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Dudley R. Herschbach

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CHEMICAL REACTIONS IN CROSSED MOLECULAR BEAMS\*

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Dudley R. Herschbach

Department of Chemistry and Lawrence Radiation Laboratory,  
University of California, Berkeley, California

Summary of a lecture presented before the July, 1961, meeting of the California Section of the American Chemical Society.

The first molecular beam experiments were carried out fifty years ago, immediately after the invention of the high speed vacuum pump had made it possible to form directed beams of neutral molecules at sufficiently low pressures to prevent their disruption by collisions. The characteristic directness of molecular beam experiments destined them to play a leading role in the evolution of modern physics.<sup>1,2</sup> However, until recent years, beam techniques have been little used in chemistry. Although the advantages of studying chemical reactions in crossed beams have occasionally been pointed out, the obvious difficulty of detecting the products at the low intensities available in beams discouraged sensible experimentalists from attempting such studies.

This pessimism has now been dispelled by recent experiments, which show that a large class of reactions of alkali metals with halogen containing compounds can be studied in crossed beams with almost rudimentary apparatus. It has been known since Michael Polanyi's work in the 1920's that many of these alkali reactions have very large cross sections, of the order of <sup>or</sup> even somewhat larger than "hard-sphere" diameters,

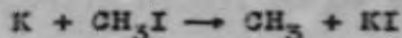
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and a remarkably sensitive and specific detector for alkali metals and their compounds has been available since Langmuir's studies of surface ionization, also over thirty years ago. This detector has been used in hundreds of molecular beam experiments. It consists simply of a heated filament of a metal such as tungsten and will ionize with nearly 100% efficiency materials having ionization potentials lower than about 4 or 5 volts, such as K, Rb, and Cs.

The feasibility of crossed beam studies of alkali reactions had been shown in two experiments before our work at Berkeley was undertaken. In 1955, Taylor and Datz<sup>3</sup> at Oak Ridge reported a study of the reaction  $K + HBr \rightarrow H + KBr$ . Although the traditional tungsten surface ionization detector is about equally sensitive to K and KBr, Taylor and Datz found that a platinum alloy is much more effective for K than for KBr. From the difference in the signals read on the two detectors, they were able to distinguish the small amount of reactively scattered KBr from the large background of elastically scattered K atoms. The experiment gave a value of about  $10^{-3}$  for the collision yield, the ratio of KBr molecules detected to K atoms scattered out of the parent beam. An activation energy of 3 kcal/mole was estimated from the variation of the yield with beam temperatures. In 1960, Greene, Roberts, and Ross<sup>4</sup> at Brown University reported a further study of this reaction. They used a mechanical rotor to select the K beam velocity and thus obtained detailed information about the energy dependence of the collision yield.



In the initial experiments at Berkeley, which were begun last Fall, we wished to study the angular distribution of reaction products. On the basis of simple theoretical considerations, to be described later, it was decided to try



and analogous reactions. The theory indicated that the distribution of KI in this reaction would yield information about the manner in which the reaction energy is partitioned between internal excitation of the products and their relative translational motion, and happily this proved to be the case. In these studies we have been very fortunate to have the collaboration of George Kwei, Sam Norris, and Dr. Jim Kinsey, and the success enjoyed in these experiments owes much to their hard work.

"It's All a Matter of Intensity"

Let us first briefly examine the apparatus and recite a favorite list of orders of magnitude involved in these experiments.

Fig. 1 shows a sketch of the apparatus, with cold shields, collimating slits, movable flags to interrupt the beams, and other details omitted. In the scattering chamber the background pressure is maintained at about  $10^{-7}$  mm or roughly  $10^{-10}$  atmospheres. This corresponds to  $10^9$  molecules/cc and a mean free path of 500 meters (compared with  $10^{19}$  molecules/cc and a mean path of  $500 \text{ \AA}$  at atmospheric pressure). This is not, however, an ultrahigh vacuum when compared with modern laboratory practice (which is striving for conditions in intergalactic space, at  $10^{-15}$  mm, 10 molecules/cc and a mean

path of 1 light-second). As the reactants are condensable, a very high pumping speed (200,000 liters/sec) is obtained by enclosing the scattering region in a copper box attached to a large liquid nitrogen trap. If air were condensable and the walls were suddenly cooled to liquid nitrogen temperature, this lecture hall would be evacuated to  $10^{-7}$  mm in less than a second.

As shown in Fig. 1, the beams are formed by thermal effusion from ovens mounted on a turntable which is rotated to sweep the angular distribution past the detector. Vertical adjustment of the detector position allows the scattering to be measured out of the plane as well as in the plane of the incident beams.

The total flux of K atoms through the oven slit (0.025 cm wide and 1 cm high) is about  $10^{17}$  molecules/sec. In chemical engineering terms, this is a flow rate of one pound per year. Widening the slit would not allow us to increase the flux, as the pressure within the oven would have to be decreased proportionately. Otherwise the condition for effusive flow, that the mean free path within the oven be greater than the slit width, would be violated and the essentially collision free character of an effusive beam would be lost because of hydrodynamic streaming. Use of a double chamber oven for K allows the beam temperature to be varied about three hundred degrees independently of the pressure which can then be maintained to provide the maximum intensity of effusive flow.

Only about  $10^{-5}$  of the total K flux passes through the collimating slits and contributes to the K beam intensity as measured at the detector (20 cm distant and 0.005 cm wide). At the peak beam intensity of  $10^{12}$  molecules/sec, it would take nearly a minute for a monolayer of atoms to build up on the detector if it were cold.

