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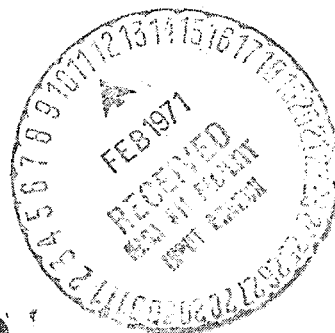
DIFFERENTIAL CROSS SECTION FOR THE
REACTIVE SCATTERING OF DEUTERIUM ATOMS
BY HYDROGEN MOLECULES: CROSS SECTIONS
FOR THE EXCITATION OF $\text{Na}(3^2\text{P})$
BY COLLISIONS WITH INTERNALLY EXCITED
MOLECULAR HYDROGEN,
DEUTERIUM AND HYDROGEN

BY

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DEUTERIUM AND NITROGEN

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B.S., Drexel Institute of Technology, 1965

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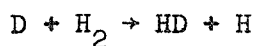
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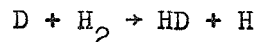
The reaction $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ has been investigated in a modulated crossed beam experiment utilizing thermal energy beams. The differential scattering cross section for reactively formed HD was measured and the mean velocity of detected HD was determined via phase spectrometry. These measurements indicate that reactive collisions in the vicinity of reaction threshold are of the direct type with the HD generally preferring to be scattered in a direction anti-parallel to that of the attacking atom without significant internal excitation. For the purpose of calibrating this cross section absolutely, the differential cross section for $\text{D} + \text{H}_2 \rightarrow \text{D} + \text{H}_2$ was studied and normalized to the known total cross section. The reactive cross section was estimated to be of order $2\text{\AA}^2$ by comparing differential signals of the reactive and elastic processes. The empirical results of this study are in general agreement with theoretical calculations performed by Micha and Karplus et al.

In another series of experiments, the collisional excitation of $\text{Na}(3^2\text{P})$ by H_2 , D_2 and N_2 was studied using modulated thermal energy crossed beams and sodium D radiation was detected. In one

configuration the effective excitation rate constants for these molecules were determined and these rates were studied as a function of molecular beam temperature. In a second configuration the molecular beam was velocity selected and the production of $\text{Na}(3^2\text{P})$ was observed as a function of molecular beam velocity and temperature. Excitation cross sections determined as a function of initial molecular vibrational state for translational and vibrational temperatures of order 1500°K and 3000°K indicate that excitation is most efficient when the electronic energy is supplied purely by molecular internal energy. The energy transfer efficiency is smaller by about one order of magnitude when molecular internal energy and the kinetic energy of collision couple to supply the energy of excitation. Effective cross sections for the inverse process derived from excitation cross sections via microscopic reversibility are in agreement with those determined in quenching studies carried out at high temperatures. Results for N_2 are in general agreement with the theory of Bauer, Fisher and Gilmore and slightly poorer agreement with the theory of Bjerre and Nikitin.

PART ONE

A MODULATED CROSS BEAM STUDY OF THE REACTION



I. INTRODUCTION

The reactive scattering or rearrangement scattering of hydrogen atoms by hydrogen molecules $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ or its isotopic variants is of fundamental importance from a chemical kinetic viewpoint. The elementary character of this bimolecular reaction makes it an excellent testing ground for theories of chemical reaction. Consequently it has been the object of many theoretical and experimental investigations.

The first attempts to calculate a chemical reaction rate stems from the initial work of London who attempted to use the H_2 electronic wave function derived by Heitler and London¹ in consideration of the H_3 problem. Many investigators have applied themselves to this problem in the last forty years not only in an effort to calculate the H_3 potential surface and the reaction rate but also more recently to calculate the differential reactive scattering cross sections for the isotopic reactions.

From the reaction dynamics viewpoint, the most interesting studies have been carried out chiefly by Karplus and co-workers. Using a semi-empirical London-Eyring-Polanyi-Sato (LEPS) potential, classical trajectory calculations² were performed for $\text{H} + \text{H}_2$ as a function of the relative kinetic energy and rotational and vibrational states of H_2 . Dynamically, the reaction followed a simple and

direct character with the H_3 reacting configuration living shorter than 3×10^{-14} sec. (short lived). Aside from showing that the average H_3 complex differs from a linear transition configuration by 20° to 30° , Monte Carlo averaging enabled the kinetic energy dependent cross sections in terms of initial H_2 states to be estimated.

In a follow up study Karplus and Tang³ calculated quantum mechanical differential cross sections for various initial states of H_2 using the same potential as before in the Distorted Wave Born approximation for various simplifying assumptions of the incoming atom-molecule interaction. While their total cross sections in this study rose more sharply than in the classical studies, the authors inferred that quantum effects are not very important.

Another quantum mechanical study of the previous type that deserves mention is the work of Micha on $D + H_2^4$ and $H + D_2^4$ in addition to $H + H_2^5$. The approach was similar to Karplus but the simplifying assumptions in carrying out the solution were different. Differential and integrated cross sections were also reported.

Experimental progress on the H_3 problem has somewhat paralleled the theoretical advances. The bulk type reaction rate constant as a function of temperature (with translational motions of reactant atoms and molecules following a Maxwell-Boltzmann distribution) was measured as early as 1930 for the para-to-ortho reaction $H + p-H_2 \rightarrow o-H_2 + H$ by A. Farkas.⁶ Other work exploiting the thermal conductivity difference between ortho and

para hydrogen for detection purposes followed.⁷ The isotopic variant hydrogen reactions have been examined by many workers⁸ employing various techniques between 250°K and 750°K. The rate for $D + H_2 \rightarrow HD + H$ has been reported for a non-Maxwell-Boltzmann distribution.⁹ These experiments have provided much needed bulk information about the hydrogen reactions; however, extraction of even the integrated cross section from the rate data is not possible.¹⁰ At best, given a particular set of reaction model assumptions, these data can determine only rigorous bounds on the energy dependence of the reactive cross section.

Recently, attempts have been made to study the hydrogen reaction dynamics in the laboratory using the well known cross beam differential scattering technique, the power of which has been demonstrated with reactions involving alkali metal species and their salts which can be detected by highly efficient surface ionization detectors. Despite the need for detailed hydrogen reaction information, data have been slow to accumulate because the presently known most efficient and practical means of detecting neutral hydrogen (electron impact) is between two and three orders of magnitude less efficient than the surface ionization technique.

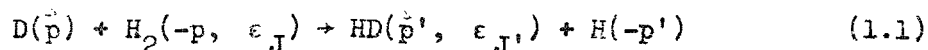
The pioneering Maxwellian hydrogen cross beam experiments were performed by Datz and Taylor¹¹ on $D + H_2 \rightarrow HD + H$ and Brackmann and Fite¹² on $H + D_2 \rightarrow HD + D$. While both of these experiments were hampered by signal-to-noise difficulties, the $D + H_2$ experiment yielded an HD laboratory angular distribution; the

$\text{H} + \text{D}_2$ experiment did not yield an angular distribution. Both experiments despite their relative success or failure appeared to confirm the theoretical notion that the reaction proceeds through a short lived reacting configuration (compared to its rotational time) and that, at center-of-mass temperature of order 1500°K , the reactively formed HD appeared to depart from the "complex" (very favorably) in a direction anti-parallel to the direction of approach of the atomic species.

Due to the compelling need for more crossed beam studies, the $\text{D} + \text{H}_2$ reaction was selected for study in this laboratory. The following sections describe an experiment which is similar to the approach of Datz and Taylor.

II. PRINCIPLES OF EXPERIMENT

When a ground state D atom collides with an H_2 molecule that is possibly rotationally excited, the atom may be elastically, inelastically or reactively scattered. The reactive process, replacement of the H - H bond by an H - D bond, for practical purposes, takes place when the relative kinetic energy exceeds the reaction threshold. The center-of-mass (CM) description of the collision near reaction threshold appears in (1.1)



The colliding partners have initial relative momentum, $|p|$, and final relative momentum $|p'|$. The rotational excitation of the randomly oriented initial and final molecules is labeled by ϵ_J and $\epsilon_{J'}$, respectively.

If a differential scattering experiment is performed in which p and ϵ_J can be reasonably well defined and if p' can be measured, it is possible to deduce $\epsilon_{J'}$, and whether the D-H-H configuration is short or long lived compared to its rotational period. The differential cross section yielded may be compared to that calculated by the theoreticians. In this way the validity of the interaction potential for the colliding species and of the approximations introduced in solving the many body problem may be checked if the experimental error is ideal.

The hydrogen chemical reaction experiment designed and performed in this laboratory with these goals in mind is represented in Fig. 1.1. D atoms are produced by thermal dissociation in a tungsten

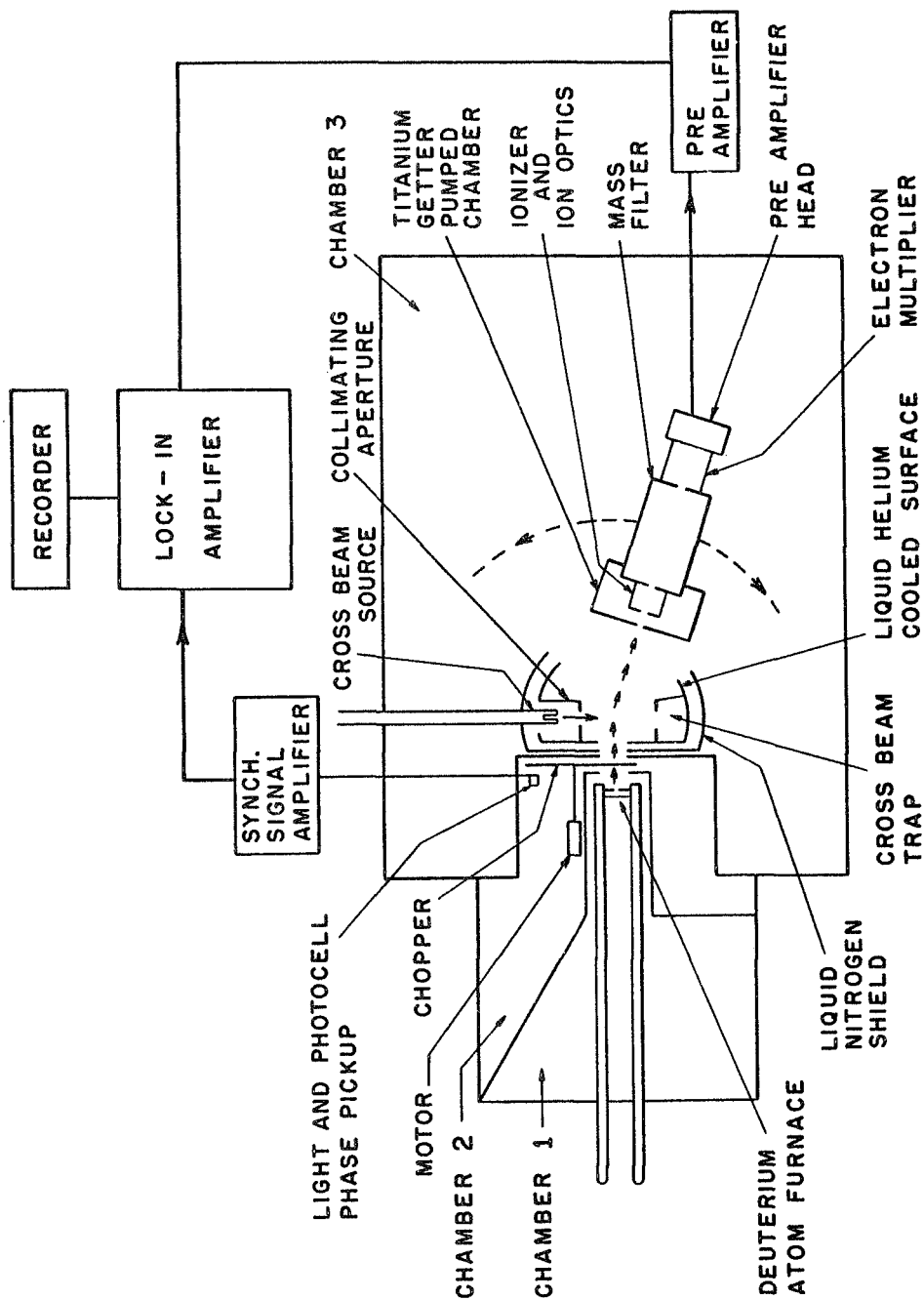


Figure 1.1. Sketch of the experimental apparatus in the beam plane. A block diagram of the signal processing equipment is also shown.

furnace operating up to 3000°K in the first of three differentially pumped vacuum chambers. This atomic beam is modulated by a mechanical chopper wheel located in Chamber Two in order that the HD resulting from collisions with H_2 and D can be distinguished from vacuum system residual mass three particles during subsequent phase sensitive detection. After entering the third chamber, this beam passes through a liquid-helium-cryopumped fourth chamber, within which the d.c. H_2 beam crosses the modulated D beam. The mass spectrometric detector rotates about the beam intersection point in the plane of the two crossed beams. The ionizer of the mass spectrometric detector is enclosed in a titanium-getter-pumped liquid-nitrogen-cooled fifth chamber to reduce the background HD pressure which is a severe source of noise in the experiment. The H_2 beam is cooled to liquid nitrogen temperature before issuing through a multichannel crinkly foil nozzle. The very dense H_2 beam is removed through condensation on liquid-helium-cooled surfaces in the fourth chamber. Neither beam is velocity-selected and the kinetic temperatures of the reactants in the center-of-mass coordinates are in a very narrow range around 1500°K .

In practice $\vec{p}$ and ϵ_j are well defined but the asymmetry inherent in the experiment implies that the center-of-mass (CM) and laboratory (LAB) frames of reference are different. It is convenient to consider the reaction in velocity space to fully understand the experimental implications. Consider the simplified velocity diagram shown in Fig. 1.2. The vector AO essentially represents the most probable LAB velocity of those D atoms coming from the 2800°K thermal

source with energies in the CM system greater than the known activation energy⁹ for the reaction $D + H_2 \rightarrow HD + H$. (Vector BO, the most probable LAB velocity of the liquid-nitrogen-cooled H_2 is small compared with AO.) CO represents the velocity of the center-of-mass for these $D + H_2$ reactive collisions. Applying conservation of linear momentum and energy assuming the initial H_2 and product HD have no internal energy, the solid circle is found to be the locus of recoil velocities for HD in the CM coordinates. The particular recoil velocity EC has a laboratory velocity EO. HD recoiling with either velocity FC or EC would be detected at a LAB angle β , but their detected velocities would be different and hence distinguishable. Tangents to the recoil circle passing through O define the LAB angles farthest removed from AO at which reactive HD could be measured for the energetics assumed for this discussion.

A major problem in this experiment is coping with the .5% HD impurity present in the D_2 admitted to the atomic source. Although dissociation runs around 95%, the undissociated HD impurity can, on elastic scattering from the H_2 target beam, give modulated HD signals comparable to the expected signals from HD formed in the reaction, particularly at small laboratory angles. The difficulty is demonstrated in Fig. 1.2 where the velocity diagram for elastic $HD + H_2$ is superimposed on the reactive diagram. Here, vector A'O represents the most probable velocity of impurity HD simultaneously emitted from the furnace. The center-of-mass is located at C' for this system. HD scattered with velocities GC' and HC' also appear at LAB angle β .

The actual signal observed in a measurement can be a superposition of four HD signals: (a) reaction product emitted generally forward in the CM system (vector EO); (b) reaction product emitted generally backward in the CM coordinates (vector FO); (c) impurity HD scattered forward in the CM coordinates (vector GO), and (d) impurity HD "hard sphere" scattered backward in CM coordinates (vector HO). It is necessary to distinguish between these contributions.

There are three principal tests that have been applied for distinguishing elastic and reactive HD. First, the HD signals can be studied as a function of LAB angle for different temperatures of the atomic furnace. At any given angle the reactive signals should rise with increased furnace temperature since the D concentration increases; elastic HD signals decrease with increased dissociation. Therefore, predominance of one process over another can be determined for a given LAB angle.

Second, knowledge of the angular distribution of the D, HD, and D_2 signals at different temperatures can be utilized to understand the different features of reactively scattered HD and elastically scattered D, HD, and D_2 with regard to angular distribution shape and relative differential cross sections. Arguments can be constructed concerning the predominance of reactive versus elastic scattering at a given angle from direct measurements of the relative number densities of the three component primary beam for a given furnace temperature.

Third, the velocities of the HD can be estimated without velocity analysis using phase spectrometry. Since the elastically and re-

actively scattered HD leave the point of beam intersection with different speeds, thus giving rise to different times-of-flight to the detector, different lock-in amplifier a.c. signal phases are measured. Knowledge of the phases as a function of LAB angle, the chopping frequency, the experimental geometry and the average velocities of D, HD, and D₂ of the direct beam enables the reaction HD velocity to be estimated. This exercise is of value not only for distinguishing reactive and elastic HD but also in verifying that the signals are predominantly forward or backward scattered molecules in the CM system.

With the reactive HD signal properly identified, the in-plane laboratory angular distribution of signals (LAB differential cross section) may be compared with theoretical signals calculated from various postulated CM differential cross sections. This entails numerically evaluating the expression for the experimental yield, S(β) in the cross beam plane. This expression is given by

$$S(\beta) = \Delta v n_1 n_2 \iint v_r f(v_1) dv_1 f(v_2) dv_2 \cdot \left\{ \iiint \frac{e(v_1')}{v_1'} \left(\frac{v_1'^2}{w_1'^2} \right) \left[\frac{d\sigma(\vec{w}_1, \vec{w}_1')}{dw_1' d\Omega} \right] dv_1' d\Omega_a \right\} \quad (1.2)$$

where $e(v_1')$ is the detection efficiency factor after number density detection has been considered; Δv is the beam intersection volume; the n_i , $i = 1, 2$ are the beam number densities; $f(v_i) dv_i$, $i = 1, 2$ are the

Maxwellian velocity distributions; v_r is the relative velocity; v_1' is the laboratory recoil velocity for the detected species; $\vec{w}_1$ and $\vec{w}_1'$ are the center-of-mass incident and recoil velocities, and $\frac{d\sigma(\vec{w}_1, \vec{w}_1')}{dw_1' d\Omega}$

is the CM differential cross section for the $\vec{w}_1 \rightarrow \vec{w}_1'$ scattering event. The CM differential cross section deduced in this manner can and has been compared with theoretical predictions.

Evidently, an expression similar to (1.2) exists for the elastic scattering of D by H_2 . If the elastic laboratory angular distribution and the total scattering cross section for these events are known, the ratio of measured reactive-to-elastic signals may be used to estimate the absolute magnitude of the reactive cross section. This exercise also has been carried out and the results have been compared with theory.

III. EXPERIMENTAL APPARATUS

The previous investigators of the hydrogen chemical reaction^{11,12} have found that the main problem with detecting the product neutral particles arises from the simultaneous ionization of vacuum system residual gas in the ionizing region. The a.c. shot noise component of the d.c. residual gas ion current can deteriorate the signal-to-noise ratio of the modulated neutral particles being detected.

For this reason it was the product HD molecules and not the H atoms which were detected. The H^+ background current is larger than the HD^+ background due to dissociative ionization of residual H_2O and H_2 . Even in the case of HD^+ detection with ionization carried out simply in Chamber Three, there is a large background signal due to the high partial pressure of HD (5×10^{-8} Torr.). Presumably this arises from the D atoms which abstract hydrogen from the adsorbed gases on the Chamber Three walls after passing cleanly through Chamber Four.

In an initial attempt to overcome the HD background problem, ionization was effected inside Chamber Four where the HD partial pressure would be expected to be quite low. This is because (a) the HD impurity in commercial grade H_2 used in the crossed beam was found to be less than $1:10^3$ and the H_2 pressure was less than 10^{-6} Torr. and (b) the D atoms that could be scattered from the primary beam and that abstract hydrogen from the cryopump walls are estimated to be capable of producing an HD partial pressure smaller than (a).

For this first attempt, electrons from a hot cathode in Chamber Three were transported through the base of Chamber Four and collected in a liquid-nitrogen-cooled Faraday cup located at the top of that chamber. This gun located 4 cm. radially from the beam intersection region was free to rotate, with the ion optics and mass filter located in Chamber Three, about a pivot passing through the reaction region.

Two difficulties were encountered with this setup. First, the electron gun became unstable after operating for a few minutes in the liquid-helium-cooled cavity. This was attributed to the charging up of the gun lenses which presumably, on cooling by radiation, became covered with a film of ice. Secondly, there was a large mass three background current which had to be attributed to H_3^+ ions formed during the long flight path from the ionization region to the mass filter mouth by the gas phase reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$.

The second and successful approach to the problem of reducing the HD background was to ionize in Chamber Three and then enclose the ionizer in a separate differentially pumped chamber(five). To this end a liquid-nitrogen-cooled titanium-getter-pumped chamber was constructed. The partial pressures of H_2 and HD in this chamber were better than 10^{-8} and 10^{-9} Torr. respectively under experimental conditions. The vacuum components, beam sources and neutral detection equipment that have been utilized in the successful effort now will be described more fully.

A. CRYOPUMPED FOURTH STAGE

The basic three-stage vacuum system described by Clendenning¹³, Ott¹⁴, and Kauppila¹⁵ is capable of performing neutral-neutral modulated crossed beam experiments using beam number densities of order 10^9 particles/cm³. The use of photon or neutral particle detectors with phase lock electronics might well be used in studying collision cross sections as small as 10^{-16} cm² with adequate signal-to-noise ratio. The D + H₂ reactive process has a cross section of similar magnitude but the basic system is inadequate for this reaction.

Three major difficulties are as follows:

(A) The use of thermal beams for studying the reaction implies that less than one D atom in ten entering the collision region is energetically eligible to react so that potential signal yield is diminished relative to the noise.

(B) Differential scattering experiments require that the collision volume and the detector solid angle be held to a minimum. The signal yield again is diminished.

(C) The hydrogen isotopes are non-condensable species at room temperature so that large background noise obscures the already small reactive signals.

A requirement for improving the signal-to-noise ratio is the increase of absolute signal yield by number density increase while simultaneously removing the higher gas flows immediately after passing through the collision region. An additional very high capacity strategically placed diffusion pump is ruled out because of restrictive geometry and pumping noise. These considerations direct one to examine

the characteristics of a cryopumped fourth stage which can maintain high vacuum pressures to at least 10^{-7} Torr. when a cross beam of 10^{13} particles/cm³ is flowing into it (pumping speeds of order 10^5 liters/sec) without serious pumping noises.

The essence of a cryopumped fourth stage is that a small, mostly closed chamber encasing the reaction region of the two crossed beams is constructed from a material of high thermal conductivity and is held at a low enough temperature such that most gas phase species emanating from the reaction region in directions other than the detecting directions are frozen out, hopefully after making only several bounces. While gaseous species may have different temperatures at which efficient gas-to-solid phase transition takes place (high sticking probability), if one reduces the chamber wall temperature low enough, all gaseous components have high sticking probability and the objective is accomplished.

In practice one anticipates this technique to yield a very high pumping speed (sticking probability ≈ 1) for major gaseous constituents of the background and beam when the chamber walls have a temperature equal to the boiling point of liquid helium. The results of Fite and Brackmann¹⁶ on reflection of beams from cold surfaces indicate that, under high vacuum pressures and temperatures about 4.2°K, the sticking probability of molecular hydrogen and other gases does approach unity, although re-evolution of H₂ occurs to give its 4.2°K vapor pressure (10^{-7} Torr.). Indications are that the capturing process is dependent on other vacuum system gaseous components, most notably water vapor

and the absolute temperature of the surface. If the walls are reduced in temperature below 4.2°K , the chamber background partial pressure of H_2 decreases.

In accord with these overall considerations, a liquid-helium-pumped fourth stage has been constructed; it is shown diagrammatically in Fig. 1.3. This stage is designed to be inserted into Chamber Three through one of two large flange holes on the top of that chamber. The stage basically consists of two stainless steel containers; one which holds liquid helium and another surrounding it which holds liquid nitrogen. The fourth chamber pumping surface constructed from annealed copper (for higher thermal conductivity) is heat sunk to the inner container; the liquid nitrogen container, from the bottom of which is suspended a second copper chamber, shields the surfaces at liquid helium temperature from the room temperature radiation that not only would dissipate the inner coolant very quickly but also would place a large enough heat load on the surfaces to raise their temperature, thus decreasing the particle sticking probability.

The liquid helium dewar constructed from .010 inch stainless steel sheet possesses a volume of seven liters. The container mass is held to a minimum in order to reduce the consumption of coolant during cool down; the small wall cross sectional area of the stem which connects the body of the container to its liquid nitrogen temperature support accounts for a helium loss rate of about $1/20$ of that due to radiation. The vacuum space (10^{-7} Torr.) between the inner and outer containers provides adequate thermal insulation to make convection heat

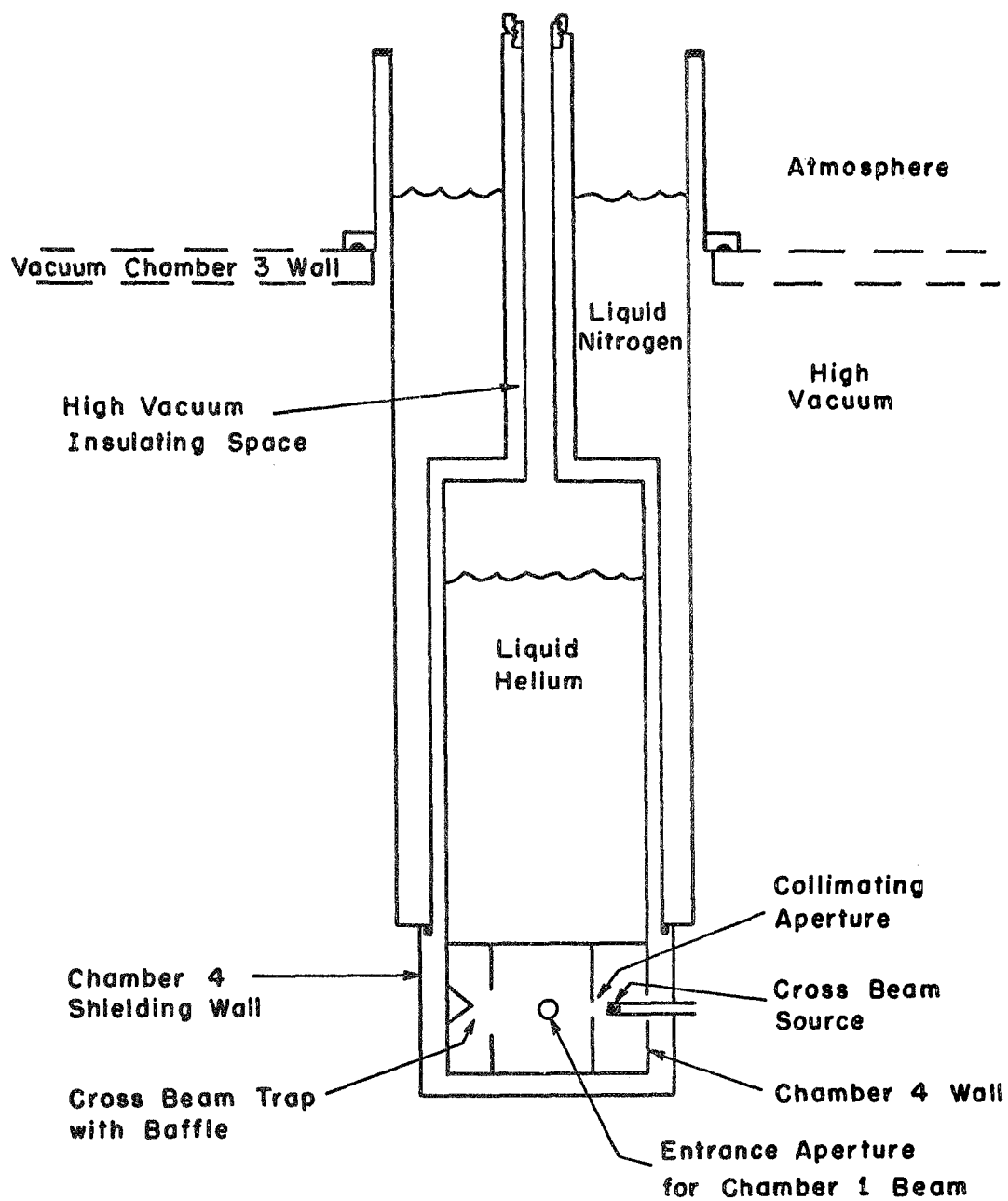


Figure 1.3. Cutaway view of the outfitted liquid helium fourth stage in the vertical plane.

losses negligible in comparison with other losses. The significant coolant loss due to heat radiation from the liquid nitrogen temperature surfaces and from the room temperature radiation sources exposed to the liquid helium surface (through holes permitting the cross beams to enter and the reaction products leave) amounts to about two liters/hour. (When a liquid-nitrogen-cooled surface intercepts room temperature radiation, helium consumption is more than halved).

The liquid nitrogen container, which also is constructed from stainless steel, holds twelve liters of coolant. The liquid nitrogen loss rate is less than two liters/hour, a rate adequate for radiation shielding over any given liquid helium fill. This container provides the support for the inner container which may be readily removed. The joint connecting the two containers is soft-soldered with additional strength provided by a nut at the joint. This construction permits easy filling of the inner container. It also permits an external mechanical vacuum pump to be connected to the joint in order to reduce the boiling point of the liquid helium if a lower fourth chamber wall temperature is desirable.

The fourth stage so far discussed is outfitted with fourth chamber wall construction that fulfills the specific requirements of the $D + H_2$ scattering experiment. The essence of this outfitting is shown in the horizontal and vertical cutaway views of Figs. 1.1 and 1.3. A narrow horizontal slit is provided in both the fourth chamber vertical walls and its shield to enable the in-plane neutral particles formed within Chamber Four to pass outside of the fourth stage to the

ionizer-mass spectrometer assembly. This assembly can be rotated 60° to either side of the Chamber One beam from outside the vacuum system enabling angular distributions of reaction region particles to be observed.

Projecting from the fourth chamber wall opposite the collimated high intensity crossed beam orifice and perpendicular to the beam from Chamber One is an annealed copper cross beam trap which is soldered to the fourth chamber wall. This trap provided with baffles increases the number of particle wall collisions for the particles entering the trap. The trap temperature and therefore the fourth chamber wall temperature can be monitored externally; a carbon resistor sensor provides the means.

The operating performance of the liquid-helium-pumped fourth stage with the basic three-stage system is illustrated in Table 1.1. Molecular hydrogen was used in the performance tests because the sticking probability for hydrogen is lower than for most other experimental gases at the representative temperatures so the results are applicable to problems other than the $D + H_2$ reactive experiment.

Table 1.1 Molecular hydrogen partial pressures in Chambers Three and Four for assorted cryopump operating conditions.

	P_3	P_4
a) no gas introduced into chamber from cross beam source without helium pumping	1×10^{-7} Torr.	1×10^{-7} Torr.
b) cross beam introduced (10^{13} particle/cm ³) without helium pumping	1×10^{-4} Torr.	1×10^{-4} Torr.
c) cross beam introduced (10^{13} particles/cm ³) with helium pumping (4.7°K)	3×10^{-7} Torr.	2×10^{-7} Torr.
d) cross beam introduced (10^{13} particles/cm ³) with helium pumping (4.3°K)	1×10^{-7} Torr.	$.7 \times 10^{-7}$ Torr.

(The liquid-nitrogen-cooled H₂ orifice is 3/16 in. diameter and 3.75 sq. in. of Chamber Four surface is open to Chamber Three).

These data show that the pumping speed for a beam of 10^{13} particles/cm³ and a fourth chamber temperature of 4.7°K is 1.5×10^5 liters/sec. and at 4.3°K is 3.5×10^5 liters/sec. The four-stage vacuum system operating under the given conditions can maintain a background Chamber Four pressure slightly better than the background of Chamber Three, when a Chamber One beam is operating with the three-stage system alone without a cross beam; this was an objective. The pumping speed upper limitation for the liquid helium pump as presently outfitted appears to be of order 10^6 liters/sec. The performance as shown brings the four-stage molecular beam apparatus within the range of examining processes involving room temperature non-condensable species whose signal-to-noise problems are as difficult as those of the

hydrogen chemical reaction.

B. IONIZER GETTER-PUMPED FIFTH STAGE

The desirability of enclosing the detector ionizer in its own differentially pumped stage for reducing noise has been noted previously; remaining is its description.

The ionizer enclosure was constructed to permit the ionizer ion-optics and a portion of the mass filter to be enveloped by a liquid-nitrogen-cooled copper cylinder shown in Fig. 1.4. The beam being detected passed through the chamber entrance aperture (see Appendix 1A for dimensions) before cleanly passing through the ionizer entrance aperture into the ionization region and then down the mass filter. This geometry enabled (a) the entire cross beam interaction region to be viewed by the ionizer; (b) the modulated scattered D atoms to pass directly into the ionization region after passing a cold aperture (rather than the very hot ionizer aperture which could provide a much greater opportunity for surface produced modulated HD), and (c) the effusion of thermalized Chamber Three HD into Chamber Five to be reduced. "O" rings sealed the enclosure cylinder to the mass filter body.

Extending from this cylinder on one side was a large pumping cylinder. Coaxial to this copper extension (23 cm x 13.5 cm dia) which possessed ample liquid nitrogen cooling coils soft-soldered to the outer surface were positioned two titanium filament rods (Varian) which continuously carried 38 amps r.m.s. of a.c. current. Titanium was then deposited on the cold pumping walls.

Pumping action for hydrogen isotopes was not experienced without the titanium-coated surfaces cooled to liquid nitrogen temperature.

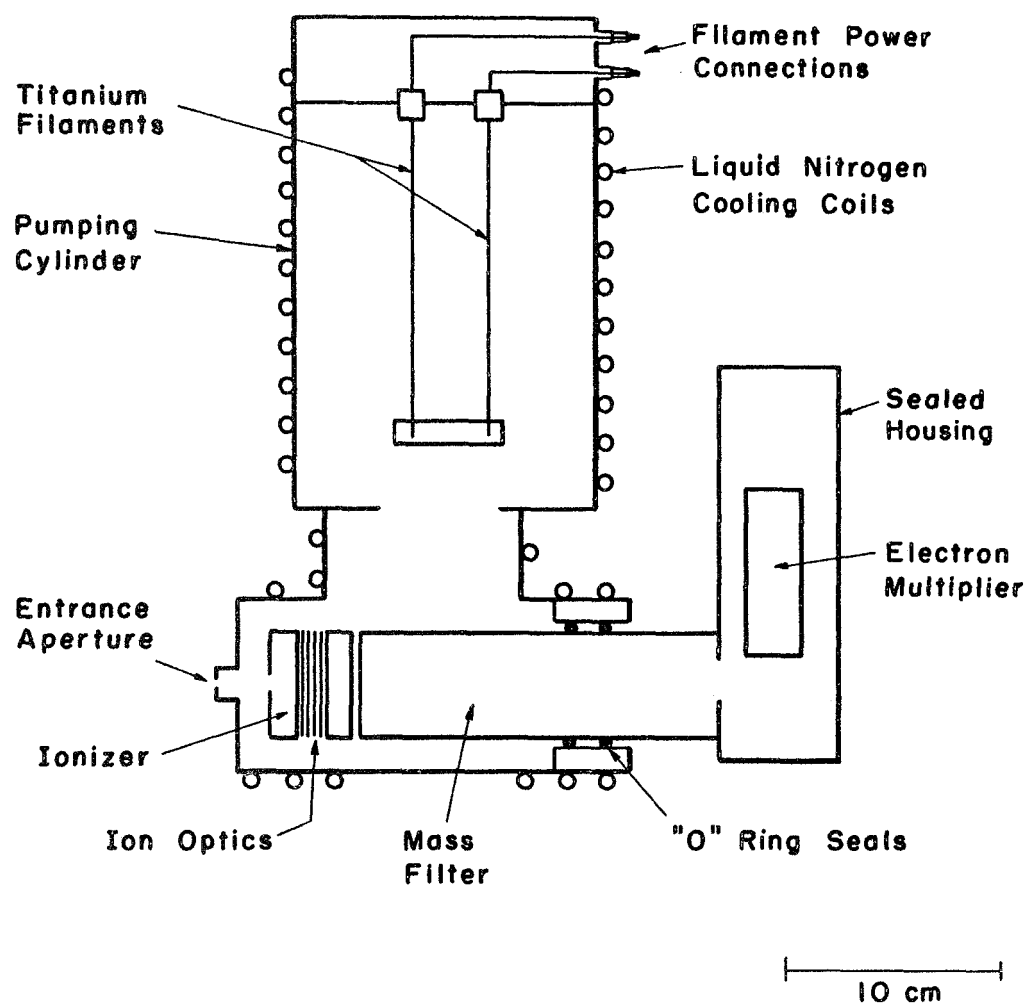


Figure 1.4. Cutaway view of the ionizer getter-pumped fifth stage. This stage is located in Chamber Three.

This may be attributed to the mechanism for removing hydrogen being less efficient at elevated temperature. The walls of this surface were responsible for removing 10^{14} particles/cm²/sec of hydrogen. As noted previously, H₂ and HD partial pressures better than 10⁻⁸ and 10⁻⁹ Torr. were typical. These pressures with getter pumping represent pressure improvements of better than one order of magnitude over the partial pressures existing in Chamber Three.

C. NEUTRAL PARTICLE DETECTION

The atomic and molecular modulated beam detection and general mass spectroscopy associated with these experiments has been carried out with a universal detector. The detector consists of a high-efficiency electron impact ionizer (Extranuclear Laboratories Inc., type II) whose axis is coincident with the axis of the quadropole mass filter (ELI Model 162-5) on which it is mounted. The ion optics consisting of two planar and two cylindrical lenses and the neutral optics preceding the ionizer ensures that each neutral particle can pass only once through the ionizer before entering the mass filter. The mass filter consists of four parallel rods of circular cross section contained within a cylindrical stainless steel case. When the rods are activated by a combination of radio frequency and d.c. electric fields, the hyperbolic fields set up allow ions of a given e/m ratio to traverse spirally the length of the filter axis. Ions of different e/m are placed on unstable orbits, resulting in their being thrown out radially.

Transmitted ions pass into the ion detector assembly, which is a 14 stage copper-beryllium electron multiplier (Dumont Laboratories, SPM-03-301). This device with nominal gain 10^5 is connected to a preamplifier (ELI) of input impedance 10 megohm which further feeds a preamplifier-electrometer (ELI) that is mounted outside the vacuum system. A lock-in amplifier (Princeton Applied Research, HR-8) is utilized in recovering modulated information.

On background analysis this ionizer produces 10 milliamperes per Torr. of mass resolved ions, and the neutral detection efficiency

exceeds 10^{-3} for thermal energy hydrogen and nitrogen beams.

The angular distribution measurements were carried out with this mass spectrometer mounted on a rotatable arm that was located in Chamber Three (see Fig. 1.1). The pivot of this arm was positioned directly below the center of the beam intersection region (approximately spherical) in order that the ionizer upon rotation would be equidistant from this region.

IV. EXPERIMENTAL PROCEDURE

The atomic and molecular beams were aligned so that their axes were perpendicular to each other and the mass spectrometer moved in the plane of the beams. The beam and detector collimating apertures were adjusted so that the ionizer would view the entire beam intersection volume (approximately spherical) at all angles at which data were to be taken. The tungsten furnace source and the detector were activated and the latter was rotated to where it intercepted the modulated D atom beam. This position was defined as $\beta = 0^\circ$.

While the detector was turned off, the pumping surfaces of Chamber Five were degassed by indirect heating (radiation from the heated titanium filaments) and then cooled to liquid nitrogen temperature with the filaments turned off. The titanium filaments were turned on again and the getter pump began to operate. The detector was turned on and the mass three partial pressure was measured to insure that this stage was operating properly.

With the detector and primary beam coaxial and the temperature-stabilized tungsten source operating, modulated signals for masses two and four were measured for the purpose of verifying that the beam was about 95 percent dissociated. The number density of the atomic species at the interaction region was then about $2 \times 10^9/\text{cm}^3$.

Liquid helium was transferred into the already liquid-nitrogen-cooled cryopumped helium dewar and this pump began operating. The H_2 crossed beam was turned on and its intensity was adjusted so that the measured D beam attenuation was less than 5 percent. The number density

of H_2 was about $2 \times 10^{13}/\text{cm}^3$ in the interaction region.

With the chopping frequency set at 1440 Hz and the primary beam stops adjusted for studying reactive scattering (see Appendix 1A), signals corresponding to masses two, three and four were measured between the LAB angles -55° to $+55^\circ$. Throughout these measurements which proceeded according to tests one and two described in Section II, the mass two signal at $\beta = 0$ was checked after approximately every two or three $\beta \neq 0$ data points to ensure that the atomic number density had not changed. The recording period of each reactive signal was 15 min. in length using an integration time constant of 100 sec. Signal-to-noise was at best 10 to 1. The length of time for a particular data run was approximately 7 hours. The data accumulated in the last hour was ignored because the pressures of Chambers Three and Four were inclined to fluctuate before the liquid helium coolant had completely evaporated.

While recording the angular distribution for mass three signals at angles closer to the primary beam than 12° , the signals were identified as primary beam, elastically scattered HD impurity. Consequently, reactive data could not be obtained at angles that lie within this 24° region.

For the purpose of velocity estimation of the mass three signals previously identified as reactive HD (test three), the primary beam chopping frequency was increased to 7.2 KHz. and a study of the lock-in amplifier phase-shifts as a function of laboratory angle and mass was carried out. With the spectrometer coaxial with the primary beam, the lock-in phase adjustment was set, as in the previous measurements, for maximum detected signal for a given mass. The phases corresponding to the respective signal maxima were recorded for each mass; the minima occurring at 90° from this phase were also noted. With the mass filter adjusted to mass three, the detector was rotated to the reactive angular regions. The phases at which the HD signals are maximum and zero (since signal changes per unit phase change around zero are greater than they are around maximum) were recorded for a variety of angles. These phase-shift data were utilized with time-of-flight arguments to calculate HD recoil velocities.

After the accumulation of these data, the chopping frequency was changed to 5.63, and 9.39 KHz, and the previous procedure was repeated for each chopping frequency. The data for 5.63, 7.2, and 9.39 KHz were used to deduce that the HD velocity estimations are in fact meaningful (see Section V. and Appendix 1C).

In a separate experiment the signal processing apparatus was examined for phase-shift characteristics as a function of chopping frequency. A properly matched square wave generator was inserted into the preamplifier input that simulated the reactive signal amplitude, and the generator was made to provide the external lock-in reference

signal. The phases corresponding to maximum and minimum signal were noted as before and the frequency was varied throughout the experimental chopping range. No detectable phase shift frequency dependence was observed so that the phase differences previously observed were attributed entirely to HD time-of-flight differences.

A check also was run to determine if the isotopic impurity HD component in the H_2 beam was being modulated and detected as the result of being scattered by the D atom beam. For this, the deuterium normally admitted to the primary source was replaced by helium. No HD signal could be detected under the same experimental conditions of the D beam.

In another separate investigation the H_2 beam was examined for the presence of polymers. For this exercise, the liquid-nitrogen-cooled wrinkle slit was mounted in Chamber One, the modulated H_2 beam was ionized and mass analyzed. A search was made for the ions H_n^+ where n is an integer. Only $n = 3$ was detected; the mass three and two signals were in the same ratio as the isotopic abundance of HD in H_2 . Mass five, if present, was at least five orders of magnitude lower in intensity than H_2^+ . Considering these results, there is no evidence of free jet expansion with consequent cooling and condensation to polymers of H_2 . The H_2 appears to have cooled to liquid nitrogen temperature and not to have cooled appreciably on further expansion; consequently, it had a velocity distribution not far from Maxwellian at 77°K.

As a result of the reactive data runs, the ratio of the different mass signals were known for a number of laboratory angles. Since

the total cross section for scattering of H by H₂ has been measured,²¹ detailed knowledge of the differential cross section for D on H₂ at angles close to the D beam could be of assistance in the estimation of the total reactive cross section using the signal ratios for mass two and three for much larger angles. For this exercise, the primary beam collimation was increased by a factor of 3 (see Appendix 1A) which in effect improves the detector angular resolution by that factor.

The procedure for studying the small angle scattering was to record the mass two signals with first the H₂ beam on and then off. The difference of these measurements is evidently proportional to the elastic differential cross section averaged over the Maxwellian beam velocity distributions. The angular range for these measurements was $-45^{\circ} \leq \beta \leq 45^{\circ}$.

V. RESULTS AND DISCUSSION.

The angular distribution results for the reactive experiment (data taken using a chopping frequency of 1440 Hz) are displayed in Fig. 1.5. Signals are not shown at angles less than 15° from the primary beam, where HD impurity in the D beam becomes significant. The error bars represent 90% confidence limits for six experimental runs.

The asymmetry of signals may be understood by comparison with the solid line, which is the signal calculated assuming that (1) $\Delta E/E = 0$ (the reaction endothermicity divided by the initial relative energy), and (2) a separable and symmetric center-of-mass differential cross section is proportional to

$$(1 - E_0/E) \cos^N M(\theta - 180^\circ) \quad E > E_0$$

$$0 \quad E \leq E_0$$

where $M = 1.35$, $N = 2.0$, and $E_0 = .33\text{ev}^9$ is the reaction activation energy and θ is measured from the forward direction (see Fig. 1B.1) over the domain where $\cos M(\theta - 180^\circ)$ is positive. The calculations (see Appendix 1B) involved transforming and averaging the cross section over the full target-detector solid angle (the half angle being $\Delta\beta = 3^\circ$, see Appendix 1A). These results were averaged once again over fourteen velocity diagrams corresponding to all significant relative velocity vectors that can lead to reaction. The reason for these assumptions [to be referred to as Assumptions (1) and (2)] will be discussed later in this section.

The mean velocities of the detected HD determined from the a.c. signal phases are shown in Fig. 1.6. These velocities are superim-

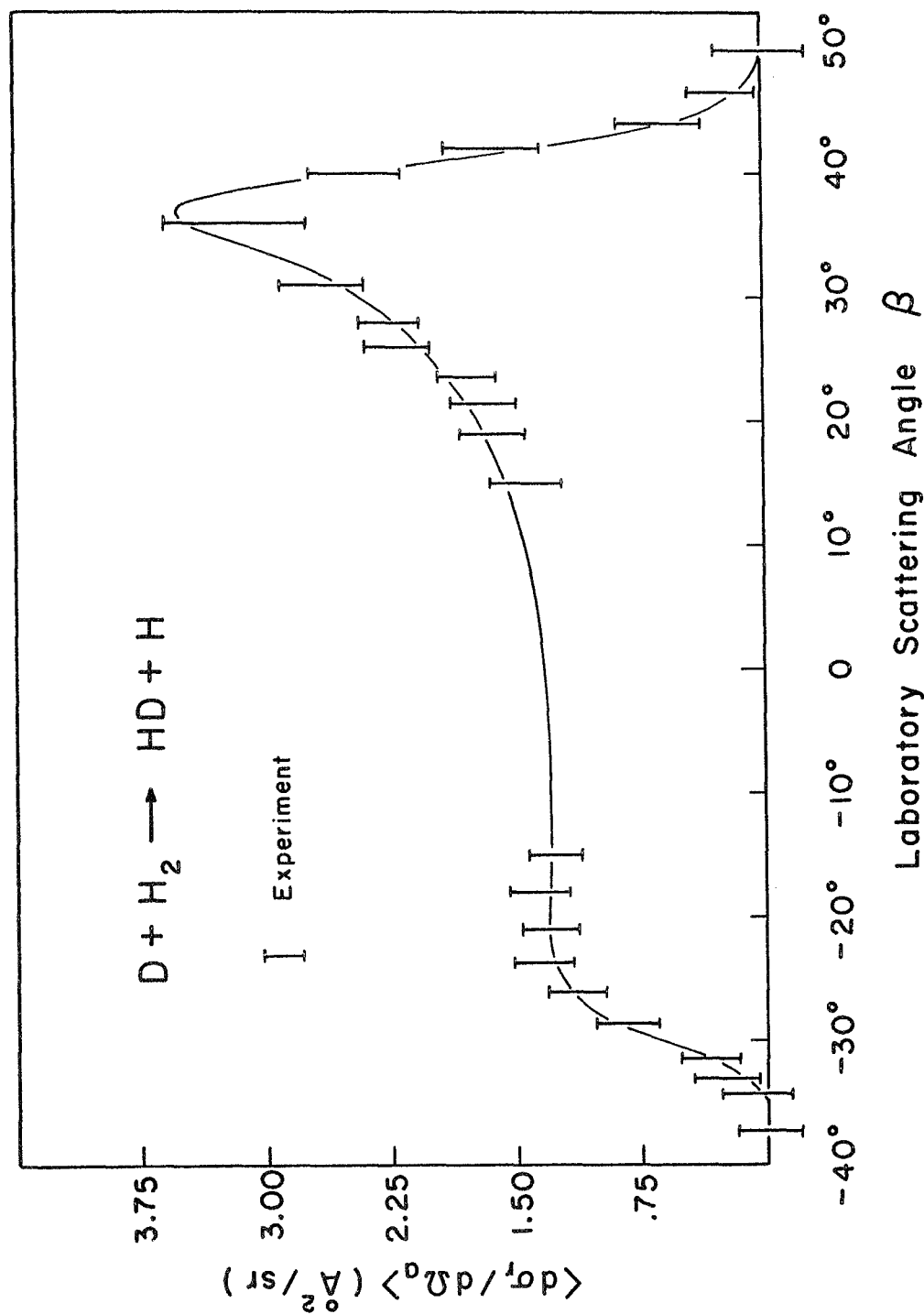


Figure 1.5. Angular distribution of detected HD. The solid curve has been calculated for Assumptions (1) and (2); see text. Absolute calibration of the differential cross section was performed by comparing mass three reactive signals with elastically scattered mass two signals.

