devised for measuring the exact population ratio is an indirect measurement. The crystal temperature was set and the detector positioned to measure molecules scattered at the direction of the surface normal. The laser was tuned to the $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{1/2}(v''=1)$ transition and scanned across the $Q_{11}+P_{21}$ rotational bandhead, $j''=1/2 - 6 1/2$, to measure the $v''=1$ population. 100 laser pulses were averaged at each wavelength. The intensity of the bandhead ($v''=1$) was measured for the scattered flux, and immediately afterward for an ambient room temperature



XBL 827-6041

Figure 4.19: The vibrational temperature of scattered NO as a function of the crystal temperature.

NO gas at a pressure of $\sim 10^{-7}$ torr. The ambient NO gas was admitted to the main chamber through a leak valve to give a pressure at which the band head would be roughly equal to the signal from the scattered molecules. The laser was then tuned to the $A^2\Sigma^+(v'=0) \rightarrow X^2\Pi(v''=0)$ transition and scanned across the $Q_{11}+P_{21}$ band head ($v''=0$) to measure first the intensity of the band head for the scattered flux and then the intensity for an ambient NO gas at a pressure of $\sim 10^{-9}$ torr. In this way the intensity of the signals from the scattered molecules in the ground and first vibrational states were referenced to signals from well defined densities of gases, using the same apparatus gain. The vibrational population ratio of the scattered molecules is given by

$$\frac{NO(v''=1)}{NO(v''=0)} = \frac{(I_{B.H.v''=1}/I_{BGv''=1})(P_{BGv''=1})}{(I_{B.H.v''=0}/I_{BGv''=0})(P_{BGv''=0})} \exp(-E_v/kT_R) \quad 4.3$$

where $I_{B.H.v''=0,1}$ is the signal intensity for the scattered molecules in the ground or first excited vibrational states respectively, $I_{BGv''=0,1}$, $P_{BGv''=0,1}$ is the signal intensity and pressure of the background reference NO gas, and the room temperature Boltzmann factor corrects for the population ratio $NO(v''=1)/NO(v''=0)$ in the ambient reference gas. The Boltzmann factor is 1.4×10^{-4} .

There are two advantages to this indirect technique. First the $v''=1$ signal and $v''=0$ signal from the scattered molecules differ by approximately two orders of magnitude while changes in gain of our experimental arrangement are difficult to accurately calibrate. By referencing the data to the signal from an ambient gas, the signal ratios are converted to effective pressure ratios, and pressures can be accurately measured over many orders of magnitude using a nude ionization gauge or mass spectrometer. Second

the excitation efficiencies from the vibrational levels may vary through the Franck-Condon factors of the resonant transition or more seriously through the unknown ionization efficiency from the upper electronic state. Two different frequencies are used to ionize the upper electronic state, and the frequency dependence of the ionization rate is unknown. Since the measurement for each vibrational level is compared to a measurement using the same transition in a reference gas, these unknown factors are eliminated, equation 4.3.

The angular distribution of scattered molecules in the first excited vibrational state is shown in figure 4.20. The angle of the incident beam was 62° and the crystal temperature was 820 K. The vibrationally excited molecules were detected in the $Q_{11}+P_{21}$ band head of the $A(v''=0) \leftarrow X(v''=1)$ transition. The angular distribution approximately matches a cosine function, shown by the solid line. This should be compared to the angular distribution of the total scattered flux at 725 K, figure 4.9b.

To investigate the degree of vibrational excitation on a more weakly interacting surface we decomposed 10 Langmuir of ethylene at 450 K on the Pt(111) surface. NO should have a much weaker interaction energy for this graphitic overlayer surface than for the strongly interacting Pt(111) surface (29 kcal/mole binding energy). A measurement of the vibrational population ratio of molecules scattered from this graphitic surface at 820 K failed to detect any signal from vibrationally excited ($v''=1$) NO molecules. This puts an upper limit of roughly 0.001 to the ratio $NO(v''=1)/NO(v''=0)$ for molecules scattered from this graphitic surface at 820 K. In contrast the Boltzmann ratio at 820 K is 0.037, and a vibrational population ratio of 0.024 was observed for NO scattered from the clean Pt(111) surface at the same temperature.

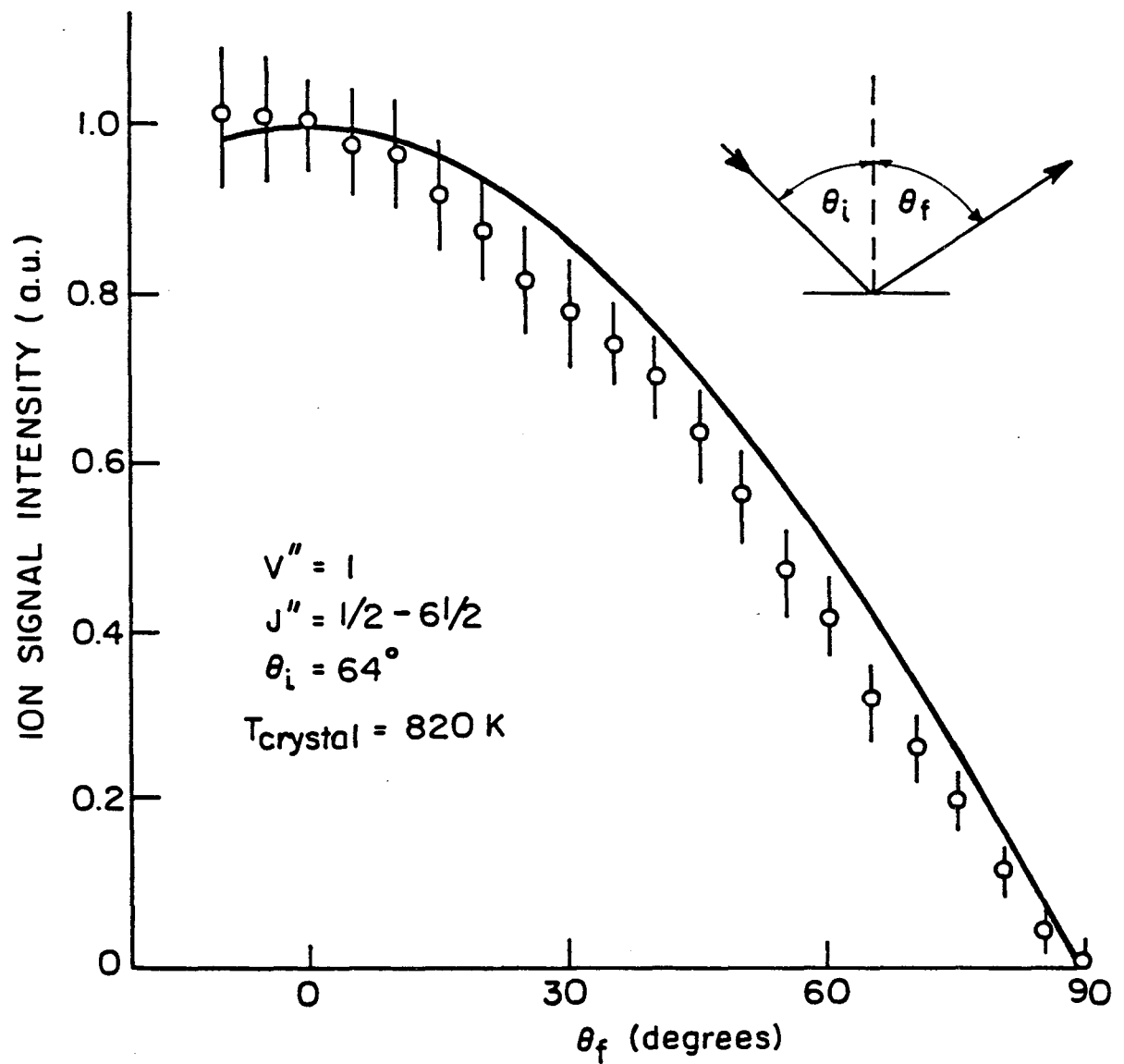


Figure 4.20: Angular distribution of vibrationally excited ($v''=1$) NO molecules scattered from the Pt(111) surface at $T_s=820\text{K}$.

4.3 Discussion

4.3.1 Accommodation

The energies, translational, rotational and vibrational, of molecules scattered from solid surfaces provide information on the extent and efficiency of gas-surface energy transfer, which is critical to understanding the microscopic processes important in gas-surface interactions. The techniques used in this chapter have been applied previously to other systems to study translational energies of inelastically scattered gases [1-4] and of surface reaction products [24-28], and internal energies of inelastically scattered molecules [6-12], of molecules in more strongly interacting systems in which the scattering primarily occurs through trapping-desorption [5] and of molecules in pure desorption experiments [13]. We have found that it is extremely useful to have instrumentation to measure the energy transferred into all modes, translational, rotational, and vibrational. The study reported in this section is the only study to date for which complete energy information has been obtained for a given gas-surface system, for each energy mode.

One means of discussing energy transfer efficiency for a given mode is in terms of the accommodation coefficient γ . The accommodation coefficient is defined in terms of the energy or equivalent temperature in a given mode as

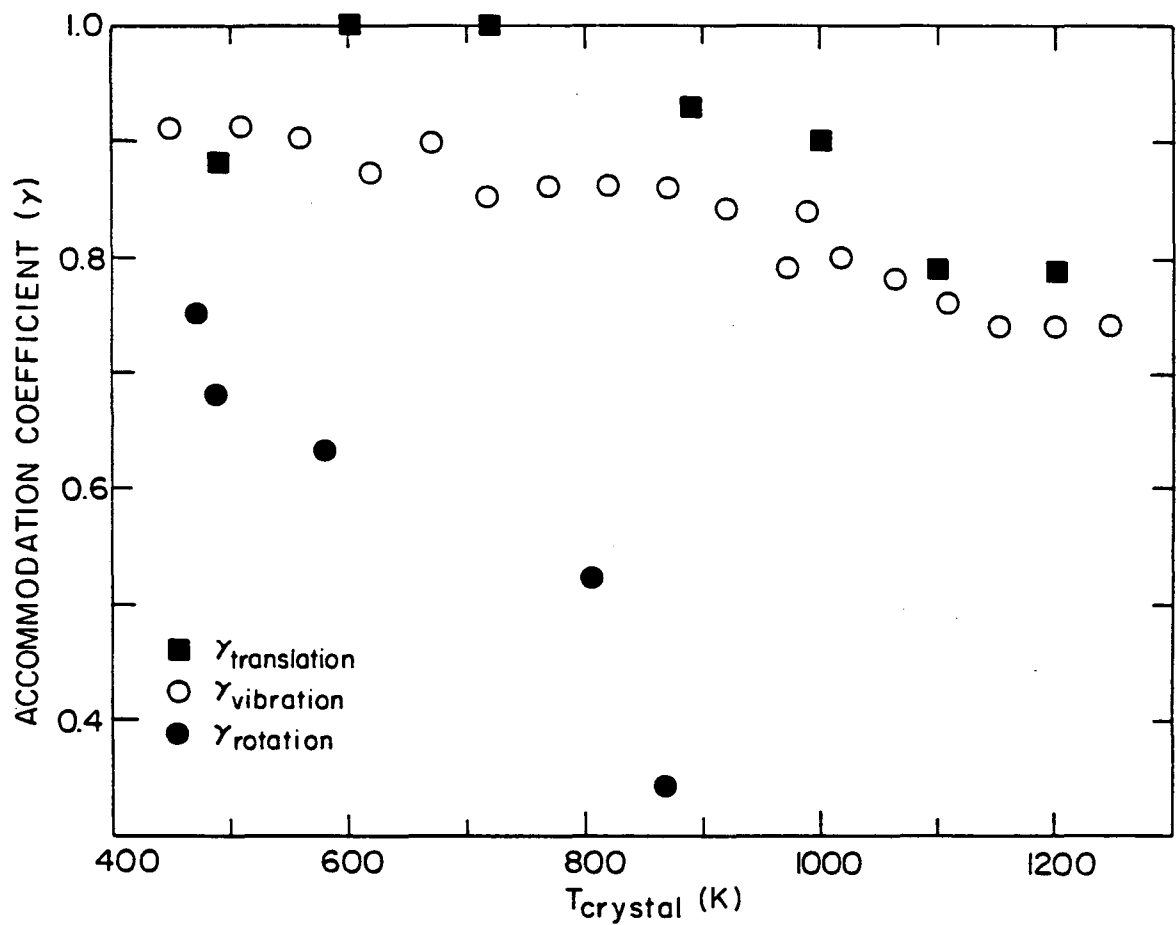
$$\gamma_J = \frac{T_f^J - T_i^J}{T_s - T_i^J} \quad 4.4$$

where γ_J is the accommodation coefficient for the energy in mode J, where J can equal T, R or V for translational, rotational or vibrational energy respectively, T_f^J is the equivalent temperature of mode J for

the scattered molecules, T_1^J the equivalent temperature for the incident molecules and T_s is the crystal temperature. From equation 4.4 it can be seen that the accommodation coefficient is the ratio of the energy change upon scattering in mode J of the gas to the energy change that would be found if the scattered gas were in equilibrium (in mode J) with the crystal. Figure 4.21 shows the data for the accommodation coefficients γ_T , γ_V and γ_R as a function of crystal temperature for NO scattered from the (111) surface of platinum. An immediate conclusion of figure 4.21 is that energy transfer in NO scattering from platinum is efficient in all modes, with the translational energy slightly more accommodated than vibrational energy, and rotational energy the most poorly accommodated mode. For translational energy the accommodation coefficient is in the range $1.0 > \gamma > 0.8$, for vibrational energy the range is $0.9 > \gamma > 0.8$ and for rotational energy the range is $0.8 > \gamma > 0.3$. Translational energy is the only mode that completely accommodates, and only to crystal temperatures of $T_s = 800$ K. It can be seen that the degree of accommodation falls with increasing crystal temperature for all modes.

The accommodation coefficient serves as a rough indicator of energy transfer efficiency, but it is important to note that incomplete accommodation does not necessarily imply inefficient energy transfer. In trapping-desorption scattering, which is the major interaction mechanism for NO on platinum surfaces, energy exchange may in fact be very efficient, allowing the molecule to reach complete equilibrium while on the surface, while the energy distribution observed in a given mode of the desorbed molecules may be far from equilibrium due to dynamic effects in the desorption process.

The translational, rotational and vibrational energies of NO



XBL 827-6043

Figure 4.21: The accommodation coefficient (γ) of the translational, rotational and vibrational modes of the scattered NO molecules as a function of crystal temperature.

molecules scattered from the Pt(111) surface show deviations from equilibrium, figure 4.21, which is fortuitous since complete equilibrium requires a statistical situation completely devoid of any microscopic information. It is the deviations from equilibrium and the differences in energy transferred into the available modes that provides the information to reach conclusions on the interesting microscopic processes that determine the energy transfer and gas-surface interaction. Causes of the translational, rotational and vibrational energy distributions observed for NO molecules scattered from the Pt(111) single crystal surface will be discussed in the following sections.

4.3.2 Scattering Mechanisms

Atomic and molecular scattering from solid surfaces is often discussed in terms of three general processes, elastic scattering, inelastic scattering and trapping-desorption scattering, the major difference in the processes being the extent of the gas-surface interaction.

In elastic scattering the molecule-surface interaction is limited to reversing the normal component of the molecular momentum. Elastic scattering is characterized by no or minimal energy transfer and by narrow angular distributions centered at the specular angle (in the absence of diffraction). Elastic scattering is usually important only for weakly interacting systems.

In inelastic scattering the interaction times are still short but with measurable energy transfer between the translational motion of the molecule and the surface or between the translational motion of the molecule and the internal rotational and vibrational modes [29], where the transfer to internal modes is mediated by the surface collision.

Inelastic scattering is characterized by broad angular distributions peaked near the specular angle and molecular energies (translational, rotational and vibrational) for the scattered gas that are functions both of the surface temperature and incident molecular energies.

Two types of inelastic scattering are often considered, direct inelastic scattering and indirect inelastic scattering. Direct inelastic scattering is usually defined to be scattering in which the normal component of the momentum of the scattered molecule changes sign only once i.e. the interaction time is minimal and the scattering process is a direct collision. Indirect inelastic scattering is defined to be inelastic scattering in which the normal component of molecular momentum changes sign multiple times. One cause of indirect inelastic scattering is deflection from lateral variations in the surface potential. Calculations of Ar scattering from platinum indicate that indirectly scattered molecules can potentially travel several hundred Angstroms along the surface before leaving [30]. In molecules, oscillation between rotational energy and translational energy of the molecule at the surface is also predicted to be an important mechanism for indirect inelastic scattering [17]. Indirectly scattered molecules will be in the surface region for several vibrational periods, so the energy transfer should be more extensive and the angular distribution broader for indirect scattering in comparison to direct scattering.

In trapping-desorption scattering the incident gas is trapped on the surface and leaves the surface by desorption independent of the trapping. Surface residence times could vary from several vibrational periods to seconds or greater, and is generally a strong function of surface temperature. Trapping-desorption scattering is characterized

by extremely broad angular distributions, often cosine distributions, centered about the surface normal and molecular energies of the scattered gas that are dependent on surface temperature but independent of incident energies. It was previously thought that desorbing molecules would be in equilibrium with the surface i.e. would have Maxwell-Boltzmann velocity distributions and equilibrium rotational and vibrational distributions [29]. However as these quantities have been measured it has become clear that the molecular energies deviate substantially from equilibrium, particularly the rotational and vibrational energies.

The angular characteristics of the scattering mechanisms provide a means of studying the behaviour of molecules scattered by the different mechanisms. The strongest inelastic behaviour, including incident energy dependence for the translational energy and translational to rotational energy transfer, should be found in molecules scattered into angles near the specular angle, and desorption behaviour should be observed in molecules scattered into angles far from specular.