The  $\text{CH}_3\text{I}$  oven slit is placed only 1.7 cm from the K beam. The intersection of the beams defines a volume of about 0.04 cc ( $0.27 \times 0.15 \times 1$  cm), within which the concentration of K is  $10^{10}$  molecules/cc or  $10^{-11}$  moles/liter, equivalent to a pressure of  $10^{-6}$  mm, and that of  $\text{CH}_3\text{I}$  is about 100-fold greater.

Of the  $10^{14}$  K atoms/sec which enter the reaction volume, about 0.1% react to form KI while about 10% are scattered elastically. As already mentioned, the reaction cross section is very large, about  $10 \text{ \AA}^2$ , and corresponded to "reaction on every collision" under the conditions of Michael Polanyi's experiments. However, in beam experiments elastic scattering always predominates, since quite weak interactions are sufficient to remove a molecule from a well collimated beam and thus count as collisions. The observed attenuation of the K beam by  $\text{CH}_3\text{I}$  implies an elastic cross section of  $1000 \text{ \AA}^2$ . This means that encounters in which the K and  $\text{CH}_3\text{I}$  pass at a distance of  $20 \text{ \AA}$  still count as collisions. At this distance the interaction comes from the long range  $r^{-6}$  van der Waals attraction term in the intermolecular potential and amounts to only 0.3 cal/mole (or  $0.1 \text{ cm}^{-1}$  in spectroscopic units).



The steady-state concentration of KI in the reaction volume is roughly  $10^7$  molecules/cc, the pressure  $10^{-9}$  mm. About  $10^{11}$  molecules/sec are formed and fly out of the reaction volume, but only a fraction of these enter the small solid angle subtended by the detector. Fortunately, the angular distribution of KI turns out to be quite anisotropic, so this dilution factor is not as severe a limitation as it might be. At the peak of the KI distribution about  $10^7$  molecules per second arrive at the detector; to deposit a monolayer of KI molecules would require more than a month and to collect a pound about 10 billion years.

In Fig. 2 are shown typical results for the  $K + CH_3I$  reaction.<sup>5</sup> The parent K beam of  $5 \times 10^{-8}$  amps is attenuated 7% by the crossed  $CH_3I$  beam. Readings on the platinum detector (solid circles) are normalized to those on tungsten (open circles) at the parent beam peak. It is seen that in this case the use of differential detection is not crucial, as the KI distribution is displaced far enough from the K beam to appear as a pronounced bump on the tungsten detector. In Fig. 2b the KI distributions are normalized so that the area under the curves gives the collision yield, which is  $5 \times 10^{-4}$  and indicates the reaction cross section is about  $7 \text{ \AA}^2$ , as expected. The circles are derived from Fig. 2a and the triangles from a replicate experiment done several months later under conditions of somewhat lower resolution. The dashed curve is calculated as described later. Measurements at several temperatures of the incident beams give practically no change in the yield and

indicate that the activation energy of the reaction is negligibly small, less than 0.3 kcal/mole.

### Mechanics of Collisions

In the analysis of the angular distribution of scattered products, we may take advantage of restrictions imposed by the conservation of energy and linear momentum.<sup>6</sup> These provide geometrical relationships between the velocity vectors in the asymptotic initial and final states of a collision. Here we need only Newton's laws, as the relationships also hold rigorously in quantum mechanics. The reason is that in these asymptotic translational states the beam particles are too far apart to interact, hence need not be precisely localized in space and can be assigned definite momenta despite Heisenberg's principle.

The observed angular distribution of KI is compared with that allowed by the conservation laws in Fig. 3, which we like to call a Newton diagram. The most probable initial velocity vectors of the reactants are shown;  $\mathbf{y}$  denotes the relative velocity vector and  $\mathbf{g}$  is the center of mass vector. As a consequence of momentum conservation,  $\mathbf{g}$  remains constant throughout a collision; only the motion relative to the center of mass involves chemical interactions. This is, of course, just the situation in the perennial freshman physics problem which requires one to show that the center of mass trajectory remains unperturbed when a cannon shell explodes in flight. Therefore we shall be



interested in what an observer riding with the center of mass would see.

As indicated in Fig. 4, the total energy available to the reaction products (omitting the constant energy of the center of mass motion) is  $E + W + \Delta D^\circ$ . In the present case,  $\Delta D^\circ$  is the difference in dissociation energy of the K-I and C-I bonds, about 22 kcal/mole (measured from the zero-point vibrational levels);  $E$  is the initial relative translational kinetic energy of the reactants and has a thermal distribution peaked about 1.3 kcal/mole;  $W$  is the internal energy of  $\text{CH}_3\text{I}$ , most of which is in the ground vibrational state, with a rotational energy distribution peaked near 0.3 kcal/mole. About 7% of the  $\text{CH}_3\text{I}$  molecules have an additional 0.7 kcal/mole in thermal excitation of the C-I stretching vibration. Formation of the products  $\text{CH}_3 + \text{KI}$  therefore frees about 24 kcal/mole to be partitioned between  $E'$ , the final relative translational energy, and  $W'$ , the vibrational and rotational excitation of the products. If all of the available energy goes into internal excitation ( $W' = 24$  kcal/mole), there would be none left for the translational energy of separation ( $E' = 0$ ), the products would stick together and their angular distribution would coincide with that of the center of mass. If the other limiting case obtains, the products would be formed in their lowest internal states ( $W' = 0$ ), all of the reaction energy would go into translational separation ( $E' = 24$  kcal/mole) and the products would recoil away from the center of mass with the maximum possible velocity.