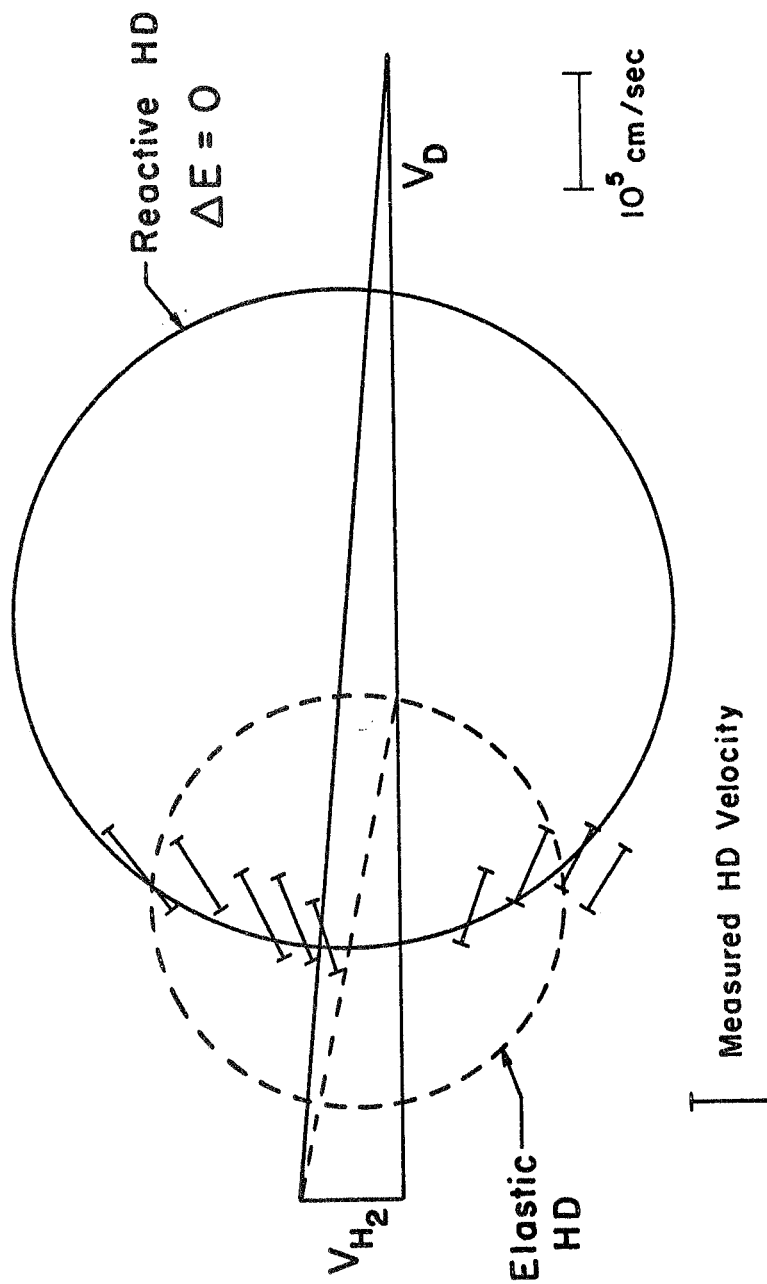


Figure 1.6. Most probable velocity diagrams for $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ and $\text{DH} + \text{H}_2 \rightarrow \text{DH} + \text{H}_2$. The measured HD velocities were determined from a.c. signal phases.

posed on two velocity diagrams. The dashed circle shows the most probable velocities for impurity HD being scattered by the H_2 beam. The solid circle shows the most probable velocities of reactive HD for Assumption (1), considering the cross section energy dependence in Assumption (2). The observed velocities appear incompatible with scattered HD impurity velocities. Both the angular distribution and the measured velocities appear compatible with the simple assumptions. These velocities may be considered as mean recoil velocities for essentially one of the four possible HD velocity contributions noted in Section II. (the reader is referred to Appendix 1C for a critical discussion of this point).

The first assumption, physically speaking, is quite appropriate for the reaction. From the binding energies of H_2 and HD in the ground state derived from spectroscopic data¹⁷, one can readily determine the ground state endothermicity for the reaction to be

$$\Delta E = D_o(H_2) - D_o(HD) = -.035 \text{ e.v.} \quad (1.3)$$

The threshold energy for reaction obtained by Kupperman and White (photolyzed mixtures of DI or DBr plus H_2 with monochromatic light, the concentration ratio $[HD]/[D_2]$ was examined) is known to be $0.33 \pm .02 \text{ e.v.}$ Evidently for the initial and final rotational states $J = 0, J' = 0, \Delta E/E_{cm} \ll 1$. Since the HD CM recoil velocity is proportional to the factor $(1 - \frac{\Delta E}{E})^{1/2}$ (see Appendix 1B, Section 2) and this factor effectively controls the width of the laboratory angular dis-

tribution for the angular dependence of (2), the solution displayed in Fig. 1.5 applies to the $J = J' = 0$ situation to good approximation.

There are, of course, other situations where $\Delta E/E_0 \ll 1$ and the $\Delta E/E = 0$ angular distribution solution applies (see Fig. 1.5).

If non-zero rotational states are considered, the kinetic energy defect becomes

$$\Delta E = -.035 + .566 \times 10^{-2} J' (J' + 1) - .754 \times 10^{-2} J(J + 1) \text{ e.v.} \quad (1.4)$$

where the rotational coefficients for the H_2 and $DH X \ ^1\Sigma_g^+$ states have been utilized in the rigid rotor approximation.¹⁷ The endothermicities for various J and J' combinations are listed in Table 1.2 in addition to $\Delta E/E_0$. Entries in Table 1.2 where $\Delta E/E_0 \ll 1$ represent those J and J' combinations where the $\Delta E/E = 0$ angular distribution solution applies.

The reason for displaying only three J values in Table 1.2 can be understood by considering the experimental situation. The H_2 nozzle source was in thermal equilibrium with the liquid nitrogen cryopump dewar, and it was operated in the effusive flow regime. As was previously discussed, there was evidence that kinetic equilibrium of the beam and source existed so that the angular distribution calculation was carried out for a beam temperature of $77^\circ K$. In fact, had a higher kinetic temperature been assumed, the calculated signals would have decayed at larger positive angles than are observed in Fig. 1.5. But equilibrium between the ortho and para molecules at

Table 1.2. $D + H_2(J) \rightarrow DH(J') + H$ Endothermicities for values of J appropriate for the experimental conditions. Entries where $\Delta E/E_0 \ll 1$, represent those J, J' combinations where the $\Delta E/E = 0$ angular distribution solution applies.

ΔE (endothermicity, e.v.)	$H_2(J)$	$DH(J')$	$\Delta E/E_0^*$
-.035	0	0	-.106
-.022	0	1	-.066
-.001	0	2	-.003
+.033	0	3	+.010
+.078	0	4	+.237
+.135	0	5	+.409
-.050	1	0	-.152
-.039	1	1	-.117
-.016	1	2	-.049
+.018	1	3	+.054
+.063	1	4	+.192
+.119	1	5	+.362
-.045	2	0	-.130
-.034	2	1	-.103
-.011	2	2	-.034
+.023	2	3	+.068
+.068	2	4	+.206
+.125	2	5	+.378

* Assumes $E_0 = .33$ ev; this measured quantity is an averaged behavior⁹

77°K most likely did not exist considering the small rate constant for ortho-to-para conversion and the fact that a catalyst for this purpose was not employed in the H₂ source. If one assumes rotational equilibrium at room temperature for the beam molecules and the usual 3:1 ratio between ortho and para molecules, the population densities listed in Table 1.3 are found. This worst case calculation indicates that the J = 0,1 and 2 states contribute more than 90 percent of the signals assuming no pathologically huge reactive cross sections for higher rotational states.

The similarity of the calculated angular distribution and the experimental data in the $\beta = -30^\circ$ and $+42^\circ$ regions (angular distribution width), in light of the previous discussions, does suggest that any or all of several J, J' combinations in which little or no product molecule excitation occurs have been observed. If HD had recoiled predominantly in rotational states $J' \approx 4$ rather than states of smaller quantum number, the total angular distribution width would have been at least 10° more narrow than was actually measured. Of course, the possibility of interpreting the results in terms of HD vibrational excitation must be dismissed entirely, because the cross sections would have to be huge in order to make up for the extremely small portion of the CM velocity distribution "tail" that can make vibrational excitations in HD energetically possible. The rapidity with which the "tail" drops off is tabulated in Appendix 1C (Table 1C.1).

Understanding the implications of the angular distribution width in terms of Assumption (1), we consider the sensitivity of the entire angular distribution with respect to change of the energy and angle terms in Assumption (2).

Table 1.3. Distribution of rotational states in the H_2 cross beam assuming equilibrium of rotational degrees of freedom at room temperature.

$$P(J) = \frac{g(2J + 1) e^{-E_{\text{rot}}/KT}}{\sum g(2J + 1) e^{-E_{\text{rot}}/KT}}$$

where $g = 1/4$ for even J

$g = 3/4$ for odd J

with Herzberg $X \frac{1}{\Sigma_g} + 17$ rigid rotator constants

J	P(J)
0	.132
1	.665
2	.116
3	.083
4	.004

The first factor of the simple differential cross section is rather inconsequential when considering the calculated signals. If one considers the energy dependence to be a step function above activation energy rather than $(1 - E_0/E)$ for $E \geq E_0$ which is specified and if one still assumes the same angular dependence, the calculated signal curve, for essential purposes, is the same as shown in Fig. 1.5. The only noticeable changes appear for $\beta > 42^\circ$ and $\beta < -23^\circ$. The new angular distribution half intensity angle $\beta \approx -30^\circ$ occurs about $1/2^\circ$ more positive than the old. (The new and old curves are parallel.) The new half intensity angle $\beta \approx 42^\circ$ occurs about 1° more positive than the old, with parallel behavior. The new curve falls within the experimental error bars. Such behavior is due to the fact that the most probable relative velocity angle occurs at a slightly larger angle for the simpler cross section. We further ignore the computational differences because (a) computational errors are difficult to estimate for these procedures and (b) reducing the target-detector half angle by 50 percent tends to reduce the half intensity positions (narrowing the distribution on the order of 2° total).

The calculated angular distribution is significantly sensitive to small changes in the CM angular distribution of Assumption (2), particularly in the roll off region on the negative side (because it receives only CM contributions from angles $215^\circ \lesssim \theta \lesssim 300^\circ$). The sensitivity of the calculation for narrower and broader CM distributions is illustrated in Fig. 1.11. For the purpose of generating intuition and demonstrating that the experimental

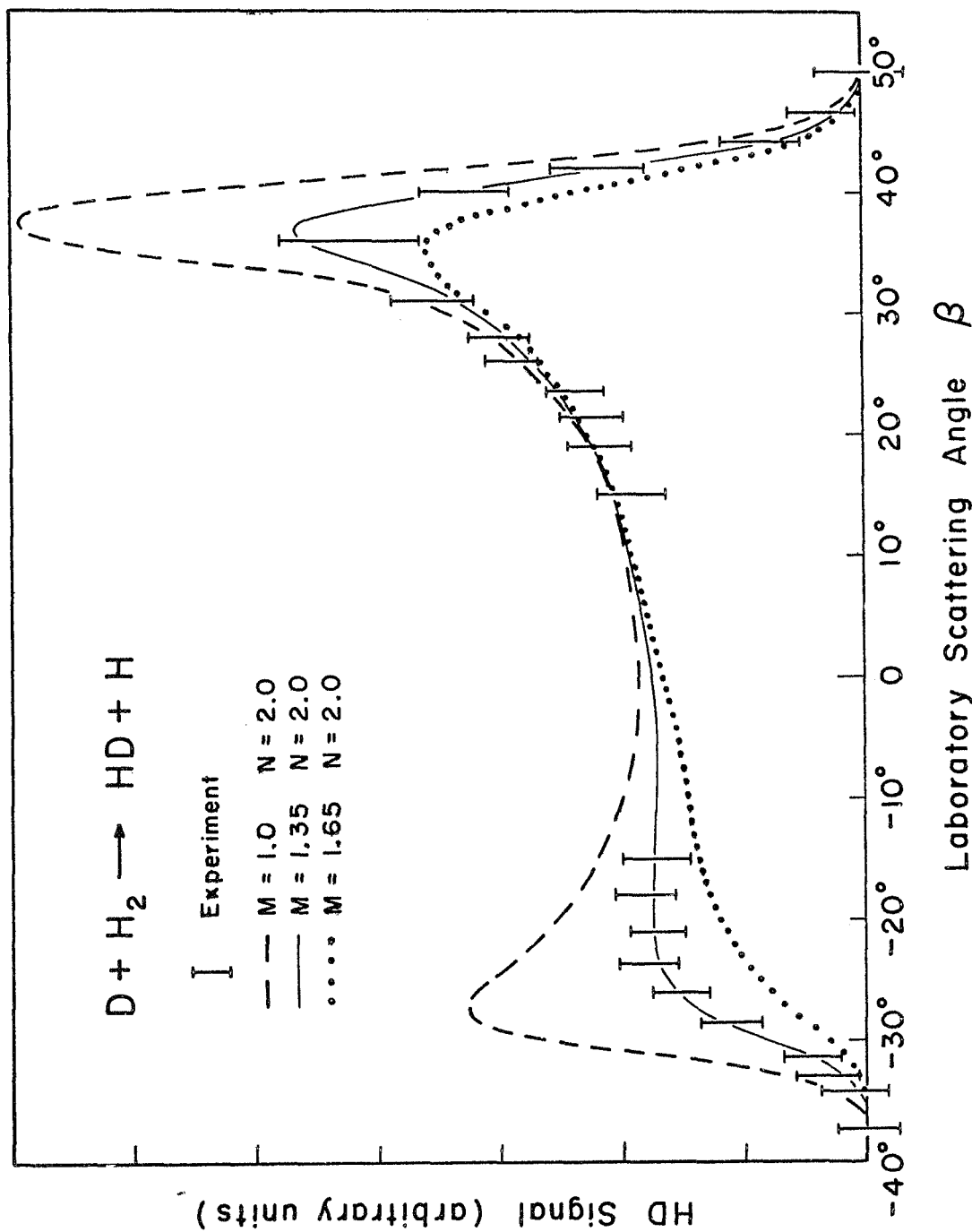


Figure 1.7. Comparison of experimental data with signals calculated for $\Delta E = 0$ and CM angular distributions of the form $\cos^N [M(\theta) - 180^\circ]$.

points simply cannot be refitted on the additional curves in any way, even if there were poor error estimates, larger deviations from Assumption (2) have been calculated than are felt to be justified.

Referring to Fig. 1.7, the curve which peaks above the data corresponds to a CM function specified by $M = 1.0$, $N = 2.0$; the curve lying below is specified by $M = 1.65$, $N = 2.0$. A noteworthy feature of the calculations is that the amplitude is essentially invariable with respect to change in M in the region $5^\circ < \beta < 25^\circ$. This is due to the fact that the functions remain relatively constant with change in M around the backward direction. Evidently the calculated signal amplitude here can be changed only by postulating a symmetric cross section which does not peak at $\theta = 180^\circ$ (i.e. removing some of the contribution from strongly backward ejection angles). In fact, subtracting the angular term $|\theta - 180^\circ|/36$ for $168^\circ \leq \theta \leq 192^\circ$ from $\cos^2(1.35(\theta - 180^\circ))$ results in a relatively flat predicted signal in this region, and the resulting curve still passes through the data points in all regions. Other arbitrary manipulation can easily produce identical results. From this discussion it is obvious that the experiment is relatively "blind" to cross section specifications in the region $170^\circ \lesssim \theta \lesssim 190^\circ$ compared to the region $215^\circ < \theta < 300^\circ$ and its symmetric counterpart.

It should be remarked that the velocity information has been of assistance in postulating a functional behavior in the latter region. If the signals in the roll off region on the negative side were due to a significant scattering contribution from angles closer

to $\theta = 300^\circ$ than 215° as postulated, the estimated velocities would have been significantly larger than observed (see Fig. 1.6). While the functional parameter $N = 2.0$ has been held constant in these discussions for reasons of convenience, any function that behaves similar to those discussed out to CM regions, about $1/10$ of the cross section amplitude 10° removed from the backward direction, would produce similar laboratory results. This fact should be kept in mind when experiment is compared with theory.

We turn now to the velocity information deduced from the phase measurements. While the energy dependence contained in Assumption (2) is arbitrary when considering the angular distribution and a mere step function energy dependence above threshold, this is not the case when considering the crude velocity information. This is demonstrated in Fig. 1.8 where the velocity measurements are superimposed upon two reactive most probable velocity diagrams (see Appendix 1C for the method in which (a) the most probable diagram specifications were determined, and (b) the velocities were calculated from lock-in phase-shifts); one diagram is for the simple step function above threshold, the other is for the energy dependence of Assumption (2). Observe that the velocity data do not fit the former energy dependence if one postulates little or no reaction product internal excitation.

The simple step function should not be abandoned immediately because more significant HD internal excitation is capable of explaining the measured velocities. This is apparent in Fig. 1.9 where the data are compared with the most probable diagrams for reaction

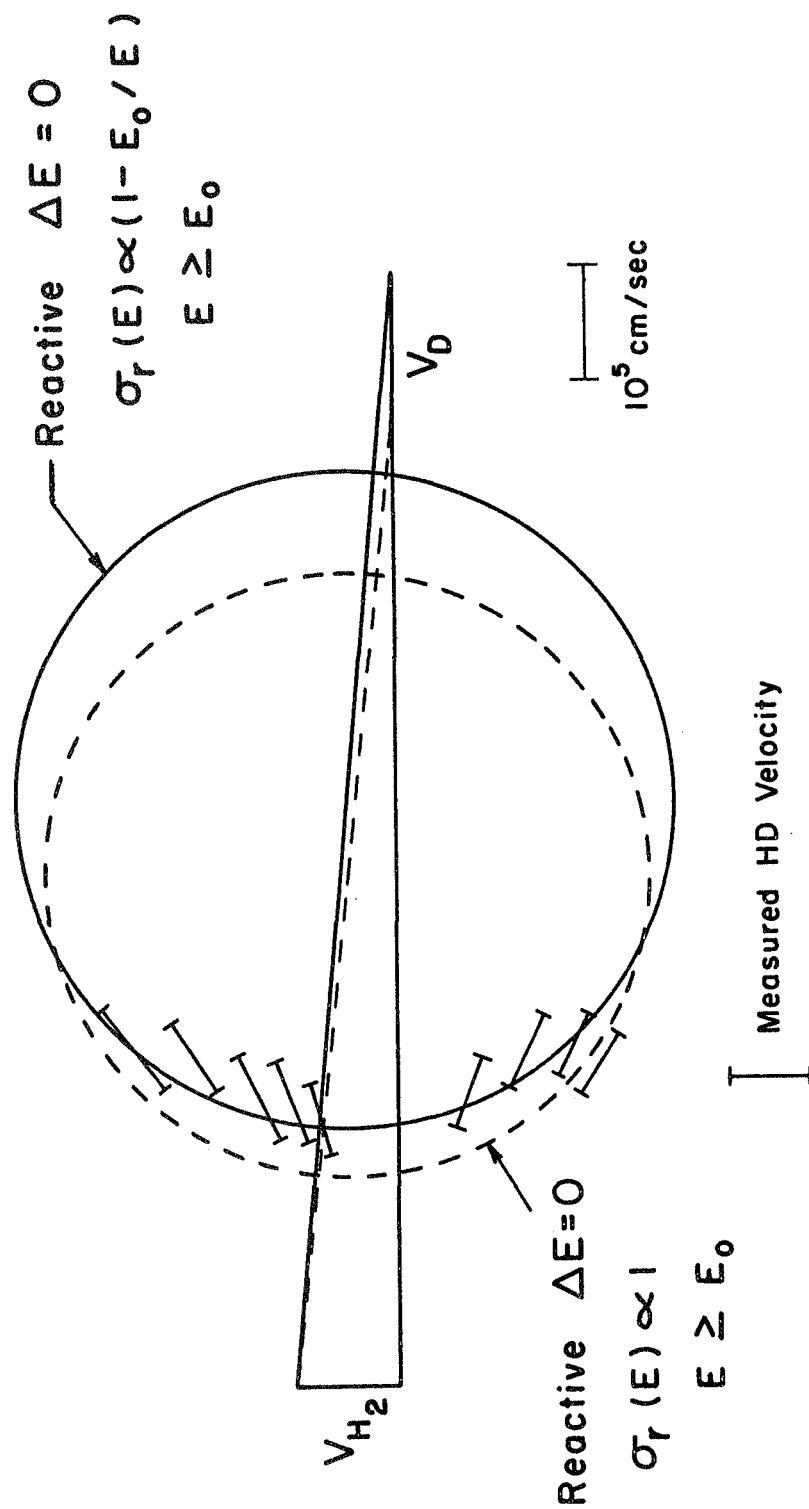


Figure 1.8. Most probable reactive velocity diagrams for two simple cross section energy dependences when $\Delta E = 0$.

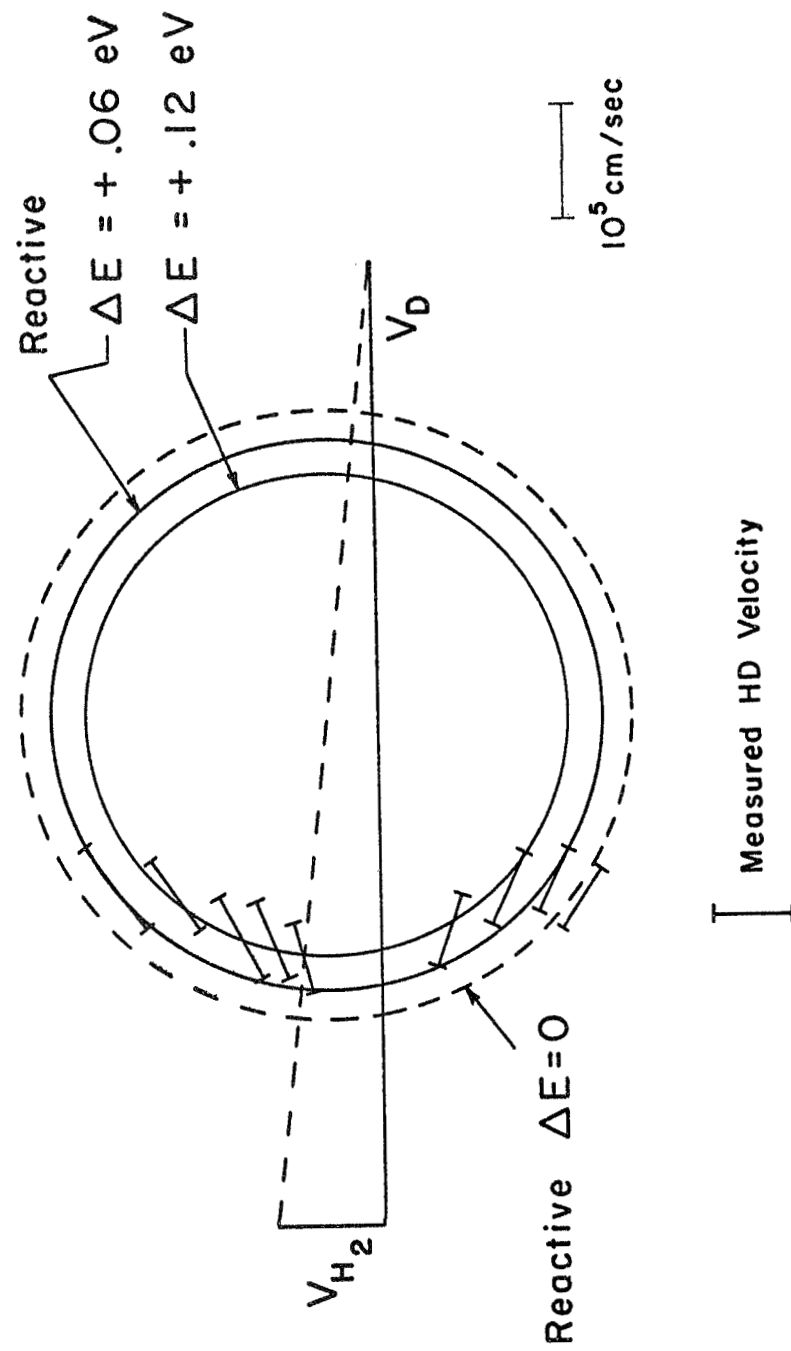


Figure 1.9. Most probable reactive velocity diagrams for a simple step function above activation energy and $\Delta E = 0$, $.06$ and $.12$.

endothermicities of .06 and .12 ev. Assuming the $J = 1$ H_2 molecules make the major contribution to the measured signals, such energies correspond to $J' - J$ equal to 3 and 4 respectively. The narrower laboratory angular distribution corresponding to larger HD excitation is to be emphasized.

If substantial HD excitation were the case, it would imply that kinetic energy can be transferred to rotational energy in times short, compared to the rotation of the D-H-H reacting configuration, a notion which is not commonly held to date.

The cross section energy dependence proposed for Assumptions (1) and (2) is certainly not unique. If average group velocity calculations had been performed rigorously for the angles at which measurements were performed (they should appear quite similar to those found by the simple most probable approach), the results would have been of questionable value in proposing a less simplified and more realistic energy dependence. The simple dependence proposed has no experimental justification by virtue of total reaction cross section measurements. The actual shape has been introduced purely for the purpose of a crude fit between the data and the most probable diagrams. The energy dependence will be further discussed in connection with theoretical calculations.

The experimental results may be compared with those of Datz and Taylor¹¹ (D and T) who have performed an equivalent experiment; the angular distribution of signals displayed in Fig. 1.10 have been

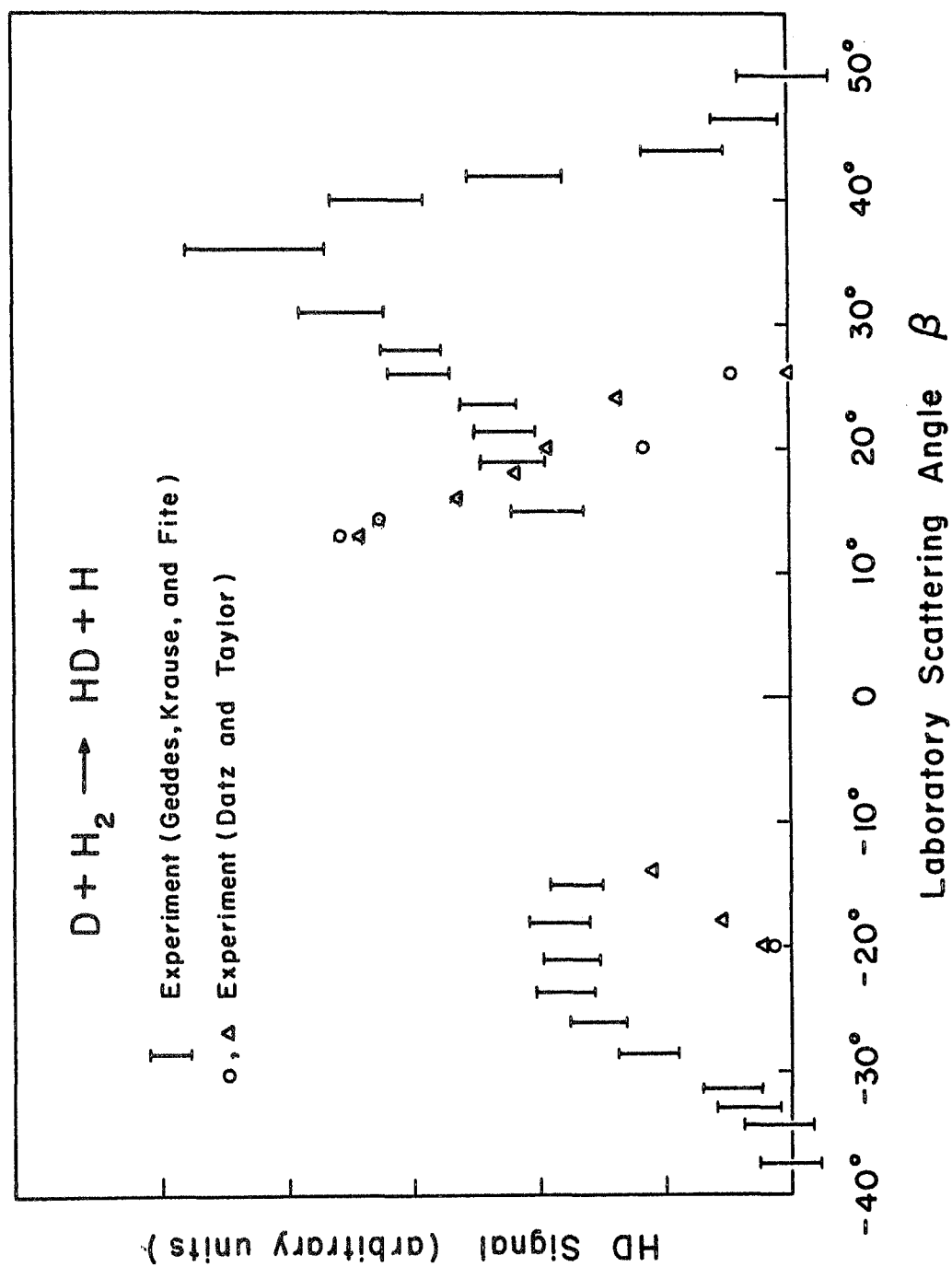


Figure 1.10. Comparison of the experimental angular distribution of Geddes, Krause and Fite with that of Datz and Taylor.

chosen to be equal at $\beta = +18^\circ$. The D and T data for the separate experimental runs are agreeable but differ from the present work.

If one attempts to understand the D and T data in terms of Assumption (1) and HD backward ejection, it is evident (recalling a previous discussion) that the backward angular dependence must be extremely narrow ($\sim 15^\circ$ half width); otherwise, the rapidly changing behavior in the $\beta = +20^\circ$ region cannot be explained. If this were the case, then the signals reported on the negative side should be zero.

A possibility of maintaining Assumption (1) arises if a forward angular dependence, broader than the backward width, is postulated. Such a dependence could be made to explain the D and T data whether it is accompanied with the backward contribution or not, because the signal deficiency on the negative side is corrected and there are no new difficulties on the positive side. However, D and T report having estimated the HD velocities in a fashion similar to the present work. The velocities were consistent with backward ejection but have not been reported. Such a finding is inconsistent with a significant forward contribution, especially since the CM to LAB Jacobian weights forward contributions about three times more heavily than backward contributions in these experimental regions. Assumption (1) does not appear to provide the basis for understanding their experiment.

Another alternative is that considerable HD rotational excitation occurs with HD backward ejection. If one postulates that

the endothermicity is of order .2ev, a laboratory distribution similar to D and T on the positive side can be produced by CM angular dependences at least twice broader than those possible for the $\Delta E = 0$ interpretation noted above. The added angular broadness tends to improve the gross disparity between the calculated signals and the data for negative LAB angles, but this approach can still not predict signals at angles less than -15° without seriously distorting the positive side.

Perhaps the difficulty of understanding the D and T results is due to the signal-to-noise difficulties that they experienced. To be sure, the difference in the respective experimental findings is not understood.

The experimental interpretations strictly speaking can be compared only with theoretical calculations for the $D + H_2$ reaction performed by Micha⁴. Using the method of distorted waves to describe the relative motions as well as an "almost-linear collision approximation" for the three body system at an energy consistent with this experiment's most probable energy range, differential cross sections for $J = 0, 1$ and 2 of the H_2 molecules have been determined. In this scheme the initial and final molecular angular momenta must be equal and the scattering amplitude is axially symmetric.

Under the assumption of a room temperature H_2 rotational state distribution, $P(J=1)$ makes the most significant contribution. Therefore in Fig. 1.11, Micha's $J = 1$ cross section is plotted with the cross section of Assumptions (1) and (2), and those earlier shown to be

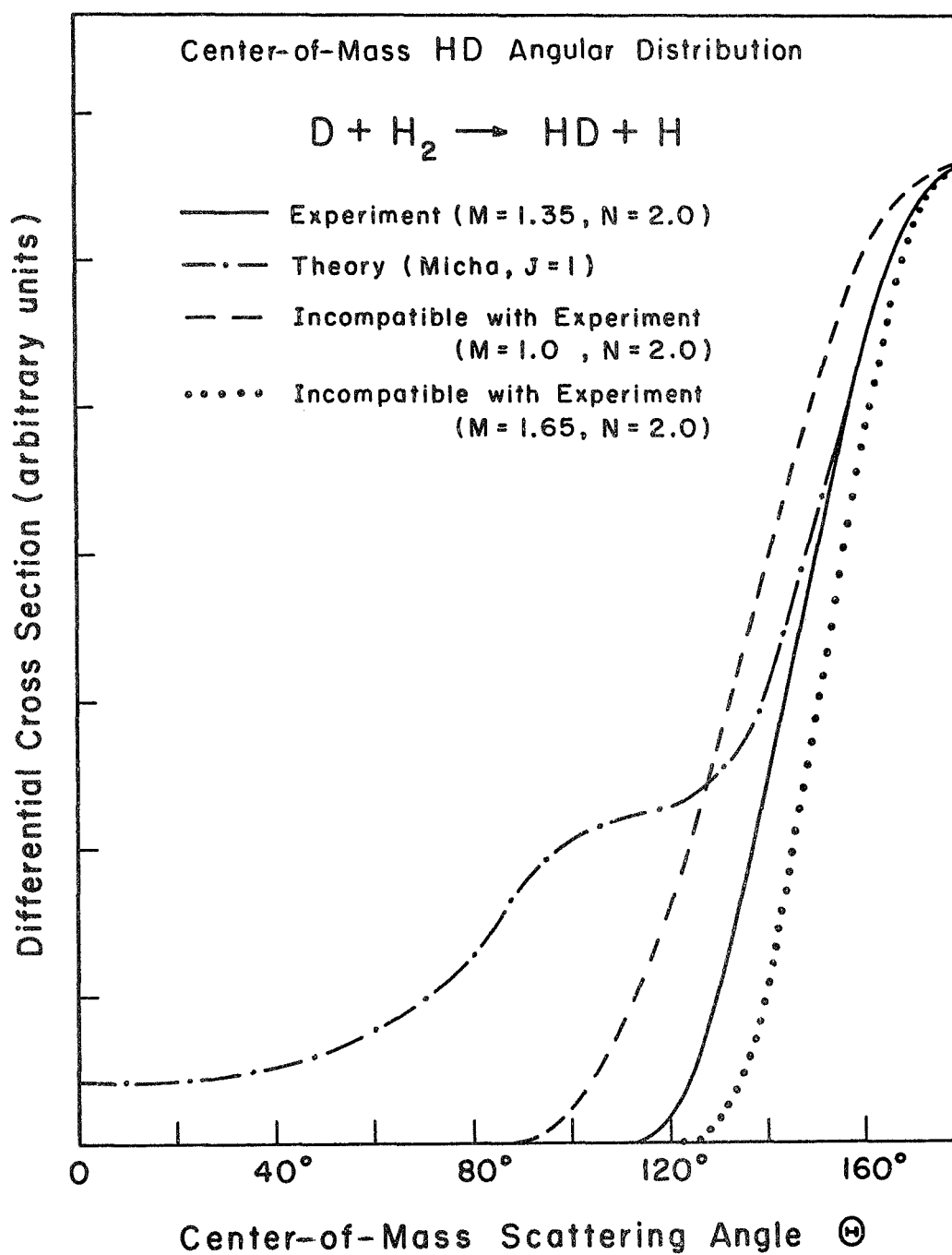


Figure 1.11. Comparison of the experimental center-of-mass angular distribution with theory. Distributions considered in experimental analysis are of the functional form $\cos^N [M(\theta - 180^\circ)]$.

drastically incompatible with experiment. The respective $\theta = 180^\circ$ magnitudes have been adjusted to be equal.

The similarity for the $J = 1$ contribution and experiment is remarkably excellent especially within 40° from the backward direction. However, a major disagreement exists for the region $60^\circ < \theta < 140^\circ$ because a distinct peak would have appeared in the laboratory angular distribution at negative angles close to $\beta = -28^\circ$. The relatively small contribution in the region $0 < \theta < 60^\circ$ is consistent with experiment because a constant contribution in these symmetric regions transforms relatively constantly into the laboratory frame. In addition, the small amplitude implies that such contributions are small perturbations on the more strongly probable backward scattering events. If one were to weight other contributions ($J = 0, 2$) with the $J = 1$ calculation, the new curve would be a very slight improvement compared with that deduced from experiment. The improvement is due to the fact that the other curves display almost identical features as the $J = 1$. This being the case, we deduce that the room temperature assumption is not critically important when comparing Micha's calculations with experiment.

With regard to angular distribution, the only other calculation available is for $H + H_2$ by Karplus and Tang³. It is by no means obvious that the $D + H_2$ and $H + H_2$ reaction calculations should be in precise agreement, although general agreement is not too much to ask for. This $H + H_2$ approximate quantum-mechanical treatment has been carried out for two limiting models in the distorted wave formulation.

In one, the molecule is unperturbed by the incoming atom and, in the other, the molecule adiabatically follows the incoming atom. The quantum results are reported to be in agreement with the quasi-classical trajectory calculations² for the same potential; at energies of interest here, the reactive H_2 is strongly peaked in the backward direction. Typical cross sections for the various initial and final molecular rotational state combinations (a different approximation than Micha's) are less strongly backward peaked than the $D + H_2$ experimental finding. The most strongly peaked distribution reported closely follows the functional shape specified by $M = 1.0$ $N = 2.0$, which was shown to be incompatible with this experiment. While Micha has considered the $H + H_2$ problem⁵, his differential cross sections have not been reported.

Before discussing the absolute reactive cross section estimated for this study, it is necessary to understand the $D + H_2$ elastic differential measurements which have been undertaken for the purpose of calibration. These angular distribution measurements were carried out for both positive and negative LAB angles between $|\beta| = 4^\circ$ and $|\beta| = 45^\circ$. Symmetry of the mass two signals about the D beam was observed to within 10%; the signals corresponding to the positive region are shown in Fig. 1.12.

The laboratory symmetry in this angular range (that contrasts with the reactive measurements) is understood in terms of the CM to LAB transformation. Two important observations concerning this problem for elastically scattered equal mass particles are the

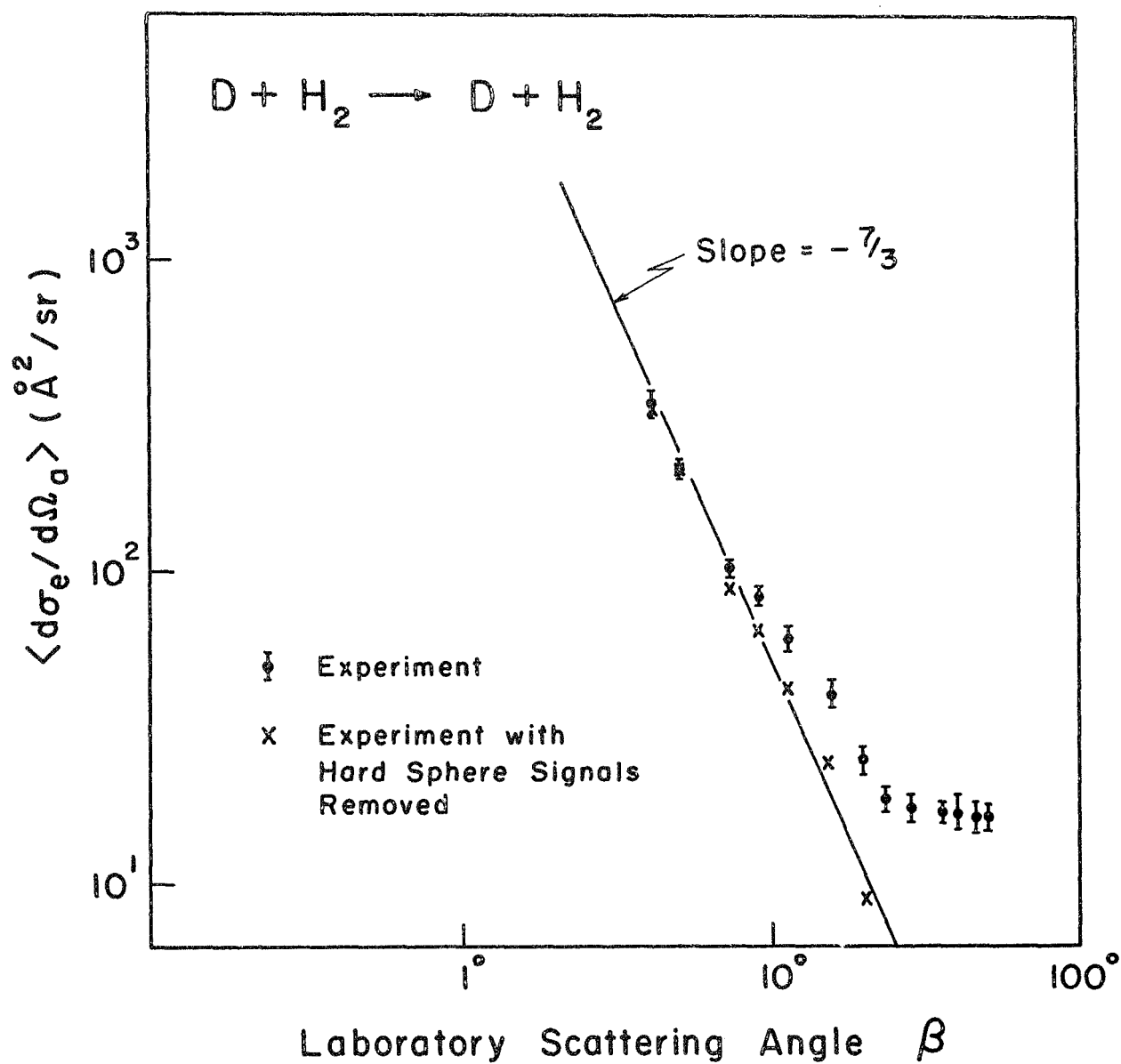


Figure 1.12 Log-log plot of the symmetric angular distribution for $D + H_2 \rightarrow D + H_2$.

following:

(A) There is a one-to-one correspondence between CM and LAB angles that is independent of both the magnitude of relative velocity, v_r and the angle the relative velocity vector makes with the primary beam, Ψ . The constant relationship is $\Theta = 2\beta$.

(B) A consequence of (A) and number density detection (ionization by electron impact) is that the solid angle relationship between the two systems is constant for any v_r and Ψ for all CM angles (no velocity bias that is LAB-angle-dependent). The fact that (A) and (B) hold for $D + H_2$ elastic scattering and not reactive scattering accounts for the respective symmetric and asymmetric laboratory angular distributions.

The behavior of the data appearing in Fig. 1.12 can be understood in terms of simple general features endemic to elastic scattering. First, the relatively constant signals found at $\beta > 25^\circ$ constitutes the "hard sphere" region for this system. The relative constancy is found at equivalent CM angles in quantum mechanical as well as classical descriptions of this elastic scattering process^{18,19}. Of a general nature for classical description, this scattering is isotropic.²⁰

Second, the strong angular dependent signals found in the region $4^\circ < \beta < 20^\circ$ also can be understood classically. If the "hard sphere" signals are subtracted from the experimental points in this region, it is noted in Fig. 1.12 that the adjusted points approximately have a slope of $-7/3$ on the log-log plot. Classical small-angle deflection theory for a potential $V = -c/r^5$ approximately

predicts an energy-angle separable differential cross section of the form .

$$\frac{d\sigma(\theta)}{d\Omega} \propto \theta^{-2(1 + \frac{1}{s})} \quad (1.5)$$

Evidently the dependence $\theta^{-7/3}$ is a consequence of the Van der Waals attraction, $s = 6$.

It is noteworthy that at CM angles less than several degrees (depends on the energy), quantum shadow scattering effects take over. This region, which was not observable in this experiment, makes a large relatively constant contribution as a function of angle except in the classical-quantum transition region. The transition region for this system considering the average energy for this experiment has been estimated to be $\theta = 2.5^\circ$.

It is to be noted that the data appearing in Fig. 1.12 are not simply D scattered by H_2 . Due to the identity of the scattered masses, the angular distribution contains an additional signal from H_2 scattered by D. The latter consideration deserves trivial attention in the large differential cross section region at angles closer to $\beta = 0$ because the hard sphere signal contributions from D on H_2 and H_2 on D are small compared with the strong angular dependent signals from D on H_2 (the recoiling H_2 from these collisions appears around $\beta = 90^\circ$). At larger angles, say $\beta = +30^\circ$, the signal is the sum of D scattered at $\theta = 60^\circ$ and the H_2 appearing at that angle which

recoiled from the D scattered at $\theta = 240^\circ$ (the latter atom appearing at $\beta = -60^\circ$). In these regions, the H_2 contributes more to the signal than the D atoms appearing at identical angle because the H_2 molecules are more efficiently ionized than the D atoms.

Despite these complications the elastic mass two signals shown in Fig. 1.12 have been normalized to the $H + H_2$ total cross section measurements of Harrison²¹ using a procedure described in Appendix 1D. This normalization has been chosen in lieu of the $D + H_2$ total cross section (should the two differ) which is unmeasured due to the problem imposed by identical mass numbers.

The absolute reactive cross section now can be estimated using the normalized elastic measurements. Since the ratio of reactive to elastic signals is proportional to the ratio of the respective differential cross sections, the measured ratio of the signals leads directly to the reactive total cross section normalized to the measured elastic total cross section. This procedure, which requires that careful attention be paid to beam distribution and angular distribution function normalizations, is discussed further in Appendix 1E. As a result of these considerations, the reactive total cross section for Assumptions (1) and (2) is found to be $3.5 \pm 1.8 \text{ \AA}^2$; the laboratory differential cross section calibration shown in Fig. 1.5 reflects this evaluation. The above quoted error refers purely to the mean deviations found in the experimental signal ratios.

Comparison of the experimental total cross section with those predicted by theory cannot be done without considering the theoretical

cross section energy dependences. Total cross section quantum-mechanical calculations have been performed by Micha on $D + H_2$ ⁴ and $H + H_2$ ⁵ and Karplus and Tang on $H + H_2$ ³. Classical $H + H_2$ determinations have been made from the classical trajectory calculations of Karplus, Porter, and Sharma.² The quantum and classical $H + H_2$ energy dependences differ considerably and the quantum results are very dependent upon the particular approximation employed. It is generally believed that the classical formulation becomes valid at energies not far from threshold, but threshold validity has been seriously questioned.³ At present it is not known whether the quantum and classical disagreements at threshold are real.