The broad angular distributions observed for the NO scattered from Pt(111) (figures 4.8, 4.9 and 4.10) indicate that most of the NO scatters by trapping-desorption scattering with some inelastic scattering accounting for the broad specular feature. The energy transfer between the platinum surface and NO molecules (figure 4.21) is consistent with substantial trapping-desorption scattering. The width of the specular peak makes separation of the contributions difficult, but integrating the intensity of the broad diffuse background over all angles (assuming a cosine angular distribution), and integrating the intensity of the specular peak above the diffuse background (assuming a distribution symmetric in angle about the maximum of the peak) gives a rough estimate of the fraction of incident

molecules trapped. The estimated trapping probability is approximately 0.90 for the most diffuse angular distribution (figure 4.9a) and 0.80 for the most specular distribution (figure 4.8c). These numbers are close to the values of the sticking coefficients found by modulated molecular beam kinetic studies, which found coverage dependent sticking probabilities for NO on platinum of 0.70 to 0.85 at low coverages [31,32].

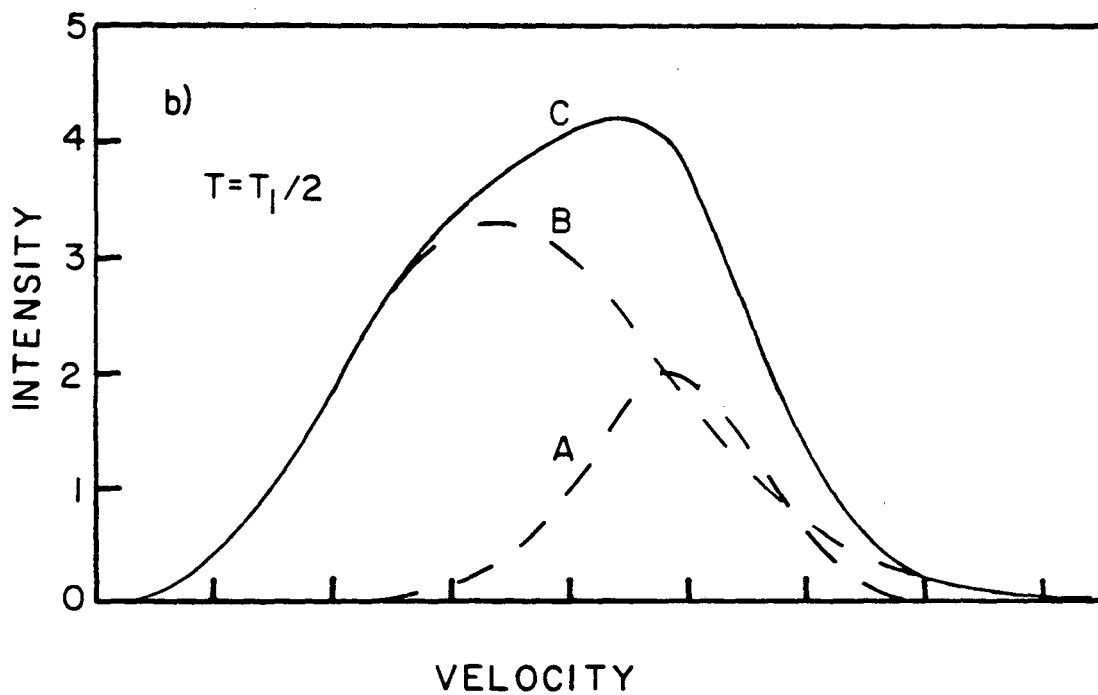
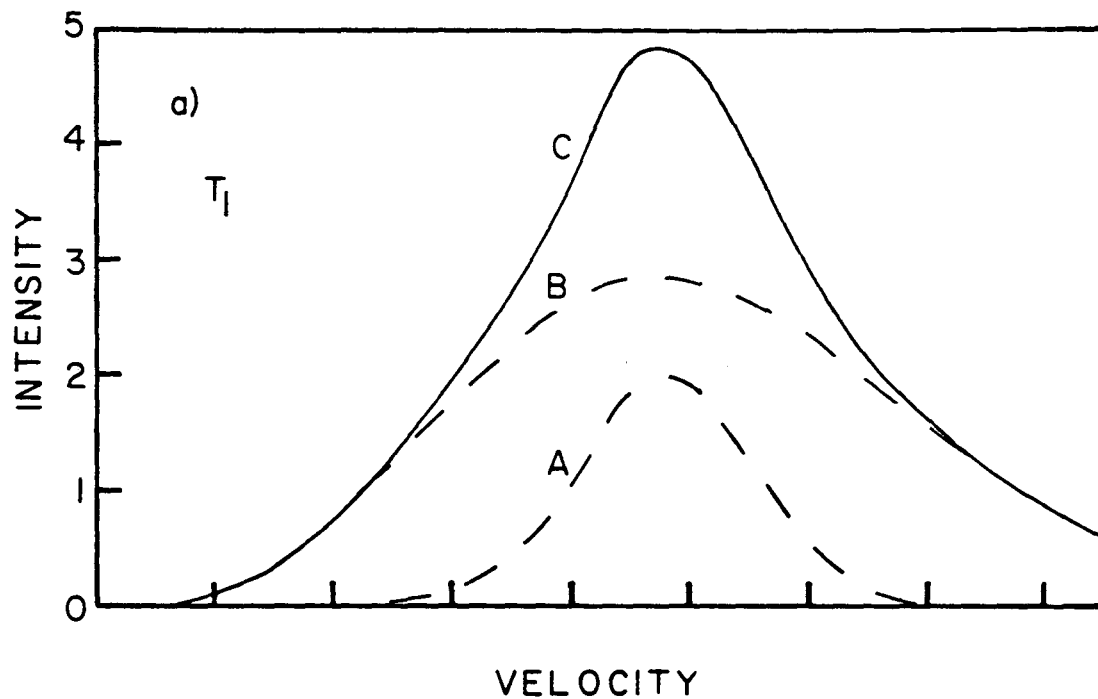
The angular distributions, figures 4.8, 4.9 and 4.10, indicate that the degree of inelastic scattering increases with increasing incident translational energy and surface temperature. The increase in inelastic scattering with translational energy reflects the greater amount of translational energy that must be transferred to the surface for trapping to occur. It also indicates that NO on Pt(111) has no or a small (<0.6 kcal/mole) activation energy barrier to adsorption. The angular distributions of He co-scattered with NO (section 4.2.2) indicate that the crystal temperature dependence to the angular distributions is not due to changes in surface roughness but is due to an increase in the degree of inelastic scattering with increasing temperature. The surface temperature dependence in trapping probability is predicted by simple hard-cube scattering models and has been observed experimentally in N₂ scattering from W [1] and Ar scattering from W [3].

4.3.3 Velocity Distributions

The angular distributions indicate that there should be two contributions to the velocity distributions: a contribution from that fraction of the molecules that scatter inelastically, and a contribution from the fraction that scatter by trapping-desorption. The superposition of the distributions from these two groups complicates the interpretation of

the velocity distributions. The average energy of the velocity distribution will be a weighted average of the separate average energies of the molecules in each fraction, and the relative width of the velocity distribution $\langle \Delta v^2 \rangle / \langle v \rangle^2$ will depend on the widths of the distributions contributed by the trapping-desorption fraction and the inelastically scattered fraction, and by the difference in the average velocity of these two groups. Figure 4.22 demonstrates these effects. If the average velocity of the inelastically scattered molecules, which is a strong function of incident translational energy, matches the average velocity of the trapping-desorption molecules, which is a strong function of crystal temperature, then the total distribution will be narrow as indicated in figure 4.22a. However at a lower temperature the average velocity of the trapped molecules will be less and the sum distribution will be wider than the distribution that would result if only one scattering mechanism were operative, figure 4.22b. This is what causes the temperature change in relative distribution width for the data for the 1390 K incident energy beam, figure 4.5b.

Velocity distributions representative of trapping-desorption should be observable near the surface normal particularly at low surface temperature and incident beam energy, and there will be greater contributions from the inelastically scattered molecules near the specular angle. But the angular distributions indicate that there will be no conditions for which only inelastic scattering is observable. It is interesting that the velocity distributions show clear signs of two scattering mechanisms, for instance in the change in distribution width with crystal temperature, figure 4.5b, and yet an extensive search varying crystal temperature, incident angle and detector angle failed to produce



XBL 8212-12091

Figure 4.22: Representation of velocity distributions resulting from a combination of trapping-desorption and inelastic scattering. a.) Both groups have similar velocities. b.) Velocity of trapped group falls at lower crystal temperature giving broader sum distribution.

velocity distributions in which the contributions of the two scattering mechanisms were discernable. This is very different from the velocity distributions of Xe scattered from Pt(111) surfaces [4], where bimodal velocity distributions were observed. The difference in this study may be the greater energy transferred in the inelastic scattering due to the stronger interaction and the availability of rotational modes, and perhaps to a larger velocity width of the inelastically scattered molecules.

One must examine the average energy of the distribution and the relative width $\langle \Delta v^2 \rangle / \langle v \rangle^2$ simultaneously to determine equilibrium of the scattered molecules with the surface. The average energy can have the equilibrium value if the inelastically scattered molecules have the right energy, but the distribution width will then be too narrow as is visually evident in figures 4.3b and 4.4b. Likewise the relative width may be artificially large if the two components have average velocities that are greatly different. Examination of figures 4.5, 4.6 and 4.7 indicate that the translational energy of scattered NO is in equilibrium with the surface only for scattering at the surface normal over the temperature range $T_s=400-900$ K and for $T_b=265$ K and 615 K. The translational energy may be in equilibrium for $T_b=1390$ K at the surface normal and for $T_s>900$ K. However the trends observed from the angular distributions is for increased inelasticity with increasing surface temperature and incident energy, so this may be only apparent equilibration.

There are several areas of unusual behaviour in the translational energy data. For $T_b=1390$ K, $T_s=475$ K and for scattering near the surface normal (figure 4.4a) there is a lack of equilibrium and yet the specular feature of the angular distribution is weak, figure 4.8a. Also for

$T_s > 900$ K, $T_B = 265$ K and 615 K, there is a decline in the accommodation coefficient, but the angular distributions again show weak specular features, especially for the 265 K incident energy beam data (figure 4.10b). The declining translational accommodation may be in part due to a non-equilibrium desorption process as discussed in section 3.3. However the degree of accommodation for scattering near the surface normal at $T_s = 1000$ K and 1195 K is lower for $T_B = 265$ K than for $T_B = 615$ K incident beam energy, figures 4.6a and 4.7, which indicates a significant contribution from inelastic scattering. From the extent of the energy transfer and from the angular spread of the inelastic scattering it appears that inelastic scattering of NO from Pt(111) must be largely indirect inelastic scattering, perhaps induced by translational to rotational energy transfer [17].

The reduced translational energy of the scattered NO, $\langle E_e \rangle / 2kT_s$, is shown as a function of the reduced incident translational energy $\langle E_i \rangle / 2kT_s$ in figure 4.23a and b for the NO molecules scattered at 7° and 51° from the surface normal respectively. Here $\langle E_e \rangle$ and $\langle E_i \rangle$ are the average translational energy of the scattered and incident beam respectively, and are reduced by an energy proportional to the crystal temperature T_s . The reduction allows comparison of data for the different energy incident beams, $T_B = 265$ K, 615 K and 1390 K. It has been shown in hard-sphere model calculations and in experimental studies that this data reduction is useful in interpreting inelastic scattering data, and that the data for translational energies of inelastically scattered molecules will lie along a straight line when plotted in this reduced energy scheme [3,33-35]. The relationship for the inelastically scattered molecules is

$$\langle E_e \rangle / 2kT_s = B_2 \langle E_i \rangle / 2kT_s + B_3$$

where B_2 and B_3 are parameters determined by the gas and surface properties, and are scattering angle, surface temperature and incident energy independent. If we let $\langle E_e^i \rangle$ and $\langle E_e^t \rangle$ be the average energy of the inelastically scattered and trapping-desorption scattered fractions respectively, and $s(\theta)$ equal the fraction of molecules observed at a given angle that were trapped, we can write for the NO case

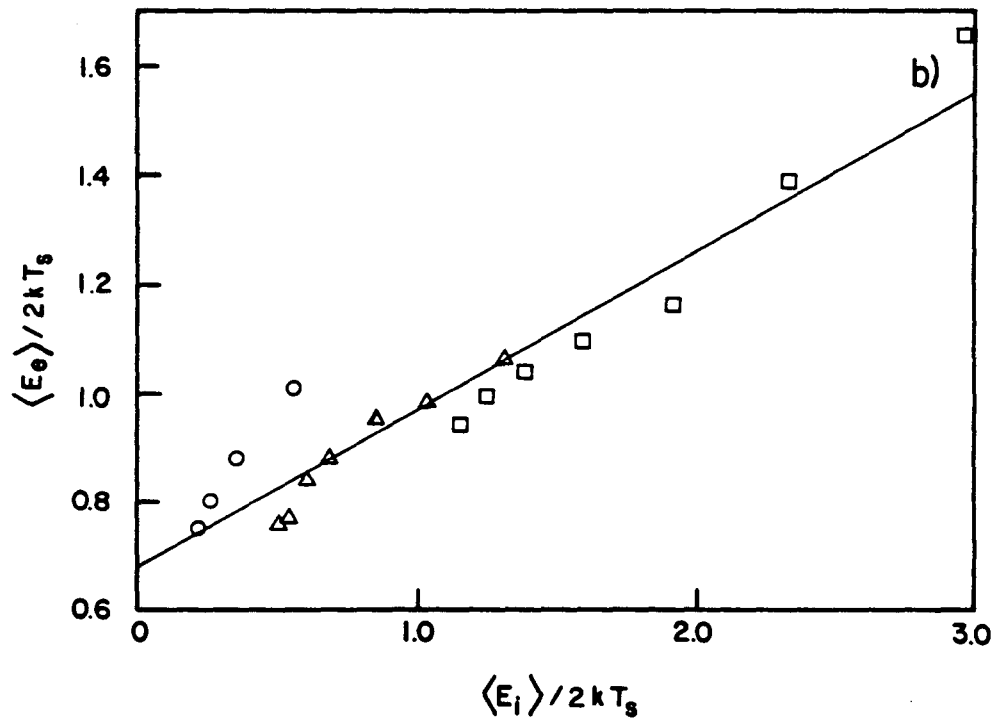
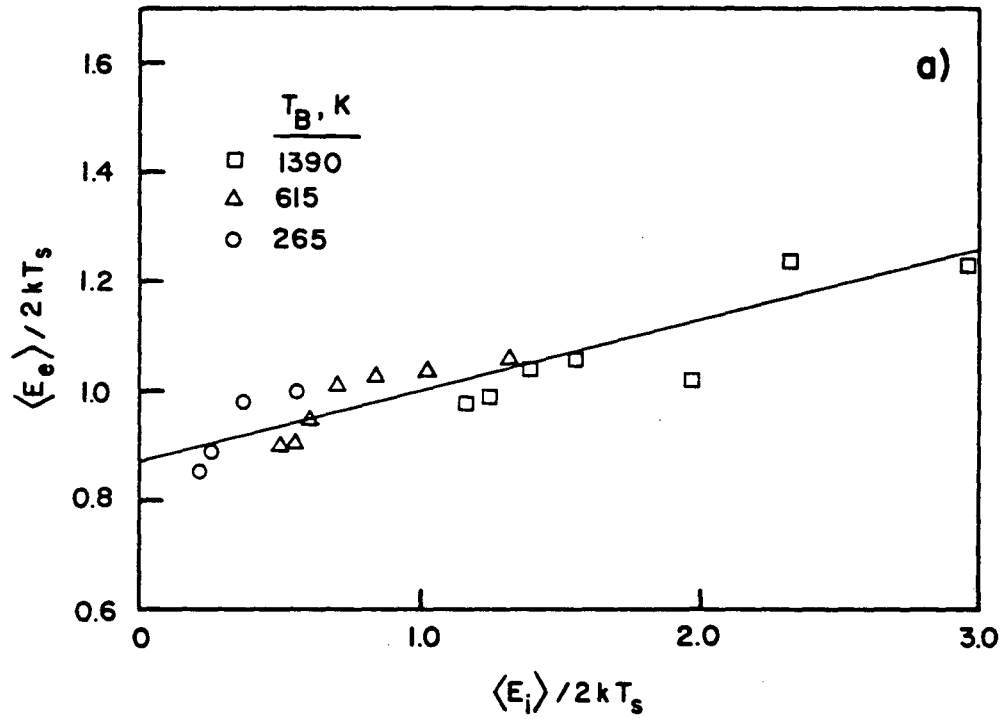
$$\begin{aligned} \langle E_e \rangle / 2kT_s &= (1-s) \langle E_e^i \rangle / 2kT_s + s \langle E_e^t \rangle / 2kT_s \\ &= (1-s) (B_2 \langle E_1 \rangle / 2kT_s + B_3) + s(2kT_s) / (2kT_s) \\ &= [(1-s)B_2] \langle E_1 \rangle / 2kT_s + [(1-s)B_3 + s] \end{aligned} \quad 4.6$$

where it is assumed that the energy of the inelastically scattered fraction can be described by equation 4.5, that the trapped fraction equilibrates with the surface, and that the fraction of trapping observed at a given angle is independent of incident energy and surface temperature.

Equation 4.6 shows that the reduced scattered energy is linear in reduced incident energy if these assumptions are valid, so that the linearity of the data can serve as a test of these assumptions. There are deviations from linearity in our NO scattering data, figures 4.23a and b, and these deviations are the strongest for molecules scattered at the specular angle. These deviations simply confirm the apparent lack of accommodation at high T_s in the trapped fraction, which was observed in the velocity distributions, and the surface temperature and incident energy dependence to the trapping probability, which was observed in the angular distributions and velocity distributions.

4.3.4 Rotational Energy Distributions

Of the three energy modes examined, the rotational energy distributions



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Figure 4.23: Reduced mean scattered energy $\langle E_e \rangle / 2kT_s$ as a function of reduced mean incident energy $\langle E_i \rangle / 2kT_s$, a.) scattering 7° from the surface normal b.) scattering 51° from the normal (specular).

are perhaps the most interesting because the rotational energy is the farthest from equilibrium with the surface (figure 4.21). In the few systems studied to date, NO scattered from silver [7-9], NO covered platinum [5], LiF [10] and graphite [11], NO desorbed from ruthenium [13], HF scattered from LiF [6] and CO scattered from LiF [12], the rotational energy distributions for the scattered molecules are significantly and consistently cold. For the case of NO scattering from the surfaces above, the equivalent rotational temperatures found were $200\text{ K} < T_R < 450\text{ K}$ for $300\text{ K} < T_g < 870\text{ K}$. This behaviour was observed in systems where the scattering mechanism was believed to be primarily inelastic scattering (NO/Ag(111), HF/LiF, CO/LiF, NO/C, and NO/LiF), primarily trapping-desorption scattering (NO/NO covered Pt and the current study of NO/Pt(111)) and in a system where only the desorption was examined (NO/Ru(001)).