Another important factor in Fig. 3 involves the mass ratio of the products. In order to balance linear momentum, the tip of  $\underline{g}$  must divide the relative velocity vector  $\underline{y}$  into segments having lengths in the inverse ratio of the masses of the collision partners, a requirement obvious to everyone who has experimented with a teeter-totter. Thus the angular distributions of the products are correlated, and a determination of the magnitude of the recoil velocity of either product will show what fraction of the reaction energy has gone into internal excitation. Since the recoil velocity might have any direction, in the Newton diagram of Fig. 3 the possible spectrum of recoil vectors for KI is represented by a set of spheres, one for each of the accessible values of  $E'$ .

#### Summary of Results

We see from the diagram that the broad peak observed near  $83^\circ$  in the laboratory corresponds to scattering in which an observer stationed at the center of mass would see KI recoil backward (and  $\text{CH}_3$  forward) with respect to the incoming K beam. Reactions producing large values of  $E'$  can contribute to this peak only if the recoil velocity vector deviates considerably from the direction of the initial relative velocity vector  $\underline{y}$ , as illustrated by the vector labeled  $\underline{g}$ . The scattering must have cylindrical symmetry about  $\underline{y}$ , however, since the incident beams contain all possible molecular orientations and impact parameters (as discussed further under Fig. 6). Therefore, the angular deviation of the KI recoil vector from  $\underline{y}$  can be



studied directly by measurement of the out-of-plane scattering. As the KI is found to be peaked about the plane of the incident beams, we may conclude that scattering close to the direction of  $\underline{y}$  with small values of  $E'$  is predominant.

The shaded region in Fig. 3 was derived by a calculation which combined the in-plane and out-of-plane data and included the influence of the thermal velocity distributions in the reactants; in order to account for the observed peak, 50% of the KI recoil vectors must lie within the doubly shaded region and 90% within the singly shaded region.

Much of the observed width of the KI peak is due just to averaging over the velocity distributions, as shown by the dashed curve in Fig. 2b. This was calculated assuming that all of the KI recoiled directly backwards along  $\underline{y}$ , with internal excitation  $W' = 21$  kcal/mole, corresponding to  $E' - E = 1.6$  kcal/mole. Although the result suggests that the products may be produced in a rather narrow range of internal states, it will be necessary to employ velocity selection to obtain a definitive test of this point.

Included at the lower right hand corner of Fig. 3 is the estimate of the most probable  $\text{CH}_3$  recoil velocity implied by the analysis of the KI distribution and conservation of momentum. If we express the velocities in terms of "translational temperatures," the KI is only slightly warm at  $340^\circ\text{K}$ , whereas the effect of the mass ratio boosts  $\text{CH}_3$  to  $1350^\circ\text{K}$ . If it were possible to measure the angular distribution of  $\text{CH}_3$ , the magnification provided by the mass ratio would enable us to



obtain much higher resolution in constructing our picture of the scattering as viewed from the center of mass.

From the results for the  $K + CH_3I$  reaction, we can predict what to expect for the angular distributions in other  $M + RX$  reactions. If we assume the products will show a similar peaking about the direction of  $y$  and a high level of internal excitation, the predictions depend only on the beam temperatures and the masses of  $M$ ,  $R$ , and  $X$ . The results found for several cases have nicely confirmed these features.<sup>7,8</sup> For the reactions of  $Rb$  and  $Cs$  atoms with  $CH_3I$ , plots analogous to Fig. 2b show peaks at  $66^\circ$  and  $52^\circ$ , respectively, within a few degrees of the predictions. Again, most of the width of the peaks is accounted for by the velocity distributions of the reactants. The activation energy for these reactions is also found to be negligibly small. The reactions of  $K$  atoms with ethyl, 1-propyl, n-propyl, and n-butyl iodides have also been studied. Under conditions similar to those of Fig. 2b, all these reactions have  $KI$  peaks in the neighborhood of  $90^\circ$ . The internal excitation of the products appears to increase slightly with the mass of the  $R$  group. It is interesting that the collision yield remains about the same as for the  $CH_3I$  reaction, since we might have expected to see some effect from "steric interference" as the  $R$  group became larger. Perhaps this offers some very circumstantial evidence for the importance of forces that tend to produce favorable alignment as the reactants approach, but this is another question to be examined in further experiments. We have not yet studied alkyl chlorides and bromides except to confirm that they are much less reactive than iodides.

Another check on the angular distribution analysis has been obtained by varying the angle of intersection of the reactant beams. It is found that the KI peak shifts to  $66^\circ$  and to  $123^\circ$  for intersection angles of  $60^\circ$  and  $135^\circ$ , respectively, in agreement with predictions derived by simply redrawing the Newton diagram of Fig. 3 for the new intersection angles. The experiment at  $135^\circ$  also provided evidence against a "sticky collision" model which predicts that the KI should scatter forward and backward along  $y$  with equal intensity.<sup>b</sup> For the perpendicular intersection used in Fig. 2, the possible presence of forward peaking of KI along  $y$  could not be definitely settled because elastic scattering hides any reactive scattering that might appear within  $\pm 30^\circ$  of the parent K beam. When a  $135^\circ$  intersection is used the whole recoil spectrum is shifted out to wider angles, and the Newton diagram shows that a prominent shoulder should have been found in the  $30^\circ$ - $50^\circ$  region if a forward peak complementary to the observed backward peak were present.

#### Role of Angular Momentum

The preceding analysis has relied only on the classical conservation laws for energy and linear momentum. These laws cannot explain why the angular distribution of alkali iodide turned out to be strongly peaked backwards or why the products are highly excited, although they provide the general relationships which enable us to deduce such features from the observations. Conservation of angular momentum is more intimately connected with the molecular mechanism of the reaction, because both

position and momentum enter into the definition of angular momentum. A rigorous treatment requires quantum mechanics. However, we shall be satisfied with a classical approximation, as it is more pictorial, and we aim only to illustrate the role of angular momentum by simple examples. First we shall consider the "sticky collision" model mentioned above, to show the close connection between the peaking of the angular distribution and angular momentum conservation. We shall also briefly describe two experiments, now being set up, in which it is expected that the excitation of the products might be strongly influenced by restrictions imposed by conservation of angular momentum.