Due to the present threshold quantum mechanical differences, the considerations here will be directed toward the classical calculations for $H + H_2$, which used a simple barrier potential of the London-Eyring-Polanyi-Sato type. The cross section energy dependence for $J = 0$ and the ground vibrational state derived from the trajectory studies is shown in Fig. 1.13 with the simple cross section energy dependences that were employed during the experimental analysis. The latter curves have the same asymptotic limits as the Karplus calculation, which is reported to vary less than 20% upward from $J = 0$ up to $J = 3$. It is noted that the theoretical energy dependence lies between the two limiting simple shapes. If this energy dependence had been assumed for the experimental cross section determination, σ_r would be lowered to about $2 \pm 1 \text{ \AA}^2$. This value and the one determined for the energy dependence of Assumption (2) is in approximate agreement

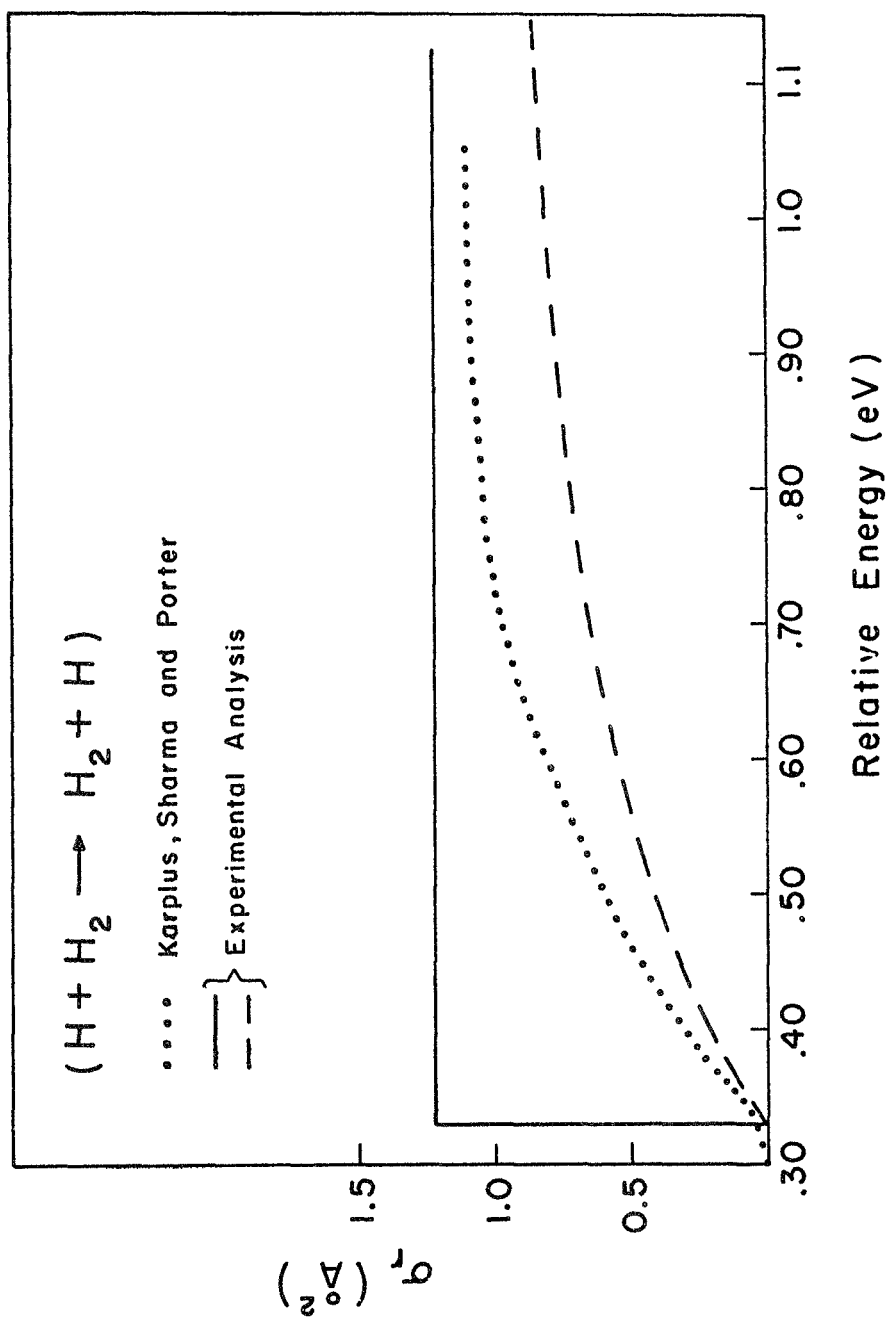


Figure 1.13. Comparison of the two simplified reactive cross section energy dependences employed in experimental analysis with classical theory for $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$.

with classical theory predictions.

VI. CONCLUSIONS.

When deuterium atoms are reactively scattered by hydrogen molecules at thermal energies, the reactively formed HD prefers leaving the D-H-H reacting configuration in times short compared with the rotational period of that configuration. On this account the present experiment appears to agree with the Datz and Taylor experiment. Most certainly it agrees with classical and quantum-mechanical calculations.

Generally speaking, most of the HD molecules recede from the collision in a direction anti-parallel to that of the attacking D atom without appreciable internal energy. The Datz and Taylor experiment is somewhat inconclusive on this point, because their results are not understood. This finding is consistent with theoretical calculations.

The angular distribution for anisotropic scattering is more strongly backward than has been predicted by theory. The absolute reactive cross section is in general agreement with that predicted by Monte Carlo averaged classical trajectory calculations.

The apparent disagreement between the respective experimental laboratory angular distributions strongly suggest that more experimental studies should be performed. Disagreement between experiment and theory concerning the sharpness of the backward scattering distribution indicates, in addition, that further theoretical study may be profitable.

APPENDIX 1A APPARATUS DIMENSIONS.

The essential apparatus dimensions for the deuterium molecular hydrogen reactive and elastic experiments are listed in Table 1A.1. The literal definitions are illustrated in Fig. 1A.1. All dimensions designated by d refer to circular diameter.

TABLE 1A.1. Reactive Geometry

	cm		cm
d_1	.13	l_1	1.5
d_2	.20	l_2	2.5
* d_3	.30	l_3	2.5
d_4	.47	l_4	4.8
d_5	.35	l_5	3.6
d_6	.20	l_6	1.7
d_7	.30	l_7	10.5
* d_8	.90	l_8	2.5

*Elastic Geometry: $d_3 = .10$, $d_8 = .30$

The effective cross beam target region (right angle intersection of two cylinders of approximately the same diameter) is estimated to be spherical to first order with diameter d_8 . The detector views the entire target region.

The apparatus angular resolution which is used when computing the theoretical laboratory (LAB) signals depends on one's criterion. The criterion for the target-detector resolution half angle has been taken to be the target-detector off-axis limiting angle for total

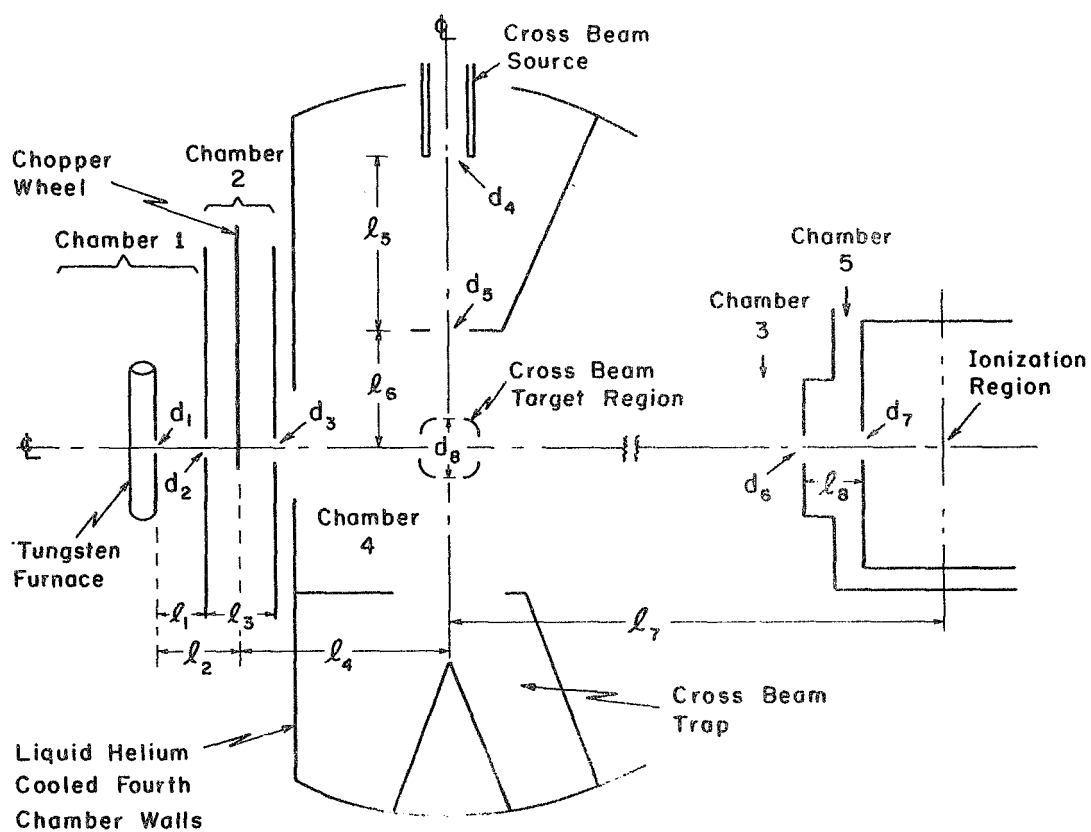


Figure 1A.1. Essential dimensional definitions for the differential scattering apparatus.

particle collection, (1A.1).

$$\Delta \beta = \frac{(d_8 + d_6)/2}{l_7} = .052 \text{ radians} \quad (1A.1)$$

This resolution is estimated to be sufficiently large to insure meaningful differential scattering measurements from the uncertainty principle viewpoint.

APPENDIX 1B ANGULAR DISTRIBUTION ANALYSIS.

The understanding of laboratory differential scattering data obtained in molecular cross beam experiments requires the investigator somehow to transform the data to the center-of-mass (CM) system. In so doing the differential cross sections of the theoretician may be compared with those deduced by the experimentalist. The most ideal situation for completing such a task is the case where the state-selected primary beams are monoenergetic and infinitesimally narrow in angular spread, and the velocity-analyzed scattered particles are detected with small enough angular resolution to make the measurement meaningful. Referring to Fig. 1B.1 which is a velocity diagram that exemplifies the ideality, it is evident that the lack of any of these situations implies that a unique CM differential cross section for specified initial and final internal energy states cannot be deduced from the experimental data. So as one digresses from this perfection on the various accounts, the possibility of transforming LAB signal into CM signal uniquely, must be abandoned.

It is noteworthy that, in practice, such purity can hardly be approached for even elastic scattering processes (large cross section), because the attainment of each perfection further reduces the signal strength with respect to the noise of the experiment. The imperfection of the $D + H_2$ reactive experiment on the various accounts, which is typical of difficult scattering experiments, implies that another approach to the transformation problem is in order.

The appropriate outlook considered exact for understanding the laboratory data is (a) to assume that the CM differential cross

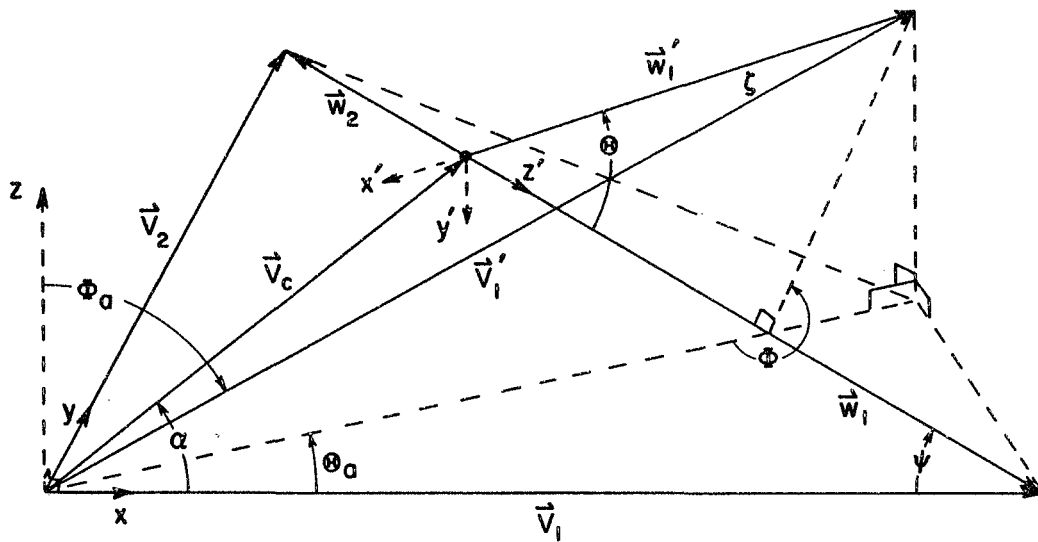


Figure 1B.1. Velocity diagram for the general case. Positive directions for angles are defined by arrows.

section in terms of relative energy, angle and internal states is known (the goal of the experiment), and (b) to transform this cross section into the laboratory (taking the practical experimental conditions into account). Upon comparison of the theoretical signal with the data, other trial cross sections may be introduced until one finds the comparison favorable.

The formalism for carrying out the above approach is well known.^{22,23,24} The actual means employed to carry out the general formulation is necessarily different, because different experimental situations lend themselves to different analytic approximations and justifiable numerical procedures.

The details of the present approach will be carefully discussed after the reader has been introduced to the well known problem.

1. General Formalism

Beginning from first principles, it is well known that the total number of particles of mass m_1 scattered per sec. in any collision experiment is expressed as

$$= n_1 n_2 \Delta v \int \int_{\substack{\text{all } \vec{v}_1 \\ \text{all } v_2}} v_r \sigma(v_r) f(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2 \quad (1B.1)$$

where the n_i , $i = 1, 2$ are the average number densities (particles/cm³) for the respective incident beams in the scattering region having volume Δv (cm³); $\sigma(v_r)$ is the total cross section for the production of particles m'_1 (cm²/particle); $f(\vec{v}_i) d\vec{v}_i$, $i = 1, 2$ are the beam number density velocity distribution functions; $v_r = |\vec{v}_r| = |\vec{v}_2 - \vec{v}_1|$ and

$$\iint f(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2 = 1. \quad (1B.2)$$

This expression is readily converted to a differential scattering form. In order to do so, consider Fig. 1B.1 which illustrates a single monoenergetic scattering event in terms of CM and LAB coordinates; the particle masses m_i $i = 1, 2$ have incident velocities $\vec{v}_i$, $i = 1, 2$ and the CM system is moving with velocity $\vec{v}_c$. LAB velocities are designated by $\vec{v}_i$ or $\vec{v}'_i$ and CM velocities are denoted by $\vec{w}_i$ or $\vec{w}'_i$, primes indicating after the scattering event. Similarly, m'_1 is here considered to be the detected scattered mass. The orientation of the rectangular right handed coordinate systems are also shown.

In the CM system, rectangular and spherical differential elements are related via (1B.4).

$$\begin{aligned} w'_{1x} &= |\vec{w}'_1| \sin \theta \cos \phi \\ w'_{1y} &= |\vec{w}'_1| \sin \theta \sin \phi \\ w'_{1z} &= |\vec{w}'_1| \cos \theta \end{aligned} \quad (1B.3)$$

$$\begin{aligned}
d^3\vec{w}_1' &= \left| \frac{\partial(w_{1x}', w_{1y}', w_{1z}')}{\partial(w_1', \theta, \phi)} \right| dw_1' d\theta d\phi \\
&= w_1'^2 \sin\theta dw_1' d\theta d\phi = w_1'^2 dw_1' d\Omega
\end{aligned} \tag{1B.4}$$

For a CM differential cross section defined as

$$\frac{d\sigma}{d\Omega dw_1'} (\vec{w}_1', \vec{w}_1') = \sigma(v_r) w_1'^2 P_c(\vec{w}_1', \vec{w}_1') \tag{1B.5}$$

evidently

$$\sigma(v_r) = \int_0^\infty \int_0^{2\pi} \int_0^\pi \frac{d\sigma}{d\Omega dw_1'} (\vec{w}_1', \vec{w}_1') \sin\theta d\theta d\phi dw_1' \tag{1B.6}$$

where $P_c(\vec{w}_1', \vec{w}_1')$ is the CM scattering probability function. The properly normalized scattering rate in terms of CM coordinates, (θ, ϕ, w_1') (1B.1, 1B.5 and 1B.6 combined) can be converted into LAB coordinates, (θ_a, ϕ_a, v_1') handily after examining the latter coordinate system.

Examining Fig. 1B.1, the system is conventional except that $\theta \rightarrow \phi_a$ and $\phi \rightarrow \theta_a$ in equations (1B.3). Therefore

$$\begin{aligned}
d^3\vec{v}_1' &= \left| \frac{\partial(v_{1x}', v_{1y}', v_{1z}')}{\partial(v_1', \theta_a, \phi_a)} \right| dv_1' d\theta_a d\phi_a \\
&= v_1'^2 \sin\phi_a dv_1' d\theta_a d\phi_a.
\end{aligned} \tag{1B.7}$$

The CM differential elements are readily transformed to the LAB variable via

$$dw'_1 d\theta d\phi = \left| \frac{\partial (w'_1, \theta, \phi)}{\partial (v'_1, \theta_a, \phi_a)} \right| dv'_1 d\theta_a d\phi_a \quad (1B.8)$$

The Jacobian in (1B.8) is readily found by noting

$$\left| \frac{\partial (w'_1, \theta, \phi)}{\partial (v'_1, \theta_a, \phi_a)} \right| = \left| \frac{\partial (w'_1, \theta, \phi)}{\partial (w'_{1x}, w'_{1y}, w'_{1z})} \right| \cdot \left| \frac{\partial (w'_{1x}, w'_{1y}, w'_{1z})}{\partial (v'_{1x}, v'_{1y}, v'_{1z})} \right| \cdot \left| \frac{\partial (v'_{1x}, v'_{1y}, v'_{1z})}{\partial (v'_1, \theta_a, \phi_a)} \right| \quad (1B.9)$$

The intermediate transformation is unitary because the rotation and translation operations necessary to make the rectangular differential elements $d^3\vec{w}'_1$ and $d^3\vec{v}'_1$ occupy the same volume are unitary.

$$\left| \frac{\partial (w'_1, \theta, \phi)}{\partial (v'_1, \theta_a, \phi_a)} \right| = \frac{v'^2_1 \sin \phi_a}{w'^2_1 \sin \theta} \quad (1B.10)$$

Combining (1B.1), (1B.5), (1B.6), (1B.8), and (1B.10), the total scattered flux in terms of $\frac{d\sigma}{d\Omega dw'_1}(\vec{w}'_1, \vec{w}'_1)$ and LAB variables is found

to be expression (1B.11).

$$n_1 n_2 \Delta v \int_{\vec{v}_2} \int_{\vec{v}_1} v_r \int_0^\infty \int_0^{2\pi} \int_0^\pi \frac{d\sigma}{d\Omega d\vec{w}_1'} (\vec{w}_1, \vec{w}_1') \frac{v_1'^2}{w_1'^2} \sin\phi_a d\phi_a d\theta_a dv_1' f(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2 \quad (1B.11)$$

The expression for the LAB signal $S(\theta_a, \phi_a)$, measured by a detector viewing a non-infinitesimal solid angle, is readily determined from (1B.11). In the case of a number density detector (ionization by electron impact) and any other arbitrary velocity dependent efficiency factor $e(v_1')$ at present unspecified, the signal is determined by (1B.12).

$$S(\theta_a, \phi_a) = n_1 n_2 \Delta v \int_{\vec{v}_2} \int_{\vec{v}_1} v_r \int_{d\Omega_a} \int_0^\infty \frac{d\sigma(\vec{w}_1, \vec{w}_1')}{d\Omega d\vec{w}_1'} e(v_1') \frac{v_1'^2}{w_1'^2} d\Omega_a dv_1' f(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2 \quad (1B.12)$$

The factor $1/v_1'$ has been explicitly inserted in order to convert flux to number density. For situations where other velocity biases of the detected signal exist, they may be included at a later point.

It is noteworthy that (1B.12) implies that (a) the beam number densities are assumed to be only slowly varying spacial functions; (b) the detected particle was not scattered after formation, and (c) multiple scattering of the incident beams is negligible.

The formulation yields to mathematical approximation with a variety of additional standard simplifications arising from lack of detailed theoretical information concerning the angular-and-recoil-velocity density function, $P_c(\vec{w}_1, \vec{w}'_1)$.²⁴ These include the following: (a) P_c can be written as the product of the angular-and-recoil velocity information that it contains. (b) The angular density can be separated into the product of a θ dependence, $f(\theta)$ and the ϕ dependence; the latter is taken to be a constant. Under these assumptions, the surface probability density of a given monoenergetic scattering event for single initial and final internal energy states may be written as (1B.13).

$$P_c(\vec{w}_1, \vec{w}'_1) = \frac{f(\theta)}{2\pi} \frac{\delta(w'_1 - w'_{10})}{w'^2_{10}} \quad (1B.13)$$

where the normalization of $f(\theta)$ is found from the requirement

$$\int w'^2_1 P_c(w_1, w'_1) dw'_1 = \sin \theta d\theta d\phi = 1. \quad (.B.14)$$

The P_c defined in (1B.13) is a gross simplification of a real atom-molecule scattering event, because it implies that only one reaction exit channel exists for each single entrance channel. One might define a new P_c to be the sum of a number of functions like (1B.13) for each single entrance and exit channel. However sophistication of this sort appears unjustified in the following cases:

(A) The velocity diagrams for the various exit channels do not differ catastrophically.

(B) The reaction products have not been velocity analyzed so that $\frac{d^3\sigma}{d^2\Omega_a dv'_1}$ is not known.

(C) P_c is taken to be separable.

These considerations are often the case for reactions other than $D + H_2 \rightarrow DH + H$ particularly for preliminary investigations. Consequently, what follows is appropriate for a P_c as previously displayed.

By inserting (1B.13) into (1B.5) and integrating (1B.12) over v'_1 after transforming $\delta(w'_1 - w'_{10})$ to $\delta(v'_1 - v'_{10}(w'_{10}))$ via relation (1B.15),

$$\delta(w'_1 - w'_{10}) = \sum_n \left| \frac{\partial w'_1}{\partial v'_1} \right|_n \delta(v'_1 - v'_{10}) \text{ wherever} \quad (1B.15)$$

$$w'_1 - w'_{10}(v'_{10}) = 0$$

and utilizing the result that $\left| \frac{\partial w'_1}{\partial v'_1} \right|_n = |\cos \zeta_n|^{24}$, the signal expression

becomes (1B.16).

$$S(\theta_a, \phi_a) = n_1 n_2 \Delta v \int_{v_2} \int_{v_1} \sigma(v_r) f(v_1) f(v_2) dv_1 dv_2$$

$$x \left\{ \sum_{n=0}^2 \int_{\Omega_a} e(v_1') \frac{f(\theta)}{2\pi} \cdot \frac{v_1' v_r d\Omega_a}{w_1'^2 |\cos \zeta_n|} \right\} \quad (1B.16)$$

The index n denotes the number of CM regions that can contribute signal to $d\Omega_a$. The bracketed portion of $S(\theta_a, \phi_a)$, (1B.16), the contribution to S from a monoenergetic pair of reacting particles v_1, v_2 (i.e. $f(v_i) = \delta(v_i - v_i')$ $i = 1, 2$) to a non-infinitesimal target-detector solid angle is seldom evaluated analytically despite the simplistic separable CM differential cross section already introduced, even in the case of elastic scattering. The intricate implicit interrelationships of the displayed quantities constitutes the difficulty. This will become apparent when the numerical solution of monoenergetic $S(\theta_a, \pi/2)$, or detection in the incident beam plane, is discussed.

Further difficulty arises when considering more indiscrete beam velocity distributions. Except for very few special kinematic situations, the bracketed quantity is dependent upon v_1 and v_2 , which is independently equivalent to saying that $v_r (= v_1 - v_2)$ and ψ (see Fig. 1B.1) variables can be used to describe $f(v_1) f(v_2) dv_1 dv_2$. In the most general case, both v_r and ψ dependences are found so that, practically speaking, one must construct a v_1, v_2 grid or its equiva-

lent in v_r , Ψ space, evaluate the bracket at the grid center, and weight these results with factor (1B.17),

$$\int_{v_1 = \bar{v}_1 - \frac{\Delta v_1}{2}}^{\bar{v}_1 + \frac{\Delta v_1}{2}} \int_{v_2 = \bar{v}_2 - \frac{\Delta v_2}{2}}^{\bar{v}_2 + \frac{\Delta v_2}{2}} \sigma(v_r) f(v_1) f(v_2) dv_1 dv_2 \quad (1B.17)$$

where $\bar{v}_1$ and $\bar{v}_2$ are the grid center velocity coordinates at which the bracket is evaluated and Δv_1 , Δv_2 are the respective grid spacings. Many of these individual results summed provide an estimation of (1B.16).

2. Formulae

The practical execution of the general formalism requires specific mathematical expressions that are convenient for later numerical solution. The presentation of formulae falls into two categories: (a) formulae required for numerically solving (1B.16) for delta function distribution functions, and (b) formulae required for estimating the effects on S caused by crossed Maxwellian beam distribution functions (i.e. a combined distribution function).

(A) Kinematic Formulae and Conventions.

Formulae for the transformation of CM and LAB angles and infinitesimal solid angles are well known.^{22,23} Unfortunately, each investigator usually derives the relationships that suit his needs and notation. To understand the generalized computer procedures developed in this study, it is appropriate to define the author's conventions and formulae which have been used in the programs.

The formulae presented (and not derived) pertain to scattering in the plane defined by the incident beams and are applicable to input and output two body elastic, inelastic, or chemical reactive scattering of perpendicular crossed beams. Perpendicularity is no severe limitation because the formulae are readily adaptable for oblique intersection should the need arise. (This would be desirable in estimating the effects of non-unidirectional beams). For reasons of uniformity, some conventions are similar to Morse and Bernstein.²² Standard definitions are listed between (1B.18) and (1B.20).

$$v_r = |\vec{v}_r| \equiv |\vec{v}_1 - \vec{v}_2| \quad (1B.18)$$

$$w_1 = v_r \frac{m_2}{(m_1 + m_2)} \quad \begin{array}{l} \text{(with an analogous formula} \\ \text{for } w_2) \end{array} \quad (1B.19)$$

$$w_1' \equiv f w_1 \quad \text{where} \quad f = \left\{ \frac{m_1 m_2'}{m_1' m_2} \left[1 - \frac{\Delta E}{E} \right] \right\}^{1/2} \quad (1B.20)$$

$E = 1/2 \mu v_r^2$ is the initial relative kinetic energy and

$$\Delta E = 1/2 \left[m_1 v_1^2 + m_2 v_2^2 - m_1' v_1'^2 - m_2' v_2'^2 \right] \text{ is the endothermicity.}$$

$$v_c = |\vec{v}_c| \equiv r w_1 \quad (1B.21)$$

where

$$r = \frac{1}{m_2 \sqrt{\left(\frac{\cos \alpha}{m_1} \right)^2 + \left(\frac{\sin \alpha}{m_2} \right)^2}}$$

holds only for $\vec{v}_1 \perp \vec{v}_2$

$$\alpha = \tan^{-1} \left[\frac{m_2}{m_1} \tan \psi \right] \quad 0 \leq \psi \leq \frac{\pi}{2} \quad 0 \leq \alpha \leq \frac{\pi}{2}$$

with positive directions defined in Fig. 1B.1. For the case, $v_1 \perp v_2$,

$\phi = 0$ and $\phi_a = \frac{\pi}{2}$ (in-plane) the LAB angle θ_a corresponding to any

CM angle θ for any relative velocity vector angle ψ , can be found

for all physically possible values of r and f by the following relations:

$$(a) \quad \theta_a = \theta_a'$$

$$\text{when } x' \geq 0$$

$$\text{where } \theta_a' = \tan^{-1} \left[\frac{y'}{x'} \right]$$

$$y' = r/f \sin \alpha + \sin (\theta - \psi)$$

$$x' = r/f \cos \alpha + \cos (\theta - \psi)$$

$$\begin{aligned}
 (b) \quad \theta_a &= 180^\circ + \theta'_a && \text{when } x' < 0 \text{ and } y' \geq 0 \\
 (c) \quad \theta_a &= -180^\circ + \theta'_a && \text{when } x' < 0 \text{ and } y' < 0
 \end{aligned} \tag{1B.22}$$

The positive sense of θ_a and θ is defined in Fig. 1B.1. The respective domains are

$$-180^\circ \leq \theta_a \leq 180^\circ \text{ and } 0 \leq \theta \leq 360^\circ.$$

For the perpendicular in-plane case, only when $f/r \leq 1$ do there exist maximum and minimum LAB angles (tangents to the recoil circle). These will be denoted β_0^+ and β_0^- respectively and are defined according to the previous conventions in (1B.23).

$$\beta_0^{(\pm)} = \arctan \left(\frac{(\pm) f/r}{\sqrt{1 - (f/r)^2}} \right) + \psi \tag{1B.23}$$

The modified CM to LAB solid angle Jacobian expression,

$$\frac{v_1'}{w_1'^2 |\cos \zeta|}, \text{ must be expressed explicitly in terms of } \theta_a \text{ and the}$$

parameters corresponding to a general reaction in order that it can be analytically integrated over a finite detector solid angle. For velocity diagrams of all possible ratios r/f , careful inspection of Fig. 1B.1 leads to the conclusion that ζ is always expressed as

$$\zeta = \theta - \psi - \theta_a . \quad (1B.24)$$

It is also apparent by the Law of Sines that

$$\frac{f}{\sin(\theta_a - \alpha)} = \frac{r}{\sin(\zeta)} \quad (1B.25)$$

From in-plane application of the Law of Cosines in the form (1B.26),

$$v_c^2 = w_1'^2 + v_1'^2 - 2v_1' w_1' \cos \zeta \quad (1B.26)$$

(1B.27) is readily shown.

$$v_1' = fw_1 \cos \zeta \pm fw_1 \left[\left(\frac{r}{f} \right)^2 - \sin^2 \zeta \right]^{1/2} \quad (1B.27)$$

By substitution of (1B.25) into (1B.27) and careful inspection of the result (considering all possible reaction geometries), one is led to the conclusion that all cases in this sign convention may be summarized as (1B.28).

$$v_1' = fw_1 \left[\cos + r/f \cos \delta (\theta_a - \alpha) \right] \quad (1B.28)$$

With (1B.28) in hand, consideration of the modified Jacobian expression leads to the results, (1B.29).

$$(a) \frac{v_1'}{w_1'^2 |\cos \zeta|} = \frac{(m_1 + m_2)}{m_2 f v_r} \left\{ 1 + \frac{r/f \cos (\theta_a - \alpha)}{\cos \zeta} \right\} \quad (1B.29)$$

everywhere for $r/f \leq 1$ and in the forward scattering quadrant when $r/f > 1$

$$(b) \frac{v_1'}{w_1'^2 |\cos \zeta|} = -1 \quad \left\{ \text{expression (a)} \right\}$$

everywhere in the reverse quadrant when $r/f > 1$

Application of (1B.24) yields an expression of $\cos \zeta$ for all cases and is defined by (1B.30).

$$\cos \zeta = \sqrt{1 - (r/f)^2 \sin^2 (\theta_a - \alpha)} \quad (1B.30)$$

Evidently, (1B.29) and (1B.30) constitute the desired in-plane expressions which are well used in Appendix 1B3.

It can be noted also that, should one wish an expression for v_1' , it is readily determined in-plane to be (1B.31).

$$\frac{v_1'}{v_r} = \frac{f m_2}{(m_1 + m_2)} \sqrt{x'^2 + y'^2} \quad (1B.31)$$

Such an expression is convenient when considering additional velocity dependent efficiency factors $e(v_1')$.

(B) Distribution Function Relations.

For (1B.17) the concept of dividing the combined distribution function into a velocity grid was discussed in the general case. In certain experimental situations such as $D + H_2 \rightarrow HD + H$ where angular and velocity recoil information suggests that $\Delta E/E \ll 0$, it is unnecessary and wasteful to go on with the most general procedure.

For the case $\Delta E/E = 0$ and $e(v_1')$ still arbitrary, invoking separability of angular and recoil velocity densities, it can be demonstrated that the delta function velocity distribution LAB signals at all angles are independent of E but still Ψ dependent. (This phenomenon appears in-plane whenever r/f is constant for all energies; since r is not energy dependent, the energy dependence of f controls this behavior). It is noteworthy that the phenomenon in this approximation is always precisely the case for elastic scattering; it usually can be approximately correct only for inelastic and reactive scattering at thermal energies.

As a result of this observation, only the averaging effects due to the variation of Ψ need be considered. The weight function for the i^{th} diagram (1B.17) expressed in v_r, Ψ coordinates appears in (1B.32),

$$\int_{\Psi_a = \Psi_i - \frac{\Delta\Psi}{2}}^{\Psi_b = \Psi_i + \frac{\Delta\Psi}{2}} \left\{ \int_{v_r = 0}^{\infty} \sigma(v_r) I(v_r, \Psi) dv_r \right\} d\Psi \quad (1B.32)$$

where the bracketed quantity can be integrated analytically even for a well behaved but pathological $\sigma(v_r)$; and the second integration (usually not analytically feasible) extends one half a Ψ grid width each side of Ψ_i where the single diagram signal of this weight is evaluated (at an arbitrary energy when $\Delta E/E$ is precisely zero). Evidently, all diagrams between $\Psi_a = 0$ and $\Psi_b = \pi/2$ must be considered, particularly if one desires to use the calculated results for the purpose of placing an absolute value on the differential cross sections.

The two specific simple total cross section energy dependences that have been considered for $D + H_2$ reactive scattering follow.

For the cross section

$$\begin{aligned} \sigma(v_r) &= \sigma & v_r &\geq v_{r_0} \\ &= 0 & 0 \leq v_r < v_{r_0} \end{aligned} \quad (1B.33)$$

where v_{r_0} is the relative velocity corresponding to activation energy, (1B.32) can be written as (1B.34),

$$4C_1 \int_{\Psi_i - \frac{\Delta\Psi}{2}}^{\Psi_i + \frac{\Delta\Psi}{2}} \sin^2(2\Psi) \left\{ x^2 - 2x + 2 \right\} \frac{e^x}{(2\Psi)^3} d\Psi \quad (1B.34)$$

where $x \equiv -\frac{2}{v_{r_0}^2}$ and $\cdot = \delta_s + \delta_d \cos(2\Psi)$ with the other definitions identical to those found in Part Two, Appendix 2D.1.

For the cross section

$$\begin{aligned} \sigma(v_r) &= \sigma \left(1 - \frac{v_{r0}^2}{v_r^2}\right) & v_r &\geq v_{r0} \\ &= 0 & 0 \leq v_r < v_{r0} \end{aligned} \quad (1B.35)$$

the i^{th} weight function becomes (1B.36)

$$4C_1 \int_{\psi_i - \frac{\Delta\psi}{2}}^{\psi_i + \frac{\Delta\psi}{2}} \sin^2(2\psi) \left\{ -x + 2 \frac{e^x}{(2)^3} \right\} d\psi \quad (1B.36)$$

3. Numerical Solution of $S(\theta_a, \phi_a = \pi/2)$ for Delta Function

Distribution Functions.

Consider

$$\sum_{n=0}^2 \int_{\Omega_{\text{det}}} e(v'_1) \frac{f(\theta)}{2\pi} \frac{v'_1 v_r}{w_1'^2 |\cos \zeta_n|} \sin \theta_a d\phi_a d\phi_a \quad (1B.37)$$

It is possible to integrate analytically (1B.37) over a small LAB detector angle. One way of accomplishing this is to choose an integration interval smaller than the angle which the detector subtends in the θ_a direction ($2\Delta\theta$) but equal to the full detector subtended angle in the ϕ_a direction ($2\Delta\phi$). (See Fig. 1B.2). With this choice we require that

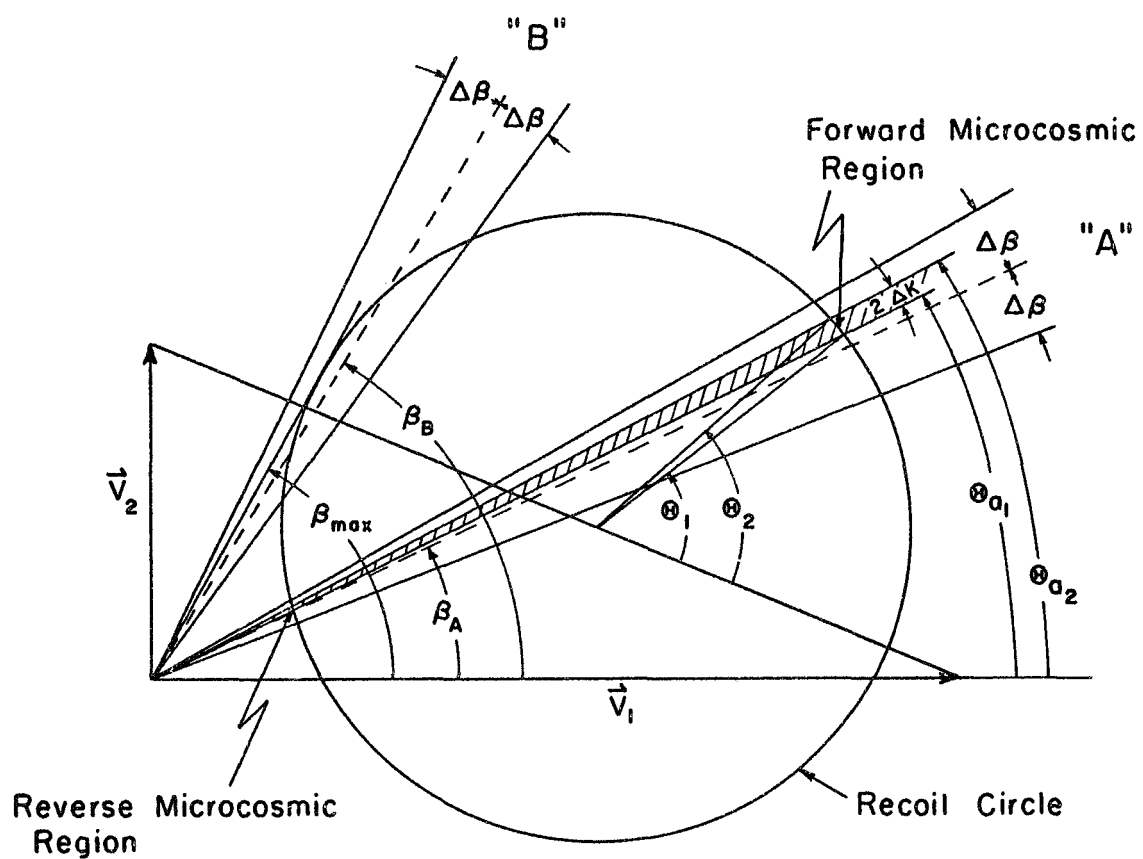


Figure 1B.2. General in-plane velocity diagram illustrating subdivision of the target-detector solid angle into microcosmic solid angles.

- (1) $f(\theta)$ be varying slowly over the integrated solid angle $4(\Delta\beta)(\Delta\beta)$;
 (2) the deviation of $\frac{v_1'}{w_1'^2 |\cos \zeta|}$ in the out-of-plane regions from the

in-plane expression be negligible so that ϕ_a does not appear in the expression, and

- (3) v_1' barely deviates from its average in-plane value over the interval (in accord with the v_1' delta function integration previously carried out).

By integrating (1B.37) first in the ϕ_a direction from $\phi_{a1} = \pi/2 - \Delta\beta$ to $\phi_{a2} = \pi/2 + \Delta\beta$ where $\Delta\beta$ is the target-detector half width, one obtains $2\Delta\beta$ assuming $\sin \phi_a = 1$ over this region. After inserting the general in-plane expression for $\frac{v_1'}{w_1'^2 |\cos \zeta|}$, (1B.29) and integrating

θ_a from $\theta_{a1} = \beta - \Delta K$ to $\theta_{a2} = \beta + \Delta K$ where β is the mean in-plane LAB angle (see Fig. 1B.2) the microcosmic signal (1B.37) becomes (1B.38) for a contribution either from the "forward" or from the "reverse" CM regions.

$$e(v_1'(\frac{\theta_1 + \theta_2}{2})) \frac{f(\frac{\theta_1 + \theta_2}{2})}{2\pi} \frac{(m_1 + m_2)}{m_2 f} (2\Delta\beta)(\theta_2 - \theta_1) \quad (1B.38)$$

where the θ_i , $i = 1, 2$ are the respective CM angles corresponding to θ_{a_i} , $i = 1, 2$ and $f(\theta)$ is evaluated at the mean CM angle. It is emphasized that in the hypothetical case shown in Fig. 1B.2 ($f/r < 1$),

the detector solid angle, $4(\Delta\beta)(\Delta\beta)$, always receives two CM contributions when the detector is at "A". When it is located at "B" there are two contributions for θ_a 's that intersect the recoil circle and zero contributions for no intersection. For the simpler case, $f/r > 1$, where the recoil circle radius is greater than the magnitude of v_c , the unique one-to-one correspondence between CM and LAB angles implies only one contribution. Examination of (1B.38) reveals that the full contribution to the detector (solid angle, $4(\Delta\beta)^2$) from any given CM region will be

$$\frac{m_1 + m_2}{m_2 f} (2 \Delta\beta) \sum_{\text{all } i} e(v'_1 \left(\frac{\theta_{i+1} + \theta_i}{2} \right)) f\left(\frac{\theta_{i+1} + \theta_i}{2}\right) / 2 \pi \cdot (\theta_{i+1} - \theta_i) \quad (1B.39)$$

where i is the number of microcosmic solid angles lying within $4(\Delta\beta)^2$ and

$$\theta(\beta + \Delta\beta) - \theta(\beta - \Delta\beta) = \sum_{\text{all } i} (\theta_{i+1} - \theta_i) \quad (1B.40)$$

These observations suggest a simple procedure for practically calculating the theoretical signal averaged over detector angle for an arbitrary $f(\theta)$ and $e(v')$.

(A). Divide the CM recoil circle into small equal increments,

$$(\theta_{i+1} - \theta_i), \text{ remembering the latter. Also compute } e(v'_1 \left(\frac{\theta_{i+1} + \theta_i}{2} \right)) f \left(\frac{\theta_{i+1} + \theta_i}{2} \right) \text{ which is the cross}$$

section properly weighted with the detection system rela-

tive weighting factor corresponding to the computed

increment. Do this operation for every θ ($0 < \theta < 360^\circ$).

(B). Consider the actual detector conic solid angle (Fig. 1B.2,

"A") and sum up all microcosmic contributions which fall

within this solid angle of $4(\Delta\beta)^2$ located at β . The sum

constitutes the signal for that β .

(C). When considering detector positions such as Fig. 1B.2,

"B", where the actual detector solid angle consistent with

the CM and LAB Jacobian transformation is $2(\Delta\beta)(\beta_{\max} -$

$(\beta_B - \Delta\beta))$, weight these sums less than in the "A" position

according to the ratio $\frac{\beta_{\max} - (\beta_B - \Delta\beta)}{2\Delta\beta_B}$

This single velocity diagram sorting operation has been computerized

for an arbitrary reaction. This procedure, Subroutine SIGNAL, is

utilized with Subroutine DIFFQ, which contains the elements $f \left(\frac{\theta_{i+1} + \theta_i}{2} \right)$

For present needs e is taken to be constant. These programs will be described subsequently.

For the case of $e(v'_1)$ different from a constant, this velocity dependence can be introduced readily when the CM to LAB angular correspondences are calculated. The modified microcosmic elements to be sorted

would then become $e^{\left(v_1' \left(\frac{\theta_{i+1} + \theta_i}{2} \right)\right)} f \left(\frac{\theta_{i+1} + \theta_i}{2} \right)$

4. Numerical Solution of the Multi-Diagram Weight Factors.

The distribution function weight factors, which appear in (1B.34) and (1B.36), have been evaluated numerically by the Gaussian Quadrature ($n = 16$) formula:²⁵

$$\int_a^b y(x) dx = 1/2(b - a) \sum_{k=1}^{16} A_k y(u_k) \quad (1B.41)$$

$$\text{where } y(u_k) = y \left\{ 1/2(b - a) u_k + 1/2(a + b) \right\}$$

U_k and A_k are the GQ tabulated constants.²⁵

The computer program for evaluating the equations of interest appears in the program listing. The normalization of (1B.34) and (1B.36) has been checked numerically for a direct error estimate. It can be concluded that the weights calculated for multi-diagram averaging have better than 5 significant figure accuracy.

5. Computer Program.

The automated procedures for carrying out the evaluation of $S(\beta, \pi/2)$ for delta function cross beam velocity distributions and for the previously discussed approximation using cross beam Maxwellian

velocity distributions have been constructed. As evidenced by the FORTRAN II listing presented in this section, the program is composed of four units: MAIN program, SUBROUTINE DIFFQ, SUBROUTINE SIGNAL and Subroutine WEIGHT.

The first three units are required for the delta function average signal. In this mode one usually selects the most probable velocity diagram and kinematics for the experiment and varies the CM differential cross section contained in a DIFFQ until the calculated LAB signal agrees in approximate shape with the experimental results. Knowing this CM function, one can use all units together for the purpose of taking the realistic beam distributions into account. It is appropriate to describe each unit and to list the definitions of FORTRAN variables in terms of those appearing in Section 1B2, following the conventions specified there.

(A) MAIN Program.

To perform any computation requires first specifying the reaction kinetics. This is accomplished by indicating the particle masses (a.m.u.) before and after reaction, the relative energy and endothermicity (e.v.) and the relative velocity angle (degrees, $\cos^{-1}(\mathbf{v}_r \cdot \mathbf{v}_l)$). The CM differential cross section function is then specified (see (B) DIFFQ).

The FORTRAN variables which specify the experimental situation are DDET and DFRAC. The former represents the target-detector conic half angle (degrees); the latter is the laboratory angle increment (degrees) at which the signals will be computed. The computation

begins at $\beta = -180 + \text{DDET}$ and automatically proceeds to $\beta = 180 - \text{DDET}$ in angular steps of DFRAC (see listing for SIGNAL).

The remaining variables for a single diagram calculation are FRACT and IMAX . The first variable specifies the CM microcosmic angular width (degrees). It must be selected small enough such that (1) the CM function is relatively constant over this interval throughout the entire domain of definition, and (2) the laboratory increment corresponding to this CM increment is small ($\sim 1/10$) compared with the full in-plane detector width ($2 \Delta\beta$) for all CM regions that make a contribution to the LAB signal. As FRACT is experimentally made smaller, the signals calculated converge closer to the actual value. In the $\text{D} + \text{H}_2$ case, FRACT was never reduced below .125 degrees, because the difference in calculated signal in the worst region ($\beta = 0$) for this value and double that value was in the third significant figure. Should this variable be reduced below .125, the array dimensions of CD , DT and TA must be expanded to accommodate the internal variable, MONEY .

IMAX is the number of diagrams to be computed for any calculation specified by the previous variables. ($\text{IMAX} = 1$ corresponds to a single diagram calculation). Since this variable is very powerful in terms of computer time, safeguards have been provided in MAIN in the event that an atrocious error arises in its singular specification.

For multi-diagram averaging to be accomplished, three additional non-zero variables must be specified: T1 , T2 , and FRAC2 . The first two are the respective beam temperatures. The last is the rela-

tive velocity angle full grid width. IMAX and FRAC2 must be selected together after studying the results of weight for the particular experimental situation. Evidently, the procedure in MAIN cannot be used in general unless the results of SIGNAL for the single diagram mode are found to be independent of energy to good approximation for fixed relative velocity angle. Also, intelligent specification of PSI in this mode requires prior knowledge of the specific weight function as a function of PSI.

When this MAIN is used with the appended subroutines, it produces absolute theoretical signal results when multiplied by the factor

$$e n_1 n_2 \Delta v \sigma N \quad (1B.42)$$

where e is the detector efficiency factor, n_i , $i = 1, 2$ are the average reaction region number densities, Δv is the reaction region volume, σ is the total cross section and N is the normalization constant for the CM differential function. N is determined from

$$N \int_0^{2\pi} \int_0^{\pi} \frac{f(\theta)}{2\pi} \sin \theta \, d\theta \, d\phi = 1. \quad (1B.43)$$

It is noteworthy that, for some types of multi-diagram averaging, N is not identical for each diagram, so in the general situation N must be included directly in DIFFQ (e.g. different separable cross sections in

multi-state summing).

(B) SUBROUTINE DIFFQ.

This program is called by MAIN to calculate , print (non-zero elements), and store the average differential cross section for each microcosmic CM interval, FRACT. In order that these results can be correctly used by SIGNAL in the sorting operation, they must be stored in the array CD(M) such that the $M = 1$ element is the first and closest evaluation near $\theta = 0^\circ$ and $M = \text{MONEY}$ is the last and closest evaluation near $\theta = 360^\circ$. These calculations are contained in a separate program so that DIFFQ can be readily changed for other circumstances.

The particular DIFFQ appearing in the listing is evidently useful for a variety of different shaped cross sections for predominantly backward scattering. The variables AM and AN, which control the angular width and the power for the cosine function centered about $\theta = 180^\circ$, are read into the program through the MAIN. FORTRAN variables not internally defined can be found in Table 1B.1.