In the strongly interacting systems, where the molecules scatter by trapping-desorption, one has to conclude that the rotational distributions are determined by dynamic effects in the desorption process and cannot be due to inefficiencies in the surface-molecule energy transfer. For the NO/Pt(111) system this conclusion is based in part on the efficiency of energy transfer to the translational and vibrational modes. It is implausible that the transfer to rotational energy could be that much less efficient, particularly in light of the long surface residence time. The surface residence time can be measured directly by modulated beam techniques at lower temperatures, and was found to vary from approximately $100\mu\text{s}$ at 600 K to greater than approximately 25ms at $T_g < 500\text{ K}$ [31]. Extrapolating these measurements to higher temperatures yields surface residence times greater than 10ns for $T_g < 1000\text{ K}$. The thermal energy of the crystal surface region can transfer to the rotational mode of the

molecule during the time it is adsorbed, but over this temperature range the rotational temperature of the scattered molecules is in the range of $300 \text{ K} < T_R < 450 \text{ K}$ (figure 4.15).

The exact configuration of NO on the Pt(111) surface is unknown. NO was reported to be in an upright configuration with a chemical bond between the N atom and the surface at $T_g < 350 \text{ K}$ [36,37]. At higher temperatures NO may be in an upright configuration, may be in a more weakly bound nearly free-tumbling state, or may pass through a tumbling state prior to desorption. The configuration of NO in the adsorbed state may not be that important to the dynamic cooling mechanisms, since similar models can be proposed for both configurations.

It was proposed previously that NO on graphite is adsorbed in the upright configuration [11]. Since the molecule is not free to rotate in this configuration it was proposed that rotational energy could not be transferred until during the desorption when the molecule finally becomes free to tumble. This then would account for the low rotational energies observed in the desorbed gas [11]. It appears however that an upright configuration for the molecule will not prevent energy transfer to rotation. Although an upright bound molecule cannot freely rotate, there are symmetrical and antisymmetrical wagging vibrations, and an instantaneous rotational energy can be defined in terms of these modes. The motion of the chemisorbed molecule can be decomposed into motion of the center of mass of the N and O atoms, and motion of the atoms around the center of mass. The latter motion can be defined as an instantaneous rotation. Neglecting the motion of the platinum atoms (which are 10 times heavier than the N or O and bound into the crystal lattice) the kinetic energy E_k can be decomposed as

$$E_k = E_{k,cm} + E_{k,R} + E_{k,v} \quad 4.7$$

where $E_{k,cm}$ is the energy of center of mass motion, $E_{k,R}$ is the energy of motion around the center of mass and $E_{k,v}$ is the energy of relative motion along the line connecting the N and O atoms. For each fixed position of the atoms R there will be some potential energy which is a function only of R, $E_p(R)$. Assuming that the adsorbed molecules have reached equilibrium, the probability of finding the molecule with a given energy will be given by a Boltzmann factor

$$P(E) = \exp(-E_p(R)\beta)\exp(-E_{k,cm}\beta)\exp(-E_{k,v}\beta)\exp(-E_{k,R}\beta) \quad 4.8$$

at a given position R. The important point is that when averaged over all positions, the instantaneous rotational energy $E_{k,R}$ will have an equilibrium energy distribution. Or in other words, if the surface-nitrogen bond could be severed in a manner allowing the NO molecule to continue on in its motion, the molecules freed in this fashion would have an equilibrium rotational distribution. This assumes that the instantaneous rotational motion can be treated classically.

If the adsorbed molecules reach thermal equilibrium with the surface then the observed rotational distributions must be determined by the desorption process. We can consider dynamic mechanisms of gas-phase unimolecular decompositions which are believed to produce sub-thermal rotational energies in the decomposition fragments [38]. The desorption process can be viewed as a unimolecular decomposition of an infinitely large molecule, so these mechanisms might be applicable to the current study. Rotational cooling is thought to occur in decompositions involving "tight complexes". These are molecules in which there is strong coupling in the transition state between the rotational motion of the decomposi-

tion fragment and the separation motion of the fragment. The transition state is the configuration of the molecule from which decomposition or return to its initial configuration could occur. The other possibility is the "loose complex" i.e. a situation at the transition state in which the rotational motion of the fragment is independent of the decomposition motion. Loose complexes are thought to result in equilibrium rotational energy in the decomposition fragments. The exact form of rotational to translational energy coupling can vary.

For the case of NO on platinum there is an attractive potential between the nitrogen atom and the surface and a repulsion for the oxygen atom [36,37]. This asymmetry of the potential could be the cause of the tight coupling. The kinetic energy needed to overcome the attractive potential of the adsorption well can come from energy transfer from the crystal, or from the rotational motion of the NO molecule. The molecules will have a range of energies in the adsorption well and a fraction will require only a small amount of additional energy to desorb. We propose that rotational to translational energy transfer in these molecules enhances the desorption and causes the rotational cooling observed in the desorbed flux. The amount of energy available for transfer increases with the rotational energy of the adsorbed molecule, so that the rotationally excited molecules are more likely to desorb through loss of rotational energy causing a cooling of the rotational temperature.

Dynamic cooling could occur regardless of the configuration of the NO adsorbate. If the NO is in a free tumbling state, the asymmetry of the NO-surface potential could couple the rotational energy to translational energy. Translational to rotational coupling was found

to be efficient in inelastic scattering studies of NO from Ag(111) surfaces [8], and it is reasonable to assume that the coupling should be equally efficient on platinum surfaces. If the NO is bonded in an upright position the repulsion of the oxygen atom could couple the instantaneous rotational energy associated with the wagging vibration to the translational energy.

A recent quantum model has successfully reproduced the experimental rotational distributions observed for some of these gas-surface systems [39]. According to this model the rotational distributions are due to overlap integrals between the molecule in a transition state and the molecule in the gas phase. The transition state used is a distortion of the molecule and surface away from the equilibrium configuration in which the molecule-surface separation is less than equilibrium and neighboring surface atoms are displaced inward. An important factor seems to be the restricted angular configuration of the adsorbate in the transition state, so that the model appears to describe in quantum mechanical terms the rotational coupling discussed classically above.

The angular dependence in rotational temperature, figure 4.14, and the difference in angular distribution as a function of rotational state, figure 4.16, are probably due to translational to rotational energy transfer in the inelastically scattered fraction of the incident molecules. This conclusion was reached because the higher rotational temperature appears to be related to the specular hump of the angular distribution, and because significant translational to rotational excitation was observed in NO inelastically scattered from a Ag(111) surface [8]. However in contradiction to this interpretation, the rotational energy does not increase for a doubling of the incident translational energy, table 4.1.

More experiments will be needed to resolve this point.

4.3.5 Vibrational Energy Distributions

This is the first study to measure vibrational population ratios of surface scattered gases. This measurement was possible in part because of the increased sensitivity of the two-photon ionization detection, but is also largely due to the fact that many of the other systems were weakly interacting systems, involving primarily inelastic scattering. As will be discussed below, it appears that vibrational excitation does not occur in inelastic scattering.

The data for the vibrational population ratio $\text{NO}(v''=1)/\text{NO}(v''=0)$ show an exponential increase in the ratio of excited molecules for $T_s < 1000$ K with increasing deviation from an exponential increase for $T_s > 1000$ K. We have assumed that the excellent agreement of the data to the exponential function $0.67\exp(-E_v/kT_s)$ over the range $400 \text{ K} < T_s < 1000 \text{ K}$ implies vibrational equilibrium of the adsorbed molecules, even though the vibrational ratio observed in the gas phase is not strictly in equilibrium with the surface. We have assumed that the increasing deviation from the exponential function indicates that the surface residence time is becoming short compared to the vibrational excitation time for $T_s > 1000$ K. Based on this assumption, the vibrational excitation will be discussed below for the two temperature ranges.

The vibrational population ratio was fit to the empirical function $\text{NO}(v''=1)/\text{NO}(v''=0) = A\exp(-E_v/kT)$ with the best fit obtained for the parameter values of $A=0.67$ and $E_v=1876 \text{ cm}^{-1}$. This equals the gas phase value of the NO vibrational energy. Since the empirical fit to the population ratio gave the NO vibrational energy, it appears that the adsorbed NO

is in equilibrium with the surface but that the desorption rates may differ for molecules in the two vibrational states. The following arguments will show how this model could give a vibrational population ratio that differs from a Boltzmann ratio by a constant multiplicative factor.

Assuming surface equilibrium of the NO, the surface ratio of molecules in the first excited and ground vibrational states is

$$\frac{[\text{NO}_{\text{ad}}(v''=1)]}{[\text{NO}_{\text{ad}}(v''=0)]} = \exp(-E_{\text{vs}}/kT_{\text{s}}) \quad 4.9$$

where E_{vs} is the vibrational energy of adsorbed NO. We assume desorption rates k_{d}^0 and k_{d}^1 for ground and vibrationally excited molecules respectively. It has been reported that NO desorbs with first order kinetics [31,34], so we take a first order Arrhenius expression for the desorption rates k_{d}^i ,

$$k_{\text{d}}^i = v^i \exp(-E_{\text{d}}^i/kT_{\text{s}}) \quad 4.10$$

where v^i and E_{d}^i are the desorption preexponential factor and desorption energy for vibrational state i . The ratio observable in the gas phase should be

$$\frac{\text{NO}(v''=1)}{\text{NO}(v''=0)} = \frac{[\text{NO}_{\text{ad}}(v''=1)]k_{\text{d}}^1}{[\text{NO}_{\text{ad}}(v''=0)]k_{\text{d}}^0} = \frac{v^1}{v^0} \exp(-E_{\text{v}}'/kT_{\text{s}}) \quad 4.11$$

where $E_{\text{v}}' = E_{\text{vs}} + E_{\text{d}}^1 - E_{\text{d}}^0$. Comparison to the data indicates that $E_{\text{v}}' = E_{\text{v}}$ and $v^1/v^0 = 0.67$ independent of temperature. Theoretically the preexponential factors v are temperature dependent [41], but they are not strong functions of temperature, and since v^1 and v^0 should have

similar temperature dependencies it is reasonable that the ratio be temperature independent. ELS studies have shown that the vibrational energy of NO adsorbed on Pt(111) is temperature and coverage dependent and at low temperatures is lower than the gas phase value ($E_{vs}=1700\text{cm}^{-1}$ - 1800cm^{-1} at $T_g=300$ - 400 K) [37,42]. There is no reason to assume that the NO surface potential energy depends on NO vibrational energy, so we assume that $E_d^1=E_d^0$. Then it appears that $E_{vs}=E_v$, which is plausible for this temperature range.

The population ratio data for $400\text{ K} < T_g < 1000\text{ K}$ are closely reproduced by this model, however the conclusion of the fit is that the preexponentials of desorption from the two vibrational states are different, the meaning of which is unclear. The common interpretation of the preexponential in terms of partition functions may mean that the two vibrational states may be slightly different due to vibrational anharmonicities. This configurational difference may cause differences in available surface sites or in the energies of the wagging vibration.

This desorption rate model successfully rationalizes the experimental population ratios, but it does not appear to be as satisfactory as the models developed for the rotational distributions above. It would be useful to apply the quantum model [39] which has been successful at describing rotational energy distributions of scattered gases to the vibrational excitation. Perhaps that model can provide additional physical insights.

We have assumed that the increasing deviation of the vibrational population from the exponential temperature dependence at $T_g > 1000\text{ K}$ indicates inefficiencies in vibrational excitation and deviations from vibrational equilibrium in the surface adsorbed NO. This would imply

that the desorption rate at these temperatures is becoming comparable to the vibrational excitation rate. The desorption rate can be roughly calculated from an extrapolation of kinetic measurements made at lower temperatures. A fit to kinetic data obtained in the range $T_s=500$ K-650 K gives an NO desorption rate from Pt(111) of $k_d=6 \times 10^{13} \exp((-29.5 \text{ kcal/mole})/kT)$ [31]. Extrapolating this rate gives a desorption rate at 1200 K of $k_d=3 \times 10^8 \text{ s}^{-1}$ (surface residence time $\sim 3 \times 10^{-9} \text{ s}$). If our assumptions are correct, the desorption starts to compete with the vibrational excitation at rate constants of 10^8 s^{-1} . Based on the NO vibrational energy and equality of the rates in equilibrium, the deexcitation rate constant would then be in the range of 10^9 s^{-1} . This calculation is unfortunately sensitive to desorption rate parameters. Serri et. al. propose that at elevated temperatures the desorption energy should be in the range of 20 kcal/mole [40], which means that the estimated deexcitation rate constant should be in the range of 10^{10} s^{-1} . This can be compared to theoretical calculations of deexcitation rates. The vibrational energy spacing (1876 cm^{-1}) is approximately 10 times the Debye phonon limit of platinum, so that energy transfer from platinum phonons is probably inefficient. The energy transfer probably occurs from the electronic levels of the metal from plasmon modes and electron hole pairs. There are several theoretical models that have had good success in predicting vibrational and electronic deexcitation rates of molecules near surfaces (10-1000Å) but separated by dielectric layers [43-45]. These models are based on energy transfer to the electronic levels of the surface as described by the dielectric function of the solid, and the dipole moment of the molecular transition (0.153 D for NO). Using

the value of the platinum dielectric function at 0.23 eV, $\epsilon(\omega) = -400 + 205i$ [46], assuming an adsorption distance of 2 Å, using the gas phase vibrational lifetime of 80 ms [47], and the formulas of Chance, Prock and Silbey [43], the calculated deexcitation rate of NO on platinum is $5 \times 10^8 \text{ s}^{-1}$, which roughly agrees with the rate inferred from our data. There is debate as to whether these simple calculations should apply to chemisorbed molecules [48,49]. The deexcitation rate of the O-H stretch vibration of methoxide on Cu(001) was recently measured to be in the range of 10^{12} s^{-1} [50], whereas the simple dielectric calculation predicted a rate of 10^9 s^{-1} . Better agreement was obtained if periodic charge transfer from the lowest antibonding orbital to the surface was included [50]. The antibonding π^* orbital of NO is occupied, in contrast to the unoccupied σ^* orbital in methoxide, so it may be that periodic charge transfer is not relevant to NO vibrational deexcitation.

It is of interest to determine what is the minimal interaction time required to produce detectable vibrational excitation. In an attempt to answer this question we reduced the surface residence time of the NO by placing a graphitic overlayer on the platinum surface. The overlayer reduces the NO-Pt energy (we estimate it might be in the range of 2-8 kcal/mole) and changes the nature of the scattering from primarily trapping-desorption to primarily inelastic scattering.

We found no detectable population in the $v''=1$ level of NO scattered from the graphitic platinum surface at $T_s = 820 \text{ K}$ which puts an upper limit of 0.001 to the population ratio $\text{NO}(v''=1)/\text{NO}(v''=0)$ of the scattered flux. Although the interaction potential of the graphitic surface is different from that of the clean (111) surface, we still expect vibrational excitation if the interaction time is long enough, particularly if the

excitation energy comes from the electronic excitations of the platinum and is transferred by dipole fluctuations (see above). However in inelastic scattering the interaction time is on the order of 10^{-12} s, which is apparently too short an interaction time. The angular distribution of molecules in the first excited vibrational level (figure 4.20) confirms the lack of vibrational excitation in the inelastically scattered molecules. The angular distribution very nearly matches a cosine function and shows no specular feature, which implies that scattered molecules in the $v''=1$ level do not originate from an inelastic scattering process. It should be noted that there was insufficient translational energy (0.1eV) to excite vibrations directly. The inelastic scattering experiments put a lower limit on the vibrational excitation time of $\tau \gg 10^{-12}$ s (excitation rate $\ll 10^{12}$ s $^{-1}$). This tends to support the conclusion above that the excitation rate is in the range of 10^8 - 10^9 s $^{-1}$.

4.3.6 State Selective Detection

A major problem in non-reactive scattering is the difficulty in separating the behaviour due to the different scattering mechanisms, elastic, inelastic and trapping-desorption. For the case of NO scattered from Pt(111) the problem is nearly tractable since there is ample evidence that approximately 85% of the incident flux adsorbs, so that most of what is observed can be ascribed to trapping-desorption scattering. However even in the current study there is always the problem of the effect of the 10-15% of the flux that is inelastically scattered.

Our discovery that vibrational excitation cannot occur during inelastic scattering from platinum may be of help to this problem. The state selectivity of the laser detector can then be used to measure the

properties of vibrationally selected molecules to determine the angular distribution of the desorbed molecules (figure 4.20), the adsorption kinetics by modulated beam techniques, the rotational energies of desorbed molecules through rotational lines of the $v''=1$ manifold, and desorption velocities either by Doppler shift techniques [51], time-of-flight techniques using laser detection, or field-free post-ionization-drift measurements using two-photon ionization. We have checked the feasibility of measurements of the angular distributions, the adsorption kinetics and the rotational distribution in the $v''=1$ manifold, and all of the techniques look extremely promising. The velocity techniques, which are listed above in approximate order of experimental difficulty, have not been tried here. It appears that state selectivity in laser detection will be extremely useful, and that we have only begun to identify the potential of it.

4.4 Conclusion

Angular distributions, and translational, rotational, and vibrational energy distributions of NO molecules scattered from the (111) single crystal surface of platinum have been measured as a function of incident translational energy and over a crystal temperature range of approximately 400-1100 K.

The angular distributions and translational energy distributions indicate that there are at least two scattering mechanisms, trapping-desorption and inelastic scattering, and that trapping-desorption is the predominant mechanism, in agreement with earlier kinetic studies [31,32]. The correlation between the translational energy and the angular distribution show that the interpretation of scattering mechanisms applied to

angular distributions are correct, at least in this case.