Before and after a collision, the total angular momentum may be divided up into the momenta of the individual collision partners (denoted by  $J$  before and  $J'$  after) and the orbital angular momentum associated with their relative motion ( $L$  before and  $L'$  after). Orbital angular momentum is familiar to anyone who has whirled a ball on a string. The axis of rotation specifies the direction of the vector  $L$ , and its magnitude is given by the mass of the ball times the tangential velocity times the length of the string. In the case of two colliding particles, indicated in Fig. 5, the initial orbital angular momentum is given by  $L = \mu vb$ . Here  $\mu = M_1 M_2 / (M_1 + M_2)$  is the reduced mass of the particles,  $v$  is their initial relative velocity and  $b$  is the "impact parameter," which would be the distance of closest approach if the particles were merely to fly by one another without any interaction. For any given velocity, there



is presumably a wide range of impact parameters which might lead to reaction. Small values of  $b$  (near direct hits) are much less probable than large ones, but the reaction probability must eventually become negligible at sufficiently large  $b$ . A representative value of  $b$  can be estimated by equating  $\pi b^2$  to the total reaction cross section.

The direction of  $\underline{L}$  is perpendicular to both the relative velocity and the impact parameter. As impact parameters with all possible azimuthal orientations about  $\underline{y}$  are equally likely to occur, the distribution of initial  $\underline{L}$  vectors may be visualized as occupying a disk with  $\underline{y}$  as axis (see Fig. 6). On the other hand, the orientations of the initial  $\underline{J}$  vectors are uniformly distributed in space regardless of the direction of  $\underline{y}$ . Thus the total angular momentum  $\underline{L} + \underline{J}$  always has a distribution with cylindrical symmetry about  $\underline{y}$ , as shown in Fig. 6.

For the final state,  $\underline{L}'$  is similarly defined in terms of  $\mu'$ ,  $v'$ , and  $b'$  for the products. However, both  $\underline{L}'$  and  $\underline{J}'$  may have anisotropic distributions about the final relative velocity vector  $\underline{y}'$ .

If we assume that the reaction proceeds via an intermediate complex of the sort invoked in the "activated complex" theory of chemical kinetics or the "compound nucleus" model of nuclear reactions,<sup>9</sup> then  $\underline{L} + \underline{J}$  is the rotational momentum of the complex. Since this rotational momentum must remain invariant throughout the reaction (and in particular equal  $\underline{L}' + \underline{J}'$  for the products), the angular velocity of the complex must vary inversely with its moment of inertia, in the same fashion as that of a ballet

dancer or ice skater executing a "spin." Thus the angular velocity of the complex will increase markedly as the reactants approach, reach a maximum, and then decrease as the products separate (corresponding to the arms out, arms in, arms out sequence for the spinning dancer). The angular velocity at the transition state is very large; a rough estimate for the  $K + CH_3I$  complex is  $10^{12}$  revolutions/sec, equivalent to a "rotational temperature" of about  $5,000^\circ K$  for a gas molecule of similar dimensions.

The analysis becomes quite simple if we suppose the complex is "sticky" enough to make its decomposition completely independent of its mode of formation -- except for the conditions imposed by conservation laws. In the chemical literature there is the overly simple and incorrect statement that the angular distribution would be isotropic in such cases and in particular whenever the complex sticks together long enough to rotate several times before decomposition. We shall see that a pronounced anisotropy will usually appear as the conservation of angular momentum can endow the products with a "memory" of the direction of the initial relative velocity vector.

This comes about because the orbital angular momentum  $L$  is much greater than the angular momentum of the reactants  $J$  in most reactive collisions. Therefore as seen from Fig. 6 most of the total angular momentum vectors  $L+J$  are nearly perpendicular to the initial relative velocity vector. The postulate of sticky collisions implies that the products are equally likely to come off at any azimuthal angle about the direction of  $L+J$ , as shown

in Fig. 7 (where  $\underline{J}$  is omitted for simplicity). To obtain the complete angular distribution we must rotate Fig. 7 about an axis along  $\underline{y}$ , since the distribution of  $\underline{L} + \underline{J}$  vectors has cylindrical symmetry about this axis. The circle shown in Fig. 7 thus generates a sphere and we see that the recoil vectors of the products will fan out around the equator and accumulate along the poles.

This strong forward and backward peaking could be suppressed if the momenta contributed by the reactants becomes comparable to or larger than the orbital angular momentum. In the limiting case with  $\underline{J}$  much larger than  $\underline{L}$ , the distribution of  $\underline{L} + \underline{J}$  becomes nearly isotropic and the direction of  $\underline{y}$  is therefore "forgotten." This limit will seldom be attained in chemical reactions, however.

The reactions of alkali metals with alkyl iodides are typical in that the most probable values of  $\underline{L}$  (corresponding to  $b$  about 1-2 Å) are five or more times larger than  $\underline{J}$  (which is here mainly due to thermal rotation of the RI molecule). Substantial peaking might therefore be expected. Since the experiments show one prominent peak in the angular distribution, not the two equal peaks required by the sticky complex model, it is necessary to assume that the motions of the M, X, and R groups are correlated by a more specific type of interaction. There are several possible mechanisms to be explored and much of the appropriate theory has yet to be worked out, to supply predictions that can be tested in further experiments. Most of the extant theories are not applicable to beam experiments, as they deal only with statistical



averages over many collisions and predict little or nothing about the state of the products after a single collision. One model, which appears capable of at least a qualitative explanation of the main features of the reactions so far studied, is based on the Franck-Condon Principle. Rather than list other speculations, we shall conclude by describing some experiments designed to test predictions which this model makes about the partitioning of the total angular momentum between the momenta of the product molecules,  $J'$ , and their orbital angular momentum,  $L'$ .