(C) SUBROUTINE SIGNAL

This program is called by the MAIN to sort out and sum all the microcosmic signals which fall within the total effective target-detector solid angle. It is set up to perform this operation according to the concepts discussed in Section 1B3 for any single in-plane velocity dia-

gram (using the calculated differential cross section results that are calculated in DIFFQ) and to multiply these results by PR, which is the desired diagram weight factor available in the MAIN. As these operations are performed, it prints all the weighted results (kinetically possible even when they are zero) that are calculated and stores them in the two-dimensional array, GA, for possible later use by the MAIN in multi-diagram summing. This unit need not be modified unless the detection efficiency factor, $e(v'_1)$, deviates from the standard neutral density detector efficiency (i.e. $e(v'_1) = \text{constant}$ in those conventions).

In the event that $e(v'_1)$ is not a constant, SIGNAL is readily modified for any circumstances. Since the analytic expression for v'_1 (1B.31) appears in terms of variables that have direct FORTRAN variable equivalence (see Table 1B.1), evidently a velocity array, $V(M)$ can be computed and stored immediately after Statement 20. All statements between 101 and 134 in which $DT(M) = CD(M)$ would become $DT(M) = CD(M) * V(M)$. This is the extent of the modification.

(D) SUBROUTINE WEIGHT

When the MAIN is operating in the multi-diagram summing mode, it calls WEIGHT prior to calling SIGNAL since PR is utilized by the latter. WEIGHT is separated to facilitate its modification for arbitrary situations.

The particular WEIGHT shown in the listing is self-explanatory. Each step is readily understood with the use of Table 1B.1 and Section

1B4.

TABLE 1B.1

(A) Definitions of COMMON Variables

FORTRAN Variable		Mathematical Variable
PSI	(degrees)	ψ
EO	(e.v.)	E_0
P1	(a.m.u.)	m_1
P2	(a.m.u.)	m_2
PP1	(a.m.u.)(detected mass)	m'_1
PP2	(a.m.u.)	m'_2
DE	(e.v.)	ΔE
DDET	(degrees)	$\Delta \beta$
DFRAC	(degrees, see text)	
FRACT	(degrees)	$(\theta_{m+1} - \theta_m)$
T1	(degrees Kelvin)	T_1
T2	(degrees Kelvin)	T_2
PR		(1B.17)(1B.34)(1B.36)
I	(diagram number index)	
FRAC2		$\Delta \Psi$, (1B.32)
AM	(see text and listing)	
AN	(see text and listing)	

(B) SUBROUTINE SIGNAL (See Section C).

FORTRAN Variable	Mathematical Variable
ALPHA	α (1B.21)
BETA	β
BZM	β_o^-
BZP	β_o^+
F	f
R	r
THA	θ_a
TH	θ
XP	x'
YP	y'

Other variables are internally defined.

(C) SUBROUTINE WEIGHT (See Section 1B4).

ALPH1	α_1
ALPH2	α_2
ALPHA	α
BOLTZ	k
C1	c_1
DELTD	δ_d
DELTS	δ_s
VRSQ1	v_{ro}^2
X	x

(D) Program Listing

PAGE 1 DUAL PURPOSE MAIN FOR CM TO LAB ANGULAR DISTRIBUTION CONVERSION

```

C    SINGLE AND MULTI-DIAGRAM AVERAGING WITH SIGNAL,DIFFQ,AND WEIGHT
C    OBSERVE CROSS SECTION NORMALIZATION RESTRICTIONS OF DIFFQ
C    OBSERVE THE NCRMALIZATION OF WEIGHT
COMMON PSI,EO,P1,P2,PP1,PP2,DE,DDET,DFRAC,FRACT,T1,T2,PR,I,FRAC2
DIMENSION CD(2880),DT(2880),TA(2880),GA(360,20),GD(360)
COMMON CD,DT,TA,GA,GD
COMMON AM,AN
100 READ 1,P1,P2,PP1,PP2,DDET,DFRAC,DE,FRACT,IMAX
    1 FORMAT (6F5.0,2F10.0,15)
    T1=0.
    T2=0.
    FRAC2=0.
    MONEY=360./FRACT
    MDET=360./DFRAC
    IF(2880-MONEY) 100,2,2
    2 IF(20-IMAX) 100,3,3
    3 IF(360-MDET) 100,4,4
    4 I=0
    IF(IMAX-1) 5,5,110
    5 READ 6,PSI,EO,AM,AN
    6 FORMAT (4F10.0)
C    LAB SIGNAL FOR ONE VELOCITY DIAGRAM
    I=I+1
    CALL DIFFQ
    PR=1.
    CALL SIGNAL
    GO TO 100
110 READ 10,PSI,EC,AM,AN,T1,T2,FRAC2
    10 FORMAT (7F10.0)
    IF(FRAC2) 100,100,116
116 IF(T1) 100,100,117
117 IF(T2) 100,100,118
118 CONTINUE
C    LAB SIGNAL FOR IMAX VELOCITY DIAGRAMS WEIGHTED AND SUMMED
C    APPROACH VALID WHEN DE/EO=0.
    CALL DIFFQ
    PSI=PSI-FRAC2/2.
120 I=I+1
    PSI=PSI+FRAC2
    CALL WEIGHT
    CALL SIGNAL
    IF(IMAX-I) 200,200,120
200 L=0
    BETA=-DFRAC-180.+DDET
205 N=0
    PRINT 301
301 FORMAT (1H122F TOTAL AVERAGED SIGNAL,
    131H (THE PRECEDING RESULTS SUMMED))

```

PAGE 2 DUAL PURPOSE MAIN FOR CM TO LAB ANGULAR DISTRIBUTION CONVERSION

```
      PRINT 302
302  FORMAT (10X 21H SPECTROMETER DEGREES,15X 13H TOTAL SIGNAL)
210  L=L+1
      BETA=BETA+DFRAC
      I=0
      GD(L)=0.
220  I=I+1
      GD(L)=GA(L,I)+GD(L)
      IF(IMAX-I) 230,230,220
230  IF(GD(L)) 245,245,235
235  PRINT 310,BETA,GD(L)
310  FORMAT (10X F10.2,15X E15.8)
      N=N+1
245  IF(180.-DDET-BETA) 100,100,250
250  IF(50-N) 205,205,210
      END
```

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SUBROUTINE SIGNAL
COMMON PSI,EO,P1,P2,PP1,PP2,DE,DDET,DFRAC,FRACT,T1,T2,PR,I,FRAC2
DIMENSION CD(2880),DT(2880),TA(2880),GA(360,20),GD(360)
COMMON CD,DT,TA,GA,GD
C SINGLE VELOCITY DIAGRAM,DENSITY DETECTOR SIGNAL
C AVERAGED OVER IN-PLANE TARGET-DETECTOR SOLID ANGLE
C FOR THE SPECIFIED DIFFQ
MONEY=360./FRACT
C COMPUTE AND STORE LAB ANGLE CORRESPONDING TO EACH CM ANGULAR
C INTERVAL END POINT
P=3.14159/180.
PSIR=PSI*P
SP=P2*SINF(PSIR)
CP=P1*COSF(PSIR)
SDC=SP/CP
ALPHR=ATANF(SCC)
ALPHA=ALPHR/P
DEDEO=DE/EO
ARITH=1.0-DEDEO
FSQ=P1*PP2*ARITH/(PP1*P2)
F=SQRTF(FSQ)
CALF=COSF(ALPHR)
SALF=SINF(ALPHR)
DENSQ=(CALF*CALF)/(P1*P1)+(SALF*SALF)/(P2*P2)
DEN=SQRTF(DENSQ)
R=1.0/(P2*DEN)
RDF=R/F
XONE=RDF*CALF
YONE=RDF*SALF
ALGEB=(P1+P2)*FRACT*P*PR/(F*P2)
M=0
TH=-FRACT
15 M=M+1
TH=TH+FRACT
THR=P*TH
DIFF=THR-PSIR
XTWO=COSF(DIFF)
YTWO=SINF(DIFF)
YP=YONE+YTWO
XP=XONE+XTWO
YDX=YP/XP
THAR=ATANF(YDX)
IF(XP) 16,17,17
16 IF(YP) 19,18,18
17 THA=THAR/P
GO TO 20
18 THA=180.+THAR/P
GO TO 20
19 THA=-180.+THAR/P
20 TA(M)=THA
IF(MONEY-M) 75,75,15
75 FDR=1./RDF
C PREPARE TO SORT MICROCOSMIC SIGNALS, COMPUTE VARIABLES NEEDED
C TO ROUTE AND SORT FOR THE SPECIFIED KINEMATICS
IF(FDR-1.0) 80,81,400
80 BRISQ=1.0-FDR*FDR
BRI=SQRTF(BRISQ)

```

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      FORDB=FDR/8RI
      BZIPR=ATANF(FCRDB)
      BZIP=BZIPR/P
      GO TO 82
81  BZIP=90.
82  BZP=BZIP+PSI
      BZM=-BZIP+PSI
      BZMM=(BZP+BZM)/2.
400  BETA=-DFRAC-180.+DDET
C    SORT,SUM,PRINT,AND STORE MICROCOSMIC SIGNALS FROM LAB ANGLES
C    -180.+DDET (DEGREES) TO 180.-DDET AT INTERVALS OF DFRAC
306  L=0
309  N=0
      PRINT 1
      1  FORMAT (1H134+ RIGHT ANGLE CROSS BEAM SCATTERING,
        142H AVERAGED SIGNAL FOR THE SHOWN  PARAMETERS,
        126H , MASS ONE PRIME DETECTED/)
      PRINT 11
      11  FORMAT (10X 9+ MASS ONE,16X 9H MASS TWO,
        111X 15H MASS CNE PRIME,10X 15H MASS TWO PRIME,
        110X 14H WEIGHT FACTOR)
      PRINT 12,P1,P2,PP1,PP2,PR
      12  FORMAT (6X F14.2,11X F14.2,11X F14.2,11X F14.2,9X E15.8)
      PRINT 2
      2  FORMAT (23H RELATIVE ENERGY (E.V.),2X 19H K.E. DEFECT (E.V.),
        16X 23H (DEFECT)/(REL. ENERGY),
        15X 26H REL. VEL. ANGLE (DEGREES))
      PRINT 3,E0,DE,DEDE0,PSI
      3  FORMAT (5X F15.8,10X F15.8,10X F15.8,20X F10.2)
      PRINT 7
      7  FORMAT (25H DETECTOR WIDTH (DEGREES),
        14X 21H SPECTRCMETER DEGREES,
        15X 20H SPECTRCMETER SIGNAL)
305  BETA=BETA+DFRAC
      ALIM=BETA-DDET
      BLIM=BETA+DDET
      WIDTH=2.0*DDET
      L=L+1
      IF(FDR-1.) 99,99,111
      99  IF(BETA-BZMM) 100,111,120
      100  IF(BLIM-BZM) 101,101,102
      102  IF(ALIM-BZM) 103,111,111
      120  IF(ALIM-BZP) 122,101,101
      122  IF(BLIM-BZP) 111,111,130
      101  DSW=0.0
      GO TO 300
      103  M=0
      105  M=M+1
      IF(TA(M)-BLIM) 104,104,106
      104  DT(M)=CD(M)
      GO TO 107
      106  DT(M)=0.0
      107  IF(MONEY-M) 108,108,105
      108  M=0
      DS=0.0
      109  M=M+1
      DS=DT(M)+DS

```

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      IF(MONEY-M) 140,140,109
140 DSW=DS*(BLIM-BZM)*P*ALGEB
    GO TO 299
111 M=0
112 M=M+1
      IF(TA(M)-BLIM) 117,117,118
117 DT(M)=CD(M)
    GO TO 119
118 DT(M)=0.0
119 IF(MONEY-M) 113,113,112
113 M=0
114 M=M+1
      IF(TA(M)-ALIM) 115,115,116
115 DT(M)=0.0
116 IF(MONEY-M) 148,148,114
148 M=0
    DS=0.0
149 M=M+1
    DS=DT(M)+DS
      IF(MONEY-M) 150,150,149
150 DSW=DS*(BLIM-ALIM)*P*ALGEB
    GO TO 299
130 M=0
131 M=M+1
      IF(TA(M)-ALIM) 132,132,133
132 DT(M)=0.0
    GO TO 134
133 DT(M)=CD(M)
134 IF(MONEY-M) 158,158,131
158 M=0
    DS=0.0
159 M=M+1
    DS=DT(M)+DS
      IF(MONEY-M) 160,160,159
160 DSW=DS*(BZP-ALIM)*P*ALGEB
    GO TO 299
299 PRINT 8,WIDTH,BETA,DSW
    8 FORMAT (8X F10.2,15X F10.2,15X E15.8)
    N=N+1
300 GA(L,I)=DSW
      IF(180.-DDET-BETA) 500,500,301
301 IF(50-N) 309,309,305
500 CONTINUE
    RETURN
  END
```

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SUBROUTINE DIFFQ
C   PREDOMINANTLY BACKWARD SCATTERING
C   BEWARE OF ABSCLUTE VALUES OF AM GREATER THAN 4.5
COMMON PSI,EO,P1,P2,PP1,PP2,DE,DDET,DFRAC,FRACT,T1,T2,PR,I,FRAC2
DIMENSION CD(2880),DT(2880),TA(2880),GA(360,20),GD(360)
COMMON CD,DT,TA,GA,GD
COMMON AM,AN
MONEY=360./FRACT
C   RESULTS OF THE MAIN ARE GOOD ABSOLUTELY TO WITHIN THE
C   CROSS SECTION NORMALIZATION CONSTANT WHICH IS FACTORABLE
C   FOR ALL DIAGRAMS IN THE RECOIL ENERGY-ANGLE SEPERABILITY
C   CASE SHOWN BELOW
C   COMPUTE AND STORE CM DIFFERENTIAL CROSS SECTION AT THE MIDPOINT
C   OF EACH CM ANGULAR INTERVAL
M=0
TH=-FRACT/2.
P=3.14159/180.
POWER=AN/2.
6  N=0
   PRINT 50
50  FORMAT (1H142F CENTER OF MASS DIFFERENTIAL CROSS SECTION,
124H (COS(M(T-ETA-180)))**N,10X 3H M=,10X 3H N=)
   PRINT 51,AM,PCWER
51  FORMAT (71X F10.2,4X F10.2)
   PRINT 52
52  FORMAT (19H T-ETA (CM DEGREES),11X 14H CROSS SECTION)
7   M=M+1
   TH=TH+FRACT
   IF(AM) 31,9,30
30  IF(AM-1.5) 9,9,32
31  IF(AM+1.5) 32,9,9
32  CONTINUE
   IF(120.-TH) 8,9,11
8   IF(240.-TH) 11,9,9
9   ARG=AM*P*(TH-180.)
   Q=COSF(ARG)
   IF(Q) 11,10,10
10  QRT=SQRTF(Q)
   QPOW=(QRT**AN)
   CD(M)=QPOW
   N=N+1
   PRINT 100,TH,CD(M)
100 FORMAT (F10.2,20X E15.8)
   GO TO 15
11  QPOW=0.
   CD(M)=QPOW
15  IF(MONEY-M) 20,20,16
16  IF(50-N) 6,6,7
20  CONTINUE
   RETURN
END

```

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SUBROUTINE WEIGHT
COMMON PSI,E0,P1,P2,PP1,PP2,DE,DDET,DFRAC,FRACT,T1,T2,PR,I,FRAC2
C THE RIGHT ANGLE MAXWELLIAN BEAM FOLDED DISTRIBUTION FUNCTION,
C I(E,PSI) ,INTEGRATED OVER ALL SPACE YIELDS 1.
C THE INTEGRAND (1-E0/E)*I(E,PSI) HAS BEEN INTEGRATED ANALYTICALLY
C FROM E0 TO INFINITY
C THIS INTEGRAL IS NUMERICALLY INTEGRATED FROM PSI-FRAC2/2. TO
C PSI+FRAC2/2. BY GAUSSIAN QUADRATURE
DIMENSION A(16),U(16)
E1=E0
PI=3.14159
P=PI/180.
CON=1.60203E-12
BOLTZ=1.38042E-16
ALPH1=(P1*1.67243E-24)/(2.0*BOLTZ*T1)
ALPH2=(P2*1.67243E-24)/(2.0*BOLTZ*T2)
AL1RT=SQRTF(ALPH1)
AL2RT=SQRTF(ALPH2)
C1=4.0*(AL1RT**3.0)*(AL2RT**3.0)/PI
REDUC=(1.67243E-24*P1*P2)/(P1+P2)
VRSQ1=(2.*E1*CON)/REDUC
DELTS=(ALPH1+ALPH2)/2.0
DELTD=(ALPH1-ALPH2)/2.0
A(1)=.0271524594
A(2)=.0622535239
A(3)=.0951585116
A(4)=.1246289712
A(5)=.1495959888
A(6)=.1691565193
A(7)=.1826034150
A(8)=.1894506104
A(9)=A(8)
A(10)=A(7)
A(11)=A(6)
A(12)=A(5)
A(13)=A(4)
A(14)=A(3)
A(15)=A(2)
A(16)=A(1)
U(16)=.9894009349
U(15)=.9445750230
U(14)=.8656312023
U(13)=.7554044083
U(12)=.6178762444
U(11)=.4580167776
U(10)=.2816035507
U(9)=.0950125098
U(1)=-U(16)
U(2)=-U(15)
U(3)=-U(14)
U(4)=-U(13)
U(5)=-U(12)
U(6)=-U(11)
U(7)=-U(10)
U(8)=-U(9)
K=0
SUM=0.