The energy measurements show good accommodation of translational energy for low incident translational energy and low crystal temperature. Under these conditions there appears to be almost complete trapping of the incident flux and translational equilibrium with the surface. The accommodation is poor for conditions where inelastic scattering was prevalent, and there were some indications of non-equilibrium desorption at higher crystal temperatures.

The accommodation of vibrational energy is almost as complete as the translational accommodation, however the rotational energy was found to be very far from equilibrium with the surface. It was shown that these deviations from full accommodation are due to dynamic effects in the desorption process. We have proposed that the rotational energy is transferred to translational energy and aids the desorption through tight coupling of the rotational and translational motion. This tight coupling is likely caused by the angular asymmetry of the molecular-surface potential. We have proposed a model which reproduces the vibrational population and is based on vibrational equilibration of the adsorbed NO and different desorption rates for molecules in different vibrational states. It was also inferred that the vibrational excitation rate is approximately 10^8 - 10^9 s⁻¹.

Finally the efficient trapping and energy exchange for NO on Pt(111) relative to other systems studied is probably due to the low incident beam energy relative to the depth of the attractive part of the the potential, and the efficient collision-induced internal transfer of translational energy to rotational energy.

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Chapter 5: Summary

The transfer of energy between the surfaces of solids and adsorbed gas molecules is a significant fundamental factor in gas-surface interactions, and it has recently become clear that the energy distributions in the translational, vibrational, rotational and electronic modes of molecules scattered from surfaces can provide important clues as to the nature of the dynamics of the gas surface interactions.

A brief review of recent theoretical and experimental studies of gas-surface energy transfer was presented in chapter one. In summary, it appears that fundamental calculations of the gas-surface interaction potential are possible only in weakly interacting systems. However methods for generating empirical potentials are being developed, and those methods have been used in some apparently accurate theoretical calculations. There has also been significant progress in simplifying the calculation of the interaction dynamics. One of the more promising methods appears to be the generalized Langevin approach.

Experimental studies have progressed rapidly since the introduction of ultra-high vacuum compatible time-of-flight spectrometers for measuring translational energy distributions and laser absorption spectrometers for measuring the internal rotational, vibrational and electronic energy distributions of surface scattered gases.

Chapter three reports the results of a study of the translational energy and angular distributions of D_2O produced from the strongly exoergic reaction of D_2 and O_2 on a (111) oriented platinum surface. It was found that none of the excess chemical energy appeared as translational energy, from which it was concluded that the energy is dissipated

in dissociative adsorption of the reactants and in the formation of intermediate OD species. The observed translational energy distributions were strongly sub-thermal with mean translational energies roughly half the equilibrium value. We have proposed that this results from a desorption-process induced perturbation of the energy distribution of the adsorbed molecules i.e. a non-equilibrium desorption model. Within this model we find that the non-equilibrium effects appear to be stronger than predicted by theoretical calculations, and we conclude that there is rapid energy transfer between the perpendicular and parallel modes of adsorbate motion. The possibility and implications of a combined product formation and desorption step were also discussed. Regardless of the mechanism responsible for the sub-thermal velocities, these results show that the common association of cosine angular distributions with gas-surface equilibrium will not always be correct.

The development of a laser absorption spectrometer based on two-photon ionization techniques was reported in chapter two. In several ways this spectrometer appears to be superior to previous spectrometers based on laser-induced fluorescence techniques. The spectrometer was developed to measure the internal rotational and vibrational energy distributions of NO scattered from Pt(111) surfaces, as reported in chapter four. Also reported are the translational energy distributions and angular distributions of the scattered NO.

From the angular and translational energy distributions we conclude that NO scatters primarily through trapping-desorption (approximately 80%) and inelastic scattering, and that the inelastic scattering appears to be primarily indirect inelastic scattering.

Molecule-surface energy transfer was found to be efficient for all molecular modes, with nearly complete accommodation found in the translational mode, efficient but noticeably less than complete accommodation found in the vibrational mode, and relatively poor accommodation found in the rotational mode. The translational energy was in equilibrium with the surface at lower crystal temperatures and incident beam energies, with the degree of inelastic scattering increasing with increasing incident beam energy or crystal temperature.

We propose that the unequilibrated rotational and vibrational energy distributions result from dynamic effects in the desorption process. We propose that the rotational and perpendicular modes of the adsorbate motion are coupled allowing rotational energy to be transferred to desorption energy and producing cooled rotational energy distributions in the desorbing flux. We have suggested a model based on vibrational equilibrium of the adsorbed NO, but with vibrational level dependent desorption rates. This model reproduces the vibrational excitation data over a large temperature range. We have also attempted to estimate the vibrational excitation rate of NO adsorbed on platinum, which we believe is in the range of $10^8 - 10^9 \text{ s}^{-1}$.

Appendix A: Laser Data Accumulation Program

A.1 Introduction

Computer control of the two-photon ionization spectrometer was originally seen as a way to increase the flexibility and control of the experiments. However we discovered that standard boxcar integrators did not have the sensitivity and time response necessary to extract the ionization signal, whereas the CAMAC charge-to-digital convertors did. Therefore computer control was essential to the data accumulation.

The program was written as a series of subroutines to aid programming and testing and to simplify future modifications. An attempt was made to have each subroutine handle a well defined function, for instance there is a subroutine to control the stepping-motor driver for the laser grating, a subroutine to control point plotting, and a subroutine to input data from the charge-to-digital convertors. With this organization a change in experimental equipment should only require modification of the subroutines of the program that handle the operation of that equipment. Presented below is a sample subroutine and its relation to the calling routine. Also the functions of some subroutines are briefly discussed along with a listing of the program.

A.2 Typical Subroutine Structure

The subroutine at location SUB is typically called from the calling routine by an indirect use of the jump to subroutine instruction (JSR @ASUB) where the location of the subroutine is stored on page zero at a pointer location (ASUB). Before the subroutine call the calling routine sets up the input parameters in the memory locations immediately

following the JSR instruction. The subroutine picks up the parameters through accumulator 3 and typically returns any results through the same memory locations. The return to the calling routine is done through accumulator 3, but offset by the size of the parameter space. A typical subroutine structure is shown below.

```

;page zero

ASUB:      SUB                      ;subroutine address.

;calling routine
.
.
.
      STA 1,PARAM1      ;set up parameters.
      STA 2,PARAM2
      JSR @ASUB         ;call subroutine.
PARAM1:                      ;space for passing parameters.
PARAM2:
      LDA .....        ;first statement executed on return from
.                        the subroutine.
.
.

;subroutine
SUB:      STA 0,ASSUB    ;save accumulators.
          STA 1,ASSUB+1
          STA 2,ASSUB+2
          LDA 0,0,3      ;access input parameters.
          LDA 1,1,3
          .
          .              ;main body of subroutine.
          .
          STA 0,0,3      ;return result.
          LDA 0,ASSUB    ;restore accumulators.
          LDA 1,ASSUB+1
          LDA 2,ASSUB+2
          JMP 2,3        ;return to next executable line in calling
                           routine.
ASSUB:    .BLK 3         ; accumulator storage space.

```

A.3 Program Listing

The program is in 4 sub-modules: MAIN9, CAMA8, UT111 and FMAT3.

Segment MAIN9 is the main program and controls program flow, CAMA8

contains routines for accessing the experimental peripherals (most of which are in the CAMAC crate), UTILL contains utility programs for handling the teletype, formatting data, etc., and FMAT3 is a series of floating point math routines for averaging and normalizing the data. Segment FMAT3 is not listed here, but a few comments are in order. For programming ease the floating point numbers are represented as a 16 bit word of mantissa and a 16 bit word of exponent. Sixteen bits of mantissa limits the number resolution. However it was anticipated that the input data would have an accuracy of 1% and that data from no more than 200 laser pulses would be averaged. For these requirements 16 bits of mantissa are adequate, however averaging of data from many more than 200 points will yield incorrect results using the current program.

MAIN9:

The group of routines in MAIN9 handle program flow. After loading, the program can be started at location 4360 (octal). The program prompts for parameters, and often comes to branching points where choices are available. A branch point is indicated by a message such as "(I,P,B,R)" on the teletype. The letter corresponding to the desired choice is typed in. The available responses and their functions are

- I - initialize. Redraws plotting axis and begins the program.
- B - boxcar mode. Causes the data system to emulate a boxcar integrator.

The emulator can be entered during a sweep.

- P - parameters. Initiates input of parameters for a spectrum sweep.
- S - sweep. Command to start a spectrum sweep.
- R - repeat. Repeat spectrum just completed.
- C - continue. Breaks program out of boxcar emulation mode. The boxcar

mode is entered automatically whenever the input digitizers overload.

CAMA8:

The group of programs in CAMA8 control the data input and output.

GPUL - Routine GPUL handles the data input from the charge-to-digital convertors. The LeCroy 2248 convertors do not generate a LAM interrupt signal at the end of the conversion, so the routine watches for a Q=0 signal indicating a conversion in progress and then a Q=1 signal indicating conversion complete.

PMON - Routine PMON outputs 2 signals through the two-channel digital-to-analog CAMAC module. These signals are the average laser intensity and the average ionization current. The outputs are used to monitor the experiment in the sweep mode, and are the channel outputs in the boxcar emulation mode.

PLOT - Routine PLOT handles the spectrum plotting, which is done through the digital-to-analog board in the computer mainframe and is plotted on a modified Hewlett-Packard x-y plotter.

MDRI - Routine MDRI controls the CAMAC stepping motor driver which in turn moves the dye laser grating.

UTI11:

The group of programs in UTI11 handle miscellaneous mathematical functions, teletype input and output, and converting binary numbers to decimal character strings and decimal character strings to binary numbers.

The program listing follows.

```
1 .TITLE MAIN9
2 .ENT ASETU
3 .EXTD AISUB ADTOB AIMUL AID12 AGCHR
4 .EXTD APCHR AGSTR APSTR APMON APLOT
5 .EXTD AGPUL AMDRI AIADD ABYUP AFAD
6 .EXTD APWE AFDIV
7 .EXTD MCPOL MCPOLH
8 .ZREL
9 APAV- PAV
10 ABRNC- BRNCH
11 AGWLN- GWLN
12 AICOM- ICOM
13 ANDPT- NDPT ;END OF SWEEP
14 ANAV- NAV ;# PULSES TO AVERAGE
15 AMDIR- MDIR ;SWEEP DIRECTION
16 ANMPS- NMPS ;FOR CALCULATING DELTA MOTOR POS
17 APWRD- PWRD ;POWER DEPENDANCE
18 ASETU- SETU ;SET UP PARAM'S
19 ASHFT- SHFT
20 ABXCR- BXCR
21 ASWEP- SWEEP ;START SWEEP
22 ARSWP- RSWP; RESTART SWEEP
23 AINIT- INIT ;INITIALIZE
24 ASWLN- SWLN ;STARTING WAVELENGTH
25 .NREL
26 START- SUB 0,0
27 DOC 0,23 ;LIFT PEN
28 JSR @APSTR ;TYPE HEADER
29 STR1
30 JSR @APSTR
31 STR2
32 JSR @ABRNC
33 2
34 .TXT /I/
35 JMP @AINIT ;INITIALIZE
36 .TXT /B/
37 JSR @ABXCR ;POWER MONITOR
38 JMP START
39 STR1- .TXT /LASER SPECTROSCOPY ACCUMULATION PROGRAM<15><12>/
40 (I,B)/
41 STR3- .TXT /<15><12>GRATING POSITION(NEAREST .02, NO DECIMAL)*/
42 STR4- .TXT /GRATING POSITION FOR START OF SCAN*/
43 ;INITIALIZE SWEEP
44 INIT- JSR @APLOT ;DRAW AXIS
45 100000
46 0
47 SETU- JSR @APSTR ;INPUT PARAM.'S
48 STR3 ;CURRENT GRATING POS
49 JSR @AGWLN
50 CWLN- .BLK 2
51 JSR @APSTR ;STARTING POS
52 STR4
53 JSR @AGWLN
54 SWLN- .BLK 2
55 JSR @APSTR ;END GRATING POS
```

```

56          STR5
57          JSR      @AGWLN
58  EWLN-    .BLK 2
59          JSR      @APSTR  ;# STEPS BETWEEN POINTS
60          STR6
61          JSR      @AGSTR
62          B
63          3
64          -1
65          JMP CONT1
66  B-       .BLK 2
67  STR5-    .TXT /END GRATING POSITION*/
68  STR6-    .TXT /# OF STEPS(ABSOLUTE VALUE) BETWEEN POINTS<15><12>
69          EACH STEP =.024 NM IN FIRST ORDER*/
70  CONT1-   JSR      @ADTOB  ;STRING TO BINARY #
71          B
72  NSTP-    .BLK 2
73          LDA      0,NSTP
74          STA      0,NPCM
75          LDA      0,NSTP+1
76          STA      0,NPCM+1
77          JSR      @AIMUL
78  NPCM-    .BLK 2          ;MULT. # STEPS *12 TO GET PICOMETERS
79          30
80          0
81          LDA      0,CWLN
82          LDA      1,CWLN+1
83          STA      0,MCPOL ;SET CURRENT MOTOR POS
84          STA      1,MCPOL
85          LDA      0,SWLN
86          LDA      1,SWLN+1
87          STA      0,MPOS1
88          STA      1,MPOS1+1
89          JSR      @AMDRI  ;MOVE MOTOR
90  MPOS1-   .BLK 2
91          STA      0,MDIR+3
92          STA      1,MDIR+4
93          LDA      0,EWLN  ;FINAL WL
94          LDA      1,EWLN+1
95          STA      0,MDIR+1
96          STA      1,MDIR+2
97          LDA      2,ANDPT
98          STA      0,0,2   ;STORE END OF SWEEP POS
99          STA      1,1,2
100         JSR      @AICOM
101  MDIR-    .BLK 5          ;END-START
102         LDA      0,NPCM  ;SET SIGN FOR STEP LENGTH
103         LDA      1,NPCM+1
104         LDA      2,MDIR
105         MOVL#    2,2 SNC ;NEG?
106         JMP      .+5     ;NO
107         COM      0,0     ;YES
108         COM      1,1
109         INCZ     0,0 SZC
110         INC      1,1

```

```

111      LDA      2,ANMPS ;ADDRESS FOR INCREMENTING MOTOR POS
112
113      STA      0,0,2   ;STORE DELTA WAVELENGTH
114      STA      1,1,2
115      JSR      @APSTR
116      STR7      ;NUMBER OF LASER SHOTS
117      JSR      @AGSTR
118      C
119      3
120      -1
121      JSR      @ADTOB
122      C
123  VAR1-      .BLK 2
124      LDA      0,VAR1
125      STA      0,@ANAV
126      JSR      @APSTR ;POWER DEPENDENCE
127      STR8
128      JSR      @AGSTR ;TAKE 2 CHAR.'S
129      C
130      3
131      -1
132      JSR      @ABYUP
133      C
134      0
135      0
136      LDA      0,.-1
137      LDA      1,RSC60
138      SUB      1,0
139      JSR      @ABYUP
140      C
141      1
142      0
143      LDA      2,.-1
144      MOV#      2,2 SNR ;NULL
145      JMP      PASTO ;YES
146      SUB      1,2
147      MOVZL     2,2
148      MOVZL     2,2
149      MOVZL     2,2
150      JMP      CONT2
151  RSC60-     60
152  C-         .BLK 2
153  STR7-      .TXT /NUMBER OF LASER SHOTS TO AVERAGE*/
154  STR8-      .TXT 'POWER DEPENDENCE-3 DIGIT OCTAL NUMBER<15><12>
155            THE BINARY REPRESENTATION IS<15><12>(A**4)(A**2,A**1,A**1/2)
156            (A**1/4,A**1/8,A**1/16)*'
157  CONT2-     ADD      2,0
158            JSR      @ABYUP
159            C
160            2
161            0
162            LDA      2,.-1
163            MOV#      2,2 SNR ;NULL?
164            JMP      PASTO
165            SUB      1,2

```

```

166      MOVZL    2,2
167      MOVZL    2,2
168      MOVZL    2,2
169      MOVZL    2,2
170      MOVZL    2,2
171      MOVZL    2,2
172      ADD      2,0
173 PASTO- STA     0,@APWRD      ;POWER DEPENDENCE
174      JSR      @APSTR
175      STR9
176      JSR      @ABRNC ;WAIT FOR FURTHER COMMANDS
177      3
178      .TXT /S/
179      JMP      @ASWEP
180      .TXT /P/      ;PARAMETER SETUP
181      JMP      @ASETU
182      .TXT /B/      ;BOXCAR, PAUSE
183      JSR      @ABXCR
184      JMP      .-12
185 STR9-  .TXT /->(S,P,B)/
186
187 ;PULSE AVERAGING SUBROUTINE
188 ;1-AVERAGE NORMALIZED SIGNAL, 12 BITS
189 ;2-AVERAGE LASER POWER, 10 BITS
190 ;3-AVERAGE SIGNAL, 10 BITS
191 ;4-OVERFLOW,LSB=L.I.,MSB=SIG
192 PAV-   STA     0,PAVAS
193      STA     1,PAVAS+1
194      STA     2,PAVAS+2
195      STA     3,PAVAS+3
196      LDA     2,NAV ;# OF PULSES TO AVERAGE
197      NEG     2,2
198      STA     2,PLCNT
199      LDA     1,OVCNT ;# OF OVERFLOWS TO IGNORE
200      SUB     0,0
201      STA     0,LPSUM ;0 SUMMING LOC.'S
202      STA     0,LPSUM+1
203      STA     0,EMSUM
204      STA     0,EMSUM+1
205      STA     0,NESUM
206      STA     0,NESUM+1
207      SUB     2,2 ;WILL HOLD OVERFLOW
208 PAVLP- JSR      @AGPUL
209 PSIG-  .BLK 3
210      LDA     0,PSIG+2 ;OVERFLOW IND
211      MOV#    0,0 SNR ;OVERFLOW?
212      JMP     .+10 ;NO
213      MOVL#   1,1 SNC ;MORE THAN MAX # OF OVERFLOWS?
214      JMP     .+3 ;YES
215      INC     1,1 ;NO,INC. COUNTER
216      JMP     PAVLP ;TAKE ANOTHER LASER SHOT
217      COM     0,0 ;OR WITH 2
218      AND     0,2
219      ADC     0,2
220      LDA     0,PSIG ;LASER INT.