The first experiment will attempt to measure the distribution of rotational states of the product MX in the reactions



In the initial state the total angular momentum is made up mainly of orbital angular momentum. However, it is expected that in the final state the orbital angular momentum will be almost negligible; that is,  $\mu'v'b'$  should be much less than  $\mu vb$ , since the reduced mass of the products (approximately just the mass of H) is far smaller than that of the reactants (26 times smaller for the K+HBr reaction, 66 for Cs+HI). If the Franck-Condon mechanism is assumed, the most probable final impact parameter should not differ from the initial one by more than a factor of about two. Likewise, the final relative velocity cannot become large enough to offset more than a fraction of the mass ratio, because the reaction is only slightly exothermic. Fig. 8 shows the relations implied by conservation of angular momentum. This is drawn with  $L$  and  $L'$  in the ratio of the reduced masses. Also, the range of  $J$  arising from the thermal

7

distribution of HX rotations is indicated. It is seen that this analysis requires the MX molecules to be formed predominantly in states with quite large rotational momentum  $J'$ . Furthermore, the orientation of  $J'$  must nearly coincide with  $L$ , so that the MX rotations will be strongly polarized, with  $J'$  aligned nearly perpendicular to the direction of the initial relative velocity vector. (The predicted alignment is much stronger than could be achieved with an external field.) If this situation actually holds, it will have a very pronounced effect on the deflection pattern obtained when the MX molecules are made to pass through an inhomogeneous electric field located between the scattering center and detector.

Incidentally, because of the small exothermicity in these reactions and the large mass ratio of MX to H, the spheres in the Newton diagrams for the recoil of MX are much smaller than in Fig. 3. In the  $K + HBr$  reaction, for example, the conservation laws confine the KBr to recoil within about  $10^\circ$  of the center of mass trajectory.<sup>6</sup> Since the entire recoil spectrum is thereby compressed into a small range of laboratory angles, these reactions are unsuitable for a study of the angular distribution of MX. This feature is an advantage for the experiment discussed above, as it increases considerably the fraction of the MX that can be focused into the inhomogeneous field region.

The second experiment takes the opposite approach and studies reactions of hydrogen atoms with alkali halides,



Here it is expected that the product HX must come off rotationally



and translationally "cool" and vibrationally "hot." Otherwise the large increase in reduced mass on formation of the products would give them far more angular momentum than allowed. Because of the wide spacing of the vibrational levels of HX and the almost thermoneutral character of these reactions, only the ground and first excited vibrational states of HX are accessible. Which state is formed makes a large difference in the translational energy available to the products and therefore in the kinematics of the scattering. Thus it may be possible to identify, in the angular distribution of the detected product M, separate regions contributed by reactions that produce HX in the ground and in the first excited vibrational state.

#### Conclusion

Even in its present primitive stage the molecular beam method promises to open up many opportunities for detailed studies of reactive collisions. The early results described here have revealed several features inaccessible to the traditional methods of kinetics. We hope this program of beam studies will ultimately provide the basis for constructing a theory of the molecular mechanics of reactions. A very encouraging aspect is that the apparatus used so far is thirty years behind modern technology. The main experimental problem, which defines the scope and resolution feasible in beam work, is detector sensitivity. By borrowing what are now everyday techniques in nuclear physics (modulation of the beams; mass analysis and counting of detected ions) it appears possible to gain from four to six orders of magnitude. However, it is the essential simplicity and directness of the