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```
DLIM=(PSI+FRAC2/2.)*P
CLIM=(PSI-FRAC2/2.)*P
C2=(DLIM-CLIM)/2.
100 K=K+1
PSIP=(DLIM-CLIM)*U(K)/2.+(DLIM+CLIM)/2.
C3=(SINF(2.*PSIP))**2.
ALPHA=DELTS+DELTC*COSF(2.*PSIP)
X=-ALPHA*VRSQ1
C4=(-X+2.)*EXP(X)
C5=4.*C1/((2.*ALPHA)**2.)
SUMK=C2*C3*C4*C5*A(K)/(2.*ALPHA)
SUM=SUM+SUMK
IF(16-K) 200,200,100
200 PR=SUM
RETURN
END
```

APPENDIX 1C ANALYSIS OF THE VELOCITY INFORMATION.

The most probable diagram specifications for elastic scattering, where the entire cross beam velocity distributions lead to those events, were determined simply by calculating the most probable velocities for each Maxwellian beam separately. The assumed temperatures for the D and H₂ beams were 2800°K and 77°K, respectively.

In the case of reactive most probable diagram specification, the combined crossed beam weight function expressed in terms of E and Ψ was divided up into a coarse two-dimensional grid and the weight factors specified by (E_i, Ψ_i) were calculated via (1C.1).

$$\begin{aligned} \Psi_b &= \Psi_i + \frac{\Delta\Psi}{2} & E_d &= E_i + \frac{\Delta E}{2} \\ \Psi_a &= \Psi_i - \frac{\Delta\Psi}{2} & E_c &= E_i - \frac{\Delta E}{2} \end{aligned} \quad \sigma(E) \int \int (E, \Psi) dE d\Psi \quad (1C.1)$$

These factors were calculated numerically by Gaussian Quadrature (16 points) for $\Delta E = .05$ ev and $\Delta\Psi = 1^\circ$. The more than adequate range, $0 < \Psi < 20^\circ$ and $.35 \text{ ev} < E < 1.0 \text{ ev}$ has been considered in the calculation.

For the cross section (1B.33), the most probable histogram coordinates for $T_1 = 2800^\circ\text{K}$, $T_2 = 77^\circ\text{K}$ were (.375 e.v., 5.5°). For the cross section (1B.35), the most probable coordinates were (.475 e.v., 4.5°).

For the purpose of demonstrating the rate at which the histogram probabilities drop with increase in energy which is appropriate in experimental analysis, integral (1C.2) is tabulated in Table 1C.1 for the first cross section.

$$\left. \begin{array}{l} E_d = E_i + \frac{\Delta E}{2} \\ E_c = E_i - \frac{\Delta E}{2} \end{array} \right\} \begin{array}{l} \psi_b = 20^\circ \\ \psi_a = 0 \end{array} \quad \sigma(E) \int_{\psi_a}^{\psi_b} \int_{E_c}^{E_d} I'(E, \psi) d\psi dE \quad (1C.2)$$

Table 1C.1. Tabulation of integral (1C.2) for cross section energy dependence (1B.33).

E_c (e.v.)	E_d (e.v.)	Integral $\times 10^2$
.35	.40	3.83
.40	.45	2.70
.45	.50	1.89
.50	.55	1.31
.55	.60	.907
.60	.65	.625
.65	.70	.429
.70	.75	.294
.75	.80	.201
.80	.85	.137
.85	.90	.093
.90	.95	.063
.95	1.0	.043

The velocities deduced from the lock-in amplifier phase shift data were determined by a single velocity argument presented below.

When the detector and primary beam are coaxial, the relative phase of the full Maxwellian D beam, in traveling from the chopper to the detector, can be expressed as (1C.3)

$$\chi_D(\alpha) = \omega \frac{l_4 + l_7}{\bar{v}_D} \quad (1C.3)$$

where l_4 and l_7 are apparatus dimensions shown in Fig. 1A.1, ω is the angular chopping frequency, and $\bar{v}_D$ is the average beam velocity.

When the detector examines reactive HD, the relative phase is (1C.4).

$$\chi_{HD}(\beta) = \omega \left(\frac{l_4}{v_D} + \frac{l_7}{v_{HD}} \right) \quad (1C.4)$$

where v_D and v_{HD} are the velocities of the respective particles before and after reaction. The relative phase shift between these measurements is defined here as (1C.5).

$$\Delta\chi = \chi_D(\alpha) - \chi_{HD}(\beta) \quad (1C.5)$$

Combining (1C.3), (1C.4) and (1C.5),

$$\frac{v_{HD}}{v_D} = \left[\frac{l_4 + l_7}{l_7} \frac{v_D}{v_D} - \frac{l_4}{l_7} - \frac{\Delta x v_D}{\omega l_7} \right]^{-1} \quad (1C.6)$$

If one estimates v_D by assuming it to correspond to the most probable diagram energy necessary for reaction, v_{HD} can be determined by substituting the data and other variables into (1C.6).

Two additional terms, excluded from the bracketed portion above, correspond to the additional phase difference between the D^+ and HD^+ particles in passing from the ionization region to the electron multiplier. These terms are expressed in (1C.7).

$$\left(\frac{l_9}{l_7} \right) \left[\frac{v_D}{v_{D^+}} - \frac{v_D}{v_{HD^+}} \right] \quad (1C.7)$$

For ionizer extraction energies of 10 e.v. these terms affect the simpler results by less than 2%. The experimental extraction energies were greater than this figure.

An important question relating to velocities calculated in this manner for the hydrogen experiment is their meaning. Here, the actual signal observed in a given measurement is the superposition of the four possible HD signals noted in Section II (reactive and elastic forward and backward scattering contributions rather than simply one). This fact is described in complex notation by relationship (1C.8)

$$C e^{i(\omega t - \chi)} = \sum_{n=1}^4 A_n e^{i\omega(t - \tau_n)} \quad (1C.8)$$

where A_n is the amplitude of the n -th signal (real number), τ_n represents the time delay for the particles from the atom beam going from the chopper to the interaction region and then on to the detector, and ω is the angular chopping frequency. Eliminating the constant $e^{i\omega t}$, the amplitudes and phases are related by (1C.9).

$$C e^{-i\chi} = \sum A_n e^{-i\omega \tau_n} \quad (1C.9)$$

Both the amplitude and the phase of the detected signal, i.e. $C(\omega)$ and $\chi(\omega)$ are functions of the modulation frequency. Upon algebraic elimination of the amplitude, C , one can write that

$$\tan \chi = \frac{\sum A_n \sin(\omega \tau_n)}{\sum A_n \cos(\omega \tau_n)} \quad (1C.10).$$

It can be noted in (1C.10) that, if any one of the A_n is very much greater than the others, then χ is proportional to ω . Linearity of phase angle with frequency is therefore a test for the predominance of one component. Deviations from linearity indicate the extent to which the less probable velocity components contribute to the total signal.

In the present experiment the signals at a given LAB angle were found to be effectively linear over the frequency range, 5.6 to 9.4 KHz. Since the scatter of points plus the statistical uncertainty in the measurements appear to admit no more than 10% contribution from velocity components other than the backward reaction HD component, the velocities calculated by the previous procedure are interpreted as single component recoil group velocities.

APPENDIX 1D CALIBRATION OF THE ELASTIC DIFFERENTIAL
CROSS SECTION MEASUREMENTS.

For elastically scattered particles of equal mass that are density-detected with no other velocity dependent efficiency factors, the averaged signal expression (1B.16) for D on H₂ and H₂ on D becomes simplified to

$$S_e(\beta) = 4n_1 n_2 \Delta v N_e \sigma_e \left\{ e_D \int_{\det} h(\theta_\beta) d\Omega_a + e_{H_2} \int_{\det} h((\theta + \pi)_\beta) d\Omega_a \right\} \quad (1D.1)$$

For all β

when the energy dependence of σ is ignored. Here,

$$N_e \int_{4\pi} h(\theta) d\Omega = 1 \quad (1D.2)$$

where $h(\theta)$ is the average CM scattering function for D on H₂; e_D and e_{H_2} are the detection efficiency factors for D and H₂ respectively, and σ_e is the total elastic cross section for D on H₂.

(1D.1) can be simplified further for the elastic measurements without introducing large error by noting that the target-detector solid angle was small enough (1° half angle) such that to good approximation, the scattering functions may be taken as invariable over $d\Omega_a$ in all angular regions. The integrals in (1D.1) are therefore removed. Direct inversion of the LAB angular distribution into

the CM system for the purpose of determining N_e would be possible if the bracketed quantity did not contain two terms.

It is proposed that one term may be eliminated and N_e determined to first order. For $\beta = 45^\circ$, ($\theta_{45} = 90^\circ$) applying z' axis symmetry of h ,

$$h(\theta_{45}) = h((\theta + \pi)_{45}) \quad (1D.3)$$

But in the LAB angular range $0 \leq \beta \leq 45^\circ$, $h((\theta + \pi)_\beta)$ scarcely varies from $h(\theta_{45})$ in the quantum mechanical studies of Dalgarno and Henry¹⁸ and Karplus and Tang¹⁹ for the energy range of interest here, as well as in the general classical description. Hence the approximation

$$h((\theta + 180)_\beta) = h(\theta_{45}) \quad (1D.4)$$

is introduced and $h(\theta_\beta)$ which does vary over the range $0 \leq \beta \leq 45^\circ$ can be determined simply by the equation

$$S_e(\beta) = 4n_1 n_2 \Delta v N_e \sigma_e \frac{d\Omega}{a} \left\{ e_D h(\theta_\beta) + e_H^2 h(\theta_{45^\circ}) \right\} \quad (1D.5)$$

$$0 \leq \beta \leq 45^\circ$$

The specific procedure for determining $h(\theta_\beta)$ $0 \leq \theta \leq 180^\circ$ is as follows:

(A) The signals (Fig. 1.12) were assumed to display a $\beta^{-7/3}$ dependence over the range $1.25^\circ \leq \beta \leq 6^\circ$. The lower limit which is the assumed quantum-classical transition angle was estimated using $\bar{v}_r = 6.5 \times 10^5$ cm/sec and $\sigma_e = 55 \times 10^{-16}$ cm² and standard methods.²⁰

(B) The signals were assumed to be constant in the shadow region $0 \leq \beta \leq 1.25^\circ$.

(C) Over the domain $0 \leq \beta \leq 45^\circ$ $\frac{e_{H_2}}{e_D + e_{H_2}}$ was $s_e(45^\circ)$

subtracted from the interpolated and measured signals. The ratio of detection efficiency factors $(e_{H_2}/(e_D + e_{H_2}))$ was taken to be .6, which corresponds to ionization cross sections of H and H₂ at 80 e.v.

(D) The conversion of angles was carried out ($h(\theta_{45}) = 1$ follows from (C)).

(E) $h(\theta_\beta)$ was assumed to be unity over the range $90^\circ \leq \theta \leq 180^\circ$.

(F) The normalization factor, N_e was determined numerically to be $1/8\pi$ by (1D.2).

The average angular scattering function for D on H₂ determined by this method is displayed in Fig. 1D.1. The averaged laboratory cross section shown in Fig. 1.12 (D on H₂, H₂ on D) is readily determined by (1D.6),

$$\frac{d\sigma(\beta)}{d\Omega_a} = 4 \frac{\sigma_e}{8\pi} [1 + h(\theta_\beta)] \quad (1D.6)$$

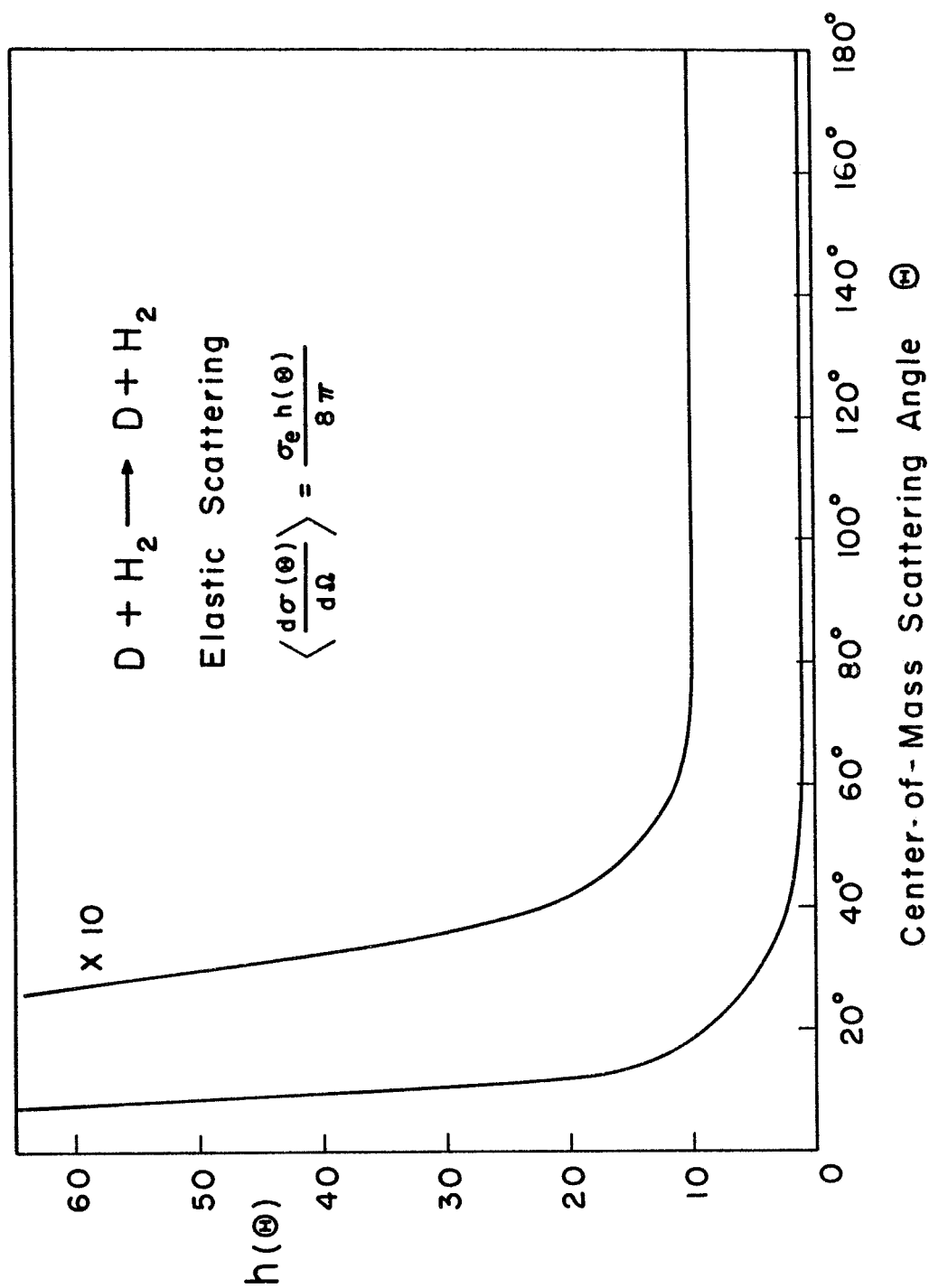


Figure 1D.1. Average center-of-mass differential cross section for $D + H_2 \rightarrow D + H_2$ inferred from the laboratory signals by removing from the data, signal contributions due to H_2 on D; see text.

taking σ_e to be identical to that for H on H_2 , which has been measured by Harrison²¹ ($55 \times 10^{-16} \text{ cm}^2$).

APPENDIX 1E CALIBRATION OF THE REACTIVE DIFFERENTIAL
CROSS SECTION MEASUREMENTS.

Knowledge of the calibrated elastic signals and the experimental reactive-to-elastic signal ratio enables the total reactive cross section to be determined irrespective of detailed knowledge of n_1 , n_2 , $d\Omega_a$ and Δv taking the ratio of (1B.42) and (1D.5).

$$\frac{S_r(\beta)}{S_e(\beta)} = \frac{e_{HD} N_r \sigma_r \text{ Computer Results}}{e_{H_2} (8.75 \times 10^{-16} \text{ cm}^2/\text{sr.}) d\Omega_a [1 + .67h(\theta_\beta)]} \quad (1E.1)$$

While $d\Omega_a$ appears explicitly in the denominator of (1E.1), it is also embedded in the computer results. The ratio, e_{HD}/e_{H_2} can be taken to be unity under the assumption that the respective ionization cross sections do not differ and the mass filter transmissions for mass two and three particles are equal.

The reactive normalization constant, N_r is calculated from

$$N_r = \frac{2\pi}{0} \int_0^\pi \int_0^{2\pi} \cos^2 [M(\theta - \pi)] \sin \theta \, d\theta \, d\phi = 1 \quad (1E.2)$$

to be

$$N_r^{-1} = 2\pi \sin^2 \left[\frac{\pi}{4M} \right] + \frac{2 \sin^2(\pi/2M)}{(1 - 2M)(1 + 2M)} \quad (1E.3)$$

whenever $M \neq \pm 1/2, \pm 1, 0$

the numerical values that the variables appearing in (1E.1) take on in the reactive cross section evaluation are listed in Table 1E.1. These values imply that $\sigma_r = (3.5 \pm 1.8) \times 10^{-16} \text{ cm}^2$ for the energy-dependent cross section of Assumption (2). The simple step function cross section is a factor of 4 smaller. The quoted error refers to the experimental mean deviation for the ratio S_r/S_e . The laboratory averaged differential cross section calibration is determined via (1E.4).

$$\frac{d\sigma_r(\beta)}{d\Omega_a} = \frac{N_r \sigma_r \text{ Computer Results}}{d\Omega_a} \quad (1E.4)$$

For $\beta = 30^\circ$ $d\sigma_r/d\Omega_a = 2.4 \times 10^{-16} \text{ cm}^2/\text{sr. (LAB)}.$

Table 1E.1. Tabulated variables required for calibrating the reactive cross section with respect to the elastic cross section normalized to total cross section measurements.

For $M = 1.35$

$$N_r = 4.68$$

$$d\Omega_a = 1.08 \times 10^{-2}$$

For $\beta = +30^\circ$

$$\text{Computer Results} = 1.6 \times 10^{-3}$$

$$\sigma(E) = \sigma_r (1 - E_o/E)$$

$$h(60^\circ) = 1.1$$

$$\frac{S_r(30^\circ)}{S_e(30^\circ)} = .16 \pm .08$$

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PART TWO
CROSS SECTIONS FOR THE EXCITATION OF $\text{Na}(3^2\text{P})$ BY COLLISIONS
WITH INTERNALLY EXCITED MOLECULAR HYDROGEN
DEUTERIUM AND NITROGEN

I. INTRODUCTION

It has been known for many years that the resonance radiation of sodium atoms is efficiently quenched in the presence of molecular gases such as H_2 , D_2 and N_2 . The high quenching efficiency for these molecules compared with inefficient quenching by atomic gases was attributed usually to efficient energy transfer involving internal molecular states. Although effective quenching cross sections for molecular gases had been studied extensively in a variety of environments¹, the electronic-internal energy transfer mechanism was speculative because the kinetic energy of neither reaction product had been determined nor had the vibrationally excited states of these product molecules been identified.

The first several experiments, which appeared to confirm that, at least for the case of sodium, the electronic-vibrational transfer hypothesis may be correct, were some investigations of the inverse process carried out in shock tubes for N_2 .² The slow rise of the sodium-line reversal temperature behind the shock front suggested to Clouston, Gaydon, and Glass³ that the excitation of sodium atoms was due to vibrationally excited N_2 molecules. Stronger evidence that this suggestion was correct came subsequently from Gaydon and Hurle⁴ and Hurle⁵ who showed that in shock-heated N_2 containing Na, the Na

excitation temperature follows the relaxing vibrational temperature of N_2 rather than the N_2 translational temperature. Hurle⁵ concluded that the transfer of excitation energy from N_2 vibrational modes proceeds with much higher probability ($\sigma > 3 \times 10^{-16} \text{ cm}^2$) than by transfer from rotational or kinetic energy modes.

This result appeared to be confirmed in a sodium excitation experiment by Starr⁶ where vibrationally excited N_2 was produced in the afterglow of a microwave discharge in flowing N_2 . In this experiment all strong sodium lines between 3100-6100Å were examined. Since a number of sodium levels were excited similarly as the $Na(3^2P)$, Starr concluded, in addition, that a close match between the vibrational and electronic levels is not requisite for the process to occur.

Around the time that Hurle and Starr offered evidence supporting the efficient interconversion of electronic and vibrational energy between Na and N_2 , Derblom⁷ positively identified the yellow emission observed in Type B aurora as due to sodium D emission. While a number of mechanisms had been postulated to explain its origin, Hunten⁸ proposed that the excitation of sodium arose through the transfer of N_2 vibrational energy from the near resonant vibrational states. Whether this proposal or an alternate possibility was tenable depended on knowledge of the sodium D excitation cross section for the near resonant vibrational states (little or no rotational or kinetic energy required to allow the reaction to proceed) and only the lower cross section limit determined by Hurle⁵ was available.

In an effort to provide the required information and to investigate the nature of the Na D excitation mechanism more precisely, a

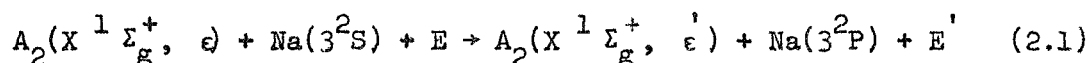
series of crossed beam excitation experiments were initiated at this laboratory using the species N_2 , H_2 , and D_2 .

In these excitation experiments, the molecular species have issued from a furnace source operating in the temperature range 2000-3000°K; the sodium atoms have effused from a 650°K source. The sodium D radiation emitted from the beam intersection region has been observed. The basic experiments for these species were addressed to the determination of the cross beam rate constants as a function of molecular beam temperature. The velocity selected molecular beam experiments performed later were directed toward a more detailed understanding of the reaction mechanism, i.e., deduction of the participating vibrational states and their cross sections for excitation transfer.

A detailed description of these experiments, experimental results and analysis of results will be described in subsequent chapters. The basic experiment for the N_2 - Na system performed by Mentall, Krause, and Fite has been previously reported⁹ accompanying preliminary analysis. The results of this previous study and the more recent studies of Krause, Fricke, and Fite¹⁰ are discussed here.

II. PRINCIPLE OF EXPERIMENT.

Excitation of the first resonance doublet of sodium by collisions with the diatomic molecules H_2 , D_2 , and N_2 is represented by (2.1) when the reacting species originate from sources operating at thermal energies:



The molecular internal energy before and after collision represented by ϵ and ϵ' is energy due to vibration and rotation. Since the atom receives electronic energy $E_0 = 2.10$ eV during the collision, conservation of energy (2.2) implies that this energy must come from the change in internal ($\Delta \epsilon$) and kinetic energy (ΔE) before and after collision.

$$\Delta \epsilon + \Delta E = E_0 \quad (2.2)$$

One method of understanding the relative roles that internal and kinetic energy play in providing the excitation energy is to observe the resonance radiation of the collisionally excited sodium atoms while ϵ and E are varied. If these energies can be varied over a wide range relative to each other so that relative excitation cross sections for various amounts of kinetic and internal energy can be deduced and if the effective reaction rate constant for these various mechanisms can be accurately measured, cross sections for the various mechanisms can be assigned. Two experiments that are capable of meet-

ing these goals when considered together now will be described.

Their common features will be described first.

The experimental arrangement which utilizes beams crossed at 90° is shown schematically in Fig. 2.1. The diatomic gas is excited thermally in a tungsten furnace operating between 2000 and 3000°K . Since each molecule makes on the average approximately 10^3 collisions with the walls before escaping into the beam, it is assumed that the gas reaches equilibrium with the furnace walls and that the degree of excitation of internal energy states is that given by the Boltzmann distribution. The slow relaxation rate for vibrational excitation in N_2 , D_2 and H_2 implies that the beam vibrational population does not differ appreciably from that in the furnace. The sodium atom beam is produced in a double-chambered oven, the temperature of the rear chamber governing the beam intensity and the temperature of the front chamber determining the beam kinetic distribution (650°K).

Sodium D line photons produced by the interaction of the molecular and Na beams are detected with a photomultiplier which views the interaction region. Wavelength discrimination is achieved by the use of a $20\text{\AA}$ pass-band interference filter preceded by a collimating lens. This bandwidth still admits a large signal due to the hot tungsten furnace light that is reflected from the blackened walls of the experimental vacuum chamber. As a convenience in separating this reflected radiation from radiation arising from the colliding beams, the sodium beam is modulated at 1440 Hz by a rotating chopper wheel. Under these circumstances the desired signal is identified

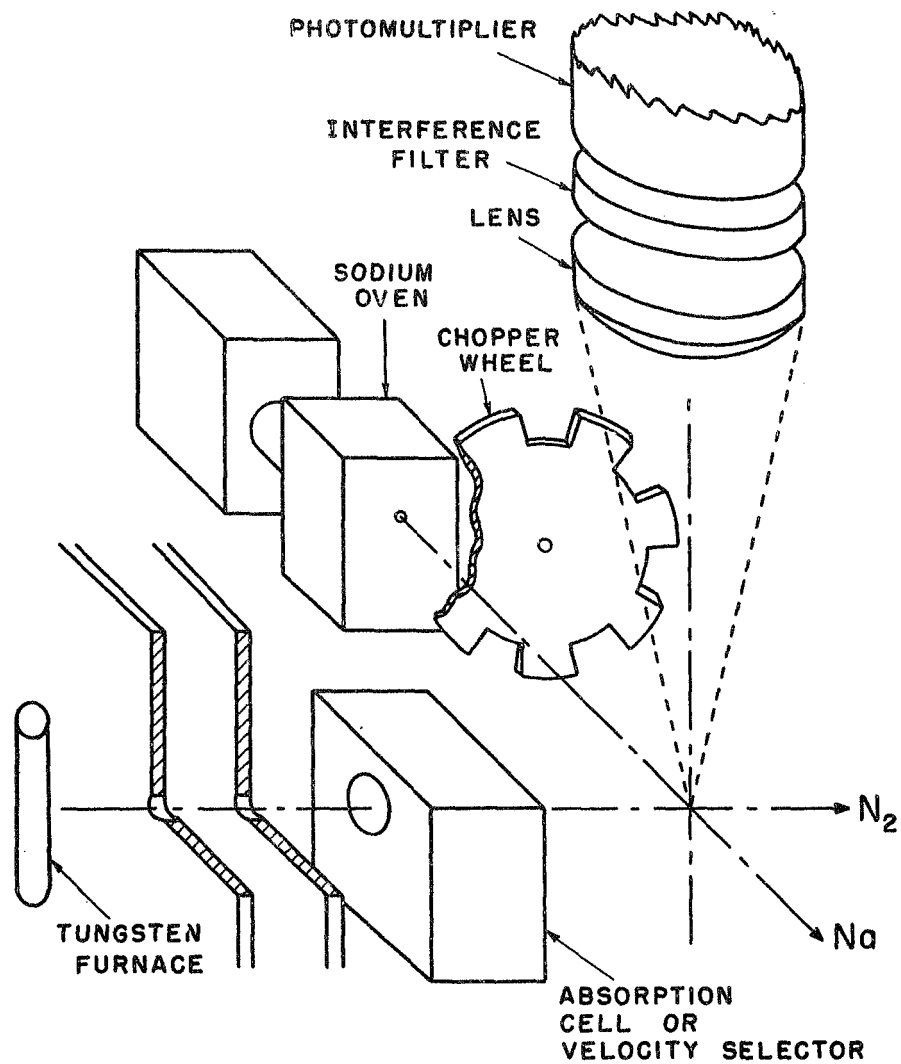


Figure 2.1. Sketch of the experimental arrangement. The figure does not show light baffles used to diminish light originating from the tungsten furnace.

by its occurring at the sodium beam modulation frequency in specified phase. This is accomplished by feeding the photomultiplier signals to lock-in amplifier circuitry.

A. . BASIC CONFIGURATION

A useful aspect of the experiment is that modulated signals, in addition to those from the interaction of the excited molecules with Na atoms, are obtained by resonant scattering of light emitted from the tungsten furnace. By making the collimation sufficiently precise so that about 90% of the light intersecting the Na beam comes from the hole in the furnace, the light to good approximation can be described by the Planck black-body radiation formula. Since the resonant scattering cross section for sodium D line radiation is known, determination of the rate constant for excitation can proceed by comparing the scattered black-body light signal to the signal produced by the atom-molecule interaction, both signals being detected by the same optical system. Effectively, the black-body radiation scattered by sodium atoms calibrates in one step both the intensity of the Na beam and the optical system characteristics.

In practice, the situation is slightly more complex because of the large intensity of the resonantly scattered black-body light compared to the light from the molecular interaction; the furnace light capable of exciting sodium D must be attenuated by about three orders of magnitude in order to observe the signals arising from reaction. The necessary attenuation is accomplished by inserting an absorption cell containing sodium vapor in the molecular beam. This addition shown in Fig. 2.1 can be made to fulfill the objective while affecting fewer than 3 per cent of the molecular beam particles during their passage through the cell.

Determination of the rate constant proceeds as follows. Once the sodium beam is established, the tungsten furnace is turned on and its temperature T_1 is measured using an optical pyrometer looking into the furnace aperture. The signal from the resonantly scattered furnace light S_s is noted. The sodium vapor absorption cell is then heated to a temperature where the resonantly scattered light signal is negligible. Molecular gas is then admitted to the furnace and the sodium light signal from particle reaction S_r is noted. The pressure change in the experimental vacuum chamber due to the molecular beam is used to calculate the molecular number density, n_1 . The reaction rate constant, k_r , conventionally defined, is determined via these measurements and (2.3) (see Appendices 2B and 2C),

$$k_r = (3\Gamma/4 \pi n_1) (A_1/L^2) (S_r/S_s) e^{-E_o/kT_1} \quad (2.3)$$

where A_1 is the tungsten furnace aperture area, L is the distance between the furnace and reaction region, Γ is the inverse of the sodium D lifetime, E_o corresponds to the D line energy, and k is the Boltzmann constant.

Studying the variation of the rate constant as a function of the tungsten furnace temperature is a gross means of understanding reaction dynamics. This can be done by comparing the experimental $k_r(T_1)$ with that calculated for various simplified reactive mechanisms using (2.4).

$$k_r = \int_{\vec{v}_2=0}^{\infty} \int_{\vec{v}_1=0}^{\infty} \left\{ \frac{\int_0^{\infty} \sigma_r(\epsilon, v_r) g(\epsilon) e^{-\epsilon/kT_1} d\epsilon}{\int_0^{\infty} g(\epsilon) e^{-\epsilon/kT_1} d\epsilon} \right. \\ \left. v_r f(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2 \right\} \quad (2.4)$$

where

$$f(\vec{v}_i) d\vec{v}_i = \left(\frac{4}{\sqrt{\pi}} \right)^{3/2} \frac{v_i^2}{v_i^3} e^{-v_i^2/v_i^2} dv_i \quad v_i^2 = m_i/2kT_i \\ i = 1, 2$$

The numerator of the bracketed quantity contains $\sigma(\epsilon, v_r)$, the cross section for energy transfer; it depends on both the relative velocity of collision, v_r , and the energy of molecular internal excitation, ϵ . Since $g(\epsilon)$ is the statistical weight density for molecular internal energy states and the population of internal states depends only on the molecular source temperature, the total quantity in brackets is the reaction cross section for a given relative velocity averaged over all internal states thermally populated. The remaining parts of (2.4) is the internally averaged cross section averaged over the Maxwell-Boltzmann velocity distributions for the crossed beams. When the molecular furnace temperature is varied, the temperature-dependent signals reflect the effect on reaction due to simultaneous changes in the molecular internal energy and kinetic energy distribution functions.

B. VELOCITY-SELECTED CONFIGURATION

Knowledge of the variation of the rate constant with temperature is not sufficient information to isolate the mechanism for reaction unambiguously; the observed temperature dependence may be ascribed to the transfer of pure internal energy, and/or internal energy combining with varying amounts of kinetic energy, to provide the required reaction endoergicity. The interpretational ambiguity, which results from the fact that the kinetic and internal energy distribution functions are changing simultaneously, can only be resolved by obtaining different experimental information. The interpretation can be clarified if the reactive signals are studied by varying the two distribution functions independent of each other.

The velocity distribution of molecules having a fixed internal energy distribution can be varied by inserting a velocity selector into the molecular beam. Since such a device can be made to pass excited molecules having little velocity dispersion over a broad range of transmitted speeds, the reaction can be studied as a function of molecular speed for each molecular furnace temperature. Appropriately, the velocity selector simultaneously removes black-body tungsten furnace photons from the beam since their velocity falls outside of the selector transmission function at molecular speeds of interest. For this reason, the sodium vapor absorption cell is not a required piece of apparatus when the velocity selector is inserted.

The molecular velocity and temperature dependent signals produced with this configuration can be understood by comparing them with calculated experimental yields for the same simplified reactive

mechanisms using an expression similar to (2.4). The modification is effected by inserting the velocity pass-band function into (2.4) before the beam velocity distribution averaging is performed. In this manner it is possible to deduce the relative importance of varying amounts of kinetic energy that go into reaction. A detailed description of the required procedures will be presented in Section V.

III. EXPERIMENTAL APPARATUS.

A. VACUUM SYSTEM.

The design and operation of the three-chamber-differentially pumped vacuum system used in these experiments has been discussed by Clendenning¹¹ and Ott¹² and its general layout has been illustrated by Kauppila.¹³ The molecular source is located in Chamber One while Chamber Three contains the remaining items necessary for the experiments. All vacuum system surfaces located in the experimental region were blackened with Aqua Dag in order to minimize stray furnace light that might easily be reflected into the optical system; photomultiplier shot noise was reduced somewhat by this care.

The first collimation aperture (see Appendix 2A) was kept smaller than the tungsten furnace hole in order to allow only the black-body photons from the Hohlraum to travel axially from Chamber One. The second collimating aperture was adjusted simultaneously to collimate the molecular beam and photons so they were required to pass through the sodium beam. This exercised care enabled the molecular beam useful to the basic experiment to be determinable from the measured Chamber Three pressure decrease (beam on-off) coupled with Chamber Three pumping speed measurements. The techniques for the latter have been described by Kauppila.¹³

The base pressures for Chamber One through Three were 3×10^{-6} , 2×10^{-6} , and 1×10^{-6} Torr., respectively. Beam-on conditions were 400×10^{-6} , 40×10^{-6} , and 4×10^{-6} Torr. respectively. Operation of the sodium beam source, absorption cell or velocity selector affected the experimental chamber pressure negligibly.

Diffusion pump speeds utilized in the calculation of source and beam number densities for the molecular species were determined by measuring the vacuum system pressure time constants of the first and third chambers for H_2 , D_2 and N_2 . The time constant of the i^{th} chamber τ_i is related to the pumping speed S_i by expression (2.5).

$$S_i = V_i / \tau_i \quad i = 1, 3 \quad (2.5)$$

V_i is the known chamber volume. The transient method for determining τ_i has been fully described by Kauppila¹³; the reader is referred to his detailed account. The results listed in Table 2.1 differ only slightly from those of Kauppila. The Chamber Three pumping speeds are approximately in the ratio of the square root of the mass ratios as expected. The Chamber One ratios deviate from these ratios; this deviation is presumably due to the greater difficulty of accurately determining the smaller Chamber One volume.

B. MOLECULAR BEAM SOURCE.

The molecular furnace was identical in construction to one described in detail by Ott¹² and the reader is referred to his account for a complete description of its design features and operation. It consisted of a sheet of tungsten (2 in. x 3 in. x .001 in.) which was rolled to form a cylinder (2 in. long and 3/16 in. diameter). A hole was sandblasted in the wall of the cylinder to permit the molecular gas to escape from the furnace as a beam. Each end of the tubular furnace was closed off with molybdenum end pieces, one piece also

TABLE 2.1

Pumping Speed Results.

Chamber	Gas	Time Constant (sec)	Chamber Volume V(liters)	Pumping Speed (liters/sec)
#1	H ₂	.057	33	580
	D ₂	.085	33	390
	N ₂	.173	33	190
#3	H ₂	.67	303	450
	D ₂	.95	303	320
	N ₂	2.42	303	125

serving as an inlet for gas molecules. This assembly was supported at the ends by two copper bus bars which conducted the a.c. current (up to 30 amps.) necessary to joule heat the furnace. The molecular gases introduced into this furnace in the course of experimentation were 99.9% pure.

The furnace geometry requires that each molecule makes on the average approximately 10^3 collisions with the walls before escaping into the beam and the use of tungsten wire wadding inside the furnace further increases contact of the gas with the hot furnace surfaces. The kinetic temperature of the beam molecules was checked as a function of furnace pressure in a separate experiment using a high resolution analyzing velocity selector (described in Section IIIF) and a mass spectrometric detector. The results of this experiment (described in Section IIIG) verify kinetic equilibrium of the gas molecules with their thermal environment at the furnace pressure (4 Torr.) utilized in the excitation experiments. These results suggest that the degree of excitation of internal energy states is that given by the Boltzmann distribution. The slow relaxation rate for vibrational excitation in N_2 , D_2 and H_2 implies that the vibrational population remains nearly that in the furnace even after the gas emerges and forms the molecular beam.

The furnace temperatures for N_2 ranged from 2000 to 3000°K; those for H_2 and D_2 ranged from 2000 to 2600°K. At these temperatures, the excitation of any molecular electronic states is extremely forbidden. (The first electronic state of H_2 and N_2 is more than 10 e.v. and 6 e.v. above the ground state respectively.) The temperature range for the hydrogen isotopes was more limited because their dissociation becomes very significant at temper-

atures approaching 2600°K . The excitation signals had to be corrected for the decrease in molecular number density at the higher experimental temperature so that the correct excitation rate constants would be determined. The precise manner in which this was carried out is discussed in Sections IV and V.

The furnace temperature was measured with an optical pyrometer (Leeds and Northrop No. 8622-C) while the molecular gases were being admitted into the furnace. It was made to view the inside of the furnace which revealed essentially the black-body temperature of the furnace.

The molecular number density in the interaction region (without velocity selection) was of order $10^{12}/\text{cm}^3$ throughout these experiments.

C. ATOMIC BEAM SOURCES.

The sodium beam source was a two-chamber oven of standard design machined from blocks of Monel metal; the reader is referred to Fig. 2.1 for visualization. Sodium metal pieces (Fisher Scientific) were placed in the chamber farthest from the beam exit aperture (rear). Sodium hydroxide was removed from the pieces in open air before they were placed in the oven; the system was immediately evacuated to avoid further contamination. Two cylindrical heaters (Vulcan TB500) were inserted into the Monel body in order to vaporize the sodium metal. This vapor was free to pass through a short stainless steel tube into the aperture chamber (front) where four identical heaters were sunk into that Monel block to raise its temperature. Once the sodium atoms thermalized in this chamber they could pass through the beam exit aperture.

During experimentation the respective chamber temperatures were separately controlled to within ± 3 percent by temperature controllers (EP Controls). The temperature of the rear chamber governed the beam intensity and the temperature of the front chamber determined the beam speed. Typical oven temperatures were 550°K and 650°K respectively. The entire furnace was set upon stainless steel point supports to reduce thermal conductive losses.

The number density of sodium in the reaction region (n_0) was typically $10^9/\text{cm}^3$ (see Appendix 2A for this beam's geometry). Since the maximum resonant scattering cross section (σ_0) for natural line width is of order 10^{-9} cm^2 for the $^2\text{P}_{3/2}$ doublet component,