```



```

221      STA      0,LPSUM+2
222      STA      0,LPPWR
223      SUB      0,0
224      STA      0,LPPWR+1
225      STA      0,EMNRM+1
226      LDA      0,PSIG+1 ;SIGNAL INT.
227      STA      0,EMSUM+2
228      STA      0,EMNRM
229      JSR      @AFAD      ;SUM SIGNAL
230  EMSUM-    .BLK 3
231          0
232      JSR      @AFAD      ;SUM LASER INT.
233  LPSUM-    .BLK 3
234          0
235      JSR      @APWE      ;RAISE LASER INT. TO THE
236  LPPWR-    .BLK 2          ;POWER DEPENDENCE
237  PWRD-     20
238          0
239      LDA      0,LPPWR
240      STA      0,EMNRM+2
241      LDA      0,LPPWR+1
242      STA      0,EMNRM+3
243      JSR      @AFDIV     ;NORMALIZE SIGNAL
244  EMNRM-    .BLK 5
245      LDA      0,EMNRM
246      STA      0,NESUM+2
247      LDA      0,EMNRM+1
248      STA      0,NESUM+3
249      JSR      @AFAD      ;SUM NORMALIZED SIGNAL
250  NESUM-    .BLK 4
251      ISZ      PLCNT
252      JMP      PAVLP
253      LDA      3,PAVAS+3 ;LOOP DONE, STORE OVERFLOW
254      STA      2,3,3
255      LDA      2,NAV      ;DIVIDE SUMS
256      STA      2,EMDI+2
257      STA      2,LPDI+2
258      STA      2,NEMDI+2
259      LDA      0,NESUM
260      STA      0,NEMDI
261      LDA      0,NESUM+1
262      STA      0,NEMDI+1
263      LDA      0,LPSUM
264      STA      0,LPDI
265      LDA      0,LPSUM+1
266      STA      0,LPDI+1
267      LDA      0,EMSUM
268      STA      0,EMDI
269      LDA      0,EMSUM+1
270      STA      0,EMDI+1
271      JMP      .+11
272  NAV-      12
273  PLCNT-    -12
274  OVCNT-    -1
275  PAVAS-    .BLK 4

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```

276 MSK1- 7777
277
278 JSR @AFDIV ;DIVIDE SIG SUM BY NAV
279 EMDI- .BLK 3
280 0
281 0
282 JSR @AFDIV ;DIVIDE LI SUM
283 LPDI- .BLK 3
284 0
285 0
286 JSR @AFDIV ;DIVIDE NORM. SIGNAL SUM
287 NEMDI- .BLK 3
288 0
289 0
290 READS 0 ;READ SWITCHES FOR SCALE FACTOR
291 LDA 1,MSK1
292 AND 1,0
293 LDA 1,NEMDI+1
294 ADD 0,1
295 MOVL# 1,1 SZC ;NEGMP .+3 ;YES
296 LDA 0,MSK2 ;NO, # TOO LARGE
297 JMP .+10
298 STA 1,NEMSH+1
299 LDA 0,NEMDI
300 STA 0,NEMSH
301 JSR @ASHFT ;SHIFT NORMALIZED SIGNAL
302 NEMSH- .BLK 2
303 LDA 0,NEMSH
304 LDA 1,MSK2 ;MAX # TO DISPLAY
305 SUB 0,1 ;TOO LARGE?
306 MOVL# 1,1 SZC
307 LDA 0,MSK2 ;YES
308 LDA 3,PAVAS+3
309 STA 0,0,3
310 LDA 0,LPDI
311 LDA 1,LPDI+1
312 STA 0,LPSH
313 STA 1,LPSH+1
314 LDA 0,EMDI
315 LDA 1,EMDI+1
316 STA 0,EMSH
317 STA 1,EMSH+1
318 JSR @ASHFT
319 LPSH- .BLK 2
320 JSR @ASHFT
321 EMSH- .BLK 2
322 LDA 3,PAVAS+3
323 LDA 2,MSK2
324 LDA 0,LPSH
325 LDA 1,EMSH
326 AND 2,0
327 AND 2,1
328 STA 0,1,3
329 STA 1,2,3
330 LDA 0,PAVAS

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```

331          LDA      1,PAVAS+1
332          LDA      2,PAVAS+2
333          JMP      4,3
334  MSK2-    7777
335  MSK3-    1777
336
337  ;FUNCTIONS AS BOXCAR, PAUSES SWEEP, C GETS OUT
338  BXCR-    STA      3,BRET
339          JSR      @APAV
340  BSIG-    .BLK 4
341          LDA      0,BSIG+3          ;CHECK OVERFLOW
342          MOVL#    0,0 SNC
343          JMP      .+4
344          JSR      @APSTR ;EM OVERFLOW
345          STR10
346          JMP      BCONT
347          MOVR#    0,0 SNC
348          JMP      BCONT
349          JSR      @APSTR ;LI OVERFLOW
350          STR11
351  BCONT-    LDA      0,BSIG+1          ;LI
352          LDA      1,BSIG+2 ;SIG
353          READS    2
354          MOVL#    2,2 SNC
355          JMP      .+3
356          LDA      0,BFSC
357          LDA      1,BFSC ;FULL SCALE FOR ADJ. METERS
358          STA      0,BOUT
359          STA      1,BOUT+1
360          JSR      @APMON ;PUT 2 SIGNALS OUT
361  BOUT-    .BLK 2
362          LDA      0,BSIG
363          SUB      1,1
364          INC      1,1
365          DOB      1,23 ;Y
366          LDA      1,BOFFS
367          SUB      1,0
368          DOA      0,23
369          SKPDN    TTI
370          JMP      BXCR+1
371          JSR      @ABRNC
372          2
373          .TXT /<177>/ ;RUBOUT
374          JMP      BXCR+1 ;CONTINUE
375          .TXT /C/ ;RETURN
376          LDA      3,BRET
377          JMP      0,3
378  BRET-    0
379  BOFFS-    4000
380  STR11-    .TXT /LASER INTENSITY OVERFLOW<15><12>/
381  STR10-    .TXT /ELECT. MULT. OVERFLOW<15><12>/
382  BFSC-    1777
383  ;SWEEP LASER, ACCUMULATE SPECTRUM
384  STR12-    .TXT /LASER INTENSITY OVERFLOW<15><12>/
385  STR13-    .TXT /ELECT. MULT. OVERFLOW<15><12>/

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386 SWEEP- LDA      0,MCPOL ;CURRENT GRATING POS.
387         LDA      1,MCPOH
388         STA      0,SMPSU
389         STA      1,SMPSU+1
390         JSR      @AIADD
391 SMPSU-  .BLK 2    ;GETS NEW WAVELENGTH
392 NMPS-   .BLK 2    ;# PICOMETERS(1ST ORDER) TO MOVE
393         LDA      0,SMPSU
394         LDA      1,SMPSU+1
395         STA      0,SNDS+1
396         STA      1,SNDS+2
397         JSR      @AICOM ;END OF SWEEP
398 SNDS-   .BLK 3
399 NDPT-   .BLK 2    ;FINAL WAVELENGTH
400         STA      0,SWMV
401         STA      1,SWMV+1
402         LDA      0,SNDS
403         MOV      0,0 SNR
404         JMP      .+4
405         LDA      1,@AMDIR ;<0>=<1>=>PAST END
406         SUB      1,0 SNR
407         JMP      SWPDN ;DONE, GET CHAR FROM TTY
408         JSR      @AMDRI
409 SWMV-   .BLK 2
410 SINR-   JSR      @APAV ;GET SIGNAL
411 SSIG-   .BLK 4
412         LDA      0,SSIG+3
413         MOVL#    0,0 SNC
414         JMP      .+5
415         JSR      @APSTR ;EM OVERFLOW
416         STR12
417         JSR      @ABXCR
418         JMP      SINR
419         MOVR#    0,0 SNC
420         JMP      SCONT
421         JSR      @APSTR ;LASER PWR OVERFLOW
422         STR13
423         JSR      @ABXCR
424         JMP      SINR
425 SCONT-  LDA      0,SSIG+1 ;L.I.
426         LDA      1,SSIG+2 ;SIG
427         STA      0,SOUT
428         STA      1,SOUT+1
429         JSR      @APMON ;PUT SIGNAL OUT
430 SOUT-   .BLK 2
431         LDA      0,SSIG ;NORM. SIGNAL
432         STA      0,SLOT
433         JSR      @APLOT ;PLOT
434 SPLOT-  0
435         100000
436         SKPDN    TTI ;TTY?
437         JMP      SWEEP ;NO, CONTINUE
438         JSR      @ABRNC ;YES
439         4
440         .TXT /R/ ;RESTART SWEEP

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441      JMP      @ARSWP
442      .TXT /P/          ;SET UP PARAM.'S
443      JMP      @ASETU
444      .TXT /<177>/      ;RUBOUT, CONTINUE
445      JMP      SWEEP
446      .TXT /B/          ;BOXCAR, PAUSE
447      JSR      @ABXCR
448      JMP      SWEEP
449  SWPDN- JSR      @APSTR
450      STR14
451      SUB      0,0        ;LIFT PEN
452      DOC      0,23
453      JSR      @ABRNC
454      4
455      .TXT /P/          ;SET UP PARAM.'S
456      JMP      @ASETU
457      .TXT /I/          ;INITIALIZE
458      JMP      @AINIT
459      .TXT /R/          ;RESWEEP
460      JMP      @ARSWP
461      .TXT /B/
462      JSR      @ABXCR    ;BOXCAR
463      JMP      .-12
464  STR14- .TXT /->(I,P,R,B)/
465  RSWP-  LDA      2,ASWLN ;GET START OF SWEEP
466      LDA      0,0,2
467      LDA      1,1,2
468      STA      0,RPOS
469      STA      1,RPOS+1
470      JSR      @AMDRI    ;REPOSITION SWEEP
471  RPOS-  .BLK 2
472      JMP      @ASWEP
473
474      ;BRANCHING PROGRAM-GET CHARACTER FROM TTY,
475      ;COMPARE TO LIST, BRANCH ACCORDING TO COMPARISON
476      ;1-# OF LETTERS, N
477      ;2*J-1FOR J=1,N- LETTER FOR COMPARISON
478      ;2*J-SUBROUTINE RETURNS HERE IF LETTER MATCHES
479  BRNCH- STA      0,BRNAS
480      STA      1,BRNAS+1
481      STA      2,BRNAS+2
482      STA      3,BRNAS+3
483      MOV      3,2
484  BRLP1- LDA      0,0,2    ;NUMBER OF COMPARISONS
485      NEG      0,0
486      JSR      @AGCHR    ;GET CHARACTER FROM TTY
487  BCHR-  0
488      LDA      1,BCHR
489  BRLP2- INC      2,2      ;INC 2,POINTS TO CHAR
490      LDA      3,0,2      ;GET CHAR
491      INC      2,2      ;POINTS TO RETURN ADD.
492      SUB      1,3
493      MOV      3,3 SNR    ;COMPARE TO TTY
494      JMP      BREX      ;SAME, EXIT
495      INC      0,0 SZR    ;END OF LIST?

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```

496          JMP      BRLP2      ;NO
497          JSR      @APCHR      ;YES
498          .TXT      /?/
499          LDA      2,BRNAS+3
500          JMP      BRLP1      ;TRY AGAIN
501  BREX-    STA      1,BRECH
502          JSR      @APCHR
503  BRECH-   0
504          JSR      @APSTR
505          BRCLF
506          MOV      2,3
507          LDA      0,BRNAS
508          LDA      1,BRNAS+1
509          LDA      2,BRNAS+2
510          JMP      0,3
511  BRNAS-   .BLK 4
512  BRCLF-   .TXT /<12><15>/
513          ;INTEGER COMPARISON
514          ;1-RETURN 1 IF A>B, 0 IF A=B, -1 IF A<B
515          ;2-LOW WORD A
516          ;3-HIGH WORD A
517          ;4-LOW WORD B
518          ;5-HIGH WORD B
519  ICOM-    STA      0,ICOAS
520          STA      1,ICOAS+1
521          STA      2,ICOAS+2
522          STA      3,ICOAS+3
523          LDA      0,1,3
524          STA      0,ICSU
525          LDA      0,2,3
526          STA      0,ICSU+1
527          LDA      0,3,3
528          STA      0,ICSU+2
529          LDA      0,4,3
530          STA      0,ICSU+3
531          JSR      @AISUB
532  ICSU-    .BLK 4
533          LDA      0,ICSU
534          LDA      1,ICSU+1
535          SUB      2,2      ;CLEAR 2
536          MOVL#    1,1 SNC ;NEG?
537          JMP      .+3      ;NO
538          COM      2,2      ;YES,<2>=-1
539          JMP      ICEX
540          MOV      0,0 SZR ;LW=0?
541          JMP      .+3      ;NO, POS
542          MOV      0,0 SNR ;YES, HW=0?
543          JMP      ICEX      ;YES, <2>=0
544          INC      2,2      ;NO, <2>=1
545  ICEX-    LDA      3,ICOAS+3
546          STA      2,0,3
547          LDA      0,ICOAS
548          LDA      1,ICOAS+1
549          LDA      2,ICOAS+2
550          JMP      5,3

```

```

551 ICOAS- .BLK 4
552 ;SHIFT FP # SO THAT EXP=0
553 ;1-MANT.
554 ;2-EXP
555 SHFT- STA 0,SHFAS
556 STA 1,SHFAS+1
557 LDA 0,0,3 ;MANT
558 LDA 1,1,3 ;EXP
559 MOVL# 1,1 SNC ;NEG?
560 JMP SHFL ;NO, SHIFT LEFT
561 SHFR- MOVZR 0,0 ;YES
562 INC 1,1 SZR
563 JMP -2
564 JMP SHFEX
565 SHFL- NEG 1,1 ;POS EXP
566 MOVZL 0,0
567 INC 1,1 SZR
568 JMP -2
569 SHFEX- STA 0,0,3
570 LDA 0,SHFAS
571 LDA 1,SHFAS+1
572 JMP 2,3
573 SHFAS- .BLK 2
574 ;INPUT GRATING POSITIONS
575 ;1-LOW WORD OF 1ST ORDER WAVELENGTH IN 10-3 NM
576 ;2-HIGH WORD
577 GWLN- STA 0,GWLAS
578 STA 1,GWLAS+1
579 STA 2,GWLAS+2
580 STA 3,GWLAS+3
581 JSR @AGSTR
582 A
583 6
584 -1
585 JSR @ADTOB
586 A
587 GWNM- .BLK 2
588 LDA 0,GWNM
589 LDA 1,GWNM+1
590 STA 0,GWM10
591 STA 1,GWM10+1
592 JSR @AIMUL
593 GWM10- .BLK 2
594 12
595 0
596 LDA 0,GWM10
597 LDA 1,GWM10+1
598 STA 0,GWD12
599 STA 1,GWD12+1
600 JSR @AID12
601 GWD12- .BLK 2
602 LDA 0,GWD12
603 LDA 1,GWD12+1
604 STA 0,GWM12
605 STA 1,GWM12+1