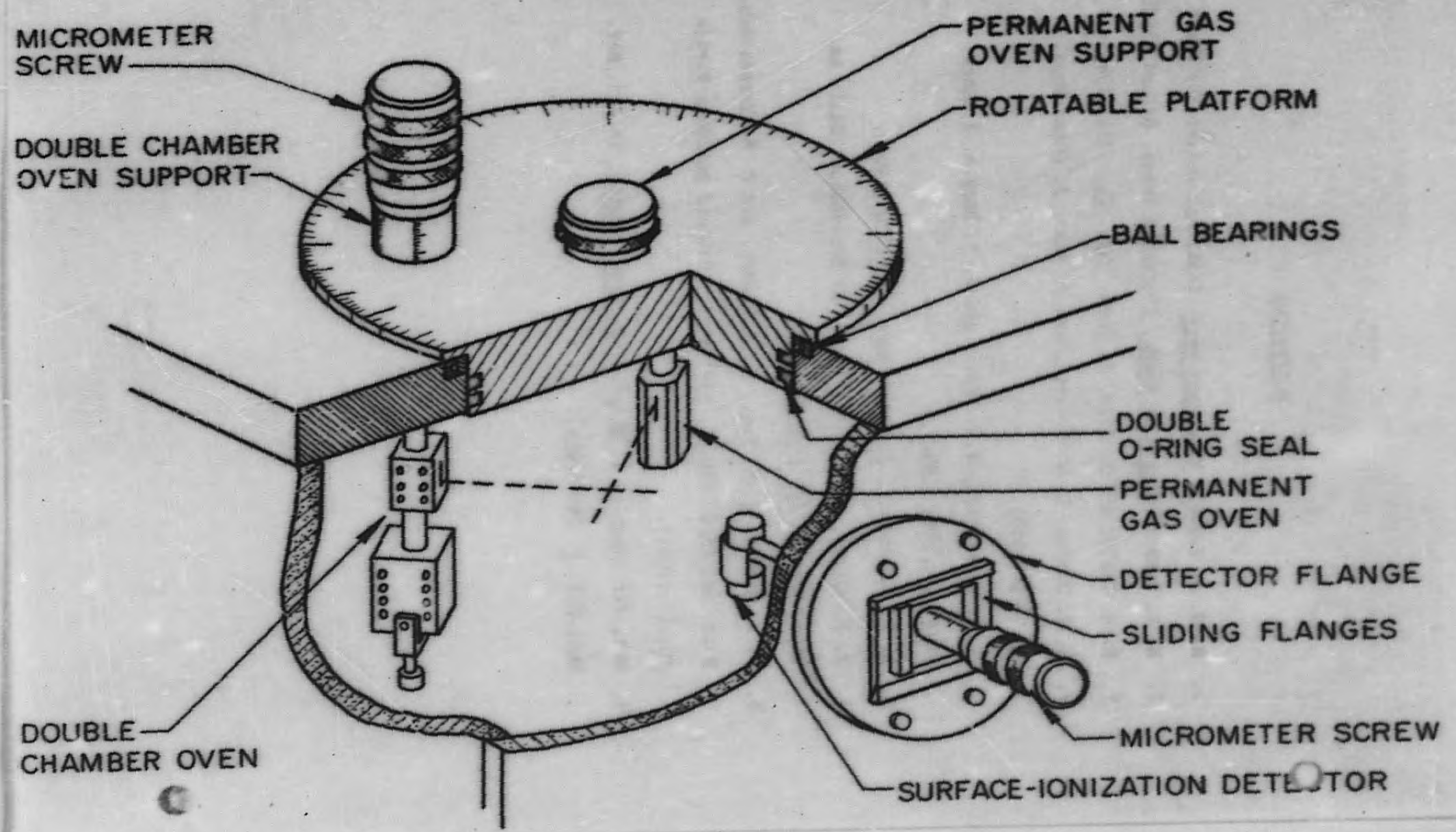


beam method which has so firmly captivated the little band of chemists now pursuing this work; that is why, even in this primitive era, they are imbued with such evangelical fervor.