$n_0\sigma_0$ could be as large as 1 in the present experiments. Taking the maximum photon path length in the interacting region to be 1 cm. (see Appendix 2A), it is evident that this region is not quite optically thin for light originating farthest from the detector. While this situation was required to obtain adequate signal in these experiments, this optical thickness, did not appear to have affected the experimental results significantly. Indeed the only effect of not having the sodium beam optically thin would be to trap a small portion of the D-line resonance radiation and to re-emit it isotropically. Such an effect would render the already good assumption of isotropically emitted radiation even better.

D. ABSORPTION CELL.

The role of this device in the basic experimental configuration has been described in Section II A; remaining is its physical description.

For all practical purposes, the basic construction corresponded to that of the sodium beam source. Unlike the source oven, the exit aperture was closed but two holes were drilled through opposite sides of one chamber (front) to allow the molecular beam to pass cleanly through. Sodium metal was placed in the other chamber. When the cell was heated, sodium vapor effused to the front chamber, where it was free to intercept the resonant furnace photons passing through. Both chambers contained one heater of the type previously described, sunk into the body in like fashion. The heaters were electrically connected in parallel and they were controlled by a temperature controller. These chambers operated at a temperature of 470°K .

It is noteworthy that the sodium number density at the temperature quoted above did not exceed $6 \times 10^{12}/\text{cm}^3$. This implies (worst case calculation) for an N_2 - Na quenching cross section assumed to be $5 \times 10^{-15} \text{ m}^2$ and an effective cell path length of 1 cm, that less than 3 percent of the molecular beam vibrational population was affected by the quenching process occurring within the cell. (The effective path length was smaller than l_3 shown in Table IA.1 because the cell absorbing cavity was less than 1 cm dia.) The proportion of molecules scattered from the beam at angles too large to escape the sodium cell or to collide with the target atoms is estimated to be considerably smaller than 3 percent.

E. OPTICAL SYSTEM AND ASSOCIATED ELECTRONICS.

Sodium D photons emitted from the reaction region were detected with an EMI 9558A photomultiplier. Wavelength discrimination was achieved using a 20 angstrom (full width half maximum) band-pass interference filter (Thin Film Products, Inc.) centered about the sodium doublet. The filter was preceded by a collimating lens. This bandwidth still admitted a large signal due to the hot furnace radiation reflected from the blackened walls of the vacuum chamber (in the basic configuration). The sodium beam modulated at 1440 Hz by a rotating chopper wheel was a convenient method to separate this large d.c. signal from the a.c. sodium D radiation originating in the intersecting beam region. The detected signals were fed to a narrow band amplifier (Extranuclear Labs Preamplifier Type II) permitting phase sensitive detection by the lock-in amplifier (PAR HR-8). The demodulated signal was displayed on a chart recorder (Texas Instrument Servo-Riter II).

The general purpose convex lens (2 in. diameter) of focal length $3 \frac{5}{8}$ in. was placed one focal length above the reaction region center; its axis was perpendicular to the plane of the incident beams. The addition of the lens and its arrangement enabled the solid angle of the detector, as seen from the reaction region, to be relatively large while insuring that all the intercepted rays would be incident normal to the interference filter surface (2 in. diameter). Under these conditions the transmission function of the filter was identical for all intercepted rays. The reader is referred to the well known general properties of

interference filters.¹⁴

The transmitted light of the filter passed through a planar piece of quartz glass (1/4 in. thick) before passing through the photomultiplier entrance window (2 in. diameter). This glass, which was in contact with the entrance window, not only helped to support the photomultiplier but also served to conduct stray furnace heat in the vicinity of the photocathode to the cylindrical photomultiplier housing cooled to 0°C. The photomultiplier housing, wrapped with copper tubing, was cooled by circulating ice water through the cooling coils surrounding it. This arrangement reduced the multiplier dark current below the d. c. currents produced by stray tungsten furnace light of the basic configuration. Thus stray furnace light transmitted through the optical system was the principal source of shot noise.

The schematic diagram of the photomultiplier and the block diagram of the signal processing equipment is shown in Fig. 2.2. The photocathode was kept at ground potential to prevent leakage currents between the cathode and the photomultiplier housing. The preamplifier was utilized in the tuned mode throughout these experiments in order to avoid a mixer overload in the lock-in amplifier.



Figure 2.2. Schematic diagram for the photomultiplier shown with the block diagram of the signal processing equipment.

F. VELOCITY SELECTORS.

Two neutral particle mechanical velocity selectors were developed and used for the excitation transfer experiments. One selector, the dual range velocity analyzer, was designed primarily to serve in general laboratory analytic capacities. These include measuring beam source velocity distributions or studying the transmission characteristics of low resolution velocity selectors, where high resolution and high speed characteristics are desirable and low transmission can be tolerated. This selector was utilized in the two specific capacities noted above.

The other selector, the coarse velocity selector, was designed specifically for velocity selecting the molecular beam in the excitation experiments. This application requires high transmission and high speed characteristics while tolerating modest velocity resolution for the molecular particles. An additional characteristic was its ability to reduce simultaneously transmitted light.

The specific description of these selectors will follow a brief review of velocity selector principles. All discussions are cast in the terminology of Hostettler and Bernstein (HB)¹⁵ and Grosser (G)¹⁶ for the purpose of uniformity.

Various mechanical velocity selectors designed to pass a velocity selected beam with no velocity "sidebands" have been reported in the literature.^{15,16,17,18,19} Of the two basic types reported (rotating helical-grooved cylinders and rotating slotted disks), the slotted disk variety is commonly preferred principally for mechanical

reasons. The slotted disk designs can be divided further into two groups: single characteristic selectors^{15,18,19} and dual range selectors.¹⁶ While those falling into the former group are at present more commonly used, the dual range type instrument is more versatile. The extent of the versatility will become evident after a short review of selector principles.

Considering the "unrolled" representation of a hypothetical dual range selector shown in Fig. 2.3a, the reader is asked to ignore disks 2 and 3. When the slots are moving to the left and a particle enters disk 4 following the $(v_0)_F$ velocity trajectory, one finds the useful relationship (2.6) when the transit time of the particle is equated with the time required for the rotor of angular speed ω to turn through the angle ϕ_F .

$$\frac{(v_0)_F}{L} = \frac{\omega_F}{\phi_F} \quad (2.6)$$

The transmitted speed expressed here in terms of rotor parameters is nominal because slightly different trajectories also can be transmitted due to the finite slit width of the disks. Considering the other possible trajectories in like manner a velocity pass-band relationship in terms of rotor geometry for any v can be derived (see HB). It is noteworthy that the maximum and minimum transmitted speeds for the nominal speed $(v_0)_F$ are expressed as

$$v_{\max} = (v_0)_F \left(\frac{1 - \beta}{1 - \gamma_F} \right) \quad v_{\min} = (v_0)_F \left(\frac{1 + \beta}{1 + \gamma_F} \right) \quad (2.7)$$

where $\beta = d/L$, $\gamma_F = l_1/r\phi_F$; d is the disk thickness; L , the rotor length (defined in Fig. 2.3(a)); and r , the particle passage radial distance. These expressions are useful in specifying the velocity resolution R for the nominal path (defined as full width half maximum).

$$R \equiv \frac{v_{\max} - v_{\min}}{2 v_{0_F}} = \frac{\gamma_F - \beta}{1 - \frac{2}{F}} \quad (2.8)$$

Evidently, resolution is determined once the geometry is fixed.

Completing the design of this one path rotor, additional disks are placed between disks 1 and 4 in a fashion such that trajectories passing through adjacent slots are interrupted. Therefore the selector is free of sidebands in the forward direction.

The two-path rotor shown in Fig. 2.3(a) contains also a reverse sideband free trajectory. Apparently, the forward path is automatically closed when the slots move to the right, and vice versa. Considering the reverse direction, the selector characteristics are given by the relationships already presented only the F subscripts are replaced by R . If the designer chooses $F \neq R$, one rotor construction can be made to possess two different velocity calibrations (v_0/ω) and resolutions. Either characteristic can be chosen during operation depending on whether the rotor is turned in one direction or the other. Two single velocity selectors for the price of one is not the only advantage of the dual rotor model over

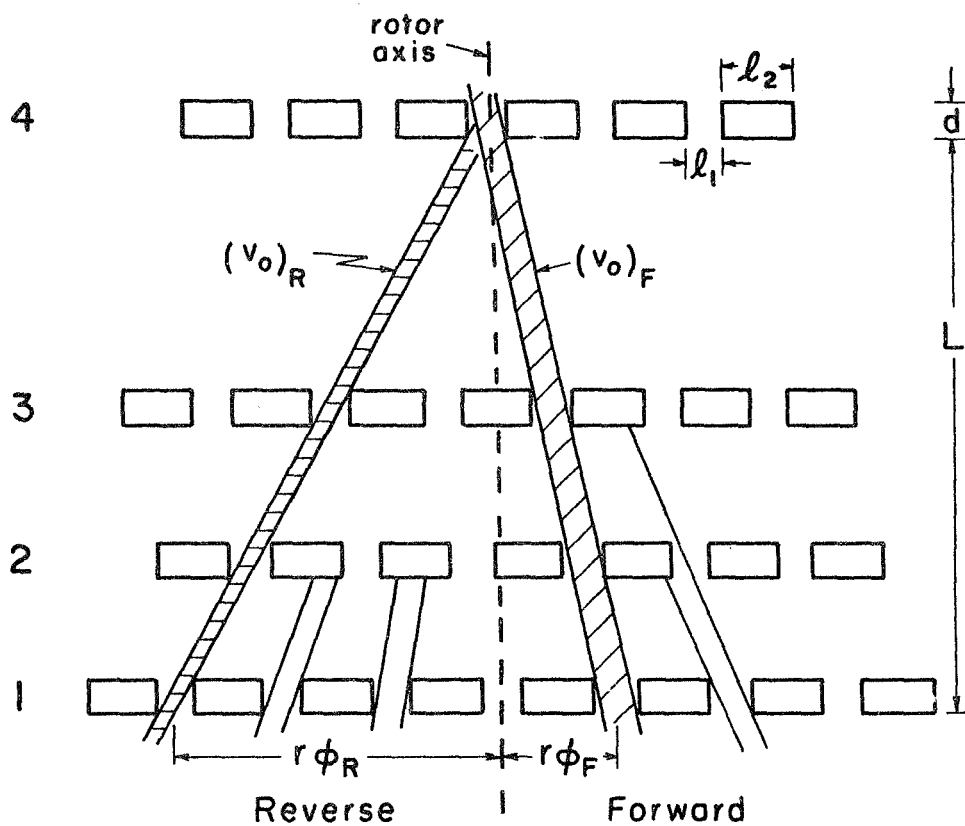


Figure 2.3(a). Unrolled graph for a hypothetical dual range velocity selector.

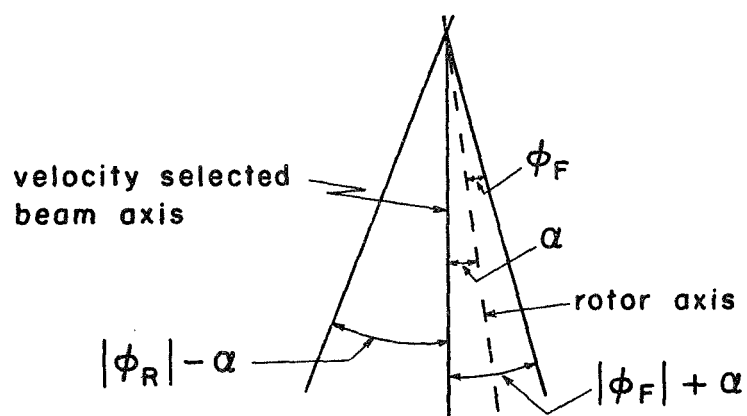


Figure 2.3(b). Diagram illustrating effect of the rotor misalignment on velocity calibration.

the single path model.

The calibration of any selector (v_0/ω) in practice is not merely given by (2.6) as defined. In general, the rotor shaft and beam particles are not parallel as was assumed in the derivation. If the rotor axis is misaligned from the beam axis by angle α , according to the arbitrary convention shown in Fig. 2.3(b), (2.6) must be modified by replacing ϕ_F by $|\phi_F| + \alpha$. This principal modification of v_0/ω for a given path requires that α be determined directly or indirectly.

Conventionally, one indirectly determines α by experimentally determining ω_{mp} , the rotor angular speed corresponding to the maximum detected signal when a particle detector follows the velocity selector and one assumes ω_{mp} to correspond to v_{mp} . This theoretical most probable velocity expression for selectors of modest-to-high resolution is readily shown to be (2.9)

$$v_{mp} = \frac{n kT}{m} \quad \begin{array}{l} n = 3 \text{ for a density detector} \\ n = 4 \text{ for a flux detector} \end{array} \quad (2.9)$$

k is the Boltzmann factor; T , the source absolute temperature; and m , the particle mass. This calibration carries additional assumptions of ideal source thermometry and effusion conditions in addition to isothermality of source and beam particles. The latter assumptions are particularly inappropriate in the event of beam streaming and free jet expansion.

The conventional calibration need not be applied when using a two-trajectory modest-to-high resolution selector. While ϕ_F is replaced by $|\phi_F| + \alpha$ in (2.6), ϕ_R is replaced by $|\phi_R| - \alpha$ in the companion relationship. If the user now experimentally determines ω_{mp} (forward) and ω_{mp} (reverse), then α is determined by the solution of these equations, mutatis mutandis; the solution is displayed in (2.10).

$$\alpha = \frac{(\omega_F/\omega_R)_{mp} |\phi_R| - |\phi_F|}{1 + (\omega_F/\omega_R)_{mp}} \quad (2.10)$$

Consequently, the correct calibrations are

$$(v_0/\omega)_F = \frac{L}{|\phi_F| + \alpha} \quad (2.11)$$

and

$$(v_0/\omega)_R = \frac{L}{|\phi_R| - \alpha} \quad (2.12)$$

This calibration for modest-to-high resolution selectors is free of the conventional assumptions. Evidently, self-calibration is possible even when using pathological velocity distributions.

1. VELOCITY ANALYZER.

The general purpose dual range velocity selector was constructed from seven slotted disks mounted on a medium length rotating shaft, the bearings of which were elastically suspended ("o" rings) to minimize vibrations resulting from rotor dynamical imbalance. The disk slots were phased and placed on the shaft such that a forward rotation of the shaft (slots moving up when particles enter disk 7, Fig. 2.4) permitted selected speeds up to at least 7.3×10^5 cm/sec (400 rps) at modest velocity resolution (12.9 percent); a reverse rotation selected up to at least 2.0×10^5 cm/sec (400 rps) at high resolution (2.8 percent). The hysteresis synchronous motor (Elinco AL841 up to 250 rps or Globe Industries LC-79A199 up to 500 rps) which drove the rotor via elastic tubular connection, was controlled by a variable frequency audio oscillator (Hewlett-Packard 200 ABR) driving a 100 watt monaural high fidelity amplifier (Bogen) that fed a phase shift network of standard design necessary for operating the particular two-phase motor mounted on the motor block.

The disk specifications, material, and machining were identical to TRR¹⁹ (see Table 2.2). The "thin" disk dual rotor was designed by trial and error using the standard principles and "unrolled" graphical methods of HB. Although the unrolled graph of this design is not presented here due to the awkward physical dimensions, the disk phase and spacing diagram which fixes the design is represented in Fig. 2.4 with the disk teeth (black) and slots enlarged for clarity. The reference line either bisects a tooth or

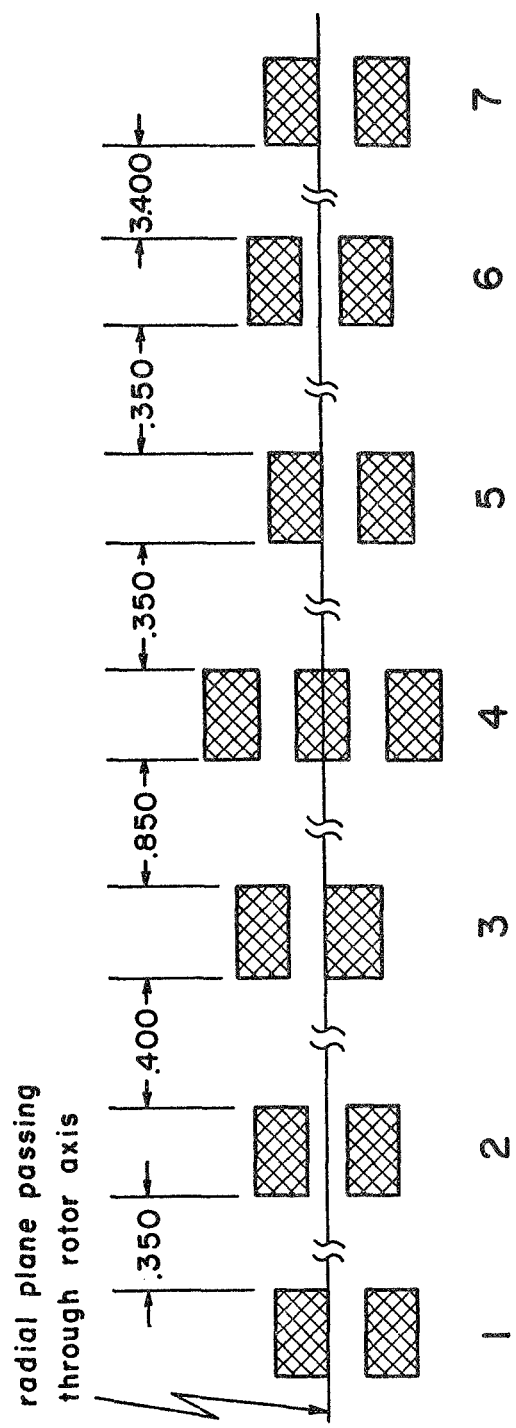


Figure 2.4. Slot phase and spacing diagram for the rotor of the seven disk dual range velocity analyzer. All dimensions are expressed in inches.

TABLE 2.2

Specifications of the Dual Range Velocity Analyzer.

Number of disks	7	
Diameter of disks	15.24 cm	
Number of slits per disk	360	
Length of slits (in radial direction)	0.635 cm	
Slit width l_1	0.051 cm	
Wall thickness between slots		
at base of slots	0.071 cm	
at top of slots	0.082 cm	
average value l_2	0.077 cm	
Average radius r	7.303 cm	
Disk thickness d	0.127 cm	
Over-all length of rotor $L + d$	15.367 cm	
L	15.240 cm	
$\beta (= d/L)$	.0083	
$\chi (= l_1/(l_1 + l_2))$	.398	
	<u>Forward</u>	<u>Reverse</u>
γ (nominal, slot base)	.1393	.0380
$ \phi $ (average)	.0526 rad	.1928 rad
γ (average)	.1328	.0362
$R (= \gamma - \beta)$	.129	.028
$\chi' (= \chi (1 - \beta/ \gamma))$	.374*	.307*
v_0 at 400 rps, $\alpha = 0$	7.3×10^5 cm/sec	2.0×10^5 cm/sec

*Assumes disks 2 and 4 do not reduce effective open time, see text.

slot, or it is tangent to a tooth. This design, the specifications of which appear in Table 2.2, possess no unwanted sidebands in either direction of rotation. However, it was a compromise because disk 2 interrupted slightly the transmitted reverse path (lowering this path's effective open time by about 25 percent) and disk 4 interrupted slightly the forward path (lowering this path's effective open time by about 15 percent). While disk 2 could have been shifted optionally one quarter slot width higher than shown in Fig. 2.4 (raising the reverse path effective open time to that shown in Table 2.2 and lowering the forward open time by an additional 25 percent without affecting sideband elimination in either direction), this option was not taken. Therefore, the selector specifications shown in Table 2.2 (using the notation of HB) reflect the characteristics of the alignment shown in Fig. 2.4, except for the ideal effective open time noted there.

The physical construction of the rotor shaft is equivalent to HB except for dimensional changes; the bearings and bearing lubrication are identical. The rotor alignment procedure and the motor-rotor connection are similar to TRR. The rotor tachometer pickup is a photodiode (GE L8F), the arrangement of which does not differ in substance from G. The photodiode feeds an oscilloscope, the output of which may be inserted into a frequency counter. The tachometer provides an independent means of checking the rotor speed.

This velocity analyzer demonstrates that high velocities (up to 10^6 cm/sec) at modest resolution (12.9 percent) and medium-to-high velocities (up to 3×10^5 cm/sec) at high resolution (2.8 percent)

can be achieved, practically, for a thin disk medium rotor length dual range selector. Grosser has demonstrated this diversity for a compact model designed for velocities up to a factor of 5 smaller and at modest resolutions (7.2 percent and 19.2 percent).

2. COARSE VELOCITY SELECTOR.

The dual range velocity selector designed for velocity selecting the molecular beam in the excitation experiment is constructed from three slotted disks mounted on a short rotating shaft (see Table 2.3), the bearings of which are elastically suspended. The disk design and the manner in which disks are phased and placed on the shaft is the resultant of an attempt to minimize transmitted light intensity and to maximize the molecular particle speed capability while minimizing beam intensity losses. The maximum selected speed ($\sim 4 \times 10^5$ cm/sec) which is limited by mechanical vibration can be attained by shaft rotation in either the forward or reverse directions with equal resolutions of 26.6 percent. The hysteresis synchronous motor (Globe Industries 75A106-2), which drives the rotor via elastic tubular connection, is controlled in the same manner as the velocity analyzer.

Like the velocity analyzer, the disks were constructed from high tensile aluminum. Unlike the analyzer disks, these disks were stacked and slotted simultaneously using the Electric-Discharge-Machining technique. This technique was chosen so that material would remain on the disk rims after slotting. The material serving as rigid spacers between slots prevents the teeth bending away from

TABLE 2.3

Specifications of the Coarse Dual Range Velocity Selector.

Number of disks	3
Diameter of disks	15.88 cm
Number of slits per disk	240
Length of slits (in radial direction)	0.635 cm
slit width l_1	0.051 cm
Wall thickness between slots	
Wall thickness at base of slots	0.132 cm
Wall thickness at top of slots	0.1487 cm
Wall thickness average value of l_2	0.1405 cm
Average radius r	7.303 cm
Disk thickness d	0.127 cm
Over-all length of rotor $L + d$	5.461 cm
L	5.334 cm
$\beta (=d/L)$	0.0238
$x (= l_1/(l_1 + l_2))$	0.2663

Primary Pass-band	Forward and Reverse
γ (nominal, slot base)	.279
$ \phi $ (average)	.026 rad
γ (average)	.266
$R (= (\gamma - \beta)/(1 - \beta^2))$	.261
$x' (= x(1 - \beta^2))$	.243
v_0 at 200 rps, $\alpha = 0$	2.52×10^5 cm/sec

their intended location. Machining more than three disks simultaneously was not possible so that all subharmonic "sidebands" are not removed. The disk specifications are shown in Table 2.3.

The unrolled graph for the resultant rotor is shown in Fig. 2.5. The design is identical for both the forward and reverse paths due to symmetry about the reference slit ($r\phi = 0$); therefore, these paths have not been distinguished separately. It is noteworthy that odd order subharmonics of the primary paths (v_0) are transmitted (v_0/n where $n = 3, 5, 7$). These subharmonics are of little concern in the excitation experiments because the transmitted number density of the spurious velocities are attenuated from the primary density roughly by the factor, $1/n$. Furthermore, the first power velocity bias of any velocity selector of this type implies that the spurious velocities are weighted an additional factor of $1/n$ compared to the primary path transmission density. The primary characteristics for this rotor appears in Table 2.3.

The rotor assembly was chemically blackened in order to reduce stray transmitted furnace light; the selector housing was blackened inside and out with Aqua Dag. All other aspects of the construction follow the velocity analyzer which has been previously discussed.

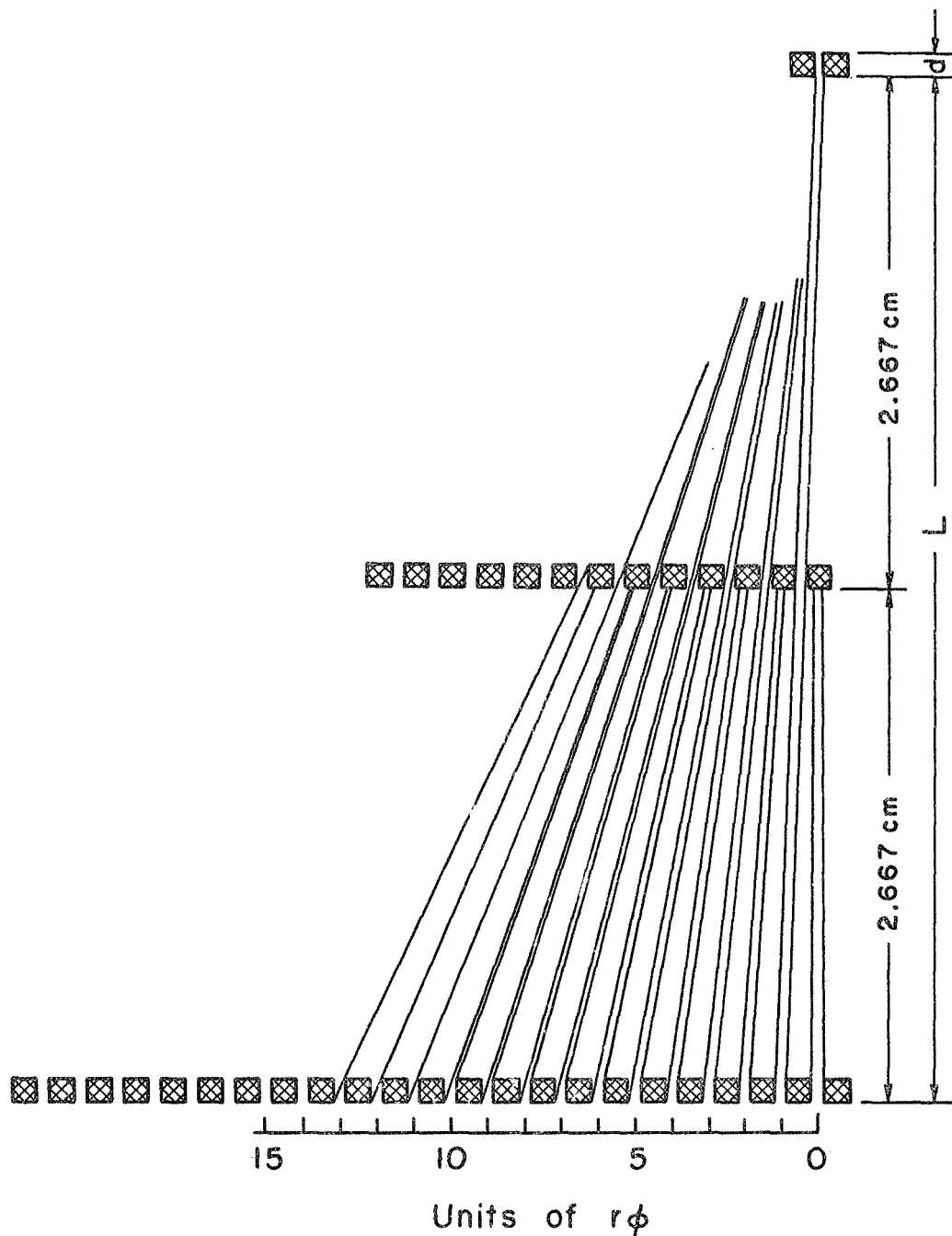


Figure 2.5. Unrolled graph for the dual range coarse velocity selector. Symmetry about the reference slot implies identical characteristics for primary and subharmonic pass-bands in either the forward or reverse direction.

G. MOLECULAR SOURCE ANALYSIS.

Beam sources operated under conditions of free molecular flow (the criterion for free molecular flow being that the mean free path for the emerging gas be of the same order of magnitude or larger than the radius of the furnace exit aperture) display Maxwell-Boltzmann velocity distributions with usually minor distortions. Sources operated under conditions violating the criterion can possess velocity distributions and perhaps internal energy distributions (the rotational possibility being most favorable), which differ from the thermal equilibrium distributions existing within the source. When performing cross beam experiments under marginal criterion source conditions, knowledge of any major velocity distribution distortions (indicative of beam thermodynamic processes) can be helpful in the interpretation of the experimental results.

The molecular beam source was operated under marginal criterion conditions throughout the excitation experiments in an effort to improve the signal-to-noise ratio. The questioning of the molecular beam properties led to the inspection of this beam's velocity distribution.

Molecular source velocity analysis is accomplished with the use of the dual range analyzer, a mechanical chopper wheel, an electron impact ionizer and quadrupole mass spectrometer, and phase lock electronics. A schematic illustration of the laboratory arrangement is presented in Fig. 2.6.

The velocity-selected beam chopper wheel is inserted before the last velocity selector disk, which is close to the ionizer. The

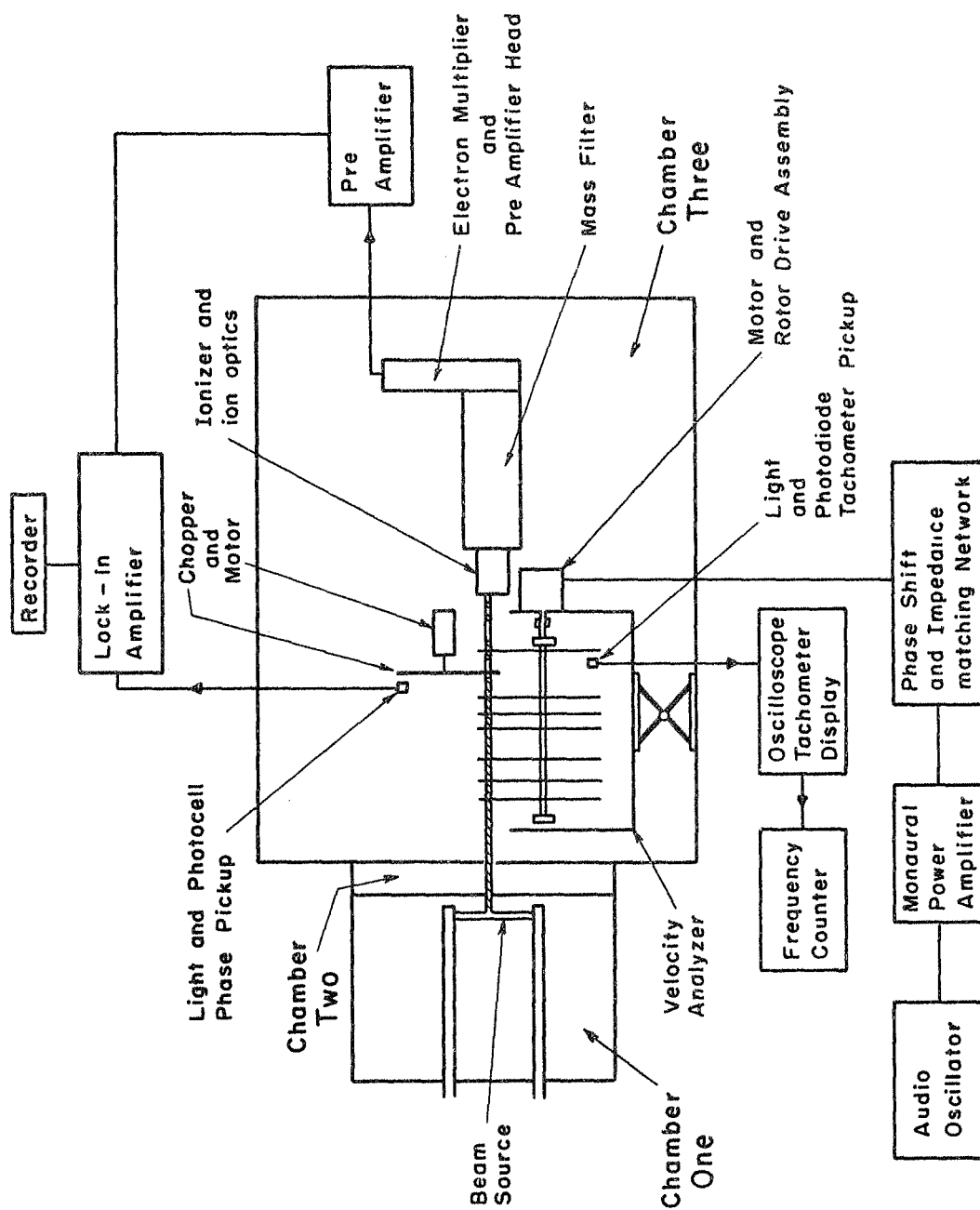


Figure 2.6. Sketch of the experimental arrangement for velocity analysis of the molecular source; a block diagram of the signal processing equipment is shown.

chopping frequency (120 Hz) and the short chopper-ionizer distance avoids appreciable phase change over the velocity range of the analyzing experiments ($0 < v_0 < 5 \times 10^5$ cm/sec). The electronic apparatus is identical to that described in the optical system and velocity analyzer sections. The ionizer, ion optics, mass filter and electron multiplier are identical to those described in Section III C of Part One.

1. PROCEDURE.

With the velocity analyzer removed from the molecular beam, gas was admitted to the molecular source which had an exit aperture of 1.5 mm. diameter. The source chamber pressure change was noted and the source number density was estimated by the method described in Section III A. The source temperature was observed by peering into the source aperture from the downstream direction with the optical pyrometer. The ionizer-mass spectrometer and phase sensitive electronics were adjusted for optimum detected signal.

The velocity analyzer was moved to its in-beam position. The velocity-analyzed beam signal was recorded versus the rotor angular speed in the 12.9 percent resolution forward direction. The angular speed was varied by adjustment of the driving audio oscillator. Knowledge of the revolutions per sec. (rps) per driving frequency, which is fixed for a given motor, enabled the rotor speed to be directly determined from the calibrated audio oscillator. The results of this method were compared with those obtained with the photo-diode tachometer. Care was exercised in determining the rotor speed corresponding to the maximum detected signal.

The voltage connections to the drive motor were changed to enable the motor to rotate in the reverse direction. The rotor speed corresponding to the maximum detected signal was noted in this direction.

For nitrogen at 2400°K the most probable rotor speeds in the forward and reverse directions were found to be 70 and 300 revolutions per sec. respectively. These values were substituted into (2.10) along with the analyzer characteristics found in Table 2.3 to determine the rotor misalignment angle, $\alpha = -.006$ radians. Relation (2.11) was used to determine the forward direction velocity calibration (2.06×10^3 cm/sec/rps). The data were recorded for three source pressures estimated to be 1, 4, and 10 Torr., which correspond to mean free paths of order 2, .5, and .2 mm. respectively.

The velocity analyzed data of the 1 and 10 Torr. runs are displayed in Fig. 2.7 along with the theoretical distribution of speeds. The 1 Torr. data closely follow the theoretical shape. A difference between this data and the 4 Torr. data was not detected. The tungsten source pressure did not exceed 4 Torr. in the excitation experiments.

The 10 Torr. data differ more significantly from the theoretical distribution. Its maximum is shifted about 1×10^4 cm/sec. to higher velocities, and the distribution is more narrow than the lower pressure data. The general observations suggest some type of kinetic cooling similar to, but far less pronounced, than is observed with nozzle type sources operating at low Mach number.

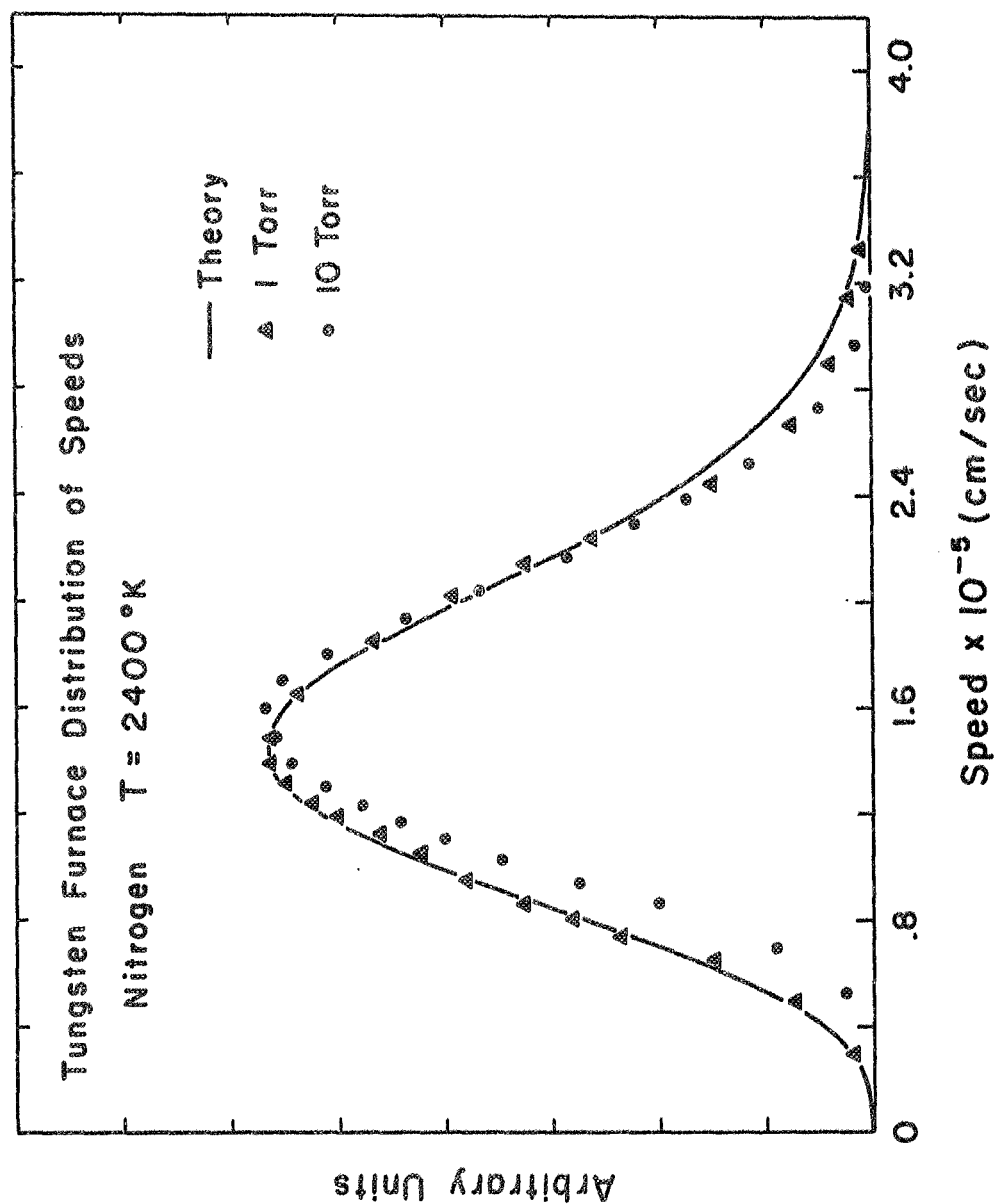


Figure 2.7. Source analysis data for nitrogen at two furnace pressures compared with the theoretical distribution of speeds; see text.

Investigations of pressure-dependent velocity distributions also were carried out for hydrogen and deuterium. No effects similar to those found for nitrogen were observed at pressures up to 10 Torr.

The theoretical distribution of velocities for nitrogen shown is calculated from a knowledge of the velocity analyzer design parameters and of the neutral detection system velocity dependence. The analytic expression for the velocity-analyzer-transmitted number density at velocity v_0 (since electron impact ionization was employed) can be written as relationship (2.13)

$$N(v_0) = \int_{v_{\min}}^{v_{\max}} B(v_0, v) I(v) dv/v \quad (2.13)$$

where $B(v_0, v)$ is the effective slitwidth (admittance) for different velocities and $I(v)$ is the velocity distribution of the incident beam. HB have derived (2.14),

$$B(v_0, v) = x' \left[1 - \frac{(1 + \beta) v_0/v - 1}{\dots} \right] \quad (2.14)$$

for $v_0 > v > v_{\min}$

and

$$B(v_0, v) = x' \left[1 + \frac{(1 - \beta) v_0/v - 1}{\dots} \right]$$

for $v_{\max} > v > v_0$

$$B(v_0, v) = 0 \text{ elsewhere}$$

$$v_{\max} = v_0 (1 - \beta)/(1 - \gamma)$$

$$v_{\min} = v_0 (1 + \beta)/(1 + \gamma)$$

χ' is the effective fractional open time to the incident beam.

$N(v_0)$ can be approximated closely by (2.15)

$$N(v_0) = \frac{I(v_0)}{v_0} \int_{v_{\min}}^{v_{\max}} B(v_0, v) dv$$

$$= \frac{\chi'}{(1 + \beta)} \ln \left[\frac{(1 + \beta)}{(1 + \gamma)} \right] + (1 - \beta) \ln \left[\frac{(1 - \beta)}{(1 - \gamma)} \right] \quad (2.15)$$

$$\times I(v_0)$$

for high-to-modest resolution selectors. The validity of this approximation has been checked for both the high and modest resolution path for nitrogen at 2400°K. This was accomplished by numerically integrating (2.13) to six significant figures. Each of the integrals $\int_{v_{\min}}^{v_0}$ and $\int_{v_0}^{v_{\max}}$ were carried out by Gaussian Quadrature ($n = 5$) for $\beta = 8.3 \times 10^{-3}$, $f = .1393$, $r = 3.62 \times 10^{-2}$ on the IBM 7090 computer. Some results of $N(v_0)/\chi'$ are displayed in Table 2.4 where exact and approximate solutions are compared. The agreement is excellent in the regime of interest even for the modest resolution path.

TABLE 2.4

Calculated Number Density Transmission of the Dual Range Analyzing Velocity
Selector for a Maxwell-Boltzmann Nitrogen Distribution (2400°K).

Velocity (cm/sec) $\times 10^{-5}$	Forward $N(v_0)/x'$		Reverse $N(v_0)/x'$	
	Approximate (2.15)	Exact	Approximate (2.15)	Exact
.2	.1298 $\times 10^{-2}$	.1325 $\times 10^{-2}$	.2244 $\times 10^{-3}$	.2247 $\times 10^{-3}$
.6	.2795 $\times 10^{-1}$	.2833 $\times 10^{-1}$	.4832 $\times 10^{-2}$	.4836 $\times 10^{-2}$
1.0	.8231 $\times 10^{-1}$	.8238 $\times 10^{-1}$	.1423 $\times 10^{-1}$	.1423 $\times 10^{-1}$
1.4	.1146	.1131	.1981 $\times 10^{-1}$	.1980 $\times 10^{-1}$
1.8	.9857 $\times 10^{-1}$	.9623 $\times 10^{-1}$	.1704 $\times 10^{-1}$	.1702 $\times 10^{-1}$
2.2	.5809 $\times 10^{-1}$	.5672 $\times 10^{-1}$	.1004 $\times 10^{-1}$	.1002 $\times 10^{-1}$
2.6	.2469 $\times 10^{-1}$	.2456 $\times 10^{-1}$	.4268 $\times 10^{-2}$	.4264 $\times 10^{-2}$
3.0	.7787 $\times 10^{-2}$	.8111 $\times 10^{-2}$	.1346 $\times 10^{-2}$	.1357 $\times 10^{-2}$
3.4	.1857 $\times 10^{-2}$	.2097 $\times 10^{-2}$	.3210 $\times 10^{-3}$	.3224 $\times 10^{-3}$
3.8	.3386 $\times 10^{-3}$	.4332 $\times 10^{-3}$	.5854 $\times 10^{-4}$	.5916 $\times 10^{-4}$

IV. EXPERIMENTAL PROCEDURE.

A. BASIC CONFIGURATION.

The cross beam sodium oven temperatures were set and permitted to stabilize for an hour. The tungsten oven was turned on and its temperature was permitted briefly to stabilize. Following this period, the molecular gas pressure in the source was brought to its operating level (~ 4 Torr), and upon rapid stabilization, the furnace temperature was measured using the optical pyrometer looking into the furnace aperture. The resonantly scattered furnace light signal was noted. Since the reactive signal was conventionally between two and three orders of magnitude smaller than this signal, the noted signal is really the resonant signal (the temperature was measured with gas admitted because cooling of order 30°C can be observed between 2000 and 3000°K).

The molecular gas was turned off. The absorption cell was heated to its temperature, resulting in a drop of the scattered light signal. The tungsten furnace temperature was adjusted between the highest and lowest values at which data were recorded in order to be assured that the signal observed with the beam off gave a common signal zero. Gas was then admitted to the furnace and the signal rise due to reaction was noted for the particular furnace temperature. Following observation of the signal for 15 min. at a 100 sec. lock-in amplifier integration time constant, the gas was turned off and the pressure change in the experimental vacuum chamber was noted. From the pumping speed for the molecular beam gas (obtained

from a separate measurement of the pressure time-constant of the system) and the pressure change on admission of the beam, the molecular beam current was obtained. The molecular furnace temperature was adjusted to a second temperature and the reactive signal was measured in like manner. After recording all desired data, the absorption cell was cooled and the ratio of the reactive signal to the resonant light signal was checked at the first temperature. This entire procedure was repeated at least three times for all experimental temperatures.

These procedures provide sufficient data to determine the excitation rate constant at all temperatures for N_2 . In the case of H_2 and D_2 an additional procedure was appended, since here the flux of molecules leaving the furnace is not constant with temperature as was the verified situation for nitrogen. The hydrogen molecular beam fluxes are temperature dependent because of thermal dissociation. It became necessary to measure the dissociation fraction at each temperature for these molecules so that number densities at which dissociation occurs could be inferred using the number densities at which dissociation does not occur.

For this purpose the optical equipment was disabled and the molecular beam was chopped. A quadrupole mass spectrometer coaxial with the molecular beam was activated and the operating molecular beam was brought to the intensity used for studying the excitation processes. The spectrometer signals (proportional to number density) for masses two and four were recorded as a function of temperature between $1800^\circ K$ and $2800^\circ K$ (holding the molecular gas flow rate constant)

when the gas admitted to the furnace was H_2 and D_2 respectively. Since there was essentially no dissociation of these species at $2000^\circ K$, the pressure rise in Chamber Three due to the molecular beam being turned on gives the correct molecular number density at that temperature. With knowledge of the spectrometer signals at various temperatures relative to the signal at $2000^\circ K$, the rate constants at the other temperatures could be determined. Other specific details are discussed with the data in Section V.

Due to the fact that H_2 and D_2 dissociate significantly near $2600^\circ K$ at furnace pressures of several Torr., it was necessary to verify that the excitation signals were, in fact, not due to the conversion of relative kinetic energy and electronic energy via atom-atom collisions. For this exercise, the tungsten furnace temperature was held constant and the molecular pressure inside the furnace was increased. Since the dissociation fraction (i.e. relative amounts of H and H_2) can be made to vary substantially by this exercise, observation of the change in dissociation fraction is a test for the predominance of either an atomic or molecular excitation mechanism. In the performance of this test while the temperature was $2800^\circ K$ and the molecular pressure was reduced so that the predominant beam component was atomic hydrogen of typical number density, no excitation signals were observed. When the furnace pressures were high (molecular hydrogen predominance), the excitation signals increased proportionally as the molecular number density. Since the signals followed the changes in molecular number density and not those of the atomic constituent, the measured signals are due to the atom-molecule inter-

action.

An additional test was performed concerning the observability of an atom-atom excitation mechanism using beam intensities comparable to those used for atom-molecule excitation. In this test, only helium gas was introduced into the molecular furnace and no excitation signals were observed.

B. VELOCITY-SELECTED CONFIGURATION.

The primary beam velocity selector was first velocity-calibrated with the sodium beam disabled, the mass spectrometer activated, and the Chamber Two chopper wheel operating, following a procedure identical to that discussed in Section III G. The dual range calibration method was performed at room temperature and checked at 2600°K for nitrogen. The verified selector characteristics appearing in Table 2.3 were utilized in this procedure. The velocity selector was kept in its calibrated in-beam position throughout experimental runs. With the apparatus required for velocity calibration disabled, the sodium cross beam source was activated according to the procedure previously discussed. With the tungsten furnace and the sodium source temperature stabilized, the velocity selector was adjusted for a particular rotational speed and the phase sensitive signal was measured when no gas was being admitted to the molecular furnace. This was continued for every rotational speed at which data would later be recorded. Molecular gas was then admitted to the furnace, at the appropriate pressure (4 Torr.) and the signals for each of the previous selector rotational speeds was recorded using an