```

```
606          JSR      @AIMUL
607 GWM12-    .BLK 2
608          30
609          0
610          LDA      0,GWM12
611          LDA      1,GWM12+1
612          LDA      3,GWLAS+3
613          STA      0,0,3
614          STA      1,1,3
615          LDA      0,GWLAS
616          LDA      1,GWLAS+1
617          LDA      2,GWLAS+2
618          JMP      2,3
619 A-        .BLK 4
620 GWLAS-    .BLK 4
621 .END START
```



```

1  .TITLE CAMA8
2  .ENT AGPUL APMON AMDRI MCPOL MCPOH APLOT
3  .EXTD ASETU AID12 AISUB APSTR AGCHR
4  .ZREL
5  AGPUL- GPUL
6  APMON- PMON
7  APLOT- PLOT
8  AMDRI- MDRI
9  MCPOL- 0
10 MCPOH- 0
11 .NREL
12 ;GET PULSE FROM LASER FIRE
13 ;1-RETURN LASER INTENSITY
14 ;2-RETURN ELECT. MULT. AMPLITUDE
15 ;3-LSB=L.I. OVERFLOW,MSB=E.M. OVERFLOW
16 GPUL- STA 0,GPUAS
17 STA 1,GPUAS+1
18 STA 2,GPUAS+2
19 SUB 0,0
20 DOC 0,40
21 LDA 0,CLRA1
22 DOAS 0,40 ;CLEAR 1
23 LDA 0,CLRA2
24 DOAS 0,40 ;CLEAR 2
25 GPWL1- LDA 0,GPREM ;WAIT FOR START OF CONV.
26 DOAS 0,40
27 SKPDZ 40 ;Q=0,CONV IN PROGRESS
28 JMP GPWL1
29 GPWL2- LDA 0,GPREM ;WAIT FOR END OF CONV.
30 DOAS 0,40
31 SKPDN 40
32 JMP GPWL2
33 LDA 0,GPRL ;CONV. DONE
34 DOAS 0,40
35 DIB 0,40 ;READ LASER
36 SUB 2,2 ;CLEAR 2
37 LDA 1,GP255 ;CHECK FOR OVERFLOW
38 SUB 0,1 SNR
39 MOVOL 2,2 ;YES
40 LDA 1,GOFFD ;GET OFFSET
41 SUB 1,0 ;SUB
42 STA 0,0,3 ;RETURN LASER AMPLITUDE
43 LDA 0,GPREM ;READ EM
44 DOAS 0,40
45 DIB 0,40
46 LDA 1,GP255
47 SUB 0,1 SZR ;OVERFLOW?
48 JMP .+3
49 MOVZL 2,2 ;YES,SET MSB
50 MOVOR 2,2
51 STA 2,2,3 ;RETURN OVERFLOW INDICTATOR
52 LDA 1,GOFFE ;OFFSET
53 SUB 1,0
54 MOVZL 0,0
55 MOVZL 0,0 ;*4

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```

56          STA      0,1,3    ;RETURN E.M. AMPLITUDE
57          LDA      0,GPUAS
58          LDA      1,GPUAS+1
59          LDA      2,GPUAS+2
60          JMP      3,3
61  GPREM- 107      ;N(4),A(7),F(0)
62  GPRL- 60       ;N(3),A(0),F(0)
63  CLRA1- 11060   ;N(3),A(0),F(9)
64  CLRA2- 11100   ;N(4),A(0),F(9)
65  GP255- 377
66  GP64- 100
67  GP48- 60
68  GOFFE- 30
69  GOFFD- 30
70  GPUAS- .BLK 3
71  ;PMON-OUTPUT LASER FIRE TO X-Y PLOTTER
72  ;1-LASER INTENSITY
73  ;2-ELECTRON MULTIPLIER
74  PMON- STA      0,PMOAS
75          STA      1,PMOAS+1
76          STA      2,PMOAS+2
77          READS    0
78          MOVL     0,0 SNC ;CHECK SWITCH #0
79          JMP      .+4      ;=0
80          LDA      0,PMFS ;=1,LOAD FULL SCALE
81          LDA      1,PMFS
82          JMP      .+3
83          LDA      0,0,3    ;GET VALUES
84          LDA      1,1,3
85          SUB      2,2
86          DOB      2,40     ;SET X-Y MODE
87          DOC      2,40
88          LDA      2,PLCON ;LOAD CONTROL MODE
89          DOAS     2,40
90          LDA      2,PMOUT ;TRANSFER DATA
91          DOA      2,40
92          DOBS     0,40     ;LASER INTEN.
93          DOBS     1,40     ;I.M.
94          LDA      0,PMOAS
95          LDA      1,PMOAS+1
96          LDA      2,PMOAS+2
97          JMP      2,3
98  PMOAS- .BLK 3
99  PLCON- 20541    ;F(16),A(1),N(22)
100 PMOUT- 21540    ;F(17),A(0),N(22)
101 PMFS- 1777
102
103 ;MOTOR DRIVER
104 ;1-LOW WORD OF DESIRED POSITION
105 ;2-HIGH WORD OF DESIRED POSITION
106 MDRI- STA      0,MDRAS
107          STA      1,MDRAS+1
108          STA      2,MDRAS+2
109          STA      3,MDRAS+3
110          SUB      0,0      ;CLEAR I

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111      DOC      0,40
112      LDA      0,MCPOL ;GET CURRENT POSITION
113      LDA      1,MCPDH
114      STA      0,MDIF+2
115      STA      1,MDIF+3
116      LDA      0,0,3 ;GET NEW POS
117      LDA      1,1,3
118      STA      0,MCPOL ;UPDATE POSITION
119      STA      1,MCPDH
120      STA      0,MDIF
121      STA      1,MDIF+1
122      JSR      @AISUB ;DIFFERENCE, AMOUNT TO MOVE
123 MDIF-   .BLK 4
124      LDA      0,MDIF
125      LDA      1,MDIF+1
126      SUB      2,2 ;CLEAR 2-INDICATES POS
127      MOVL#    1,1 SNC ;NEG?
128      JMP      .+6 ;NO
129      COM      1,1 ;YES,MAKE POS
130      COM      0,0
131      INCZ     0,0 SZC
132      INC      1,1
133      COM      2,2 ;SET FLAG TO IND. NEG.
134      STA      0,MNTST
135      STA      1,MNTST+1
136      JSR      @AID12 ;DIVIDE TO GET # OF STEPS
137 MNTST-  .BLK 2
138      LDA      0,MNTST
139      LDA      1,MNTST+1
140      STA      0,MNST
141      STA      1,MNST+1
142 MDLP-   JSR      @AISUB ;SUBTRACT MAX # OF STEPS
143 MNST-   .BLK 2
144      77777
145      0
146      LDA      3,MNST+1
147      MOVL#    3,3 SNC ;GREATER THAN MAX?
148      LDA      0,MNST+2 ;YES
149      MOV#     2,2 SNR ;NEG?
150      JMP      .+3 ;NO
151      MOVZL    0,0 ;YES,SET MSB
152      MOVOR    0,0
153      LDA      1,MMOV
154      DOA      1,40
155      DOBS     0,40 ;START MOTOR
156      SKPDN    40 ;Q=0?
157      JMP      MLIM ;YES
158      LDA      1,MRST ;READ STATUS
159      DOAS     1,40
160      DIB      0,40
161      MOVR     0,0 SNC
162      JMP      .-3
163      LDA      0,MNST ;MORE TO GO?
164      LDA      1,MNST+1
165      MOVL#    1,1 SZC ;REMAINDER POS?

```

```

166      JMP      MDEX      ;NO, QUIT
167      MOVL#    1,1 SZR ;YES,-0?
168      JMP      MDLP
169      MOVL#    0,0 SZR
170      JMP      MDLP      ;NO,CONTINUE
171 MDEX-  LDA      0,MDRAS
172      LDA      1,MDRAS+1
173      LDA      2,MDRAS+2
174      LDA      3,MDRAS+3
175      JMP      2,3
176 MLIM-  JSR      @APSTR  ;MOTOR AT LIMITS,SEND MESSAGE
177      MERMS
178      JMP      @ASETU
179 MDRAS-  .BLK 4
180 MMOV-  20040      ;F(16) A(0) N(2)
181 MRST-  1054      ;F(1) A(12) N(2)
182 MERMS-  .TXT /GRATING MOTOR OFF OR AT LIMITS. CORRECT.<15><12>/
183
184      ;PLOT-PUT POINTS TO X-Y PLOTTER
185      ;1-Y POS IN 12 LOWER BITS,MSB=1=>RESET X,DRAW AXIS, DON'T PLOT
186      ;2-X POS IN LOWER 12 BITS,MSB=1=>INCREMENT X
187 PLOT-  STA      0,PLAS
188      STA      1,PLAS+1
189      STA      2,PLAS+2
190      STA      3,PLAS+3
191      LDA      2,PRTC      ;SET RTC TO 100HZ
192      DOAS      2,14
193      LDA      0,0,3
194      MOVL#    0,0 SNC ;AXIS?
195      JMP      .+5
196      JSR      PAXIS      ;YES
197      SUB      0,0      ;RESET X
198      STA      0,PNX
199      JMP      PEX
200      LDA      1,1,3
201      MOVL#    1,1 SNC ;INCREMENT X?
202      JMP      .+6      ;NO
203      LDA      1,PNX      ;NEXT X POS
204      LDA      2,PDELX ;AMOUNT TO INCREMENT X
205      ADD      2,1
206      STA      1,PNX      ;STORE NEW X
207      LDA      2,PXMx      ;XMAX
208      SUB      1,2
209      MOVL#    2,2 SNC ;X TOO LARGE?
210      JMP      .+10      ;NO
211      JSR      @APSTR  ;MESSAGE FOR NEW PAPER
212      PNEWP
213      JSR      @AGCHR  ;TTY RESPONSE
214      0
215      JSR      PAXIS
216      SUB      1,1
217      STA      1,PNX
218      LDA      2,POFFS
219      SUB      2,0
220      SUB      2,1

```

```
221      SUB      2,2
222      DOB      2,23      ;X
223      DOA      1,23
224      INC      2,2      ;Y
225      DOB      2,23
226      DOAS     0,23
227 PEX-   LDA      0,PLAS
228      LDA      1,PLAS+1
229      LDA      2,PLAS+2
230      LDA      3,PLAS+3
231      JMP      2,3
232 PLAS-   .BLK 4
233 PDELX-  14
234 PNx-    0
235 POFFS-  4000
236 PXMx-   7777
237 PNEWp-  .TXT /INSERT NEW PLOTTER PAPER,TYPE ANY KEY<15><12>/
238 PAXIS-  STA      3,PTEMP
239      SUB      2,2
240      DOC      2,23      ;LIFT PEN
241      JSR      PWAIT
242      -1
243      LDA      1,PFSC
244      DOB      2,23      ;X
245      DOA      1,23      ;X=MAX
246      LDA      1,POFFS
247      INC      2,2
248      DOB      2,23      ;Y
249      DOA      1,23      ;Y=MIN
250      JSR      PWAIT
251      -200
252      SUB      2,2
253      DOB      2,23      ;X
254      INC      2,2      ;PEN DOWN
255      DOC      2,23
256      JSR      PWAIT      ;WAIT
257      -1
258      LDA      1,POFFS
259      DOA      1,23      ;X=MIN,XAXIS
260      JSR      PWAIT
261      -200
262      DOB      2,23      ;Y
263      LDA      1,PFSC
264      DOA      1,23      ;Y=YMAX,Y AXIS
265      JSR      PWAIT
266      -200
267      SUB      2,2
268      DOC      2,23      ;LIFT PEN
269      JSR      PWAIT
270      -1
271      LDA      3,PTEMP
272      JMP      0,3
273 PTEMP-  0
274 PFSC-   3777
275 PRTC-   2
```

```
276 PWAIT- LDA      1,0,3
277          STA      1,PCCNT
278 PWLP-   NIOS      14
279          SKPDN     14
280          JMP       -1
281          ISZ       PCCNT
282          JMP       PWLP
283          JMP       1,3
284 PCCNT-   0
285 .END
```

```

1  .TITLE UT111
2  .RDX 8
3  .ENT AIADD AISUB AIMUL
4  .ENT AID12 APCHR AGCHR
5  .ENT ABYPA ABYUP ADTOB
6  .ENT ABTOD AGSTR APSTR
7  ;
8  .ZREL
9  AIADD- IADD
10 AISUB- ISUB
11 AIMUL- IMUL
12 AID12- ID12
13 APCHR- PCHR
14 AGCHR- GCHR
15 ABYPA- BYPA
16 ABYUP- BYUP
17 ADTOB- DTOB
18 ABTOD- BTOD
19 AGSTR- GSTR
20 APSTR- PSTR
21 ;
22 .NREL
23 ;INTEGER ADD
24 ;1-PASS A, RETURN SUM
25 ;2
26 ;3-PASS B
27 ;4
28 IADD- STA 0,IADAS ;STORE ACC'S
29        STA 1,IADAS+1
30        STA 2,IADAS+2
31        STA 3,IADAS+3
32        LDA 0,0,3 ;LOW WORD OF A
33        LDA 1,2,3 ;LOW WORD OF B
34        SUBO 2,2 ;CLEAR 2
35        ADDZ 0,1 ;ADD
36        MOVL 2,2 ;SHIFT CARRY INTO 2
37        STA 1,0,3 ;STORE LOW WORD OF SUM
38        LDA 0,1,3 ;HIGH WORD A
39        ADD 0,2 ;ADD CARRY
40        LDA 0,3,3 ;HIGH WORD B
41        ADD 0,2 ;ADD
42        STA 2,1,3 ;STORE HIGH WORD OF SUM
43        LDA 0,IADAS
44        LDA 1,IADAS+1
45        LDA 2,IADAS+2
46        LDA 3,IADAS+3
47        JMP 4,3
48 IADAS- .BLK 4
49 ;INTEGER SUBTRACT
50 ;1-PASS A, RETURN DIFFERENCE, LOW WORD
51 ;2-HIGH WORD
52 ;3-PASS LOW WORD OF B
53 ;4-HIGH WORD
54 ISUB- STA 0,ISUAS ;STORE ACC'S
55        STA 1,ISUAS+1

```

```

56          STA      2,ISUAS+2
57          STA      3,ISUAS+3
58          LDA      0,0,3    ;LOW WORD A
59          LDA      1,1,3    ;HIGH WORD A
60          STA      0,ISUBT
61          STA      1,ISUBT+1
62          LDA      0,2,3    ;B
63          LDA      1,3,3
64          COM      0,0      ;MAKE B NEG
65          COM      1,1
66          INCZ     0,0 SZC ;ADD 1 TO COMPLETE
67          INC      1,1      ;2'S COMPLEMENT
68          STA      0,ISUBT+2
69          STA      1,ISUBT+3
70          JSR      @AIADD
71  ISUBT-   .BLK 4
72          LDA      0,ISUBT
73          LDA      1,ISUBT+1
74          LDA      3,ISUAS+3
75          STA      0,0,3    ;RETURN DIFF.
76          STA      1,1,3
77          LDA      0,ISUAS
78          LDA      1,ISUAS+1
79          LDA      2,ISUAS+2
80          JMP      4,3
81  ISUAS-   .BLK 4
82          ;INTEGER MULTIPLY
83          ;1-PASS A, RETURN PRODUCT, LOW WORD
84          ;2-HIGH WORD
85          ;3-PASS LOW WORD OF B
86          ;4-HIGH WORD
87  IMUL-    STA      0,IMUAS
88          STA      1,IMUAS+1
89          STA      2,IMUAS+2
90          STA      3,IMUAS+3
91          LDA      0,0,3    ;LOW WORD OF A
92          LDA      1,1,3    ;HIGH WORD
93          STA      0,IMUAC+2
94          STA      1,IMUAC+3
95          SUB      0,0      ;CLEAR ACCUMULATION LOC.
96          STA      0,IMUAC
97          STA      1,IMUAC+1
98          LDA      0,2,3    ;LOW WORD OF B
99          LDA      1,3,3    ;HIGH WORD
100         STA      0,IMBST
101         STA      1,IMBST+1
102         LDA      2,IMM32 ; -32
103  IMLP-    LDA      0,IMBST
104         LDA      1,IMBST+1
105         MOVZR     1,1      ;SHIFT B RIGHT
106         STA      1,IMBST+1;AND STORE
107         MOVR      0,0
108         STA      0,IMBST
109         MOV      0,0 SNC ;LSB B=1?
110         JMP      IMUSH    ;NO

```



```

111      JSR      @AIADD  ;YES, ADD
112 IMUAC-  .BLK 4
113 IMUSH-  LDA      0,IMUAC+2
114          LDA      1,IMUAC+3
115          MOVZL    0,0      ;SHIFT A LEFT
116          MOVL     1,1
117          STA      0,IMUAC+2
118          STA      1,IMUAC+3
119          INC      2,2 SZR ;CHECK COUNT
120          JMP      IMLP
121          LDA      0,IMUAC ;GET PRODUCT
122          LDA      1,IMUAC+1
123          LDA      3,IMUAS+3
124          STA      0,0,3
125          STA      1,1,3
126          LDA      0,IMUAS
127          LDA      1,IMUAS+1
128          LDA      2,IMUAS+2
129          JMP      4,3
130 IMUAS-  .BLK 4
131 IMBST-  .BLK 2
132 IMM32-  -40
133 ;DIVIDE BY 12
134 ;1-PASS AND RETURN LOW WORD
135 ;2-HIGH WORD
136 ID12-   STA      0,IDIAS ;STORE ACC'S
137          STA      1,IDIAS+1
138          STA      2,IDIAS+2
139          STA      3,IDIAS+3
140          LDA      0,0,3  ;LOW WORD
141          LDA      1,1,3  ;HIGH WORD
142          MOVZR    1,1    ;DIVIDE BY 8
143          MOVR     0,0
144          MOVZR    1,1
145          MOVR     0,0
146          MOVZR    1,1
147          MOVR     0,0
148          STA      0,ID1AC
149          STA      1,ID1AC+1
150          LDA      1,IDC3 ;DIVISOR
151          SUB      0,0
152          STA      0,ID1AC+2
153          STA      1,ID1AC+3
154          LDA      2,IDM30 ; -30
155          SUBO     0,0    ;CLEAR, WILL RECEIVE
156          SUBO     1,1    ;ANSWER
157 ID1LP-  LDA      3,ID1AC
158          STA      3,IDIST ;TEMP. STORE
159          LDA      3,ID1AC+1
160          STA      3,IDIST+1
161          JSR      @AISUB ;SUB.
162 ID1AC-  .BLK 4
163          LDA      3,ID1AC+1;HIGH WORD OF DIFF.
164          MOVL     3,3 SNC ;CHECK SIGN
165          JMP      IDIPO ;POS.