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Fig. 1





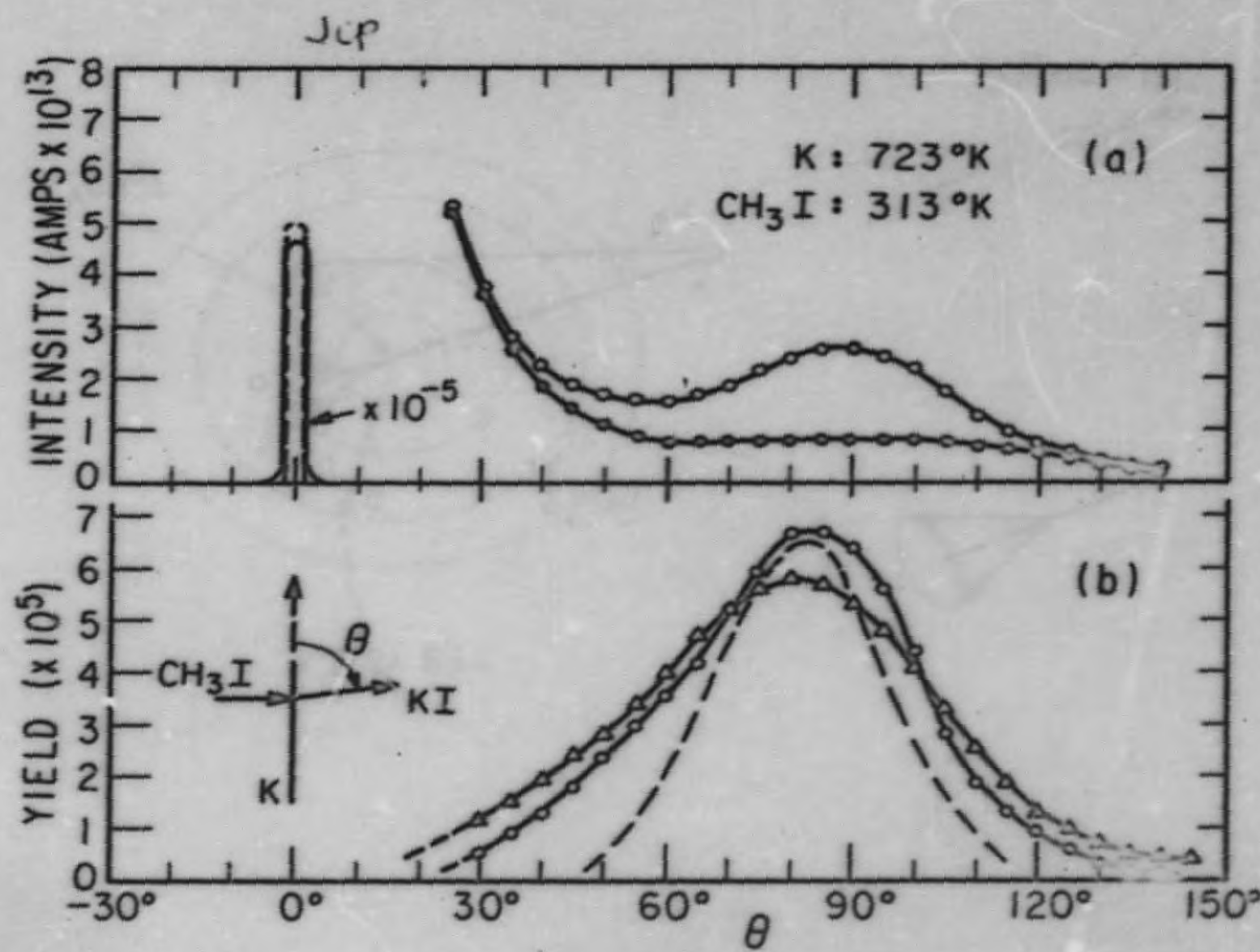


Fig 2

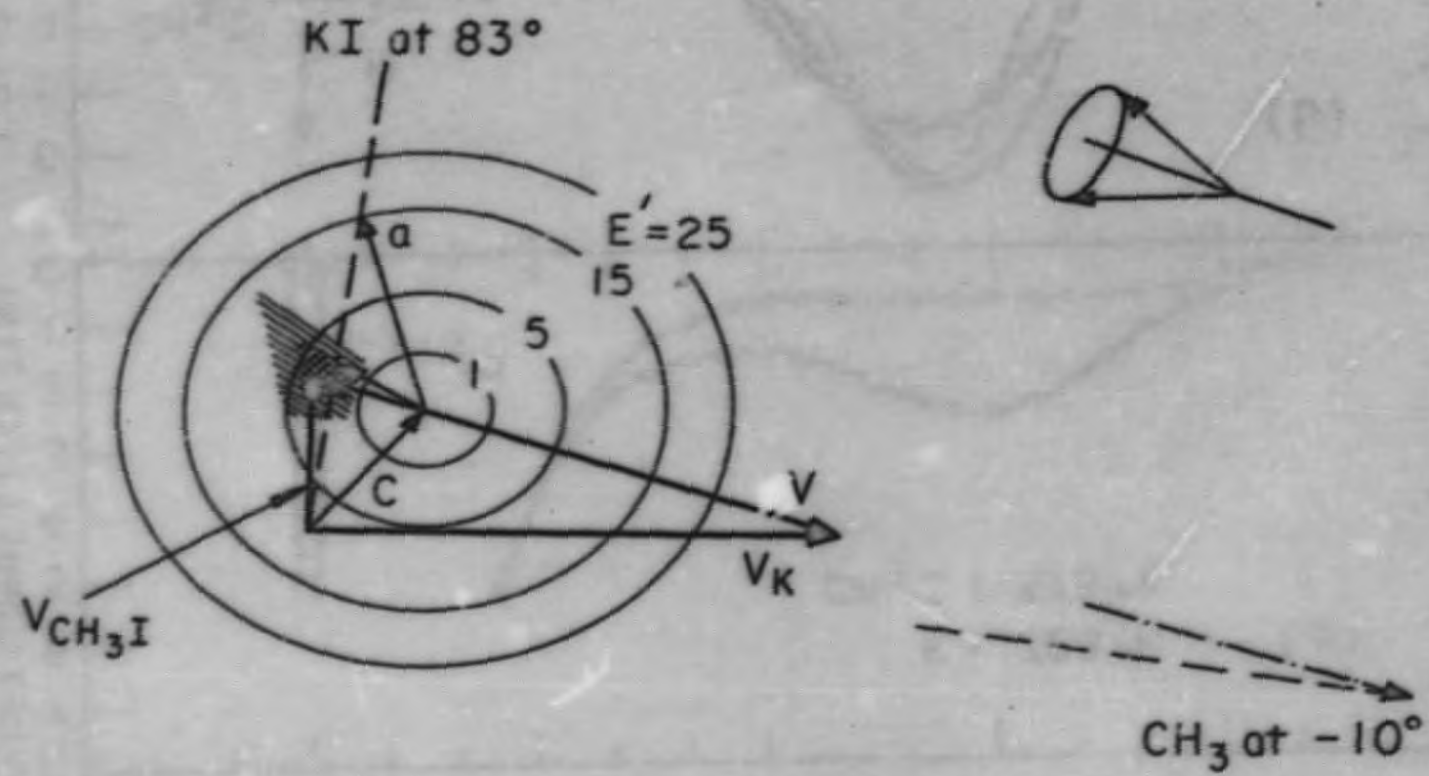


Fig 3



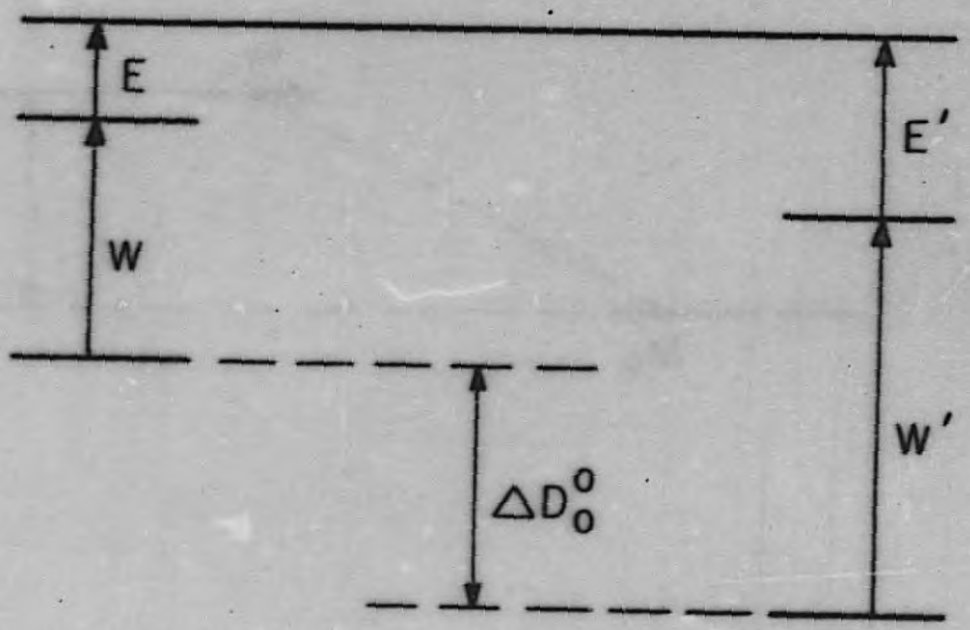