integration time constant of 30 sec. for 10 min./point.

Every two or three points, the rotational speed was brought back to an arbitrary reference speed for the purpose of verifying constancy of the experimental conditions throughout the time period required to gather these data. For nitrogen, velocity contours were taken at 2600°K and 2900°K; for hydrogen and deuterium, 2600°K was the only molecular beam temperature.

Following this data collection, in a separate measurement the signals for each species were studied relative to one another at an arbitrarily chosen velocity selector speed where all three signals were observable. Having obtained the three signals, the velocity selector was lowered out of the beam and the relative number densities for the respective beams were determined via the mass spectrometer procedures utilized in the basic configuration. Knowledge of the signals relative to each other enabled all velocity signals to be plotted on the same arbitrary experimental scale.

V. RESULTS.

The temperature dependent effective rate constants determined with the basic configuration for H_2 , D_2 and N_2 are shown in Fig. 2.8. Referring to Fig. 2.8, the ordinate n defined by (2.16) is the rate constant for molecules having sufficient energy to react.

$$n(T_1) \equiv k_r(T_1, T_2 = 650^\circ K) e^{E_0/kT_1} \quad (2.16)$$

k_r is the conventionally defined reaction rate constant displayed in (2.4). E_0 ($= 2.10$ ev.) is the required energy for excitation. T_1 is the molecular furnace temperature. This definition has been chosen for the purpose of displaying a temperature dependence that is more abated than that of $k_r(T_1)$.

The excitation rate for N_2 was determined absolutely at $2200^\circ K$ using the procedure of comparing reactive signals with resonantly scattered furnace light signals as described in Sections IIA and IVA. This determination is appropriate to the assumptions that (a) all beam molecules entering the experimental chamber (and passing through the target atoms) also leave via that chamber's diffusion pump; (b) the light produced in particle collisions is isotropically distributed (the angular distribution of the resonantly scattered light is only 2 percent non-isotropic²⁰ and this correction was not made in treating the data); (c) the $Na(3^2P)$ lifetime is known.²¹ Since the ionization gauge was calibrated against a McLeod gauge for this gas, the absolute calibration carried out at $2200^\circ K$ only depends further on three factors: the repeatability of the ionization gauge in measuring an absolute Chamber

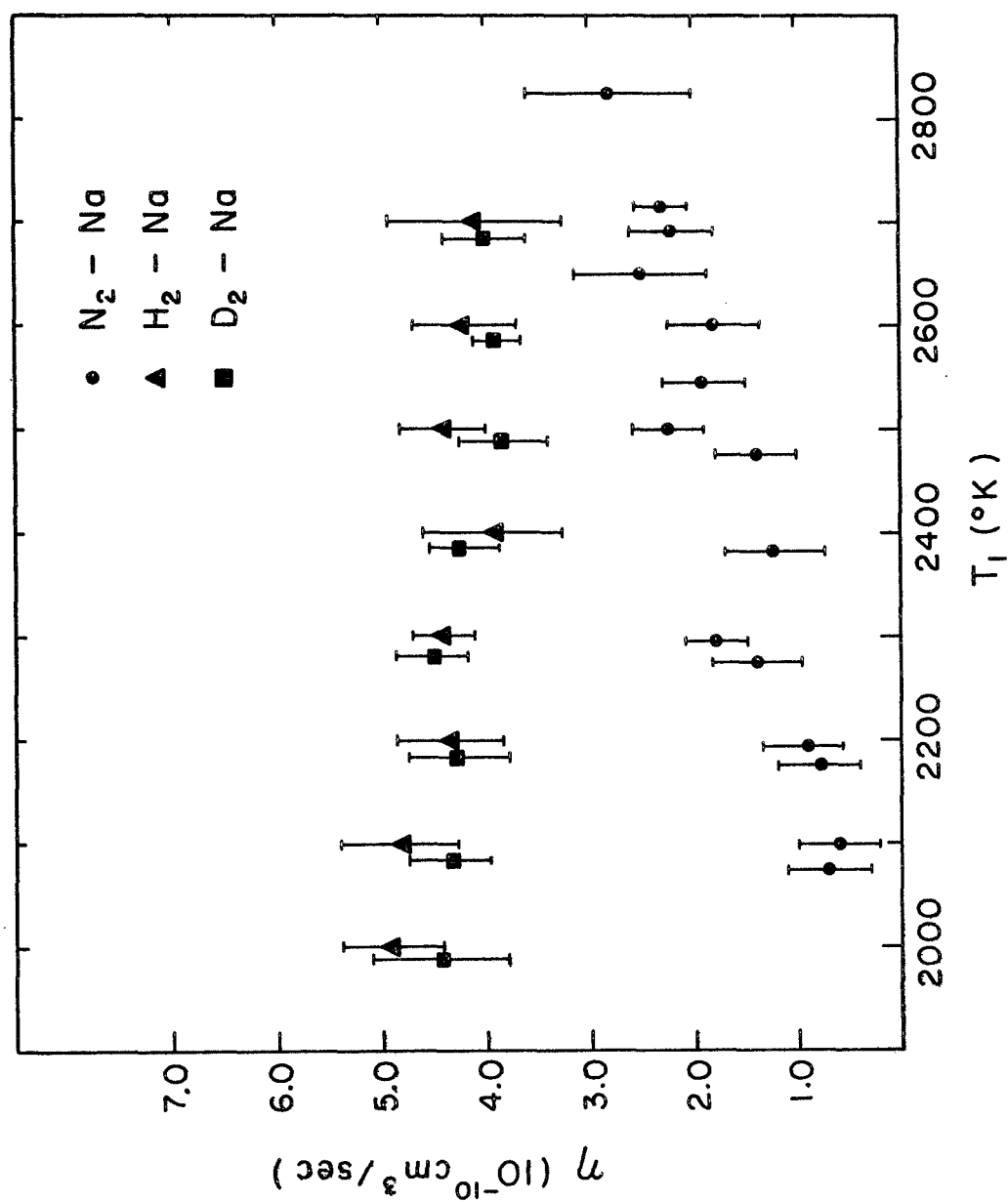


Figure 2.8. Basic configuration effective rate constants for $\text{Na}(3^2\text{P})$ excitation transfer from H_2 , D_2 and N_2 at temperature T_1 .

Three pressure change, the determination of that chamber's diffusion pumping speed (Section IIIA), and measured primary beam geometry (Appendix 2A).

The absolute rates for H_2 and D_2 were determined by comparing the reactive signals for these gases with the N_2 signal at $2200^\circ K$. These determinations carry additional assumptions that (a) the ionization gauge relative efficiency factors are known (N_2 is more efficiently detected than H_2 and D_2 by a factor of 2.4), and (b) the diffusion pumping speeds for H_2 and D_2 relative to N_2 are related by the inverse square root of the mass ratios (correct to first order, see Section IIIA).

The rate constants at temperatures other than $2200^\circ K$ were determined for each gas from relative measurements of that gas with respect to $2200^\circ K$. All quoted error bars in Fig. 2.8 refer solely to the reproducibility of data at each point; their magnitude corresponds to mean deviation of the average signals displayed on the chart recorder output. (The mean deviation of chart recorder signals about the average for different experimental runs was usually large compared with the mean deviation of averaged signals in one run.)

The velocity-selected signals obtained for H_2 and D_2 at $2600^\circ K$ are displayed in Fig. 2.9; those for N_2 at 2600 and $2900^\circ K$ are shown in Fig. 2.10. The abscissa of each, V_0 , is the nominal laboratory speed of molecules prior to excitation collisions. It is noteworthy that the data of both figures are plotted using the same arbitrary units for signal. The respective signals were adjusted to the same scales as a result of taking relative velocity measurements at $V_0 = 3 \times 10^5$ cm/sec and measuring the relative molecular beam densities

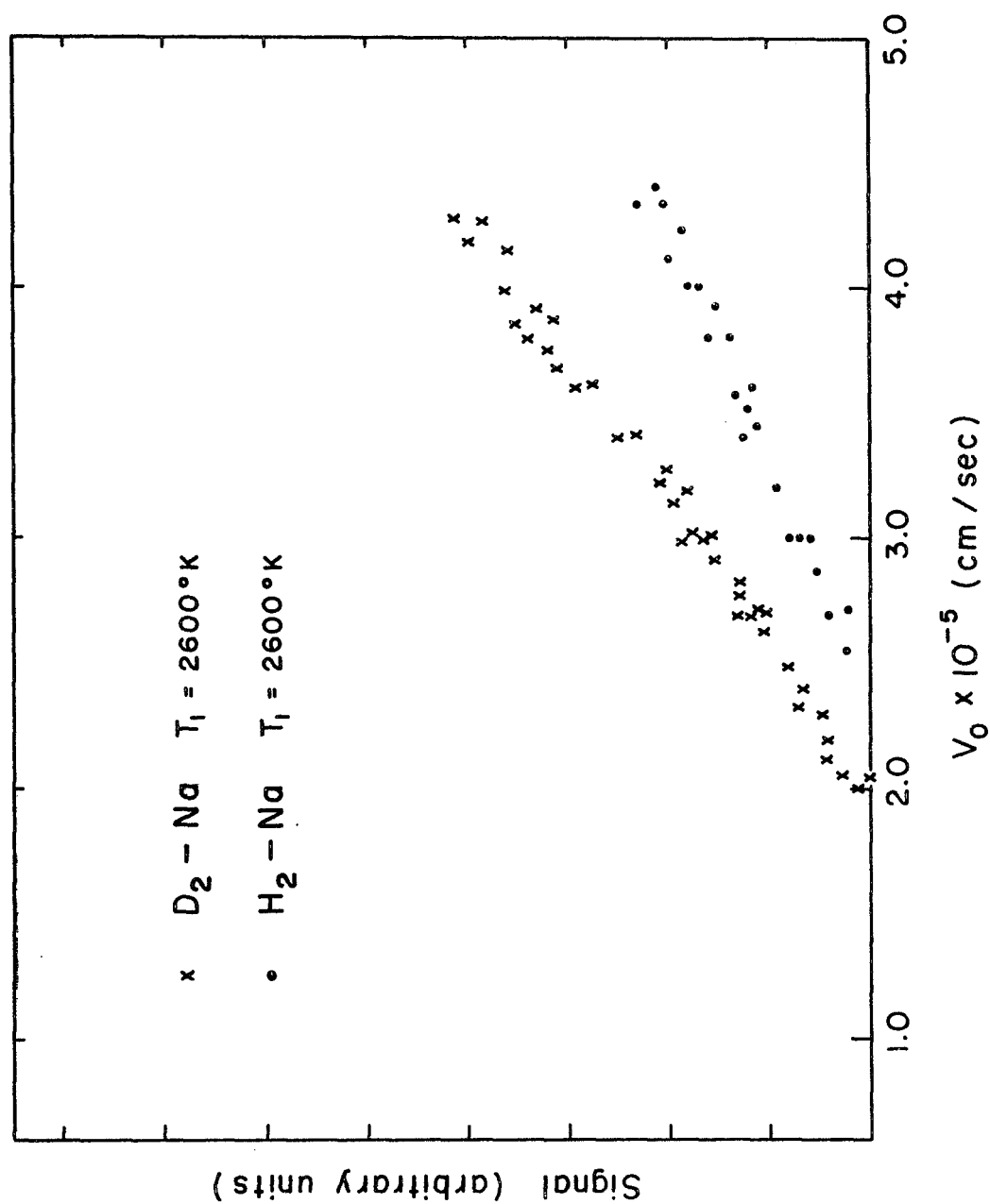


Figure 2.9. $Na(3^2P)$ signals measured for velocity-selected H_2 and D_2 at $2600^\circ K$.

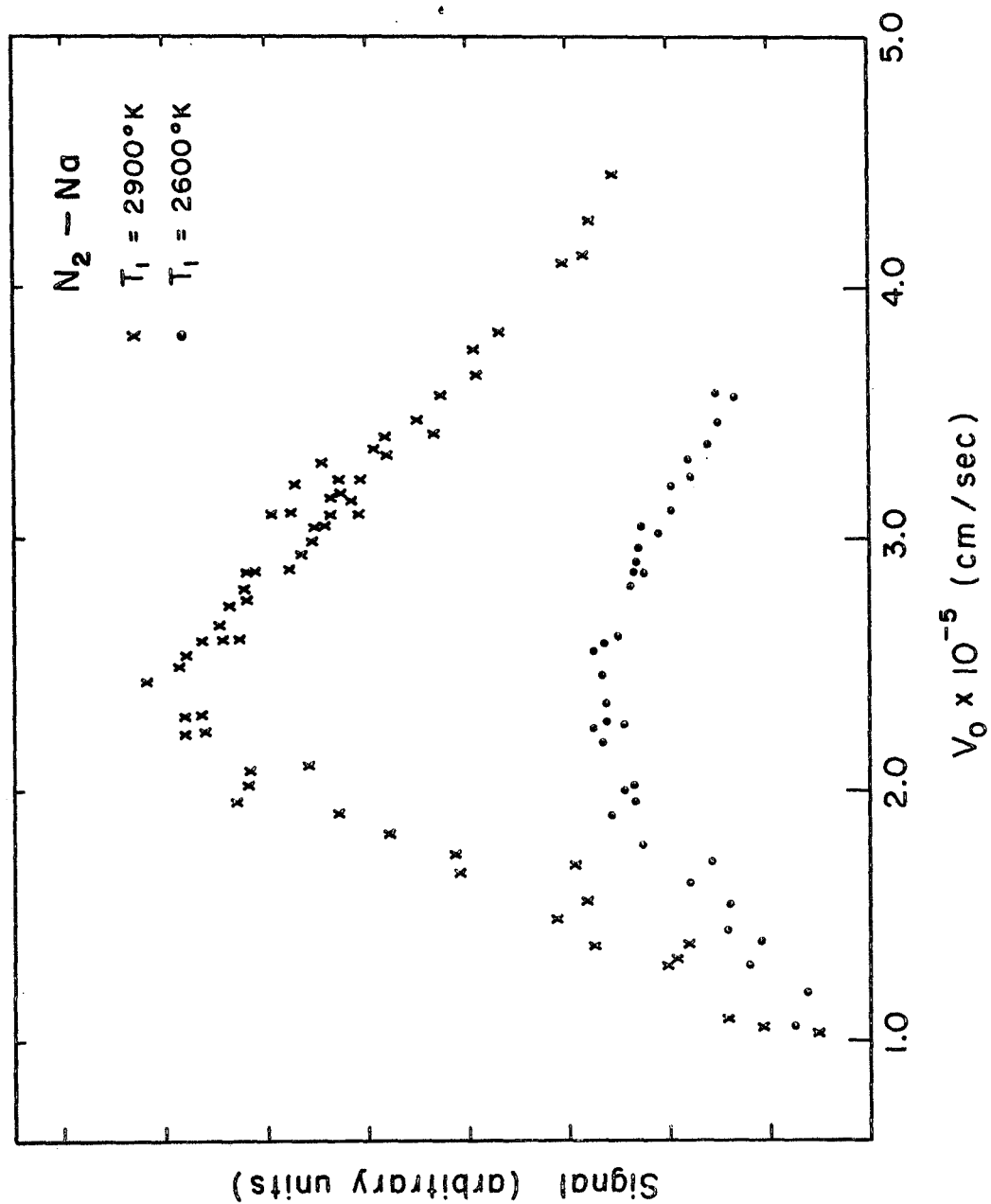


Figure 2.10. $Na(3^2P)$ signals measured for velocity-selected N_2 at 2600 and 2900 K.

without velocity selection. Similarly, as in the basic configuration, the relative scaling is known only to within the same relative pressure gauge efficiency factors and diffusion pumping speeds. These signals, like those of the preceding experiment are displayed without the mean deviations of signal for a given experimental run.

The results of these experiments have been analyzed assuming that vibrational energy and the kinetic energy of collision are the sole sources of excitation energy. If one also assumes the effective cross section is given by (2.17), it is shown in Appendix 2D that the basic and velocity-selected experimental yields are given by (2.18) and (2.19) respectively.

$$\sigma(\epsilon, v_r) = \sum_v \sum_{v'} \sigma_{v,v'} R_{\Delta v}(v_r) \delta(\epsilon - \epsilon_v) \quad (2.17)$$

$\sigma_{v,v'} R_{\Delta v}(v_r)$ is a velocity-dependent excitation cross section for molecules in vibrational state v averaged over the rotational energy distribution being de-excited to vibrational state v' after collision.

$\sigma_{v,v'}$ is a constant and its magnitude represents the cross section maximum value. $R_{\Delta v}(v_r)$, which represents the velocity dependence of the cross section, has the value 1 where the cross section is maximum. $R_{\Delta v}(v_r)$ is identical for fixed $\Delta v (= v - v')$ when vibrational energies are given in the simple harmonic approximation. $\delta(\epsilon - \epsilon_v)$ is a delta function with vibrational energy argument.

In the basic experiment the rate coefficient η is given by

$$\eta(T_1) = \sum_v \sum_{v'} \sigma_{v,v'} \alpha_{v,v'}(T_1) \equiv \sum_{\Delta v=0}^{\infty} a_{\Delta v}(T_1) \alpha_{\Delta v,0}(T_1) \quad (2.18)$$

where $\alpha_{v,v'}(T_1) = e^{E_0/kT_1} \left\{ P_{\Delta v}(T_1) \frac{e^{-\epsilon_v/kT_1}}{\sum_{\text{all } v} e^{-\epsilon_v/kT_1}} \right\}$ and

$$P_{\Delta v}(T_1) = \int_{v_1=0}^{\infty} \int_{v_2=0}^{\infty} R_{\Delta v}(v_r) v_r f(\vec{v}_1) f(\vec{v}_2) dv_1 dv_2. \quad \text{The signals in}$$

the velocity-selected experiment are given by

$$S(V_0, T_1) = K' \sum_v \sum_{v'} \alpha_{v,v'} \beta_{v,v'}(V_0, T_1) \quad (2.19)$$

$$= K' \sum_{\Delta v=0}^m a_{\Delta v}(T_1) \beta_{\Delta v,0}(V_0, T_1)$$

where $\beta_{v,v'}(V_0, T_1) = Q_{\Delta v}(V_0, T_1) \frac{e^{-\epsilon_v/kT_1}}{\sum_{\text{all } v} e^{-\epsilon_v/kT_1}}$ and

$$Q_{\Delta v}(V_0, T_1) = \int_{v_1=0}^{\infty} \int_{v_2=0}^{\infty} B(V_0, v_1) R_{\Delta v}(v_r) v_r f(\vec{v}_1) f(\vec{v}_2) dv_1 dv_2$$

$$a_{\Delta v}(T_1) \equiv \sigma_{\Delta v,0} + \sigma_{\Delta v+1,1} e^{-\epsilon_{\Delta v=1}/kT_1} + \sigma_{\Delta v+2,2} e^{-\epsilon_{\Delta v=2}/kT_1} + \dots$$

$$\Delta v = 1, \dots, m \quad (2.20)$$

m is the smallest number of vibrational quanta required for excitation by pure vibrational energy transfer.

The experimental rate of the basic configuration displayed in Fig. 2.8 is equal to the superposition of the rate constants $\alpha_{v,v'} \alpha_{v,v'}(T_1)$ in (2.18) for molecules having initial and final states v and v' and having sufficient energy to react. The conventionally defined rate constant, $\alpha_{v,v'} e^{-E_0/kT_1}$, is composed of a kinetic factor $P_{\Delta v}(T_1)$

which depends on $R_{\Delta v}(v_r)$ and the Maxwellian velocity distribution function of the crossed beams.

The velocity-selected signals displayed in Fig. 2.9 and 2.10 are proportional to the superposition of the velocity-selected rate constants $\sigma_{v,v'}$, $\beta_{v,v'}$, (V_0 , T_1) in (2.19) via an unknown constant proportionality factor K . Component rates $\sigma_{v,v'}$, $\beta_{v,v'}$, depend on the nominal laboratory velocity, V_0 , of the molecules as well as on T_1 because $Q_{\Delta v}(V_0, T_1)$, the analogue of $P_{\Delta v}(T_1)$, additionally contains the velocity selector pass-band function.

The alternate way of expressing the experimental yields in (2.18) and (2.19) involving (2.20) emphasizes the fact that if $\sigma_{\Delta v,0} = \sigma_{\Delta v+i,i}$ for all i , the predominant rate measured in either experiment for fixed Δv is that corresponding to complete vibrational de-excitation after collision, $\sigma_{\Delta v,0}(T_1)$. The possible predominance of one rate $\sigma_{\Delta v,0}(T_1)$ $\beta_{\Delta v,0}(V_0, T_1)$

in list (2.20) is helpful in analysis.

The fact that rate constants for the velocity-selected configuration depend on the laboratory speeds of the molecules with excitation rates for pure vibrational energy transfer predominating at small V_0 ($\Delta v=m$) and excitation rates for pure kinetic energy transfer predominating for high V_0 ($\Delta v = 0$) suggests that this experiment is capable of determining the relative rates for different Δv . Substitution of the relative rates determined via (2.19) into (2.18) enables absolute determination of cross sections.

If $\eta(T_1)$ and $S(V_0, T_1)$ are determined experimentally at a variety of temperatures, and at one temperature for a variety of velocity selector

speeds V_0 respectively, then equations (2.18) and (2.19) suggest the following recipe for extracting a limited number of $\sigma_{v,v'}$ from these data.

- (A). Assume a functional form for $R_{\Delta v}(v_r)$ and calculate the functions $\beta_{\Delta v,0}$ for all appropriate Δv and one temperature, $T_1^{(1)}$.
- (B). Owing to the fact that $\beta_{\Delta v,0}(V_0, T_1^{(1)})$ differ greatly for different Δv (demonstrated in Appendix 2D.2) a unique superposition of the $\beta_{\Delta v,0}$ can explain $S(V_0, T_1^{(1)})$. By fitting find the ratio $a_m(T_1^{(1)}): a_{m-1}(T_1^{(1)}) \dots a_0(T_1^{(1)})$ which explains $S(V_0, T_1^{(1)})$.
- (C). Calculate the $\alpha_{v,v'}(T_1)$ at $T_1^{(2)}$ and at least another temperature, $T_1^{(3)}$. Compare the calculated temperature dependences $u = \alpha_{v,v'}(T_1^{(3)})/\alpha_{v,v'}(T_1^{(2)})$, with that measured $\eta(T_1^{(3)})/\eta(T_1^{(2)})$ and arbitrarily select only one $\sigma_{v,v'}$ for each fixed Δv that appears in the long list (2.20) which together explain the temperature dependence. Knowing the ratios of the $a_{\Delta v}(T_1^{(1)})$ $\Delta v = 0 \dots m$, determine the ratios of these $\sigma_{v,v'}$, which form a set of cross sections consistent with the temperature data.
- (D). If velocity data are available at a second temperature $(T_1^{(4)})$, then substitute the $\sigma_{v,v'}$ determined in (C) into (2.19) and calculate $S(V_0, T_1^{(4)})$. $S(V_0, T_1^{(4)})$ should agree with the experimental data if the $\sigma_{v,v'}$ guessed in (C) are consistent with the data of both experiments.
- (E). When a set of predominant terms in equation (2.20) are capable of explaining all data consistently, determine the absolute values for the selected $\sigma_{v,v'}$ using (2.18)

and the absolute rate data in Fig. 2.8.

This prescription has been applied using the two different assumed $R_{\Delta v}(v_r)$ appearing below. $E(\equiv 1/2 \mu v_r^2)$ is the relative kinetic energy. $E_t(\geq 0)$ is the minimum relative kinetic energy required for reaction.

$$\begin{aligned} R_{\Delta v}(v_r) &= 1 & E &\geq E_t \\ &= 0 & E &< E_t \end{aligned} \quad (2.21)$$

$$\begin{aligned} R_{\Delta v}(v_r) &= 1 - E_t/E & E &\geq E_t \\ &= 0 & E &< E_t \end{aligned} \quad (2.22)$$

where $E_t = E_0 - (\epsilon_v - \epsilon_{v'})$ when $E_0 - (\epsilon_v - \epsilon_{v'}) \geq 0$

$E_t = 0$ when $E_0 - (\epsilon_v - \epsilon_{v'}) < 0$

Energy dependences (2.21) and (2.22) are consistent through detailed balance arguments with the results of $\text{Na}(3^2\text{P})$ quenching experiments carried out in high and low temperature environments. (Refer to Appendix 2D for these arguments). While there appears to be more justification for (2.22) in the case of N_2 , D_2 and H_2 , (2.21) also has been utilized to estimate the sensitivity of the analysis on functional form of the excitation function.

Armed with these procedures, one finds it necessary only to specify the vibrational energy levels ϵ_v before carrying out the required calculations. These levels for the $X^1\Sigma_g^+$ states of H_2 , D_2 and N_2 are well known from recent spectroscopic data of Herzberg

TABLE 2.5

 $X \ ^1\Sigma_g^+$ VIBRATIONAL ENERGY LEVELS.

<u>v</u>	H ₂ Energy (e.v.)	D ₂ Energy (e.v)	N ₂ Energy (e.v.)
0	0.0	0.0	0.0
1	.516	.371	.289
2	1.002	.727	.574
3	1.460	1.069	.856
4	1.890	1.396	1.134
5	2.292	1.710	1.408
6	2.666	2.009	1.680
7	3.011	2.294	1.947
8	3.326	2.565	2.211
9	3.610	2.822	2.471
10	3.861	3.065	2.728
11	4.076	3.292	2.981
12	4.252	3.505	3.230
13	4.382	3.702	3.476
14	4.459	3.882	3.718
15		4.044	3.957
16		4.188	4.191
17		4.311	4.423
18		4.412	4.650
19		4.489	4.874
20		4.536	5.094
21		4.550	5.310

and Howe²², Takezawa, Innes, and Tanaka²³, and Wallace²⁴ respectively; a listing of the levels appears in Table 2.5. Readily apparent from this listing is the fact that pure vibrational transfer for H_2 , D_2 and N_2 requires 5, 7, and 8 quanta respectively. If fewer than these number of quanta participate in reaction, kinetic energy must assist since rotational energy is being ignored. Also neglected is the possibility of any bona fide reaction activation energies. These are the maximum number of kinetic functions ($P_{\Delta v}$ and $Q_{\Delta v}$) that must be calculated.

When steps (A) and (B) are carried out using energy dependence (2.21) for H_2 and D_2 at 2600°K, the measured velocity data can be fitted, as shown in Fig. 2.11. For these molecules, the data (with error bars assigned) are only sufficient to verify the participation of pure internal energy and a limited amount of kinetic energy going into reaction. The calculated signal for H_2 is understood to be the superposition of 4 and 5 vibrational quanta transfers ($a_5 : a_4 = 1 : 1/10$); for D_2 , 5, 6 and 7 quanta transfers are taking place ($a_7 : a_6 : a_5 = 1 : 1/5 : 1/50$). The fitted data using energy dependence (2.22) are shown in Fig. 2.12 (H_2 , $a_5 : a_4 = 1 : 1$; D_2 , $a_7 : a_6 : a_5 = 1 : 1/2 : 1/4$). Inability to detect larger amounts of kinetic energy is due to the fact that the velocity selector could not be operated at higher velocities, if in fact the contribution of larger amounts of kinetic energy is possible.

In the case of N_2 where the reduced mass is considerably larger, the velocity data are sufficient to demonstrate that excitation can still occur when only about half of the excitation energy

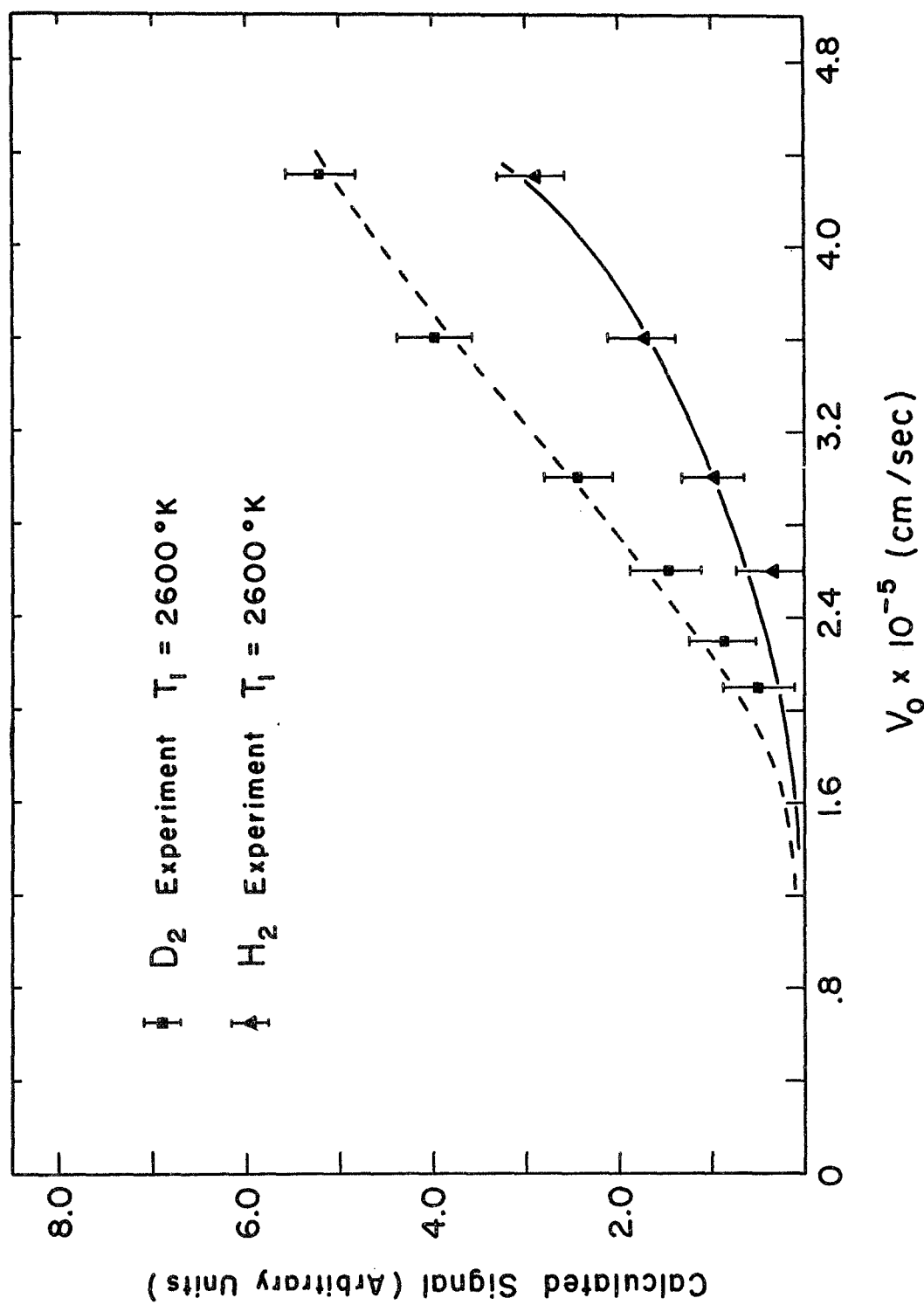


Figure 2.11. Comparison of H_2 and D_2 experimental data with signals calculated assuming a cross section velocity dependence (2.21) for all participating vibrational states; see text.

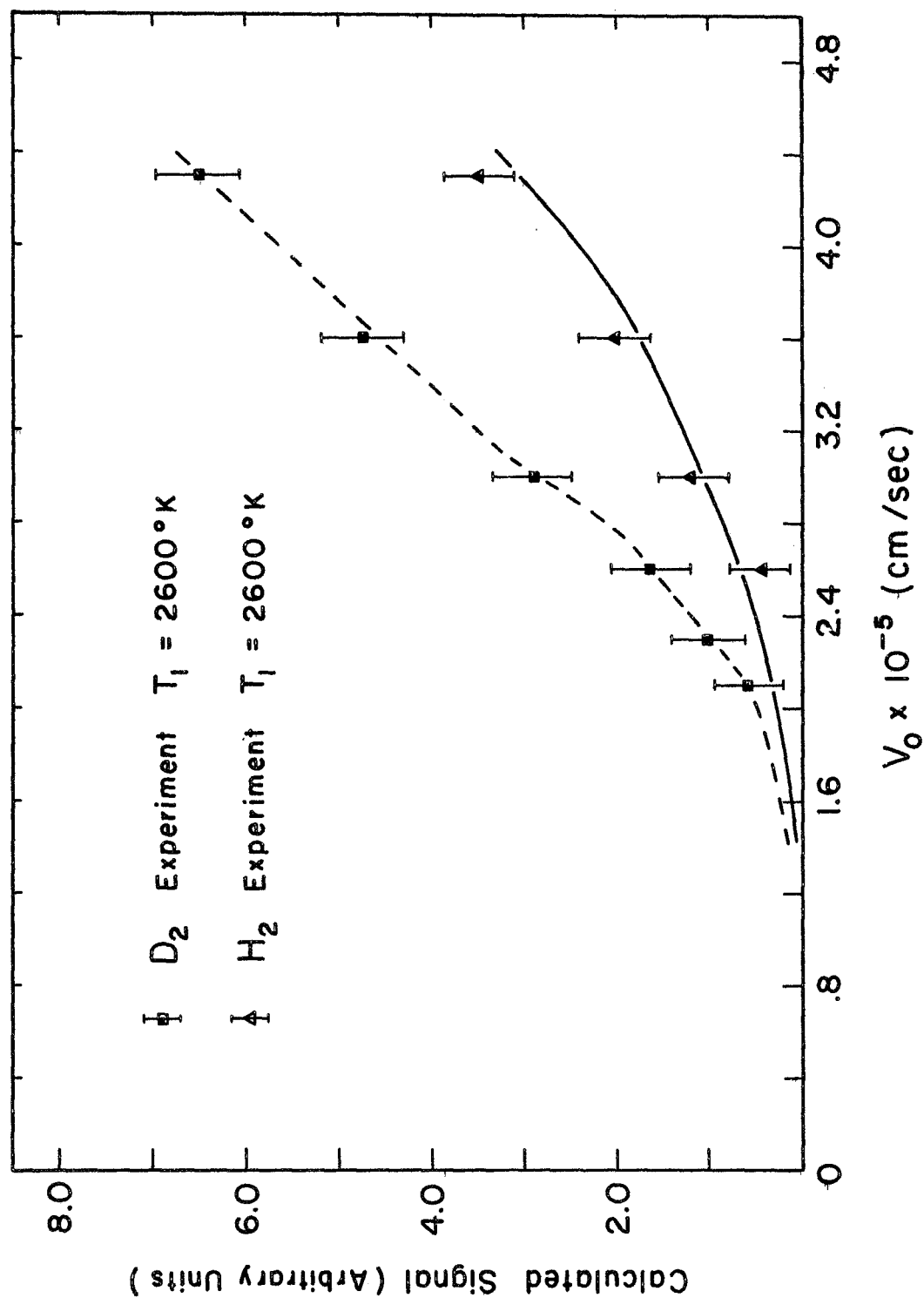


Figure 2.12. Comparison of H_2 and D_2 experimental data with signals calculated assuming a cross section² velocity dependence (2.22) for all participating vibrational states; see text.

comes from internal energy (4 quanta transferred). Like the hydrogen isotopes, multiple quanta transfers up to pure vibrational transfer have been observed. In the case of energy dependence (2.21), when the 2900°K data are fitted using $a_8 : a_7 : a_6 : a_5 : a_4 = 1/2 : 1 : 1 : 1 : 1$, one obtains the 2900°K curve in Fig. 2.13. The fit at this temperature for (2.22) using $a_8 : a_7 : a_6 : a_5 : a_4 = 1/5 : 1/2 : 1 : 1 : 3$ is shown in Fig. 2.14.

It is noteworthy that the experimental data of Fig. 2.13 and Fig. 2.14 like those of Fig. 2.11 and Fig. 2.12 for H_2 and D_2 represent the signals due purely to the primary velocity selector pass-band. In the case of H_2 and D_2 , secondary contributions are negligible and no corrections have been applied to the data. For N_2 , secondary contributions have been removed from the data appearing in Fig. 2.10 (i.e. Fig. 2.13 and Fig. 2.14 represent $S(V_0, T_1) - S(V_0/3, T_1)/9$). A discussion of secondary velocity selector characteristics appears in Section IIIF.

Proceeding to step (C), if one calculates the $\alpha_{v,v'}(T_1)$ at many temperatures in the experimental range examined for any of the species, then it is evident that the $\alpha_{v,v'}(T_1)$ depend essentially linearly on T_1 in the range $2000 \leq T_1 \leq 2800^\circ K$. One can adequately summarize the results of these calculations by specifying the magnitude of the $\alpha_{v,v'}$ at one temperature and presenting the ratio $u = \alpha_{v,v'}(T_1^{(3)}) / \alpha_{v,v'}(T_1^{(2)})$ at two different temperatures as noted in (C). The results for H_2 , D_2 and N_2 using (2.21) appear in Tables 2.6, 2.7 and 2.8 respectively; those using (2.22) appear in Tables 2.9, 2.10 and 2.11.

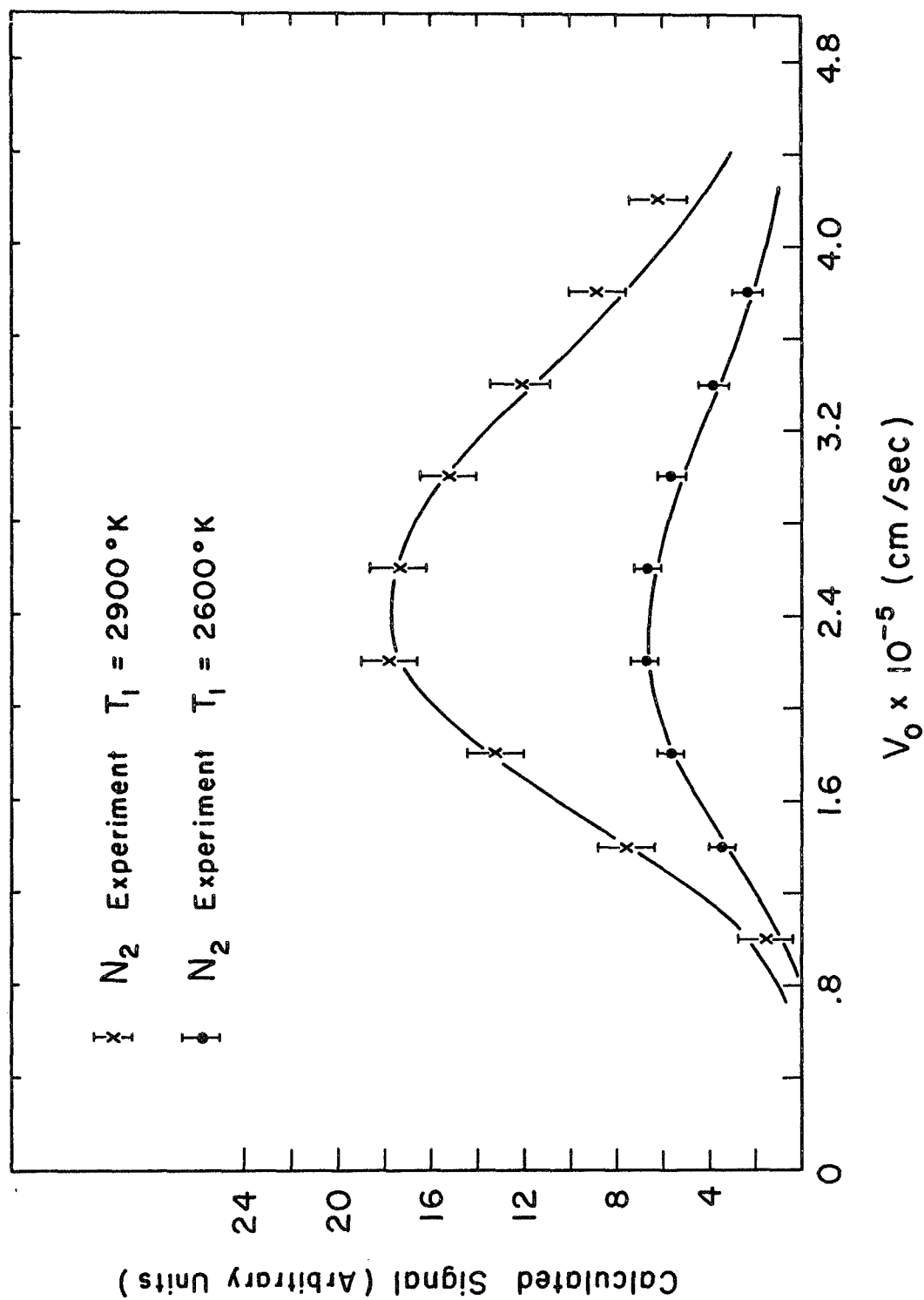


Figure 2.13. Comparison of N_2 experimental data with signals calculated assuming a cross section velocity dependence (2.21) for all participating vibrational states; see text.

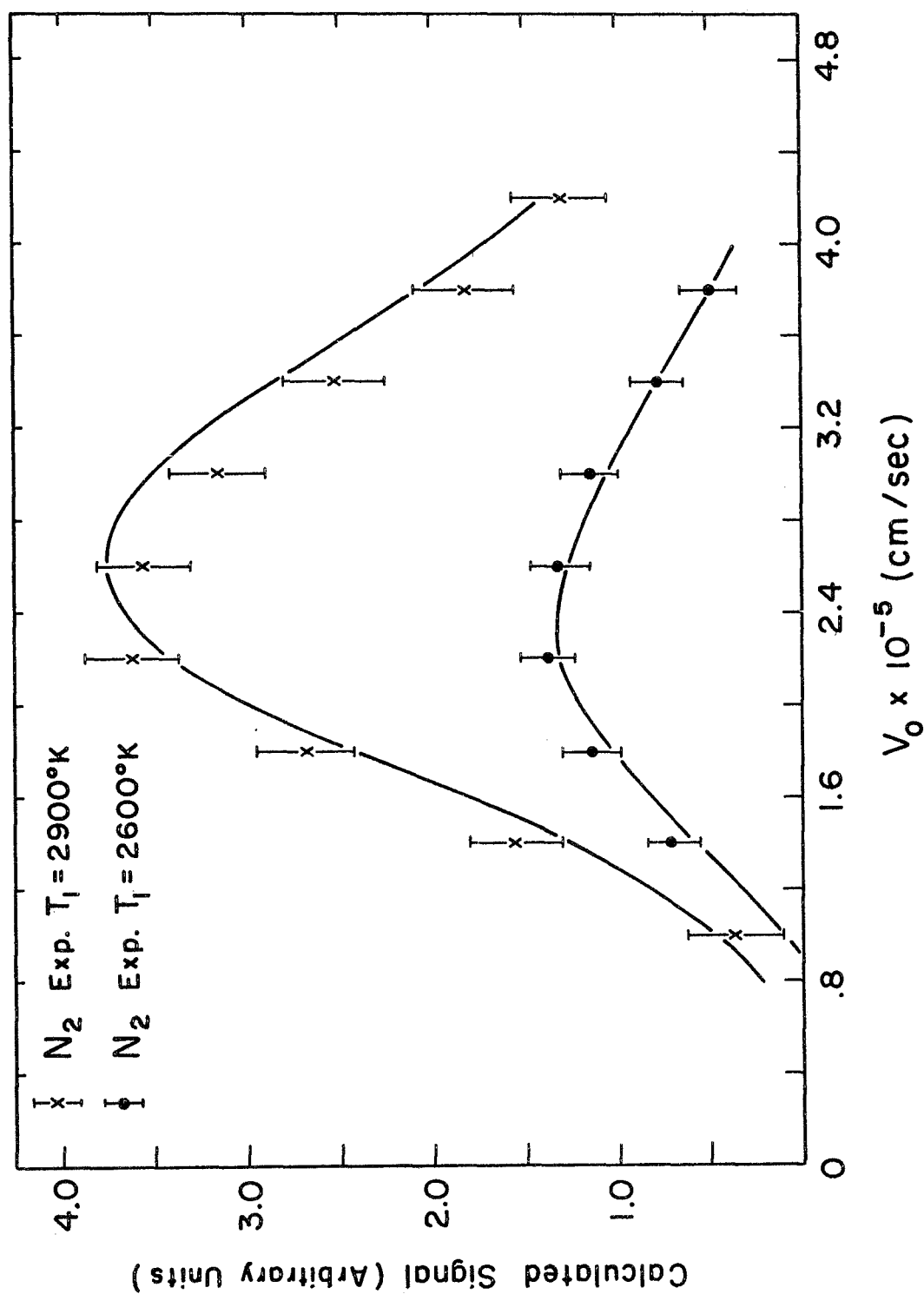


Figure 2.14. Comparison of N_2 experimental data with signals calculated assuming a cross section velocity dependence (2.22) for all participating vibrational states; see text.

Table 2.6. Basic Configuration calculated results for hydrogen using cross section (2.21).

v	$E_t(e.v)$	Δv	0	.21	.64	1.20	1.58	2.10
0								
1			5	4	3	2	1	0
2								
3								
4								
5								
6								
7								

$u = 1.13$	$u = 1.01$	$u = .976$	$u = .946$	$u = .955$	$u = 1.38$	$u = 1.674$	$u = 3.603$
2.33×10^6	2.22×10^6	2.05×10^6	1.65×10^6	9.55×10^5	1.50×10^5	1.71×10^4	2.33×10^3
		$u = 1.95$	$u = 1.89$	$u = 1.63$	$u = 1.63$	$u = 2.694$	
		1.32×10^5	1.44×10^5	1.36×10^5	9.27×10^4	1.06×10^4	
		$u = 3.62$	$u = 3.29$				
		9.25×10^3	1.19×10^4				

$u = \frac{\alpha_{v,v'}(2600)}{\alpha_{v,v'}(2000)}$	Entries appearing below u are $\alpha_{v,v'}(2000)$
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Table 2.7. Basic Configuration calculated results for Deuterium using cross section (2.21).

E_t (e.v.)	0.0	.09	.39	.70	1.03	1.37	1.73	2.10
v	7	6	5	4	3	2	1	0
0								$u = 6.93$ 6.4×10^5
1							$u = 1.20$ 6.9×10^5	7.4×10^4
2						$u = 1.22$ 8.0×10^5	$u = 1.94$ 8.7×10^4	
3				$u = 1.04$ 8.7×10^5	$u = 1.77$ 1.09×10^5			
4			$u = .98$ 8.8×10^5	$u = 1.60$ 1.3×10^5			$u \equiv \frac{\alpha_{v,v'}}{\alpha_{v,v'}} \quad (2600)$ $\alpha_{v,v'} \quad (2000)$	
5		$u = .93$ 7.7×10^5	$u = 1.48$ 1.4×10^5					
6		$u = .95$ 4.6×10^5	$u = 1.43$ 1.4×10^5					
7	$u = 1.33$ 9.9×10^4	$u = 1.40$ 8.7×10^4						
8	$u = 1.92$ 2.1×10^4							

Entries appearing below
u are $\alpha_{v,v'}$ (2000)

Table 2.8. Basic Configuration calculated results for Nitrogen using cross section (2.21).

$E_t(e.v)$	Δv	0.0	.16	.43	.70	.97	1.25	1.53	1.82	2.10
v	Δv	8	7	6	5	4	3	2	1	0
0										$u = 13.7$
1									$u = 8.33$	
2								$u = 5.62$	3.66×10^1	8.56
3							$u = 3.81$	1.92×10^2		
4						$u = 2.66$	$u = 5.17$			
5					$u = 1.85$	$u = 3.57$	$u = 7.05$			
6				$u = 1.27$	$u = 2.5$	$u = 4.85$				
7		$u = .95$	$u = 1.66 \times 10^5$	$u = 1.72$	$u = 3.34$	$u = 6.55$		$u = \frac{\alpha_{v,v'}}{\alpha_{v,v'}} (2800)$		
8	$u = 1.10$	$u = 1.28$	$u = 1.72$	$u = 2.3$	$u = 4.67$	$u = 6.18 \times 10^1$		$u = \frac{\alpha_{v,v'}}{\alpha_{v,v'}} (2200)$		
9	$u = 1.47$	$u = 1.72$	$u = 3.13$	$u = 3.13$	$u = 4.67$	$u = 6.18 \times 10^1$				
10	$u = 1.98$	$u = 2.29$	$u = 2.70 \times 10^3$	$u = 2.70 \times 10^3$	$u = 2.70 \times 10^3$	$u = 2.70 \times 10^3$				
11	$u = 2.58$	$u = 2.58$	$u = 2.58$	$u = 2.58$	$u = 2.58$	$u = 2.58$				

Entries appearing below
u are $\alpha_{v,v'}$ (2200)

Table 2.10. Basic Configuration calculated results for Deuterium
using cross section (2.22).

$E_t(e.v)$	0.0	.09	.39	.70	1.03	1.37	1.73	2.10
$v \Delta y$	7	6	5	4	3	2	1	0
0								
1							$u = 1.54^4$ 5.3×10^4	
2						$u = 1.42^4$ 7.7×10^4		
3					$u = 1.32^5$ 1.1×10^5			$u \equiv \frac{\alpha_{v,v'}(2600)}{\alpha_{v,v'}(2000)}$
4				$u = 1.22^5$ 1.5×10^5				Entries appearing below u are $\alpha_{v,v'}(2000)$
5			$u = 1.12^5$ 2.1×10^5					
6		$u = 1.05^5$ 2.8×10^5						
7	$u = 1.33^4$ 9.9×10^4							

Table 2.11. Basic configuration calculated results for Nitrogen
using cross section (2.22).

E_t (e.v.)	0.0	.16	.43	.70	.97	1.25	1.53	1.82	2.10
Δv	8	7	6	5	4	3	2	1	0
0									
1								$u = 10.4$ 1.65	
2							$u = 7.05$ 10.2		
3						$u = 4.76$ 6.21×10^{-1}			
4					$u = 3.26$ 3.68×10^2	$u = 6.6$ 1.41×10^{-1}			
5				$u = 2.22$ 2.13×10^3	$u = 4.36$ 8.60×10^{-1}				
6			$u = 1.55$ 1.18×10^4	$u = 3.03$ 5.09×10^2	$u = 6.1$ 2.05×10^{-1}		$u = \frac{\alpha_{v,v'}(2800)}{\alpha_{v,v'}(2200)}$		
7		$u = 1.09$ 6.06×10^4	$u = 2.10$ 2.88×10^3	$u = 4.10$ 1.24×10^2					
8	$u = 1.10$ 6.9×10^{-4}	$u = 1.48$ 1.50×10^{-4}	$u = 2.82$ 7.15×10^{-2}	$u = 5.50$ 3.09×10^{-1}					
9	$u = 1.47$ 1.75×10^{-7}	$u = 1.98$ 3.82×10^{-3}	$u = 3.80$ 1.8×10^{-2}						
10	$u = 1.98$ 4.5×10^3	$u = 2.66$ 9.80×10^{-2}							
11	$u = 2.58$ 1.2×10^{-7}								

Entries appearing below
u are $\alpha_{v,v'}$ (2200)

It is noteworthy that a number of v, v' combinations are unspecified in the upper left portions of each chart. These transitions are impossible via conservation of energy when vibrational and kinetic energy are the only excitation energy sources. The unspecified u and $\alpha_{v, v'}$ in the lower right portion of the charts are rejected because here u is too large and α is too small to conform to measured values of η . With regard to calculated features, as expected, the effects of the first entry in each column ($v \rightarrow v' = 0$ transitions) are the most probable of being observed in these experiments as evidenced by comparing the "reaction velocities" $\alpha_{v, 0}$ with those for constant Δv lying immediately below, $\alpha_{v, v-\Delta v}$. Another general feature for all species is the fact that for fixed Δv , the temperature slopes u increase as v increases; this behavior is no surprise in light of equation (2.20).

Considering the temperature dependences of Tables 2.6 and 2.9 for H_2 , one observes that $\alpha_{5,0}$ and $\alpha_{4,0}$ possess temperature slopes corresponding most nearly to those observed in Fig. 2.8; only $\Delta v = 5$ and 4 quanta transfers were identified in the velocity data. Ascribing Fig. 2.8 data to these transitions, $\sigma_{5,0} : \sigma_{4,0} = a_5 : a_4$ for either (2.21) or (2.22). Proceeding to step (E), these cross section ratios imply that $\sigma_{5,0} : \sigma_{4,0} = 19\text{\AA} : 1.9\text{\AA}$ for (2.21) and $\sigma_{5,0} : \sigma_{4,0} = 8.7\text{\AA}^2$ for (2.22).

The apparent large dependence of these cross sections on cross section velocity dependence can be partially attributed instead to lack of velocity-selected information at high velocities. The fact that the velocity data below $V_0 = 3.8 \times 10^5$ cm/sec are

signals entirely from $\sigma_{5,0}$ means that only the velocity threshold for $\sigma_{4,0}$ was measured. Since the $Q_{\Delta v}(V_0, T_1)$ are very sensitive to $R_{\Delta v}(v_r)$ at threshold and rather insensitive for larger V_0 , the ratios $a_5 : a_4$ may be incorrectly determined (particularly for (2.22) where the $Q_4(V_0, T_1)$ threshold lies close to 4×10^5 cm/sec).

In the case of D_2 , Tables 2.7 and 2.10 indicate that $\alpha_{7,0}$, $\alpha_{6,0}$ and $\alpha_{5,0}$ are consistent with the data of Fig. 2.8. Therefore, ascribing the principal features of the data to these transitions means that $\sigma_{7,0} : \sigma_{6,0} : \sigma_{5,0} = a_7 : a_6 : a_5$. In the case of (2.21), these ratios imply that $\sigma_{7,0} : \sigma_{6,0} : \sigma_{5,0} = 19\text{\AA}^2 : 3.9\text{\AA}^2 : 3.9\text{\AA}^2$; for (2.22) $\sigma_{7,0} : \sigma_{6,0} : \sigma_{5,0} = 8.7\text{\AA}^2 : 4.3\text{\AA}^2 : 2.2\text{\AA}^2$. Both cross section velocity dependences suggest that the transfer of pure internal energy is more efficient than when less internal energy leads to excitation. Comparing the $\sigma_{5,0}$ for H_2 with $\sigma_{7,0}$ for D_2 one finds agreement regardless of the particular cross section velocity dependence chosen.

Considering the temperature dependences of Tables 2.8 and 2.11 for N_2 , one finds that $\alpha_{8,0}$, $\alpha_{7,0}$, $\alpha_{6,0}$ are in serious disagreement with the measured temperature dependence of the basic experiment (similar to $\alpha_{5,0}$). Regardless of this disagreement, if one believes that the $\alpha_{5,0}$ and $\alpha_{4,0}$ could be dominating the data of Fig. 2.8 then substitution of $\sigma_{8,0} : \sigma_{7,0} : \sigma_{6,0} : \sigma_{5,0} : \sigma_{4,0} = a_8 : a_7 : a_6 : a_5 : a_4$ into (2.18) should predict the temperature dependence observed. The fact that this simple list of cross sections cannot explain the data can be shown from the large magnitude of $\sigma_{8,0}$ $\alpha_{8,0}$ compared with $\sigma_{5,0}$ $\alpha_{5,0}$ (see Tables

2.8 and 2.11). This reason for failure of the complete vibrational de-excitation scheme and the fact that $\sigma_{11,3}$ does predict the observed temperature dependences instructs us to ascribe the 8 quanta contribution to $\sigma_{11,3}$ while still maintaining the $\sigma_{v,0}$ scheme for $v = 4, 5, 6, 7$. In this case $\sigma_{11,3} : \sigma_{7,0} : \sigma_{6,0} : \sigma_{5,0} : \sigma_{4,0} = 58 a_8 : a_7 : a_6 : a_5 : a_4$ ($e^{(\epsilon_{11} - \epsilon_8)/kT_1} = 58$, $T_1 = 2700^\circ\text{K}$) and these cross sections can explain the data. With this simple interpretation (2.21) suggests the cross sections $\sigma_{11,3} = 95\text{\AA}^2$ and $\sigma_{v,0} = 3.3\text{\AA}^2$ for $v = 4, 5, 6, 7$. Velocity dependence (2.22) suggests that $\sigma_{11,3} : \sigma_{7,0} : \sigma_{6,0} : \sigma_{5,0} : \sigma_{4,0} = 200\text{\AA}^2 : 8.6\text{\AA}^2 : 17.3\text{\AA}^2 : 17.3\text{\AA}^2 : 52\text{\AA}^2$. When these cross sections (for either velocity dependence) are used with step (D), the calculated $S(V_0, T_1 - 2600)$ are consistent with the measured 2600° velocity contour, as shown in Fig. 2.13 and Fig. 2.14.

If one attempts to explain the N_2 temperature dependence of the basic experiment without asserting the approximate predominance in the signals of $\Delta v = 8$ transitions originating from high lying vibrational states such as $v = 10, 11$ or 12 , one is impressed by the inability of finding an interpretation that is consistent with the velocity selected results. It can be seen by considering Tables 2.8 and 2.11, that the ratio a_5/a_8 , determined by analyzing the velocity data, would have to be larger by at least one or two orders of magnitude than was found in order to support the notion that $\sigma_{5,0}$ signals predominate over $\sigma_{8,0}$ in the basic experiment. Approximate pure internal energy transfer predominance enables one to deduce that $\sigma_{8,0} \approx \sigma_{11,3}/58 = 3.5\text{\AA}^2$.

Concerning the N_2 cross sections, it is noteworthy that the $\Delta v = 7, 6$ signals optionally could be principally attributed to $v > 7, 6$ respectively rather than to complete vibrational de-excitation assumed in the previous interpretation. For example, in Table 2.11 it will be noted that $\alpha_{9,2}$ and $\alpha_{7,1}$ possess temperature dependences which more nearly correspond to those found experimentally than $\alpha_{7,0}$ and $\alpha_{6,0}$. Assuming that $\sigma_{7,0} \ll \sigma_{9,2} e^{-\epsilon_2/kT}$ and $\sigma_{6,0} \ll \sigma_{7,0} e^{-\epsilon_1/kT}$ then $\sigma_{9,2} \sim 130 \text{ \AA}^2$ and $\sigma_{7,0} \sim 70 \text{ \AA}^2$ for velocity dependence (2.22) and the cross sections $\sigma_{11,3}$, $\sigma_{5,0}$, $\sigma_{4,0}$ do not change. While the N_2 molecules may in fact prefer not being completely vibrationally de-excited when kinetic and vibrational energy couple with the electronic mode, this notion is not as appealing as when the $v = 11 \rightarrow v' = 3$ transition is the only possibility for not being completely de-excited. A larger number of vibrational states not being completely de-excited appears to contradict the temperature dependent results found in quenching experiments carried out at high and low temperatures.

A notion often discussed in the literature is that the cross section for interconversion of vibrational and electronic energies may depend strongly on the closeness of match between the vibrational energy given and the electronic energy received (energy resonance). Since $\sigma_{5,0}$ for H_2 and $\sigma_{7,0}$ for D_2 have been found to be equivalent and large compared with $\sigma_{8,0}$ for N_2 in this study, this notion certainly deserves attention. In this regard, the reaction energy defects, $\Delta \epsilon_v - E_0$, have been tabulated for those species using the vibrational energies appearing in Table 2.5. Examining Table 2.12

Table 2.12. Reaction energy defects, $\Delta \epsilon - E_0$, for pure vibrational energy transfer.

(a) $H_2 (X^1\Sigma_g^+)^{22}$				(b) $D_2 (X^1\Sigma_g^+)^{23}$			
v	v'	$\Delta \epsilon = \epsilon_v - \epsilon_{v'} \text{ (e.v.)}$	$\Delta \epsilon - E_0$	v	v'	$\Delta \epsilon = \epsilon_v - \epsilon_{v'} \text{ (e.v.)}$	$\Delta \epsilon - E_0$
5	0	2.292	.187	7	0	2.294	.189
6	1	2.150	.045	8	1	2.194	.089
7	2	2.008	-.097	9	2	2.095	-.010
8	3	1.865	-.24	10	3	1.956	-.149

$N_2 (X^1\Sigma_g^+)^{24}$			
v	v'	$\Delta \epsilon = \epsilon_v - \epsilon_{v'} \text{ (e.v.)}$	$\Delta \epsilon - E_0$
8	0	2.211	.106
9	1	2.182	.077
10	2	2.154	.049
11	3	2.125	.020
12	4	2.096	-.009
13	5	2.068	-.037

$$E_0 = 2.105 \text{ e.v.} \quad P_{3/2}$$

(a) , (b) for these results one notes that the $v = 5 \rightarrow v' = 0$ and $v = 7 \rightarrow v' = 0$ energy defects of H_2 and D_2 are almost identical and large compared with those for $v = 6 \rightarrow v' = 1$ and $v = 8 \rightarrow v' = 1$ respectively. If energy defect is important then the latter transitions should have been observed for these molecules. Looking at Table 2.12 (c) for N_2 one notes that the defect for $v = 8 \rightarrow v' = 0$ is almost half that found for complete de-excitation of the hydrogen molecules. But the defect for $v = 11 \rightarrow v' = 3$ is small compared with that for $v = 8 \rightarrow v' = 0$ and the former has been implicated in these experiments. These correlations suggest that the sharp type of energy defect resonance theoretically found by Dickens, Linnett, and Sovers²⁵ (in consideration of the $N_2 - N_2$ (^2P) and Hg (^3P) - CO , N_2 , NO quenching reactions) may in fact be valid for the $N_2 - Na$ (^2P) system. The validity of this concept for the hydrogen - Na systems appears to be questionable, experimentally speaking.

The present experimental finding that for $N_2, \sigma_{11,3} \gg \sigma_{8,0}$ correlates with energy defect, appears to be the only experimentally suggested evidence yet reported in favor of the sharp resonance idea. Hurle⁵ suggested that excitation proceeds via the transfer of pure vibrational energy but he did not suggest any priorities among various vibrational states that could lead to excitation. After examining the excitation of several lines of Na other than the 3^2P , Starr⁶ concluded that resonances are not important because his observations were similar for all strong Na lines between 3100 and 6100Å. While at face value his conclusion is in disagreement with the present finding, one can question whether his evidence provides sufficient

detailed information to warrant the conclusion. In particular, a detailed knowledge of Starr's initial distribution of vibrationally excited states would be helpful in evaluating the certainty of his conclusion.

It is noteworthy that the present findings, demonstrating that electronic energy also can couple with vibrational energy in a highly non-resonant manner with moderate efficiency, have been observed in other systems. Polanyi and co-workers were the first to observe directly this phenomenon by studying the infrared emission induced in both CO^{26} and NO^{27} through the quenching of $\text{Hg}(6^3\text{P})$. This type of coupling also has been directly observed recently in a shock wave environment for the $\text{CO} - \text{Na}(3^2\text{P})$ system.²⁸

If the excitation cross sections determined in this study are valid, then via microscopic reversibility one would expect them to be in general agreement with the effective cross sections measured when $\text{Na}(3^2\text{P})$ is quenched in the presence of H_2 , D_2 and N_2 .^{5,29,30,31,32,33,34} When both multiplet components ($^2\text{P}_{3/2}$, $^2\text{P}_{1/2}$) excited by collision appear in their natural statistical ratio (observed in Starr's excitation experiment for N_2), then the partial quenching cross sections, $\sigma_{v',v}$, for excitation velocity dependence (2.22) are given by (2.23)

$$\sigma_{v',v} = \sigma_{v,v'}/3. \quad (2.23)$$

Substitution of the previously determined $\sigma_{v,v'}$ into (2.23) yields the partial quenching cross sections appearing in Table 2.13.

Table 2.13. Quenching cross sections calculated from excitation cross sections for velocity dependence (2.22) using microscopic reversibility.

H_2	$\sigma_{0,5}$	$2.9 \text{ \AA}^2$
	$\sigma_{0,4}$	2.9
	$\sigma_{0,3}$	?
	$\sigma_q = \sigma_{0,4}$	2.9
D_2	$\sigma_{0,7}$	$2.9 \text{ \AA}^2$
	$\sigma_{0,6}$	1.4
	$\sigma_{0,5}$	.7
	$\sigma_{0,4}$	?
	$\sigma_q = \sum_{v=5,6} \sigma_{0,v}$	2.1
N_2	$\sigma_{3,11}$	$67. \text{ \AA}^2$
	$\sigma_{0,8}$	<3.5
	$\sigma_{0,7}$	2.8
	$\sigma_{0,6}$	5.8
	$\sigma_{0,5}$	5.8
	$\sigma_{0,4}$	17.3
	$\sigma_{0,3}$	?
	$\sigma_q = \sum_{v=4,5,6,7} \sigma_{0,v}$	35.2