```

```

166      MOVZL    0,0      ;NEG., SHIFT 0 INTO
167      MOVL     1,1      ;QUOTIENT
168      LDA      3,ID1ST ;TEMP. STORE =>
169      STA      3,ID1AC ;DIVISION ACCUM.
170      LDA      3,ID1ST+1
171      STA      3,ID1AC+1
172      JMP      ID1SH
173 ID1PO- MOVOL    0,0      ;POS., SHIFT 1 INTO
174      MOVL     1,1      ;QUOTIENT
175      LDA      3,ID1AC ;UPDATE TEMP. STORE
176      STA      3,ID1ST
177      LDA      3,ID1AC+1
178      STA      3,ID1ST+1
179 ID1SH- LDA      3,ID1AC+3
180      MOVZR     3,3      ;SHIFT HIGH WORD OF DIVISOR
181      STA      3,ID1AC+3
182      LDA      3,ID1AC+2
183      MOVR      3,3      ;SHIFT LOW WORD
184      STA      3,ID1AC+2
185      INC       2,2 SZR ;TEST COUNT
186      JMP      ID1LP
187      LDA      3,ID1AS+3      ;DONE
188      STA      0,0,3
189      STA      1,1,3
190      LDA      0,ID1AS
191      LDA      1,ID1AS+1
192      LDA      2,ID1AS+2
193      JMP      2,3
194 ID1AS- .BLK 4
195 ID1ST- .BLK 2
196 IDM30- -36
197 IDC3-  60000
198
199 ;PUT CHARACTER TO TTY
200 ;1-PASS CHARACTER IN LOW BYTE
201 PCHR-   STA     0,PCHAS
202         LDA     0,0,3
203         SKPBZ   TTO
204         JMP     .-1
205         DOAS    0,TTO
206         LDA     0,PCHAS
207         JMP     1,3
208 PCHAS-  0
209 ;GET CHARACTER FROM TTY
210 ;1-RETURN CHARACTER IN LOW BYTE
211 GCHR-   STA     0,GCHAS
212         STA     1,GCHAS+1
213         SKPDN   TTI
214         JMP     .-1
215         DIAC    0,TTI
216         LDA     1,GCHMS
217         AND     1,0
218         STA     0,0,3
219         LDA     0,GCHAS
220         LDA     1,GCHAS+1

```

```

221          JMP      1,3
222 GCHAS-   .BLK 2
223 GCHMS-   177
224 ;BYTE PACKER
225 ;1-PASS BASE ADDRESS OF STRING
226 ;2-PASS INDEX FROM BASE
227 ;3-PASS BYTE IN LOWER HALF
228 BYPA-    STA      0,BYPAS
229          STA      1,BYPAS+1
230          STA      2,BYPAS+2
231          STA      3,BYPAS+3
232          LDA      2,0,3 ;BASE
233          LDA      1,1,3 ;BYTE INDEX
234          MOVZR    1,0 ;WORD INDEX FROM BASE
235          ADD      0,2
236          LDA      0,2,3 ;BYTE IN AO
237          LDA      3,BYPMS ;MASK(377)
238          AND      3,0 ;MAKE SURE HIGH=0
239          MOVR#    1,1 SZC ;HIGH BYTE?
240          MOVS     0,0 ;YES, SWAP
241          STA      0,BYPWD
242          LDA      0,0,2 ;WORD IN AO
243          LDA      3,BYPMS ;MASK
244          MOVR#    1,1 SNC ;HIGH BYTE?
245          MOVS     3,3 ;NO, MASK HIGH
246          AND      3,0
247          LDA      3,BYPWD ;GET BYTE
248          ADD      3,0 ;ADD
249          STA      0,0,2 ;STORE
250          LDA      0,BYPAS
251          LDA      1,BYPAS+1
252          LDA      2,BYPAS+2
253          LDA      3,BYPAS+3
254          JMP      3,3
255 BYPMS-   377
256 BYPWD-   0
257 BYPAS-   .BLK 4
258 ;BYTE UNPACKER
259 ;1-PASS BASE ADDRESS OF STRING
260 ;2-PASS INDEX FROM BASE
261 ;3-RETURN BYTE IN LOW HALF
262 BYUP-    STA      0,BYUAS
263          STA      1,BYUAS+1
264          STA      2,BYUAS+2
265          STA      3,BYUAS+3
266          LDA      2,0,3 ;BASE
267          LDA      1,1,3
268          MOVZR    1,0 ;INDEX FROM BASE
269          ADD      0,2 ;ADDRESS OF WORD
270          LDA      0,0,2 ;LOAD WORD
271          MOVR     1,1 SZC ;HIGH BYTE?
272          MOVS     0,0 ;YES, SWAP
273          LDA      1,BYUMS ;MASK(377)
274          AND      1,0
275          STA      0,2,3

```

```

276          LDA      0,BYUAS
277          LDA      1,BYUAS+1
278          LDA      2,BYUAS+2
279          JMP      3,3
280  BYUAS-   .BLK 4
281  BYUMS-   377
282
283  ;DECIMAL STRING TO BINARY CONVERTER
284  ;1-PASS ADDRESS OF DEC STRING(MUST TERMINATE IN A NULL)
285  ;2-RETURN LOW WORD OF BINARY STRING
286  ;3-RETURN HIGH WORD OF BINARY STRING
287  DTOB-    STA      0,DTOAS ;STORE ACC'S
288          STA      1,DTOAS+1
289          STA      2,DTOAS+2
290          STA      3,DTOAS+3
291          LDA      2,0,3 ;ADDRESS
292          STA      2,DTONS ;SEARCH FOR NULL
293          SUB      2,2
294          STA      2,DTONS+1;COUNTER,BYTE INDEX
295  DTLPI-    JSR      @ABYUP
296  DTONS-    .BLK 3
297          LDA      2,DTONS+2;CHARACTER
298          MOV      2,2 SNR ;NULL?
299          JMP      .+3 ;YES
300          ISZ      DTONS+1 ;NO,NEXT BYTE
301          JMP      DTLPI
302          LDA      0,DTONS+1;1ST NULL BYTE
303          NEG      0,0 ; -1
304          COM      0,0
305          STA      0,DTOCN+1;STORE BYTE INDEX
306          LDA      0,DTONS
307          STA      0,DTOCN ;1ST WORD
308          SUB      0,0
309          STA      0,DTOAD ;SET ACCUM
310          STA      0,DTOAD+1
311          STA      0,DTON ;SET SIGN TO POS
312          LDA      2,ADP10 ;ADDRESS OF POWERS OF 10
313  DTLPI-    JSR      @ABYUP ;GET DIGITS
314  DTOCN-    .BLK 3
315          LDA      0,DTOCN+2
316          LDA      1,DTONS ;MINUS SIGN?
317          SUB      0,1 SZR
318          JMP      .+3 ;NO
319          STA      0,DTON ;YES, SAVE SIGN
320          JMP      DTNX
321          LDA      1,DTC60 ;60
322          SUB      1,0 ;STRIP,>=0?
323          MOVL#    0,0 SZC
324          JMP      DTNX ;NO
325          LDA      1,DTC10 ;10
326          SUB      0,1 ;GE 10?
327          MOVL#    1,1 SZC
328          JMP      DTNX ;YES
329          STA      0,DTMU ;STORE DIGIT TO MULT.
330          SUB      0,0

```

```

331      STA      0,DTMU+1
332      LDA      0,0,2 ;GET POWER OF 10
333      INC      2,2
334      STA      0,DTMU+2
335      LDA      0,0,2
336      INC      2,2
337      STA      0,DTMU+3
338      JSR      @AIMUL ;MULTIPLY
339  DTMU-    .BLK 4
340      LDA      0,DTMU ;PRODUCT
341      STA      0,DTOAD+2;STORE TO ADD
342      LDA      0,DTMU+1
343      STA      0,DTOAD+3
344      JSR      @AIADD ;ADD
345  DTOAD-   .BLK 4
346  DTNX-   LDA      0,DTOCN+1;BYTE COUNTER
347          NEG      0,0 ;-1
348          COM      0,0
349          STA      0,DTOCN+1
350          INC      0,0 SZR ;LAST DIGIT?
351          JMP      DTLF2
352          LDA      0,DTOAD ;GET BIN RESULT
353          LDA      1,DTOAD+1
354          LDA      2,DTON ;SIGN
355          MOV      2,2 SNR
356          JMP      DTPOS ;POS
357          COM      0,0 ;NEG., MAKE 2'S COMP.
358          COM      1,1
359          SUBZL    2,2 ;1
360          ADDZ     2,0 SZC ;ADD 1
361          ADD      2,1 ;ADD TO HIGH IF C=1
362  DTPOS-   LDA      3,DTOAS+3
363          STA      0,1,3
364          STA      1,2,3
365          LDA      0,DTOAS
366          LDA      1,DTOAS+1
367          LDA      2,DTOAS+2
368          JMP      3,3
369  DTOAS-   .BLK 4
370  DTC10-   12
371  DTC60-   60
372  DTON-    0
373  DTOMS-   .TXT/-/
374  ADP10-   DP10
375  DP10-    1 ;1
376          0
377  .RDX 10
378          10 ;10
379          0
380          100 ;100
381          0
382          1000 ;1000
383          0
384          10000 ;10000
385          0

```

```

386 .RDX 8
387      103240 ;100000
388      1
389      41100 ;1,000,000
390      17
391      113200 ;10,000,000
392      230
393      160400 ;100,000,000
394      2765
395      145000 ;1,000,000,000
396      35632
397 ;CONVERT BINARY NUMBER TO DECIMAL STRING
398 ;1-PASS ADDRESS TO RETURN STRING(6 WORDS)
399 ;2-PASS LOW WORD OF BINARY NUMBER
400 ;3-PASS HIGH WORD
401 BTOD- STA 0,BTOAS
402      STA 1,BTOAS+1
403      STA 2,BTOAS+2
404      STA 3,BTOAS+3
405      LDA 2,0,3 ;ADDRESS OF STRING
406      STA 2,BTDSI
407      STA 2,BTDPA ;STORE ADDRESS FOR
408      SUBZL 0,0 ;BYTE PACK
409      STA 0,BTDPA+1
410      SUB , STA 0,0,2 ;CLEAR MEM
411      INC 2,2
412      INC 1,1 SZR
413      JMP .-3
414      LDA 0,1,3 ;LOAD BINARY NUMB.
415      LDA 1,2,3
416      MOVL# 1,1 SNC ;SIGN?
417      JMP BTDP0 ;POS
418      LDA 2,BTDSI ;NEG., MINUS SIGN
419      COM 0,0 ;MAKE POS.
420      COM 1,1
421      SUBZL 3,3
422      ADDZ 3,0 SZC
423      ADD 3,2
424      JMP .+2
425 BTDP0- LDA 2,BTDBL ;BLANK
426      STA 2,BTDSI+2
427      SUB 2,2
428      STA 2,BTDSI+1
429      JSR @ABYPA
430 BTDSI- .BLK 3
431      LDA 2,BTM10 ;-10
432      STA 2,BTLCT ;LOOP COUNTER
433 BDLPI- LDA 2,ADPI0
434      LDA 3,BTLCT
435      COM 3,3 ;CNT-1
436      MOVZL 3,3 ;(CNT-1)*2
437      ADD 3,2
438      LDA 3,0,2 ;STORE POWER OF 10
439      STA 3,BTDSU+2
440      LDA 3,1,2

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```

441      STA      3,BTDSU+3
442      SUB      2,2      ;CLEAR 2, WILL HOLD # OF THIS POW
443      STA      0,BTDSU
444      STA      1,BTDSU+1
445 BDLP2- JSR      @AISUB
446 BTDSU- .BLK 4
447      LDA      3,BTDSU+1;HIGH WORD
448      MOVL#    3,3 SZC ;POS?
449      JMP      BTDCH    ;NO
450      INC      2,2      ;INCR. CONV REG.
451      LDA      0,BTDSU ;UPDATE DIFF
452      LDA      1,BTDSU+1
453      JMP      BDLP2
454 BTDCH- LDA      3,BTD60 ;60
455      ADD      3,2      ;CALC. ASCII CODE
456      STA      2,BTDPA+2
457      JSR      @ABYPA   ;PACK
458 BTDPA- .BLK 3
459      ISZ      BTDPA+1 ;INCR. BYTE POINTER
460      ISZ      BTLCT    ;CHECK LOOP COUNT
461      JMP      BDLP1
462      LDA      0,BTOAS
463      LDA      1,BTOAS+1
464      LDA      2,BTOAS+2
465      LDA      3,BTOAS+3
466      JMP      3,3
467 BTM10- -12
468 BTDM6- -6
469 BTDMS- .TXT/-/
470 BTDBL- .TXT/ /
471 BTLCT- 0
472 BTD60- 60
473 BTOAS- .BLK 4
474
475 ;PUT STRING TO TELETYPE
476 ;1-PASS ADDRESS OF STRING
477 PSTR- STA      0,PSAS
478      STA      1,PSAS+1
479      STA      2,PSAS+2
480      STA      3,PSAS+3
481      LDA      0,0,3
482      STA      0,PSGC
483      SUB      0,0
484      STA      0,PSGC+1
485 PSLP- JSR      @ABYUP
486 PSGC- .BLK 3
487      LDA      0,PSGC+2
488      MOV      0,0 SNR
489      JMP      PSTEX
490      STA      0,PSPC
491      JSR      @APCHR
492 PSPC- 0
493      ISZ      PSGC+1
494      JMP      PSLP
495 PSTEX- LDA      0,PSAS

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496         LDA      1,PSAS+1
497         LDA      2,PSAS+2
498         LDA      3,PSAS+3
499         JMP      1,3
500 PSAS-     .BLK 4
501 ;GET STRING FROM TTY
502 ;1-PASS ADDRESS OF STRING (GE.(#CHAR/2+1)WORDS)
503 ;2-PASS MAX # OF CHARACTERS
504 ;3-SPECIAL FLAG,-1 MEANS TAKE ONLY NUMBERS
505 GSTR-     STA      0,GSTAS
506         STA      1,GSTAS+1
507         STA      2,GSTAS+2
508         STA      3,GSTAS+3
509         NIOC      TTI
510         LDA      0,0,3 ;STRING STORE ADDRESS
511         LDA      2,1,3 ;MAX # CHAR'S
512         STA      0,GSTNU ;FINAL NULL
513         STA      0,GSTPC ;PACK CHARACTERS
514         STA      0,GSTUC ;UNPACK CHAR'S
515         SUB      0,0
516         STA      0,GSTPC+1;CHAR COUNTER
517 GSTLP-    JSR      @AGCHR
518 GSTGC-    0
519         LDA      0,GSTGC
520         LDA      1,GSRET ;RETURN?
521         SUB      0,1 SNR
522         JMP      GSTEX ;YES,EXIT
523         LDA      1,GS RUB ;RUBOUT?
524         SUB      0,1 SNR
525         JMP      GSTRB ;YES, RUBOUT CHAR
526         LDA      1,GSTPC+1;CHAR COUNTER
527         SUB      2,1 SNR ;TOO MANY CHAR'S?
528         JMP      GSTEX ;YES, EXIT
529         LDA      3,GSTAS+3
530         LDA      1,2,3
531         INC      1,1 SZR ;NUMBERS?
532         JMP      GSSTO ;NO, PROCEED
533         LDA      1,GSTMI ;MINUS SIGN
534         SUB      0,1 SZR
535         JMP      .+4 ;NO
536         LDA      1,GSTPC+1;YES,CHAR COUNT
537         MOV      1,1 SNR ;1ST CHAR?
538         JMP      GSSTO ;YES,OK
539         LDA      1,GSC60 ;60
540         MOV      0,3 ;STRIP ASCII CODE
541         SUB      1,3 ;GE 0?
542         MOVL#    3,3 SZC
543         JMP      GSTWC ;NO, NOT A #
544         LDA      1,GSC9
545         SUB      3,1 ;LT 10?
546         MOVL#    1,1 SNC
547         JMP      GSSTO ;YES,OK
548 GSTWC-    JSR      @APCHR ;NO, SEND '?'
549         .TXT/?/
550         JMP      GSTLP ;GET NEXT CHAR