Fig 4



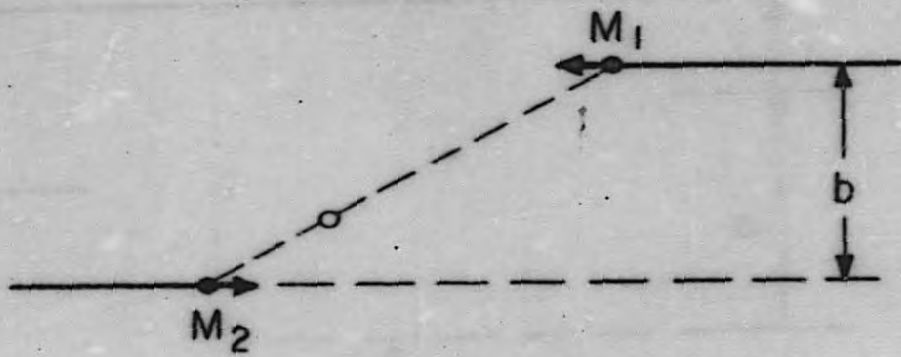


fig 5

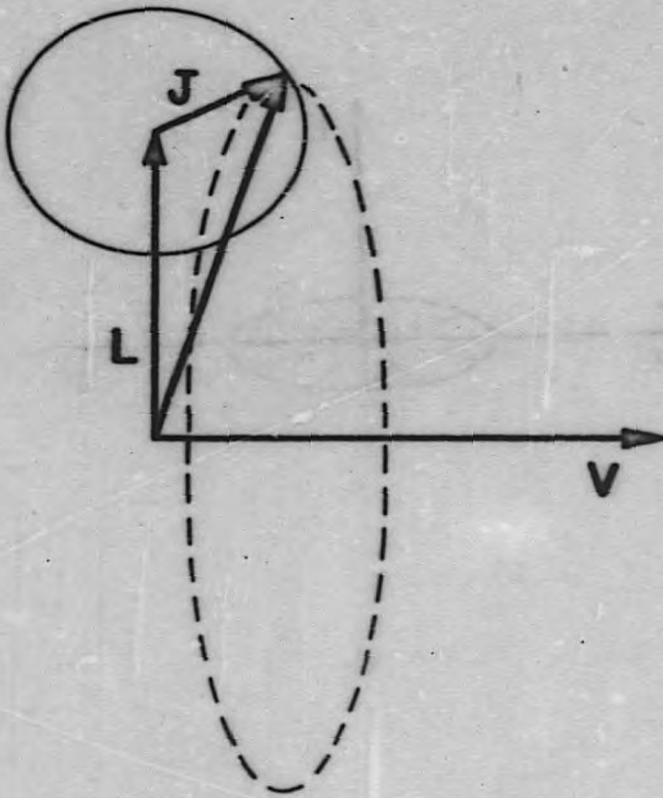


fig 6

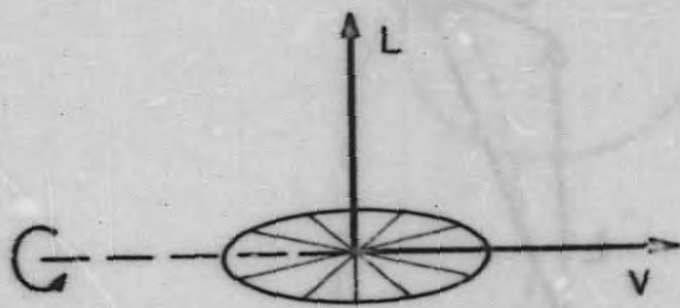


fig 7



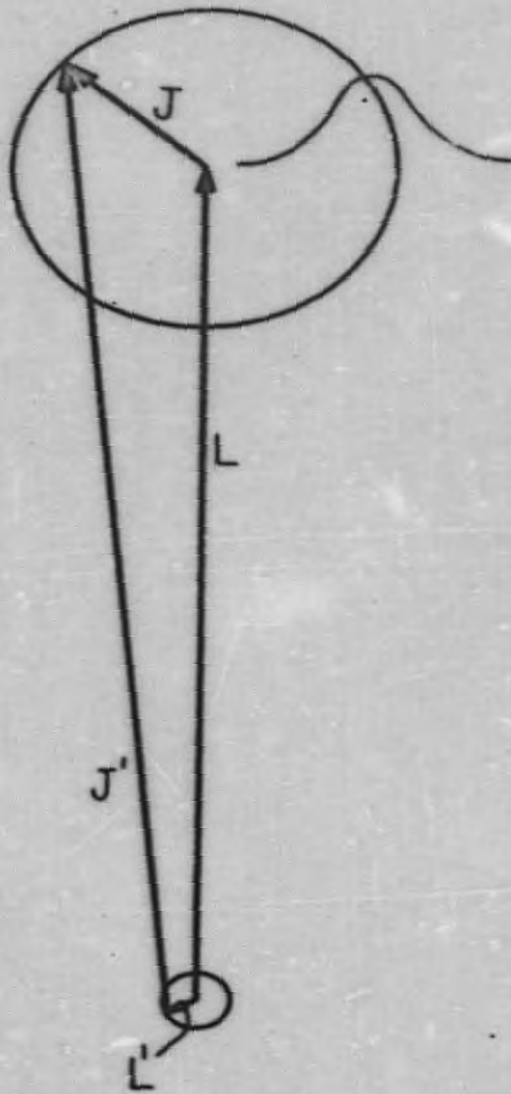


fig 8

**END**