Comparing the deduced effective quenching cross sections σ_q (including only energetically allowed $\sigma_{0,v}$) given in this Table with some of the measured quenching cross sections determined in a variety of environments (see Table 2.14), one finds the general agreement expected. One also notes excellent agreement with experiments carried out at center-of-mass temperatures, equivalent to those of the present study, and poorer agreement with the bulk studies carried out at lower temperatures. The fact that the estimated cross sections fall within the range of the low temperature ($\sim 500^\circ\text{K}$) bulk results and the high temperature studies tends to speak reassuringly for the analytical techniques employed in this study.

In comparing the σ_q with the results of quenching studies in greater detail, it should be emphasized that only the partial quenching cross sections for initial ground vibrational states energetically allowed in quenching experiments have been included in σ_q (see Table 2.13). In the case of N_2 where $\sigma_{3,11}$ is within 0.02 e.v of being energetically allowed, no attempt has been made to include it in the effective cross section before comparing with the results for any environment. Strictly speaking, one should specifically weight this cross section with the $\sigma_{0,v}$ before comparing σ_q with quenching results. However, not knowing $\sigma_{0,3}$ for N_2 implies that only thermal distribution considerations can be applied in the weighting procedures. Depending on the size of $\sigma_{0,3}$, this consideration may be important along with significant vibrational relaxation rates. It is for these reasons that σ_q has been kept simplified and a more

Table 2.14. Effective collision cross section for quenching of $\text{Na}(3^2\text{P})$.

Source	H_2	D_2	N_2
This work, estimated via microscopic reversibility			
$\sigma_q; R_{\Delta v}(v_r)$ (2.22)	$> 2.9 \text{ \AA}^2$	$> 2.1 \text{ \AA}^2$	$> 35.2 \text{ \AA}^2$
Kibble, Copley, and L. Krause ²⁹ (Bulk)	16.2 ± 0.3	9.8 ± 0.3	40.3 ± 0.3
Norrish and Smith ³⁰ (Bulk)	23.2		45.6
Mankopff, Cross Section determined by Mitchell and Zemansky (1961) ³¹ (Bulk)	17		61.
Jenkins ³² (flame)	2.87		21.8 (1400-1800°K)
Hanson ³³ (photo-dissociation of NaI by u.v. light)	2.77 - 3.06		
Hurle ⁵ (shock tube, 1700-4500°K).			~10
Tsuchiya, Koratani ³⁴ (shock tube, 2300-2500°K)			10 to 20

See Jenkins³² for additional investigations.

Table 2.15. Comparison of theoretical results for quenching by N_2 with those deduced from experimental excitation cross sections. All cross sections are expressed in $\text{\AA}^2$. α represents the polarizability assumed in the Bauer et al. theory.

v	$\sigma_{0,v}$ Theory ³⁵			$\sigma_{0,v}$ Experiment $R_{\Delta v}(v_r), (2.22)$	$\sigma_{0,v}$ Theory ³⁸ *
	$\alpha = 0\text{\AA}^3$	$\alpha = 10\text{\AA}^3$	$\alpha = 100\text{\AA}^3$		
8	0.00	0.00	0.00	<3.5	2.3×10^{-3}
7	1.27	1.90	5.89	2.8	3.8×10^{-2}
6	5.12	6.03	6.56	5.8	4.6×10^{-2}
5	10.50	7.81	7.65	5.8	.69
4	1.06	5.86	8.21	17.3	1.5
3	0.30	3.74	8.81	?	10.
2	0.00	0.21	8.74	?	15.
1	0.00	0.00	5.75	?	6.2
0	0.00	0.00	4.38	?	0

* Bjerre and Nikitin calculated quenching rate constants for the bulk temperature $T = 1000^\circ\text{K}$. Cross sections displayed above have been determined by dividing the rate constants by $\bar{v}_r = \sqrt{\frac{8kT}{\pi\mu}} = 1.3 \times 10^5 \text{ cm/sec}$

exhaustive detailed quenching cross section comparison has not been carried out.

Not only can the implications of the excitation findings be compared with other experimental studies but in the case of N_2 they can be compared with the recent semi quantitative theoretical studies of Bauer, Fischer and Gilmore.³⁵ After postulating an intermediate ionic state involving $Na^+ N_2^-$ as first suggested by Magee and Ri³⁶ and Laidler³⁷ in an attempt to explain the large quenching cross sections generally measured, Bauer et al. calculated $Na(3^2P)$ quenching cross sections for N_2 as a function of initial kinetic energy and of final vibrational state. These calculations were carried out for three arbitrarily chosen polarizability corrections (α) to the simple coulomb term of the potential. Some of these results for initial kinetic energy of .1 e.v. appear in Table 2.15. Referring to Table 2.15, one finds some agreement between the partial cross sections of Table 2.13 and the Bauer results, particularly for the larger polarizations. Aside from the differences in the cross section absolute values, the only general disagreement appears to deal with the importance of resonance effects in this process.

In consideration of the same problem, Bjerre and Nikitin³⁸ (BN) calculated rate constants for the quenching of $Na(3^2P)$ by N_2 , also assuming the intermediate ionic state. Comparing their deduced cross sections with the cross sections of Bauer et al. (see Table 2.15), one finds significant differences. BN suggest that N_2 prefers being excited in the lower vibrational states with a maximum

population occurring for $v = 2$ rather than the broader more constant vibrational distribution favoring $v = 5$ suggested by Bauer et al. Besides the lack of agreement between the BN and experimental results concerning vibrational resonance for $\Delta v = 8$, the BN cross sections $\sigma_{0,6}$ and $\sigma_{0,7}$ contrast with the corresponding experimental cross sections.

Finally we are in a position to discuss the auroral sodium D excitation problem that provided the motivation for these studies. Hunten⁸ considered this problem and concluded that direct excitation of the sodium by energetic electrons is untenable. The competition for these electrons at the auroral altitudes is overwhelmingly won by the much more abundant N_2 molecules, which become vibrationally excited with large cross section.³⁹ Hunten's proposal that the excitation of sodium arises through transfer of the $v = 8$ energy in N_2 is possible because there are a large number of secondary electrons with energy near 2.9 e.v. at auroral altitudes, and the cross section for the production of N_2 ($v = 8$) by electron impact peaks at this energy. While electrons at these energies also can excite lower vibrational states, the participation of these states via coupled kinetic energy supplying the reaction energy defect in aurora is remote unless cross sections for these phenomena are huge. (The temperature of this environment is of order $200^\circ K$). Also, an auroral mechanism due to N_2 ($v > 8$) is unattractive because vibrational excitation of N_2 for $v > 8$ by electrons appears to take place with too small a cross section.³⁹ Evidently, Hunten's proposal is valid only if the excitation cross sections $\sigma_{7,0}$ and $\sigma_{8,0}$

are sufficiently large to explain the observed auroral yellow emission.

The experimentally determined excitation cross sections ($\sigma_{7,0} \approx 9\text{\AA}^2$ and $\sigma_{8,0} \approx 3.5\text{\AA}^2$) of this study are in sharp contrast with the cross section ($\sim 30\text{\AA}^2$) that Hunten proposed for explaining Na D auroral excitation. Even allowing for a possible overestimate of his required rate, it appears that neither $\sigma_{7,0}$ nor $\sigma_{8,0}$ are sufficiently large to support the Hunten hypothesis. This conclusion does not appear to change unless $\sigma_{8,0}$ should rise about a factor of 10 in going from translational temperatures of order 1500°K to those existing in the cool auroral environments.

VI. CONCLUSIONS.

At translational and vibrational temperatures of order 1500°K and 3000°K respectively, the interconversion of energy between pure internal modes of H_2 , D_2 and N_2 and the sodium 3^2P levels is the most efficient means of energy transfer. While H_2 and D_2 transfer pure internal energy similarly, their behavior differs from that of N_2 . This type of transfer for N_2 tends to take place when the change of internal energy by collision is more nearly identical to the electronic energy. There is no such apparent preference in the case of H_2 and D_2 .

For the previously stated experimental conditions when internal and translational energy combine to couple with electronic energy, the efficiency of transfer is about an order of magnitude less than when internal and electronic modes couple alone. At least one third of the electronic energy transferred can come from translational in the case of the hydrogen isotopes, and at least one half can come from translation for nitrogen-sodium collisions. For the hydrogen systems, the efficiency via this mechanism appears to decrease when larger amounts of translational energy couple, whereas the efficiency for N_2 appears to rise for greater kinetic energy contributions.

The present findings for the collisional excitation of $\text{Na}(3^2\text{P})$ are in general agreement with the results of $\text{Na}(3^2\text{P})$ quenching experiments carried out in high temperature environments via microscopic reversibility arguments. For the N_2 - Na system there is general agreement between experiment and the Bauer et al. theory except for the theoretically predicted insignificance of internal energy and electronic energy resonance effects. There is slightly poorer

agreement with the theory of Bjerre and Nikitin.

The excitation results for N_2 applied to the auroral sodium excitation problem suggest that Hunten's proposal is incorrect. Alternate mechanisms should be sought to explain the yellow emission of type B aurora.

APPENDIX 2A

APPARATUS DIMENSIONS

The essential dimensions for the sodium excitation experiments appear in Tables 2A.1 and 2A.2. The literal definitions are illustrated in Fig. 2A.1. Dimensions designated by d refer to circular diameter unless otherwise specified.

TABLE 2A.1

Basic Configuration.

	cm		cm
d_1	.15	l_1	1.5
d_2	.12	l_2	2.5
d_3	.20	l_3	3.9
d_4	.68	l_4	2.4
d_5	.84	l_5	9.7
d_6^*	.05	l_6	2.8
d_7	.75		
d_8	.8		

*Two holes placed .3 cm apart.

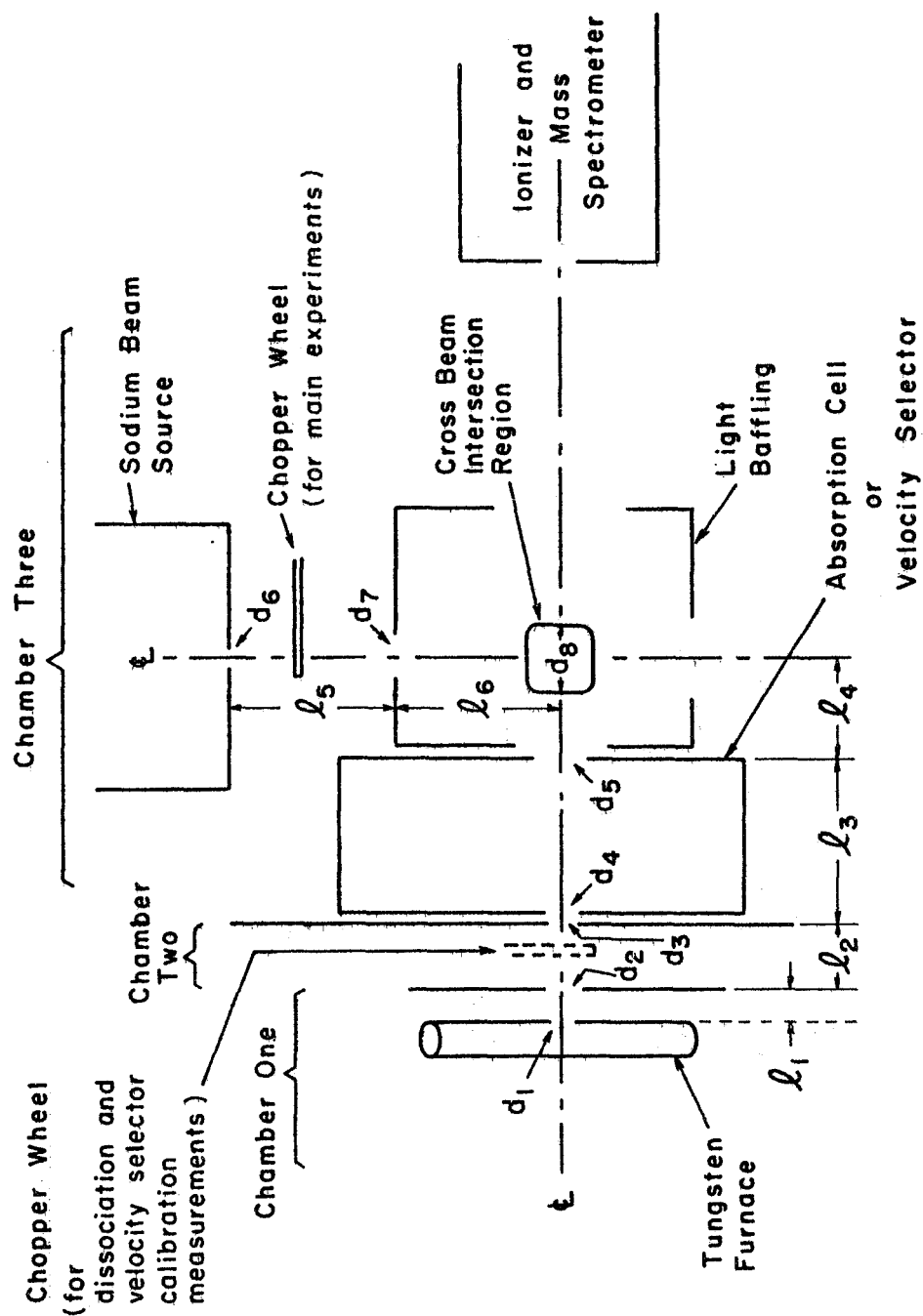


Figure 2A.1. Essential dimensional definitions for the excitation experiment layout.

TABLE 2A.2

Velocity Selected Configuration.

	cm		cm
d_1	.13	l_1	1.5
d_2	.20	l_2	2.5
d_3	.35	l_3	8.0
d_4^{**}	.2 x .50	l_4	2.4
d_5^{**}	.25 x .50	l_5	9.7
d_6^*	.05	l_6	2.8
d_7	.75		
d_8	.8		

** Rectangular slits similar to those of velocity selector disks.

APPENDIX 2B. EVALUATION OF S_s FROM THE KNOWN
CROSS SECTION FOR RESONANT ABSORPTION FLUORESCENCE.

In the basic configuration when the sodium absorption cell is at room temperature, large sodium D signals are measured when the molecular source is heated and the molecular beam is turned off. These signals, as noted in Section II, are due to resonant absorption-fluorescence of black-body furnace light by the target sodium atoms. These signals can be calculated via (2B.1).

$$S_s = n_2 x \sum_{D_1, D_2} e(\omega) \sigma(\omega) I(\omega) d\omega \quad (2B.1)$$

$e(\omega)$ represents the geometrical, optical transmission and detection efficiency factors for sodium D; $\sigma(\omega)$ is the total cross section for resonance-fluorescence; $I(\omega)d\omega$ is the black-body photon flux incident upon the target region between angular frequencies ω and $\omega + d\omega$; n_2 is the atom target number density; and x is the target path length for the photons. The sum over both doublet lines (D_1, D_2) must be carried out for the apparatus previously described.

Assuming the fluorescence to be isotropic, the total cross section, $\sigma(\omega)$, for this process is given by (2B.2).⁴⁰

$$\sigma(\omega) = \frac{\pi}{2} \left(\frac{\lambda_0}{2\pi} \right)^2 \frac{(2J_{\text{excited}} + 1)}{(2J_{\text{ground}} + 1)} \frac{\Gamma^2}{(\omega - \omega_0)^2 + (\Gamma_t/2)^2} \quad (2B.2)$$

where λ_0 and ω_0 are the resonant wavelength and frequency, respectively; $\Gamma_t = (\omega/\omega_0)^2 \Gamma$ is the Lorentz line shape half width, and Γ^{-1} is the lifetime. Combining (2B.1) with (2B.2) and substituting for $I(\omega)d\omega$, S_s becomes (2B.3).

$$S_s = A_1 d\Omega_f \sum_{D_1, D_2} \frac{(2J_{ex} + 1)}{(2J_{gr} + 1)} \frac{e(\omega)}{8\pi^2} \frac{1}{(e^{\hbar\omega/kT_1} - 1)} \cdot \frac{\Gamma^2 d\omega}{[(\omega - \omega_0)^2 + (\Gamma_t/2)^2]} \quad (2B.3)$$

A_1 is the tungsten furnace aperture area; $d\Omega_f$ is photon flux solid angle.

The resonant term in the integrand of (2B.3) changes rapidly compared to the other ω dependent terms. The integral therefore is carried out with these terms treated as constants. It is readily shown that insignificant error is introduced by conveniently extending the limits of integration imposed by $e(\omega)$ to the region $0 \leq \omega < \infty$. Under these assumptions and since $e^{\hbar\omega/kT_1} \gg 1$, (2B.4) follows.

$$S_s = eA_1 \frac{\Delta V}{L^2} n_2 \sum_{D_1, D_2} \frac{(2J_{ex} + 1)}{4\pi(2J_{gr} + 1)} \Gamma e^{-\hbar\omega_0/kT_1} \quad (2B.4)$$

ΔV is the reaction region volume and L is the distance between tungsten furnace and reaction region. This result is valid even if Doppler absorption is considered.³¹

The excited state designations are ${}^2P_{3/2}$ and ${}^2P_{1/2}$ and the ground state designation is ${}^2S_{1/2}$, neglecting nuclear spin, so

$$\sum_{D_1, D_2} \frac{(2J_{\text{ex}} + 1)}{(2J_{\text{gr}} + 1)} = 3 \quad (2B.5)$$

The substitution of (2B.5) into (2B.4) completes the evaluation of S_s .

APPENDIX 2C. EXPERIMENTAL DETERMINATION OF THE
REACTION RATE CONSTANT.

As noted in Section II, the ratio of reactive-to-scattered furnace light signals can be used to approximate the reaction rate constant. Considering the expression for signals due to reaction, (2C.1), and taking the ratio of (2C.1) and (2B.4), (2C.2) results. Refer to Appendix 2B for symbol definitions.

$$S_R = e n_1 n_2 \Delta V k_r \quad (2C.1)$$

$$\frac{S_R}{S_S} = \frac{4\pi n_1^2 L^2 k_r e^{h\nu_0/kT_1}}{3 A_1 r} \quad (2C.2)$$

The left side of (2C.2) is experimentally determined directly as are L and A_1 , the distance between the furnace and reaction region and the furnace aperture area, respectively. The reaction region number density, n_1 , can be experimentally determined indirectly by equating the molecular particle flux passing through the reaction region to the experimental chamber exhaustion rate.

$$n_1 = \frac{\Delta P_3 S_3}{A_2 \bar{v}_B} \quad (2C.3)$$

This technique requires the measurement of ΔP_3 , the experimental chamber pressure difference when the molecular beam is turned off, and of S_3 , the diffusion pumping speed for the particular molecular

gas. The latter is readily determined by measuring the experimental chamber pressure time constant, a technique previously described by Kauppila.¹³ The reaction region cross sectional area, A_2 , is readily determinable via geometry and knowledge of the primary beam apertures (Tables 2A.1). The average beam velocity is readily calculated via (2C.3).

$$\bar{v}_B = \frac{8}{\pi} \frac{kT_1}{m_1} \quad (2C.3)$$

The inverse of the sodium D lifetime, Γ , is known from the work of Demtroeder²¹ to be $1.49 \times 10^7 \text{ sec}^{-1}$.

This technique has been utilized only in the calibration of nitrogen on sodium. The calibration of molecular hydrogen and deuterium on sodium follows from the nitrogen calibration via relative signal measurements corrected for equal reaction region number densities between the respective species, as discussed in Section V.

APPENDIX 2D. ANALYSIS OF THE EXCITATION RESULTS.

There are two basic mathematical approaches available for the analysis of either of the two excitation experiments. One approach is to attempt to extract the cross section $\sigma(\epsilon, v_r)$ directly by an operational mathematical approach to invert the measured signals. The second method is to postulate cross sections that hopefully are physically meaningful, to calculate the experimental consequences of these cross sections, and to compare the calculated results with experiment. Considering the experimental situation and the fact that previous theoretical and experimental studies can assist in the selection of reasonable cross section energy dependences, the second method has been chosen as the method of attack for each experiment.

For this method of analysis a simple separable $\sigma(\epsilon, v_r)$ has been chosen which does not contain rotational energy. See Section V where equations (2.17), (2.21) and (2.22) define this cross section.

Indirect support for a cross section similar to (2.22) for the hydrogen-sodium system comes from a quenching experiment performed by Hanson.³³ In this experiment the effective quenching cross section for $\text{Na}(3^2\text{P})$ arising from the photo-dissociation of the sodium iodide molecule was determined as a function of the sodium atom energy by measuring the D line radiation. The velocities of the excited sodium atoms after dissociation were determined from experimentally gained knowledge of the repulsive potential curve

for an excited sodium atom and a normal iodine atom. Hanson found the quenching cross section to be velocity independent between the velocities 2.6 to 3.1×10^5 cm/sec. Microscopic reversibility applied to such an energy dependence for quenching implies the excitation cross section (2.22).

Hanson's result of quenching cross section energy independence was later verified by an experiment carried out in flame by Jenkins.³² In this experiment in which the reactants possessed Maxwell-Boltzmann velocity distributions, the effective quenching cross section was found to be temperature independent over the range 1600 to 1800°K . Jenkins's cross section is in agreement with that of Hanson.

There is not unanimous support for cross section (2.22), however. The bulk quenching data of Norrish and Smith³⁰ and other investigators at lower average impact velocities ($< 2 \times 10^5$ cm/sec) coupled with those of Hanson and Jenkins suggest an excitation cross section that rises at low energies more slowly than the inverse of the average relative energy for the quenching collisions. Such an excitation cross section can be approximated by the simple step function exceeding the energy required for exciting collisions. This is the sole support for a cross section of form (2.21).

Experimental support for an N_2 excitation cross section of form (2.22) comes also from the quenching experiments of Jenkins; the quenching cross section for N_2 was also found to be temperature independent. The theoretical support for applicability of this cross section to N_2 comes from the recent calculations of Bauer,

Fisher and Gilmore.³⁵ They have reported energy independent effective quenching cross sections for N_2 ending up in any of 8 vibrational states.

When (2.17) is inserted into (2.4), the rate constants for the basic and velocity-selected configurations expressed as a function of experimental variables become (2D.1).

$$\left\{ \begin{array}{l} k_r(T_1) \\ k'_r(V_0, T_1) \end{array} \right. = \sum_v \sum_{v'} \frac{P_{\Delta v}(T_1)}{Q_{\Delta v}(V_0, T_1)} \frac{\sigma_{v,v'} e^{-\epsilon_v/kT_1}}{\sum_{\text{all } v} e^{-\epsilon_v/kT_1}} \quad (2D.1)$$

Variables T_1 and V_0 are defined as the tungsten furnace temperature and the velocity selector nominal velocity, respectively. The kinetic factor for the basic configuration is expressed in (2D.2); that for the velocity-selected experiment is expressed in (2D.3)

$$P_{\Delta v}(T_1) = \int_{v_2=0}^{\infty} \int_{v_1=0}^{\infty} R_{\Delta v}(v_r) v_r f(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2 \quad (2D.2)$$

$$Q_{\Delta v}(V_0, T_1) = \int_{v_2=0}^{\infty} \int_{v_1=0}^{\infty} B(V_0, V_1) R_{\Delta v}(v_r) v_r f(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2 \quad (2D.3)$$

where $B(V_0, V_1)$ is the velocity selector pass-band function (see Section IIIF). These factors carry a vibrational state subscript

because the cross sections for the participation of each Δv differ by conservation of energy considerations.

The way in which energy considerations give rise to different kinetic energy dependent cross sections can be illustrated by a generalized example. Ignoring anharmonicity of vibrational states, let m represent the number of vibrational quanta that must be transferred to the sodium 3p electron in order that excitation is energetically allowed. Since all of the excitation energy comes from internal energy, the cross section should allow collisions of all beam relative velocities (activation energy considerations are ignored). Evidently, this cross section is appropriate for all initial vibrational states $v \geq m$. If the reaction can take place when only $\Delta v = m - n$ quanta go into reaction where $n < m$, then the cross section must exclude collisions lacking center-of-mass kinetic energy at least as large as n quanta of vibration energy. The initial vibrational states allowed for these collisions are $v \geq m - n$. In this analysis no other cross section restrictions derive from other conservation principles.

The effective rate constant for either of the two experiments (2D.1) can be expanded in a more lucid form when these simple energy restrictions are applied. In the case of the basic configuration, the rate becomes (2D.4).

$$k_r(T_1) = P_m(T_1) e^{-\frac{\epsilon_m}{kT_1}} (\sigma_{m,0} + \sigma_{m+1,1} e^{-\frac{\epsilon_1}{kT_1}} + \sigma_{m+2,2} e^{-\frac{\epsilon_2}{kT_1}} + \dots)$$

$$\begin{aligned}
& + P_{m-1}(T_1) e^{-\frac{\epsilon_{m-1}}{kT_1}} (\sigma_{m-1,0} + \sigma_{m,1} e^{-\epsilon_1/kT_1} + \dots) \\
& \vdots \\
& + P_0(T_1) (\sigma_{0,0} + \sigma_{1,0} e^{-\epsilon_1/kT_1} + \dots) / \Sigma e^{-\epsilon_v/kT_1}
\end{aligned}
\tag{2D.4}$$

The rate expression for the velocity-selected experiment is obtained by substituting $Q_{\Delta v}$ factors in place of $P_{\Delta v}$. Since anharmonicity has been neglected, the kinetic factors for vibrational transitions of constant Δv have been taken to be equal; they are therefore shown factored in (2D.4). It is apparent from (2D.4) that signals measured in these two experiments can be a very complex superposition of different vibrational transitions but some information can be extracted. The precise procedure employed for the present experiments appears in Section V.

Steps (A) and (C) of the analytical recipe appearing in Section V involve the calculation of the $Q_{\Delta v}(V_0, T_1)$ and $P_{\Delta v}(T_1)$ respectively. The manner in which the $P_{\Delta v}(T_1)$ have been calculated is described in Appendix 2D Section 1. The way in which the $Q_{\Delta v}(V_0, T_1)$ have been calculated is described in Appendix 2D Section 2.

1. Evaluation of the Kinetic Factors for the Basic Configuration.

The evaluation of $P_{\Delta v}(T_1)$, (2D.2), (and the weight factor expression (1B.32) used in the analysis of the $D + H_2$ study) can be carried out once $f(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2$ is expressed in terms of relative velocity. This combined distribution function for two crossed Maxwellian cross beams $I(v_r, \Psi)$ (where v_r is the magnitude of the relative velocity and Ψ is the relative velocity vector angle between $\vec{v}_r$ and $\vec{v}_1$) is well known.⁴¹

The beam velocity distribution functions are defined as

$$f(v_i) = 4\pi (\alpha_i/\pi)^{3/2} v_i^2 e^{-\alpha_i v_i^2} \quad (2D.7)$$

where $\alpha_i = m_i/2kT_i$. m_i is the mass of the i^{th} beam particles. T_i is the temperature of the i^{th} beam particles.

$$\int_0^\infty f(v_i) dv_i = 1 \quad i = 1, 2.$$

$$\text{The combined probability,} \quad \int_{v_1=0}^\infty \int_{v_2=0}^\infty f(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2, \quad \Psi = \pi/2$$

is readily transformed in any case to the form $\int_{v_r=0}^\infty \int_{\Psi=0}^\pi I(v_r, \Psi) dv_r d\Psi$.

$d\Psi = 1$. For the special case, $\vec{v}_1 \perp \vec{v}_2$, (2D.8) gives the transformation of velocity differentials. $v_1 \equiv v_r \cos \Psi$, $v_2 \equiv v_r \sin \Psi$

$$dv_1 dv_2 = \frac{\partial(v_1, v_2)}{\partial(v_r, \psi)} dv_r d\psi = v_r dv_r d\psi \quad (2D.8)$$

The transformed probability density, (2D.10) follows immediately from definitions (2D.9). $\alpha_1 v_1^2 + \alpha_2 v_2^2 = \alpha v_r^2$ where

$$\alpha = \delta_s + \delta_d \cos(2\psi)$$

$$\delta_s = \frac{(\alpha_1 + \alpha_2)}{2} \quad \delta_d = \frac{(\alpha_1 - \alpha_2)}{2} \quad (2D.9)$$

$$I(v_r, \psi) = C_1 v_r^5 \sin^2(2\psi) e^{-\alpha v_r^2} \quad \text{for } C_1 = 4\pi^2 (\alpha_1/\pi)^{3/2} (\alpha_2/\pi)^{3/2} \quad (2D.10)$$

In the evaluation of (2D.2), (2D.11) results when $I(v_r, \psi) dv_r d\psi$ is substituted for $f_1(\vec{v}_1) f(\vec{v}_2) d\vec{v}_1 d\vec{v}_2$.

$$P_{\Delta v}^{(T)} = \int_{v_r=0}^{\infty} \int_{\psi=0}^{\pi/2} C_1 R_{\Delta v}(v_r) v_r^6 \sin^2(2\psi) e^{-\alpha v_r^2} dv_r d\psi \quad (2D.11)$$

The ψ integration can be performed analytically; the result is expressed in (2D.12).

$$P_{\Delta v}(T_1) = \int_{v_r=0}^{\infty} \frac{\pi C_1}{2(-\delta_d)} R_{\Delta v}(v_r) v_r^3 I_1(-v_r^2 \delta_d) e^{-\delta_s v_r^2} dv_r \quad (2D.12)$$

I_1 is the first order modified Bessel function of the first kind.

The kinetic factors $P_{\Delta v}(T_1)$ required in the data analysis have been calculated by numerically integrating (2D.12) using the Gaussian Quadrature formula (1B.41). The 16 point integrations carried out on the IBM 7090 were found to be accurate to more than 4 significant digits.

2. Evaluation of the Kinetic Factors for the Velocity-Selected Configuration.

The evaluation of $Q_{\Delta v}(V_0, T_1)$ in (2D.3) can be performed similarly as $P_{\Delta v}(T_1)$ but with a few minor complications. Considering the piecewise nature of $B(V_0, v_1)$ defined in Section IIIIF, (2D.13) results when (2.14) is inserted into (2D.3) before the transformation to v_r, ψ coordinates is carried out.

$$\begin{aligned}
 Q_{\Delta v}(V_0, T_1) = & \left(1 + \frac{1}{\beta}\right) \bar{v} - \frac{(1 + \beta)}{2} V_0 \int_{J_{ab}}^{v_b=V_0} \int_{v_a=\frac{(1+\beta)}{(1+\beta)}} V_0 \\
 & + \left(1 - \frac{1}{\beta}\right) \bar{v} + \frac{(1 - \beta)}{2} V_0 \int_{J_{ab}}^{v_b=\frac{(1-\beta)}{(1-\beta)}} V_0 \int_{v_a=V_0}
 \end{aligned}
 \tag{2D.13}$$

$$\text{where } \bar{v} = \frac{v_a + v_b}{2}$$

$$J_{ab} = 4C_1 \chi' \int_{\psi} \cos \psi \sin^2 \psi d\psi \int_{v_r} R_{\Delta v}(v_r) v_r^5 e^{-v_r^2/\alpha} dv_r \tag{2D.14}$$

β and α are velocity selector design parameters. The first term of (2D.13) is a contribution to the kinetic factor from molecular velocities below the selector nominal transmission velocity V_0 ; the second term is that for velocities above V_0 .

Actually, (2D.13) is an approximation because, strictly speaking, (2D.14) results only for a term of $B(V_0, v_1) \propto (1/v_1)$. The rigorous integral expression for a term of $B(V_0, v_1) \propto 1$

contains an additional $v_r \cos \Psi$ in excess of the integrand of (2D.14). This more complicated integrand has been expressed in terms of (2D.13) and (2D.14) because (2D.14) is the more easily evaluated when $R_{\Delta v}(v_r)$ is proportional to even powers of v_r . It happens in such a situation that one of the two integrations of (2D.14), the v_r integration, can be readily carried out analytically, thus avoiding the need of performing any double numerical integrations when (2D.3) is evaluated.

The approximated terms of (2D.13), those containing $\bar{V}$, result from the fact that the molecular beam velocity distribution can be expressed as (2D.15) before the transformation from v_1, v_2 coordinates is carried out.

$$v_1^2 e^{-\alpha_1 v_1^2} \quad \bar{V} v_1 e^{-\alpha_1 v_1^2} \quad (2D.15)$$

for $v_a \leq v_1 \leq v_b$

Expression (2D.15) is a good approximation because the velocity extrema in the velocity selector pass-band, v_a and v_b , do not differ greatly from v_1 . The replacement of one v_1 by $\bar{V}$ implies a very small error indeed after the integration is carried out.

The evaluation of (2D.14) is straight forward once the limits of integration are determined. When the maximum and minimum speeds transmitted by the velocity selector are v_b and v_a , respectively, and this transmitted distribution of speeds is folded with a complete Maxwellian distribution for the crossed beam, the combina-

tions of v_r and Ψ that are possible candidates for collision are those represented in Fig. 2D.1 which lie between the curves $v_r = v_b \sec \Psi$ and $v_r = v_a \sec \Psi$, $0 \leq \Psi \leq \pi/2$. A minimum relative collision velocity V_{R_0} that enters via the cross section further limits the combinations of v_r and Ψ which deserve consideration. Evidently, evaluation of (2D.14) should proceed according to (2D.16)

$$J_{ab} = \int_{\Psi=\Psi_1}^{\Psi_{\max}} \int_{v_r=V_{R_0}}^{v_b \sec \Psi} (2D.14) - \int_{\Psi=\Psi_2}^{\Psi_{\max}} \int_{v_r=V_{R_0}}^{v_a \sec \Psi} (2D.14) \quad (2D.16)$$

where $\Psi_{\max} = \pi/2$. Of course, $\Psi_{\max}$ can be less than $\pi/2$ in the evaluation (as shown in Fig. 2D.1) if insignificant error is introduced by lowering that upper limit. This conveniently applies in the evaluations carried out for H_2 , D_2 and N_2 with Na at the experimental temperatures.

When these considerations are applied, (2D.16) can be evaluated by (2D.17).

$$J_{ab} = I(\Psi_{\min} = \Psi_1, \Psi_{\max}) - K(\Psi_{\min} = \Psi_1, \Psi_{\max}, C = v_b^2) + I(\Psi_{\min} = \Psi_2, \Psi_{\max}) - K(\Psi_{\min} = \Psi_2, \Psi_{\max}, C = v_a^2) \quad (2D.17)$$

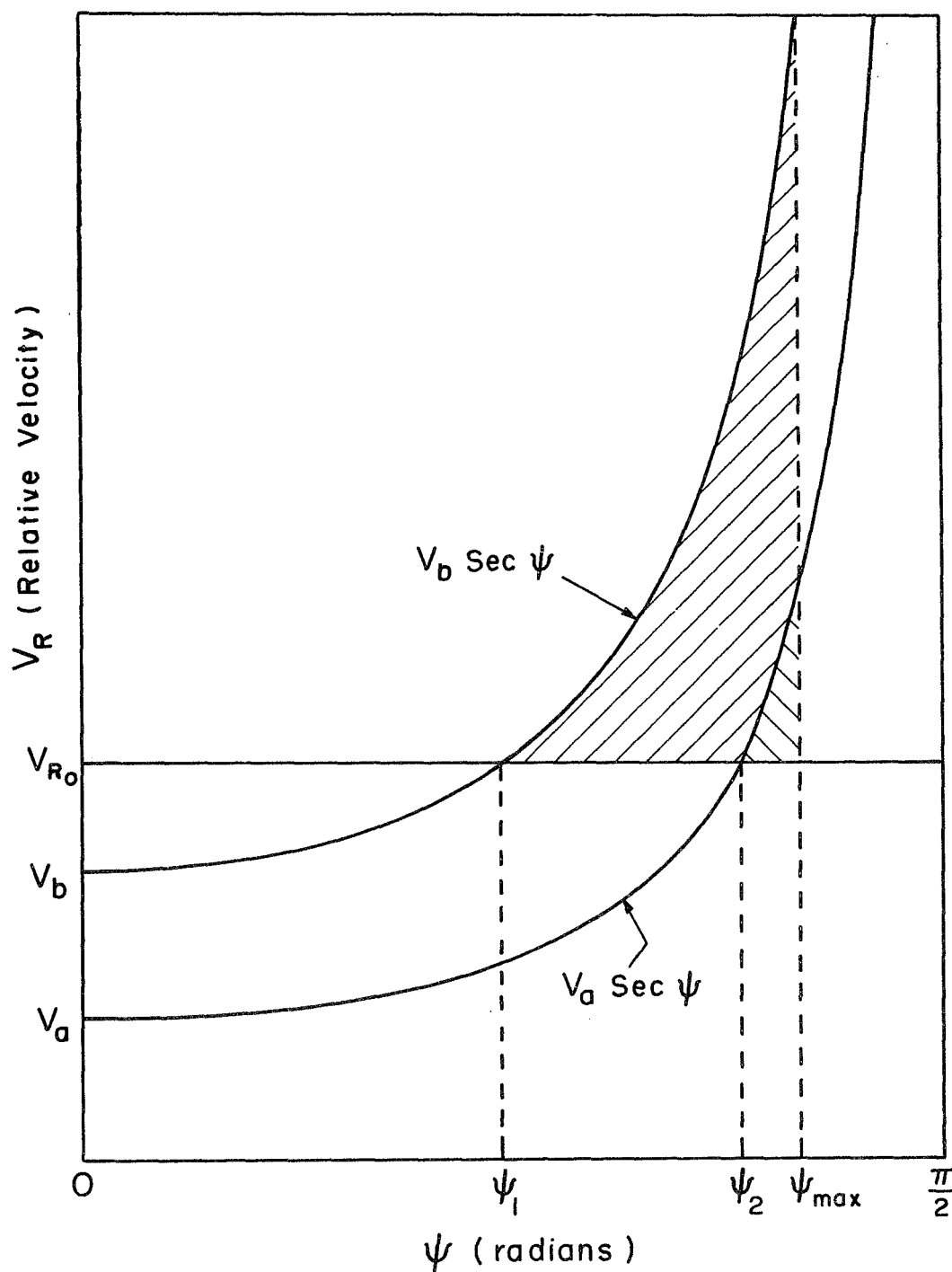


Figure 2D.1. Diagram that generally illustrates the v_r, ψ region that must be considered in the velocity-selected experiment.

For cross section velocity dependence (2.21), $I(\psi_{\min}, \psi_{\max})$ and $K(\psi_{\min}, \psi_{\max}, C)$ are defined by (2D.18) and (2D.19), respectively.

$$I(\psi_{\min}, \psi_{\max}) = \frac{C_1 D^{3/2}}{(-2\delta_d)^{3/2}} \int_{y_{\min}}^{y_{\max}} \frac{y - 2D\delta_d - D\alpha_2}{y^3} (y^2 + 2y + 2) e^{-y} dy \quad (2D.18)$$

$$\text{where } D = \frac{v_{R_0}^2}{\alpha_2}, \quad y_{\max} = D [2\delta_d \cos^2 \psi_{\max} + \alpha_2], \quad y_{\min} = D [2\delta_d \cos^2 \psi_{\min} + \alpha_2]$$

$$K(\psi_{\min}, \psi_{\max}, C) = \frac{C_1 C}{\alpha_2^2} \int_{z_{\min}}^{z_{\max}} \frac{z - 2C\delta_d - C\alpha_2}{z^3} (z^2 + 2z + 2) e^{-z} dz \quad (2D.19)$$

$$\text{where } z_{\max} = C [2\delta_d + \alpha_2 \sec^2 \psi_{\max}] \text{ and } z_{\min} = C [2\delta_d + \alpha_2 \sec^2 \psi_{\min}]$$

When cross section velocity dependence (2.22) is considered and $I \rightarrow I'$ and $K \rightarrow K'$ in (2D.17), $I'(\psi_{\min}, \psi_{\max})$ and $K'(\psi_{\min}, \psi_{\max}, C)$ are defined by (2D.20) and (2D.21).

$$I'(\psi_{\min}, \psi_{\max}) = I(\psi_{\min}, \psi_{\max}) - \frac{C_1 v_{R_0}^2 D^{1/2}}{(-2\delta_d)^{3/2}}$$

$$\int_{y_{\min}}^{y_{\max}} \frac{y - 2D\delta_d - D\alpha_2}{y^2} (y + 1) e^{-y} dy \quad (2D.20)$$

$$K'(\psi_{\min}, \psi_{\max}, C) = K(\psi_{\min}, \psi_{\max}, C) - \frac{C_1 C v_{R_0}^2}{a^2}$$

$$\int_{z_{\min}}^{z_{\max}} \frac{z - 2C\delta_d - C/a^2}{z^2(z - 2C\delta_d)} (z+1) e^{-z} dz$$

(2D.21)

There are three different cases that must be considered when $\psi_{\min}$ is determined; $\psi_{\max}$ can be chosen arbitrary to insure that all significant contributions from the integrands of (2D.18), (2D.19), (2D.20) and (2D.21) have been summed. The three cases are listed in (2D.22).

$$(a) \quad V_{R_0} > V_b > V_a$$

$$\psi_1 = \arccos \left[V_b/V_{R_0} \right]$$

$$\psi_2 = \arccos \left[V_a/V_{R_0} \right]$$

$$(b) \quad V_b \geq V_{R_0} \geq V_a$$

$$\psi_1 = 0$$

$$\psi_2 = \arccos \left[V_a/V_{R_0} \right]$$

$$(c) \quad V_{R_0} \leq V_a < V_b$$

$$\psi_1 = 0$$

$$\psi_2 = 0$$

(2D.22)

The actual evaluation of (2D.13) via (2D.17), (2D.18), (2D.19), (2D.20), and (2D.21) employing conditions (2D.22) has been carried out numerically on the IBM 7090 computer using Gaussian Quadrature for $n = 16$. The program was set up to choose the largest $\psi_{\max}$ for which all integrals could be evaluated without causing an underflow. Arbitrary manipulation of $\psi_{\max}$ in the program demonstrated that $Q_{\Delta V}(V_0, T_1)$ had converged to more than three significant digits at all V_0 and T_1 at which calculations were performed for H_2 , D_2 and N_2 .

Partial results of the calculated $\beta_{\Delta V,0}(=Q_{\Delta V}(V_0, T_1))$. $\left(\frac{e^{-\epsilon_v/kT_1}}{\sum e^{-\epsilon_v/kT_1}} \right)$ for cross section velocity dependence (2.21) appear in Figs. 2D.2, 2D.3, 2D.4 and 2D.5. Those for (2.22) appear in Figs. 2D.6, 2D.7, 2D.8 and 2D.9. The calculations of $\beta_{5,0}$ for H_2 , $\beta_{7,0}$ for D_2 and $\beta_{8,0}$ for N_2 are necessarily identical for either (2.21) or (2.22). The curves appearing on succeeding pages have been employed for fitting the experimental velocity-selected data, as described in Section V.

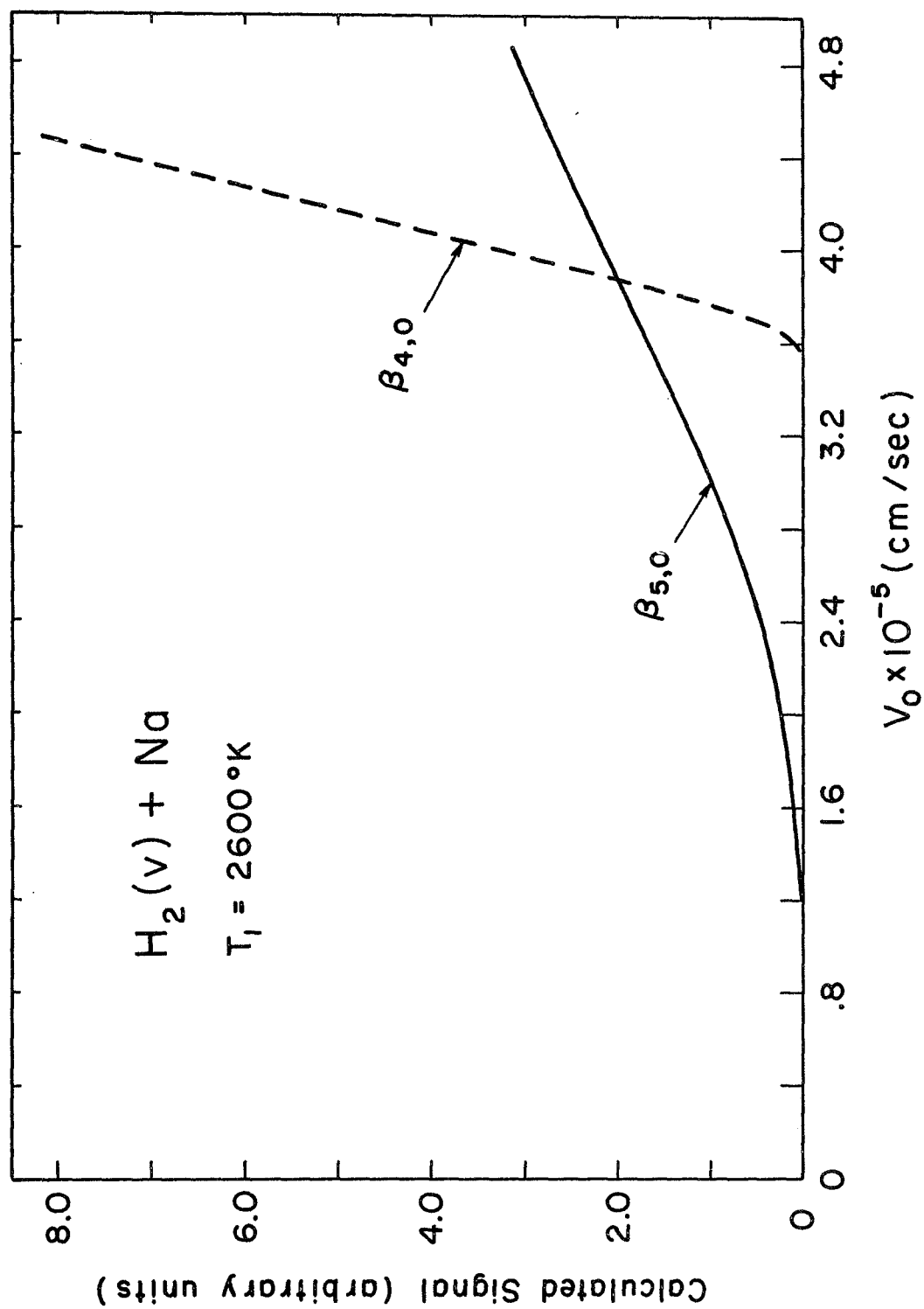


Figure 2D.2. Temperature-velocity functions $\beta_{v,0}$ calculated using cross section (2.21). The experimental data have been fitted for a weighted superposition of these functions.

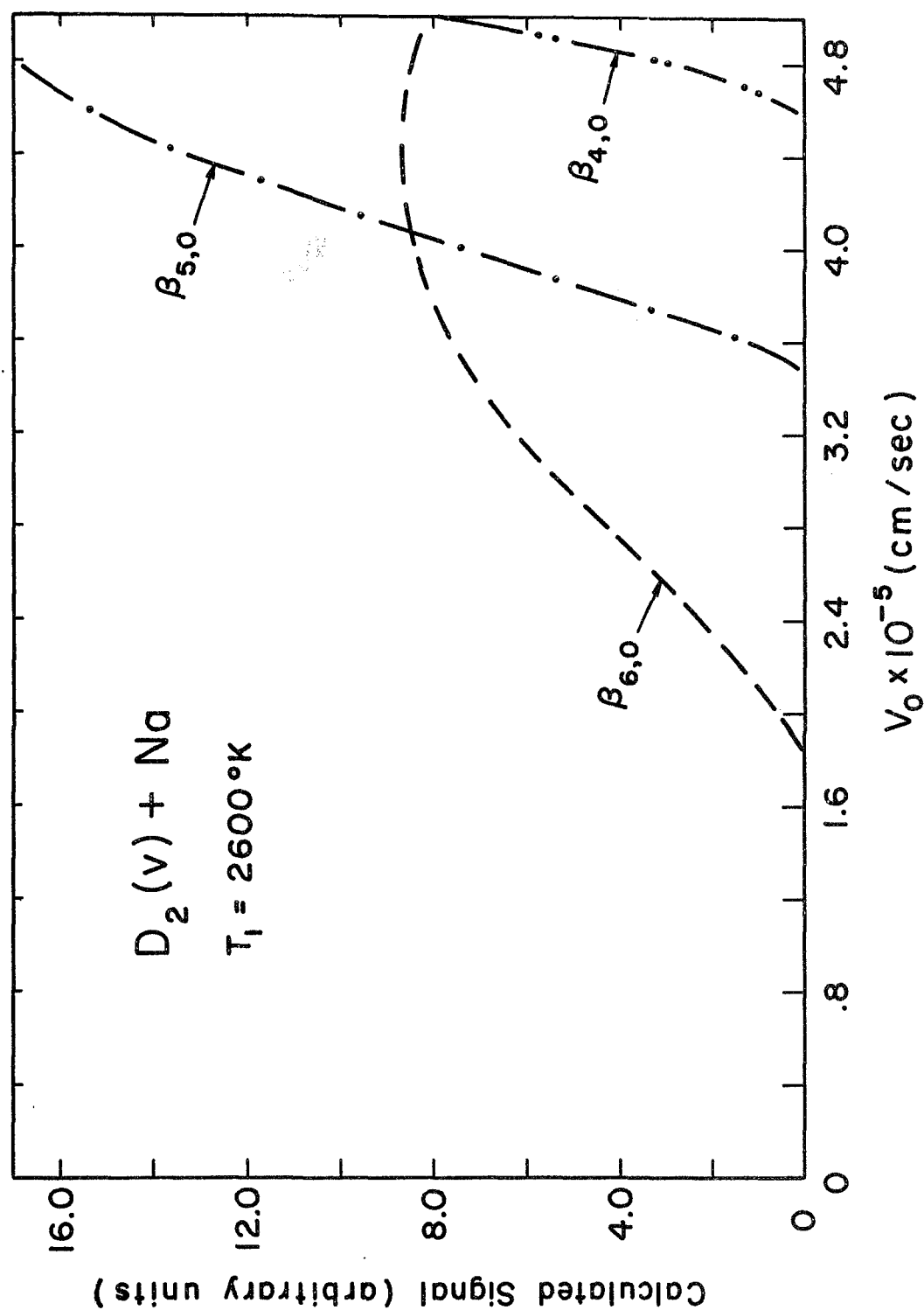


Figure 2D.3. Temperature-velocity functions $\beta_{v,0}$ calculated using cross section (2.21). The experimental data have been fitted for a weighted superposition of these functions.

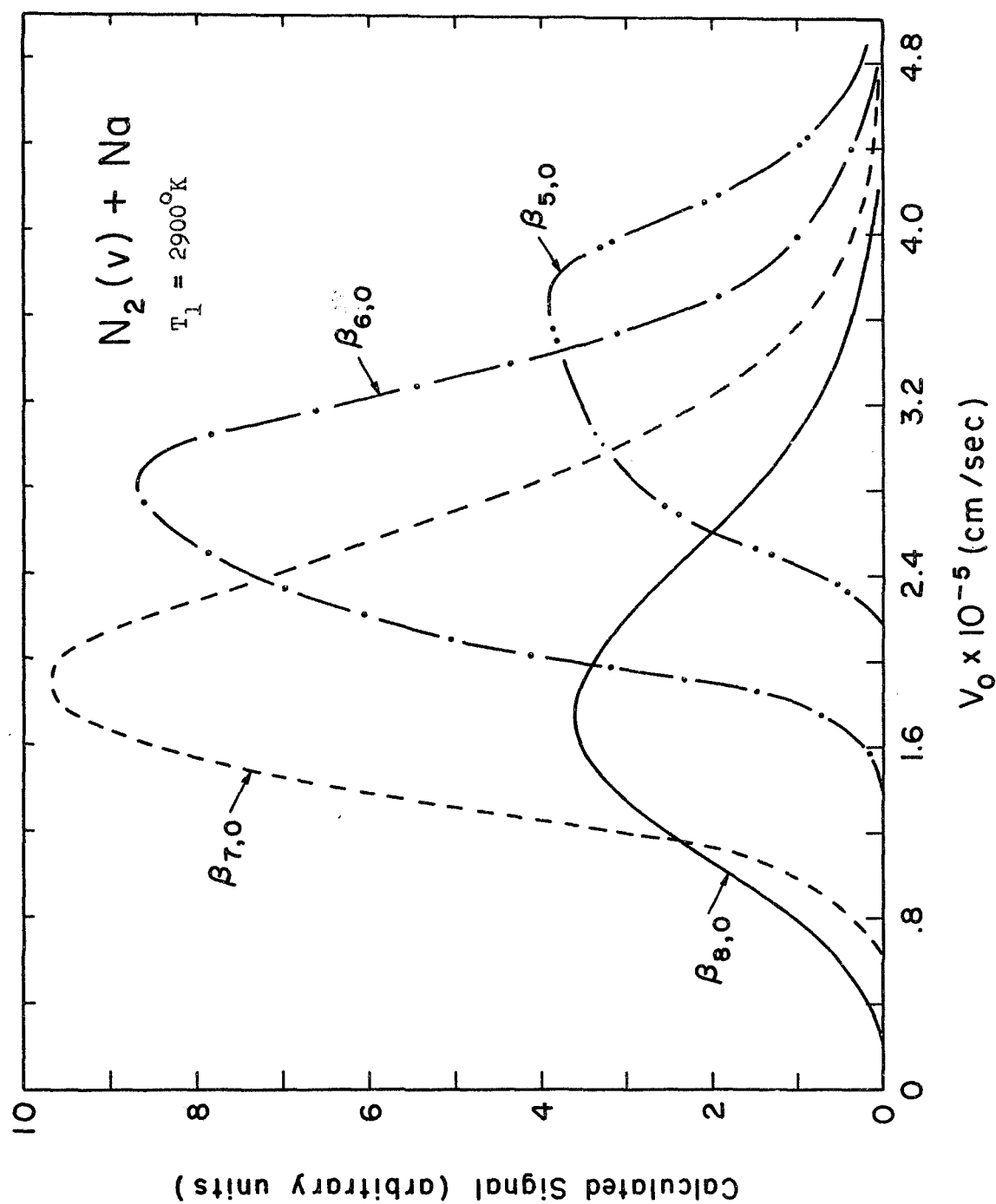


Figure 2D.4. Temperature-velocity functions $\beta_{v,0}$ calculated using cross section (2.21). The experimental data have been fitted for a weighted superposition of these functions.

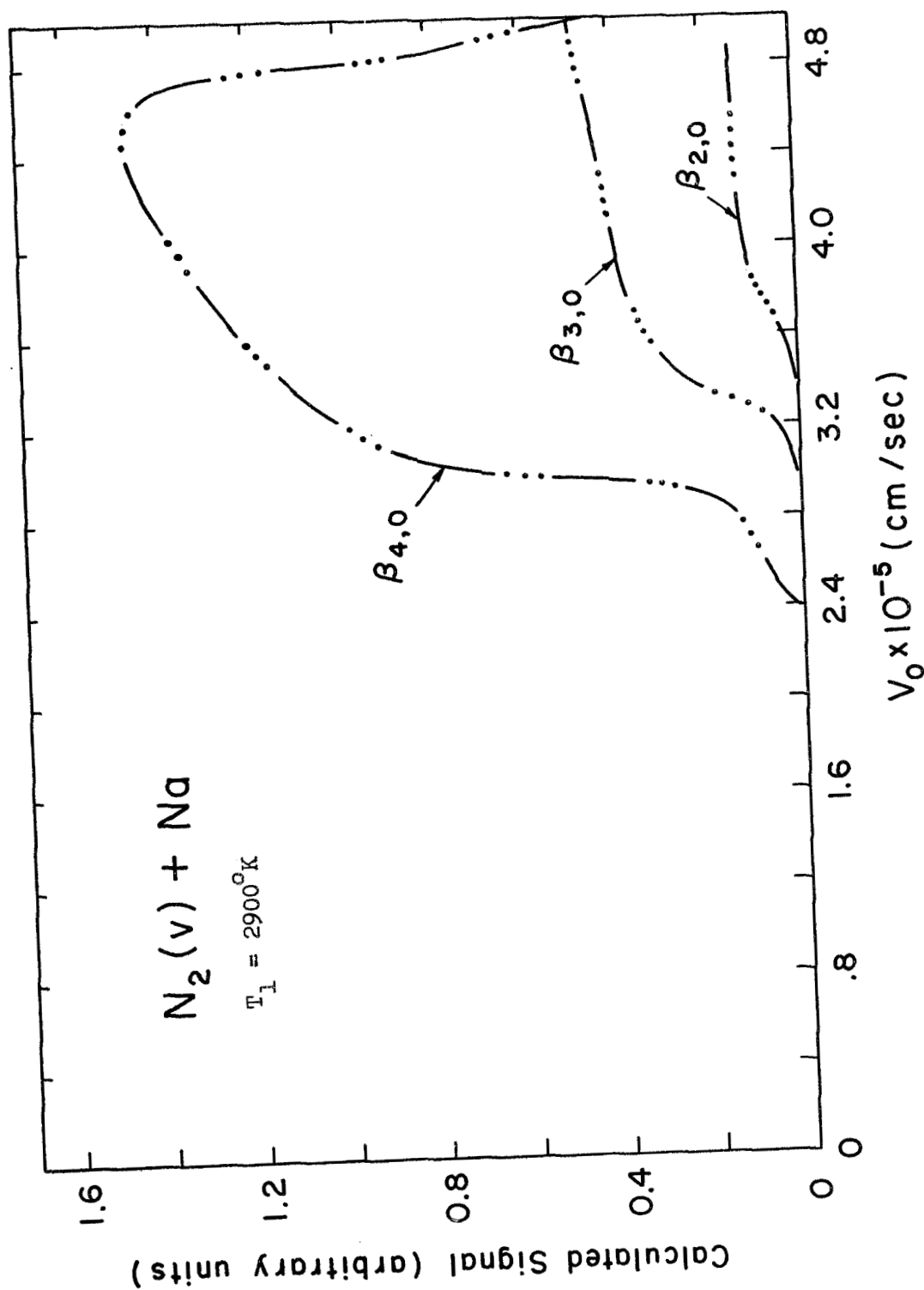


Figure 2D.5. Temperature-velocity functions $\beta_{v,0}$ calculated using cross section (2.21). The experimental data have been fitted for a weighted superposition of these functions.

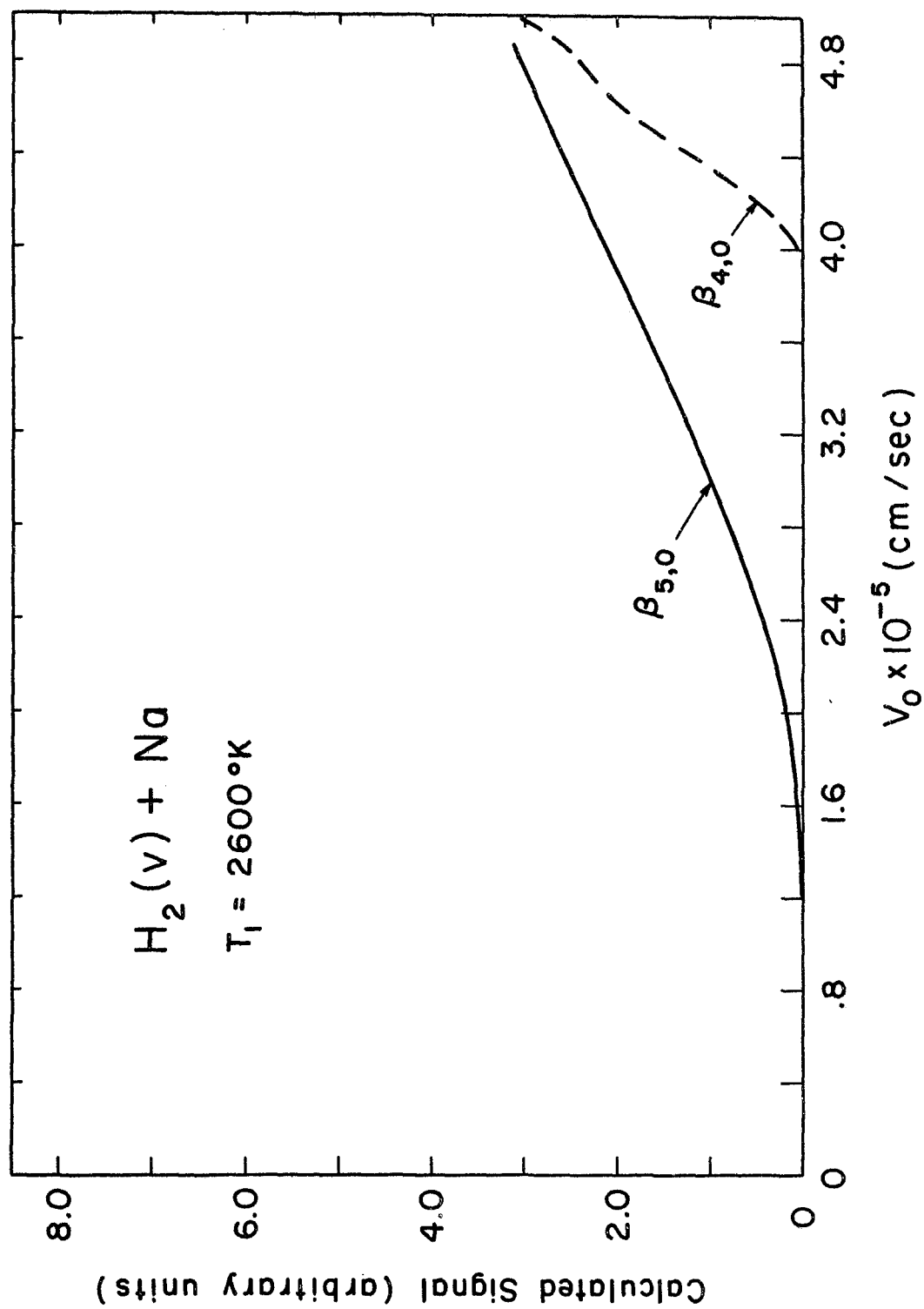


Figure 2D.6. Temperature-velocity functions $\beta_{v,0}$ calculated using cross section (2.22). The experimental data have been fitted for a weighted superposition of these functions.

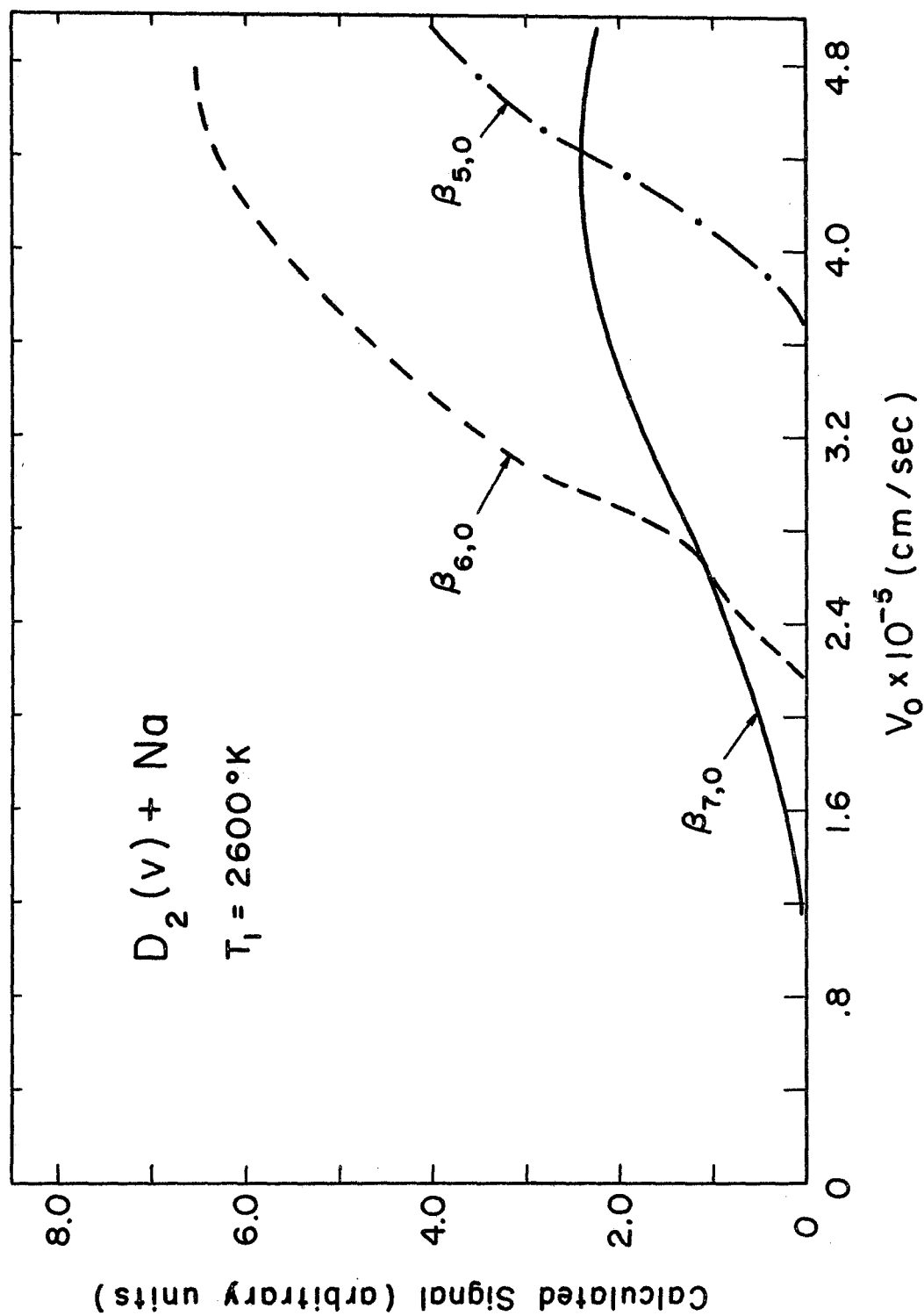


Figure 2D.7. Temperature-velocity functions $\beta_{v,0}$ calculated using cross section (2.22). The experimental data have been fitted for a weighted superposition of these functions.

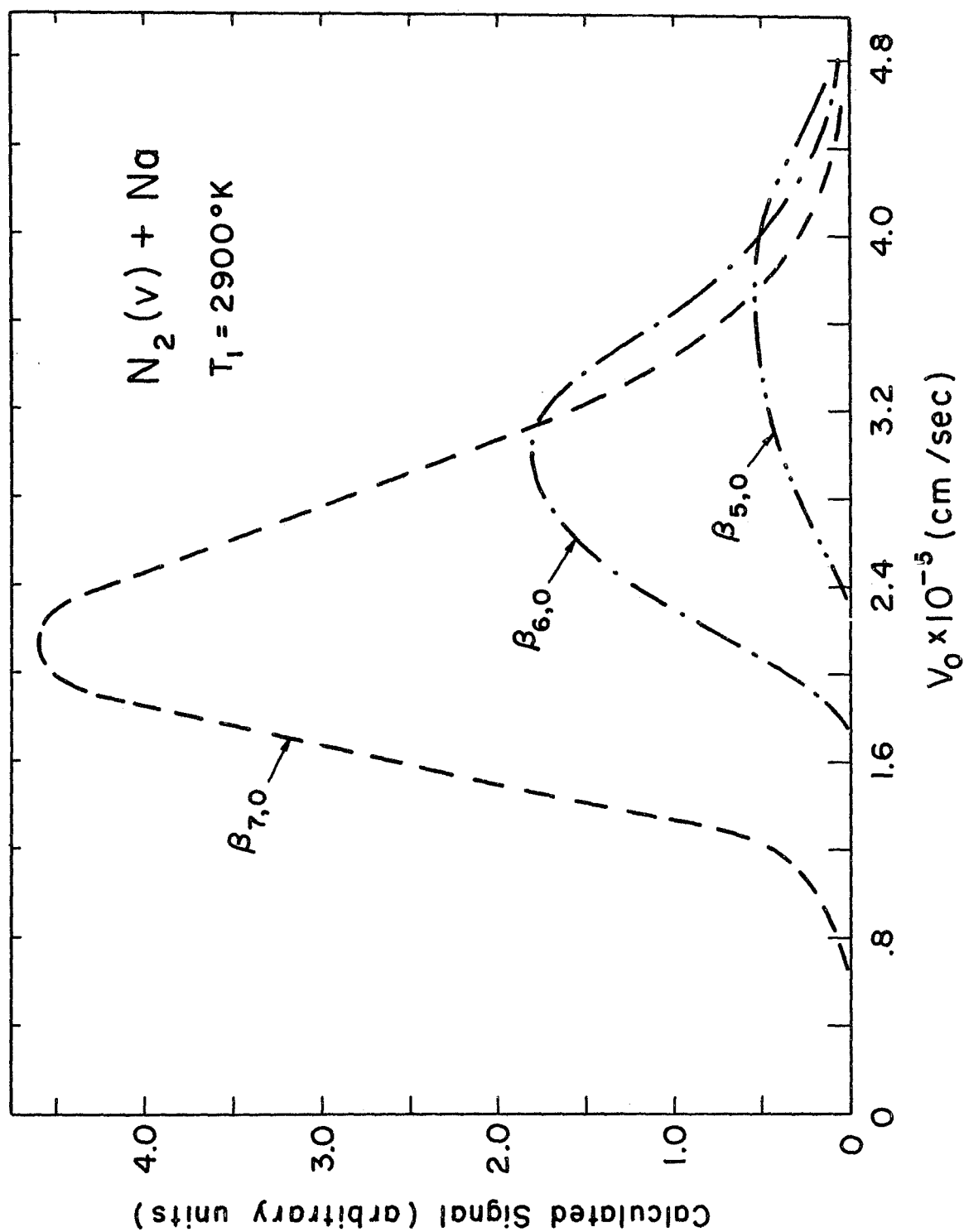


Figure 2D.8. Temperature-velocity functions $\beta_{v,0}$ calculated using cross section (2.22). The experimental data have been fitted for a weighted superposition of these functions.

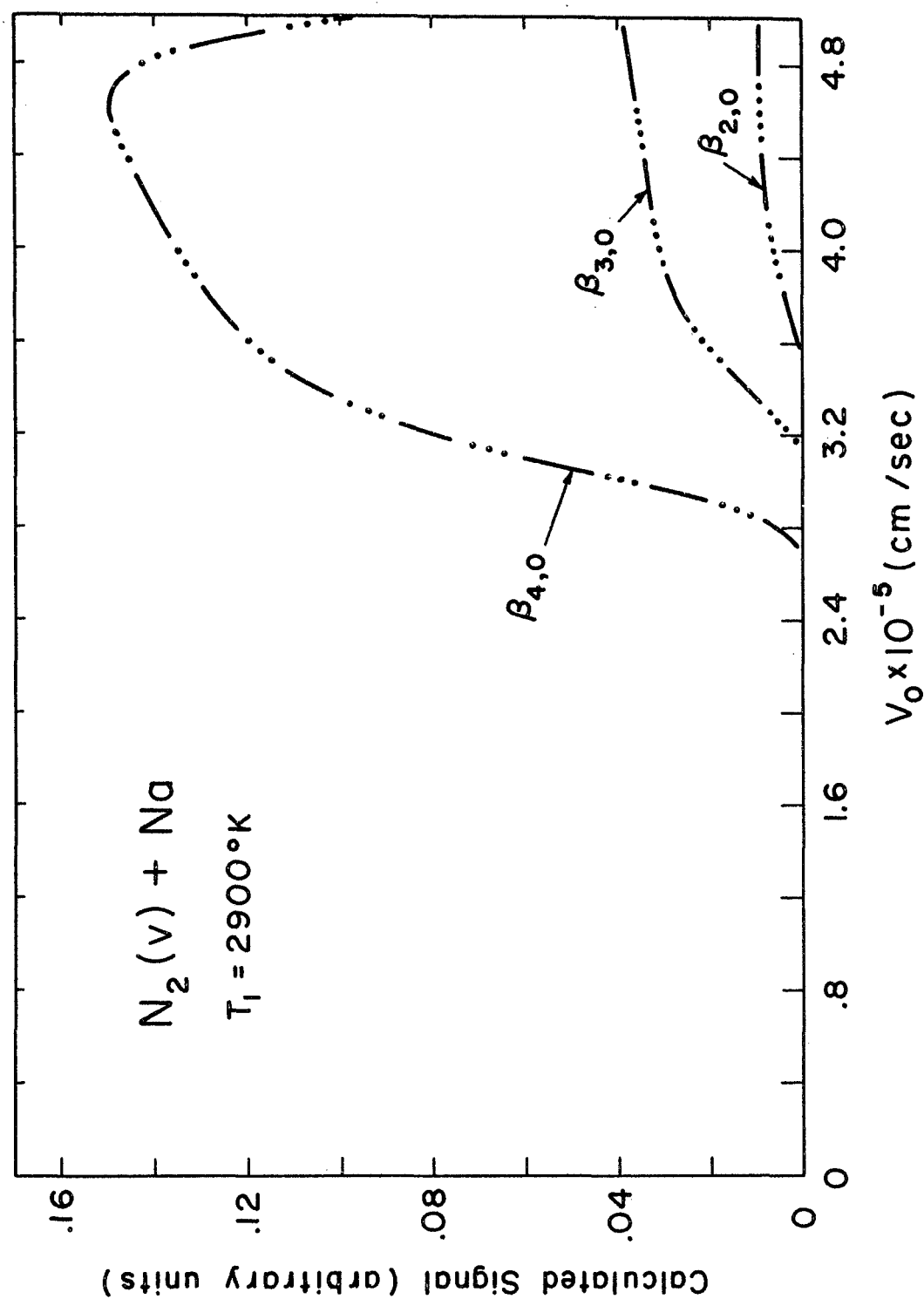


Figure 2D.9. Temperature-velocity functions $\beta_{v,0}$ calculated using cross section (2.22). The experimental data have been fitted for a weighted superposition of these functions.

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