```



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551 GSSTO- STA      0,GSTPC+2
552      JSR      @ABYPA ;STORE CHAR
553 GSTPC- .BLK 3
554      STA      0,GSTEC ;ECHO CHAR
555      JSR      @APCHR
556 GSTEC- 0
557      ISZ      GSTPC+1 ;INCREMENT CHAR POINTER
558      JMP      GSTLP
559 GSTRB- LDA      0,GSTPC+1;CHAR POINTER
560      NEG      0,0      ;-1
561      COM      0,0
562      MOVL#     0,0 SZC ;ALREADY AT BEG. OF STRING?
563      JMP      GSCLF ;YES,SEND LF CR
564      STA      0,GSTPC+1;DECREMENT CHAR POINTER
565      STA      0,GSTUC+1
566      JSR      @APCHR ;SEND '\
567      .TXT/\/
568      JSR      @ABYUP ;GET LAST CHAR IN STRING
569 GSTUC- .BLK 3
570      LDA      1,GSTUC+2
571      STA      1,GSRB1
572      JSR      @APCHR ;SEND LAST CHAR
573 GSRB1- 0
574      JMP      GSTLP
575 GSCLF- JSR      @APSTR ;SEND CR LF
576      GSCRL
577      JMP      GSTLP
578 GSTEX- LDA      0,GSTPC+1
579      STA      0,GSTNU+1
580      JSR      @ABYPA ;PACK NULL TO END STRING
581 GSTNU- .BLK 2
582      0          ;NULL
583      JSR      @APSTR ;SEND CR LF
584      GSCRL
585      LDA      0,GSTAS
586      LDA      1,GSTAS+1
587      LDA      2,GSTAS+2
588      LDA      3,GSTAS+3
589      JMP      3,3
590 GSCRL- .TXT/<15><12>/ ;CR LF
591 GSRUB- .TXT/<177>/ ;RUBOUT
592 GSRET- .TXT/<15>/ ;CR
593 GSTMI- .TXT/-/
594 GSC60- 60
595 GSC9- 11
596 GSTAS- .BLK 4
597 .END

```

Appendix B: Usefull Diagrams

B.1 Trigger Sensor

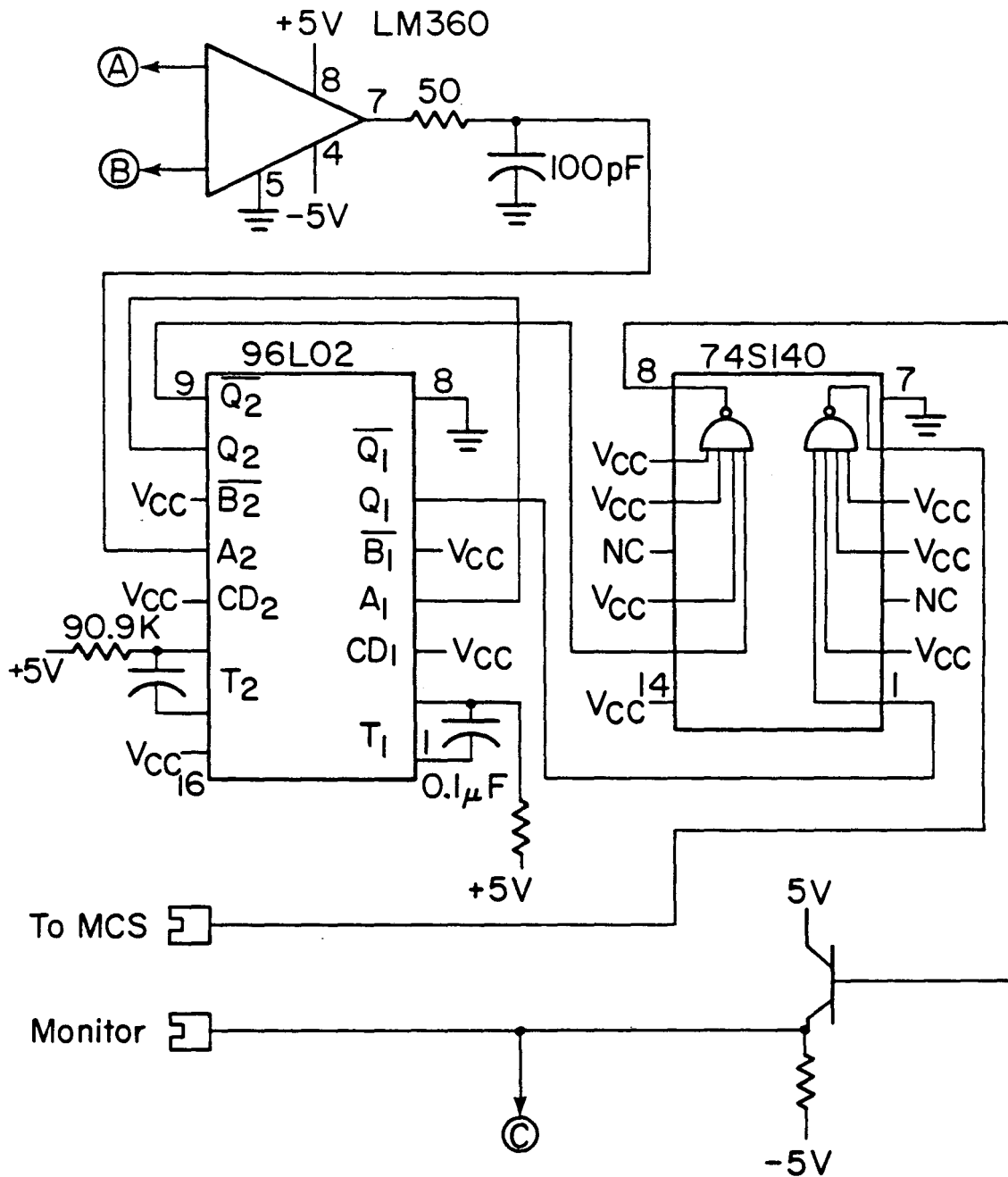
A circuit was built to amplify the reference trigger signal from the photodiode-LED pair associated with the cross-correlation chopper, and to generate the timing pulse for the multi-channel scalar. The amplifier has a rise time of 2 μ s. The output pulse is generated when the photodiode signal crosses the reference trigger level voltage. The trigger level voltage is derived from a fixed fraction of the difference between the maximum voltage and minimum voltage of the photodiode signal. This makes the trigger point insensitive to gain changes. A 300 ns pulse is generated for the MCS and a ms pulse is generated for monitoring. There is a subcircuit to monitor the period of the chopper rotation.

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Figure B.1 a

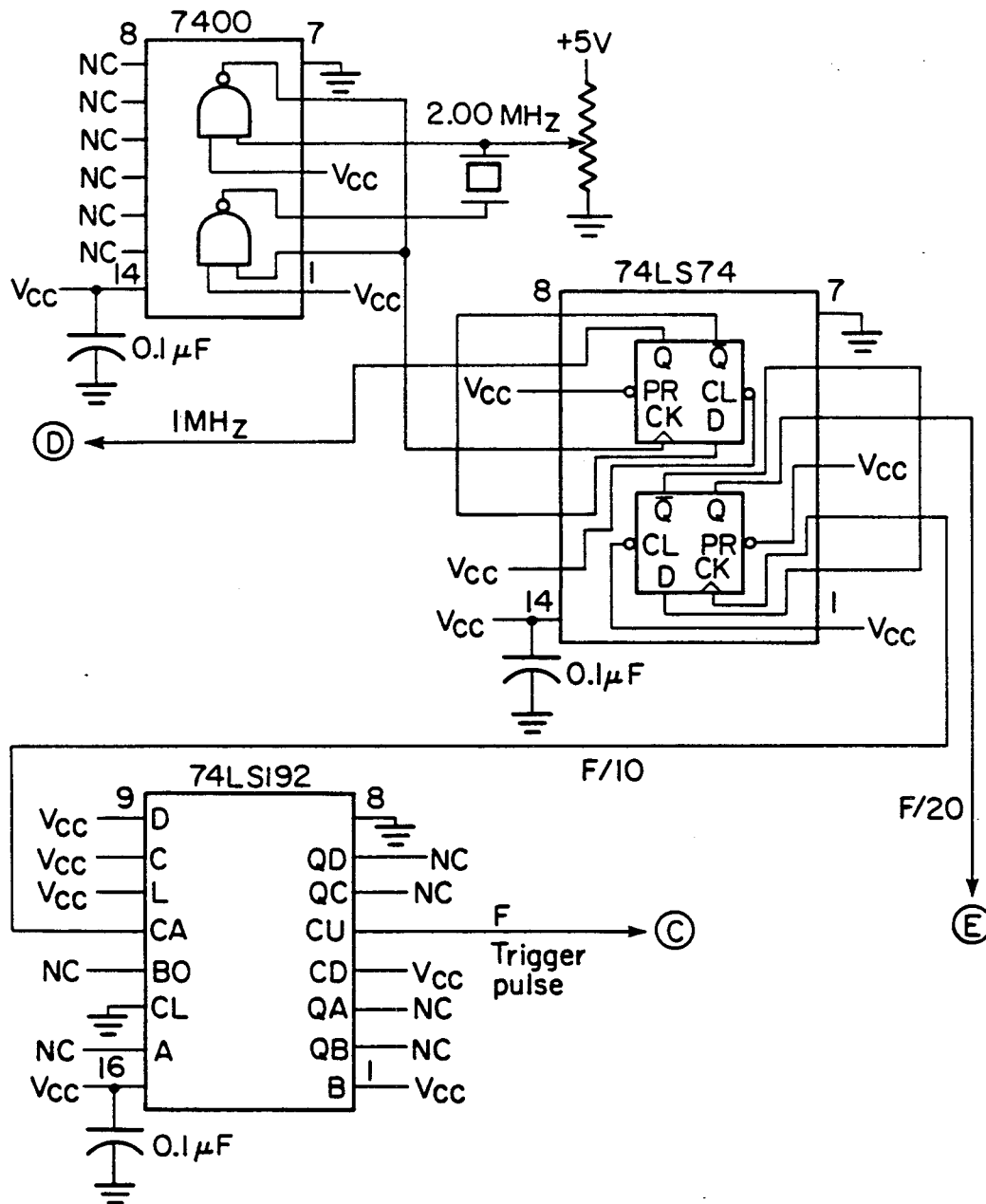
TRIGGER SENSOR (b) TRIGGER PULSE GENERATOR



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Figure B.1 b

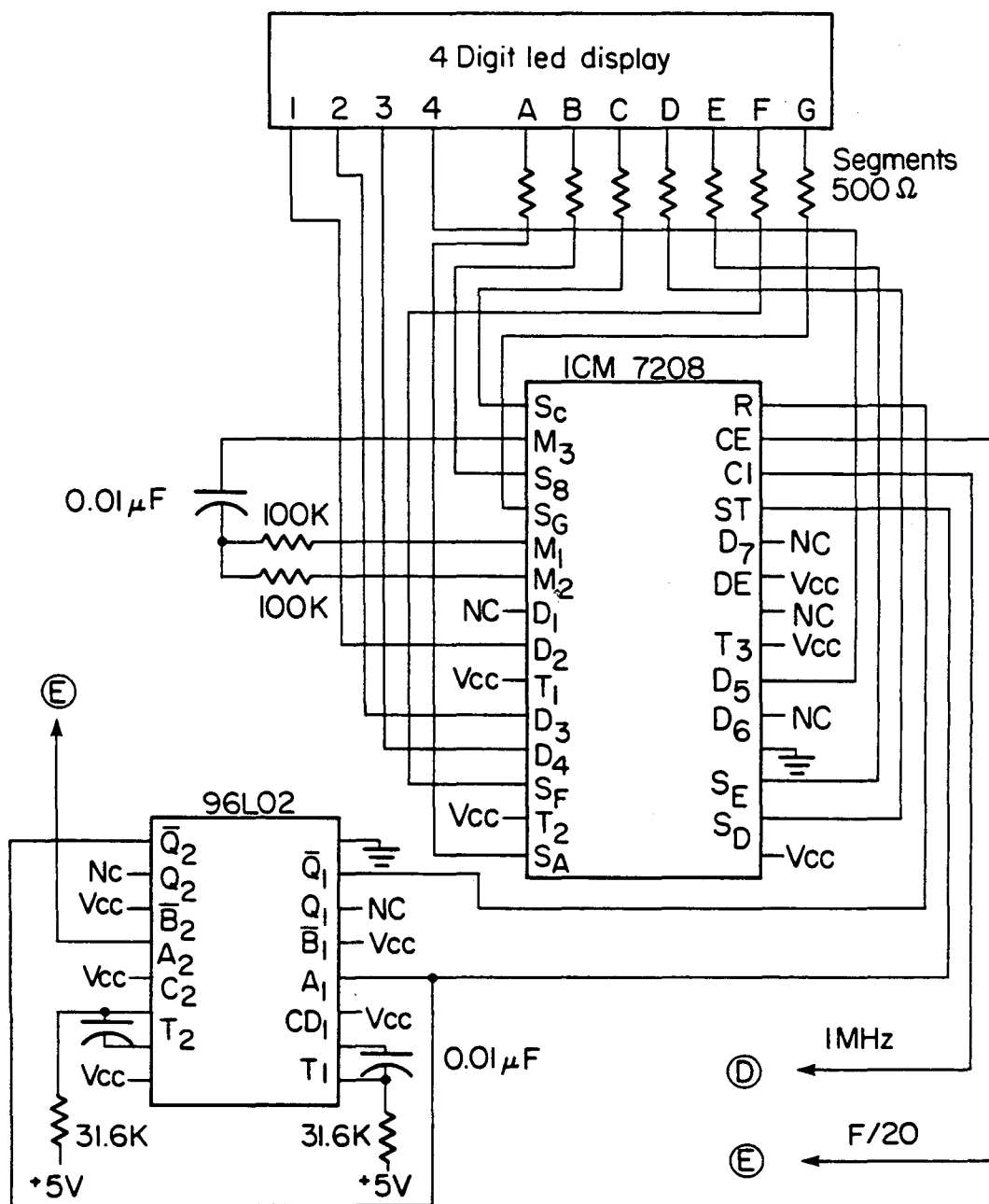
TRIGGER SENSOR (c) OSCILLATOR AND PULSE SCALER



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Figure B.1 c

TRIGGER SENSOR (d) PERIOD MONITOR



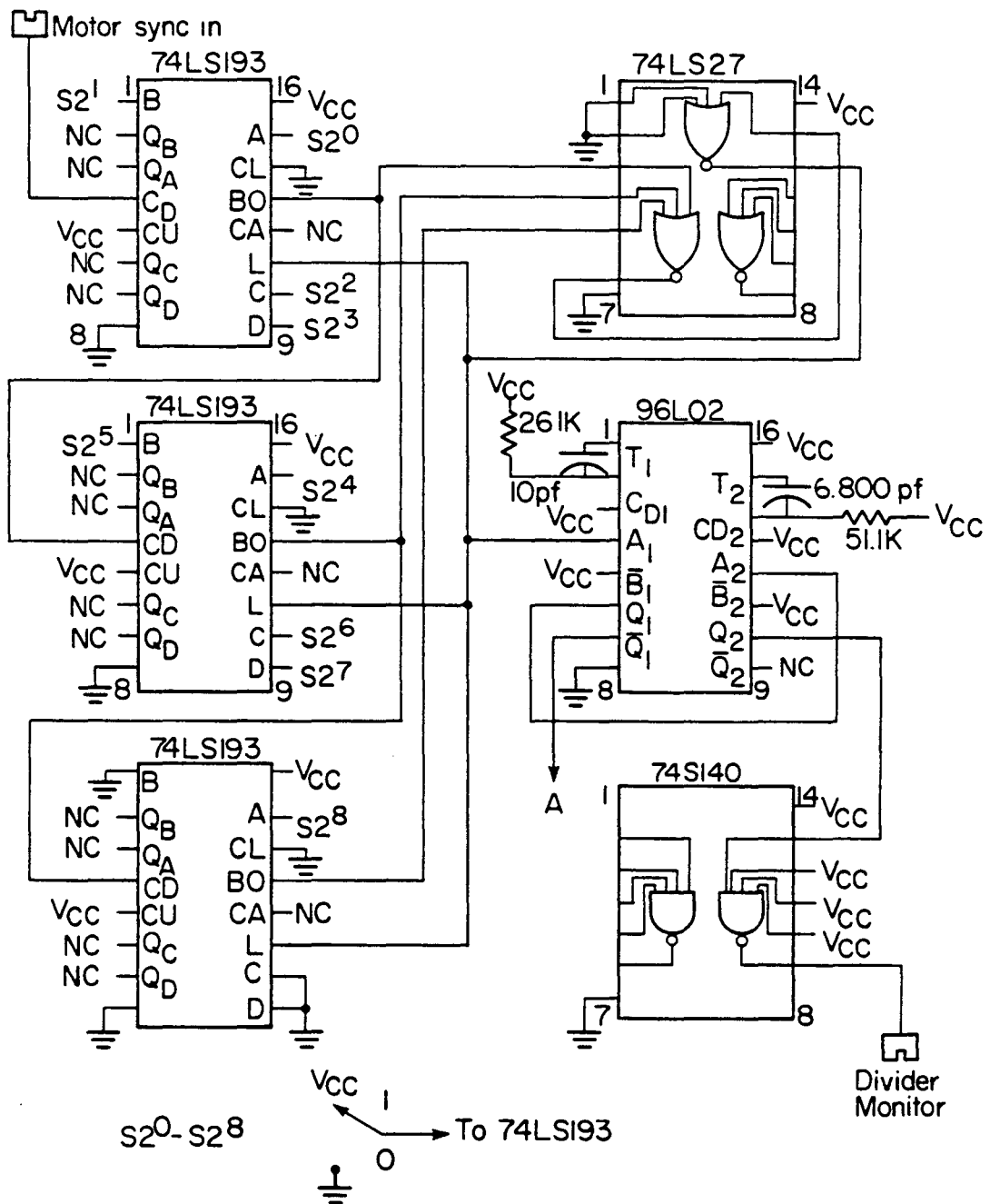
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Figure B.1 d

B.2 Motor Synchronization Scalar

The motor synchronization scalar takes the channel pulses from the multi-channel scalar and generates chopper motor drive pulses. The divider section is a programmable counter and should be set for the number of channels per rotation by the front switches (255 channels for single sequence, 510 channels for double sequence). The X4 section is a phase-lock loop which generates the four pulses needed per motor revolution.

MOTOR SYNCHRONIZATION SCALAR (a) DIVIDER SECTION



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Figure B.2 a

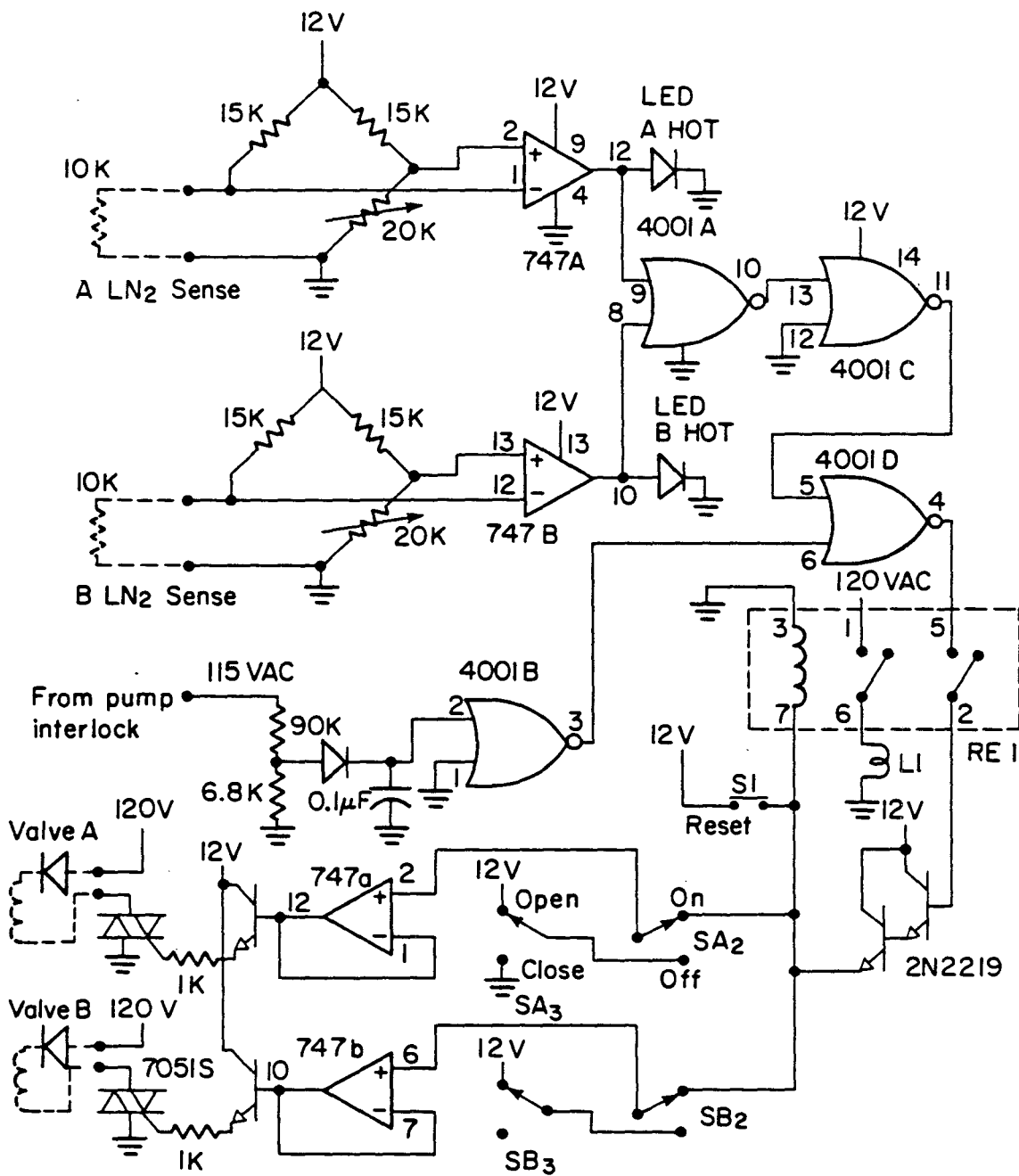
5

Figure B.2 b

B.3 Valve Interlock Controller

One section of the valve interlock controller is shown. Interlock control is based on the signal from the pump power interlock controller (water flow, temperature, foreline pressure) and the liquid nitrogen level in the pump trap. The response to low LN_2 levels can be suppressed by removing the appropriate sense resistor lines in the back of the controller.

VALVE INTELOCK CONTROL VALVE A+B (C+D Same, E similar)



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Figure B.3

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