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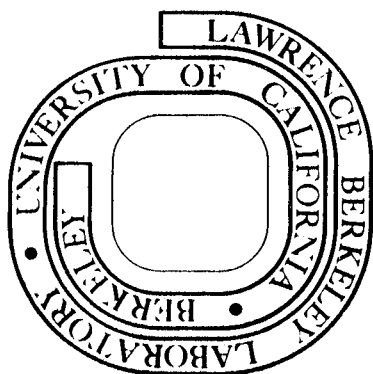
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DYNAMICS OF  $\text{CO}_2^+$  -  $\text{D}_2$  COLLISIONS

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## ABSTRACT

We have measured complete velocity vector distributions for several of the products of collisions between  $\text{CO}_2^+$  and  $\text{D}_2$ . The reactions  $\text{CO}_2^+(\text{D}_2, \text{D})\text{DCO}_2^+$  and  $\text{CO}_2^+(\text{D}_2, \text{OD})\text{DCO}^+$  are the principal chemical processes in the range of relative energies from 1 to 15 eV. The former proceeds principally by a direct interaction mechanism, with some smaller contribution from the decay of a  $\text{D}_2\text{CO}_2^+$  persistent complex. The  $\text{DCO}^+$  appears to come exclusively from the decay of this persistent complex at low relative energies, and from a complicated direction interaction process at very high energies. Other energetically accessible products such as  $\text{CO}^+$ ,  $\text{O}^+$ ,  $\text{D}_2\text{O}^+$  and  $\text{OD}^+$  prove to be of minor or no importance.

As part of a program intended to elucidate the relation between molecular structure and reaction dynamics, we have used the ion beam scattering technique to investigate the reactive and non-reactive collisions of  $\text{CO}_2^+$  with  $\text{H}_2$ ,  $\text{D}_2$ , and HD. Previous investigations in this series have dealt largely with the reactions of atomic and diatomic ions with the isotopic hydrogen molecules.<sup>1</sup> Examples of both direct interaction<sup>2,3</sup> and long-lived complex<sup>4,5</sup> reaction mechanisms have been found, and the use of molecular orbital and electronic state correlation diagrams to rationalize or predict the gross features of reaction dynamics has been explored.<sup>6</sup> The  $\text{CO}_2^+$  -  $\text{H}_2$  system was chosen for study with the hope of providing an example of a reaction in which an intermediate complex might exist transiently before decomposing into one of several product channels.

The possible ionic products of  $\text{CO}_2^+$  -  $\text{H}_2$  collisions are numerous, and include  $\text{CO}_2^+$ ,  $\text{HCO}_2^+$ ,  $\text{HCO}^+$ ,  $\text{OH}^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{H}_2^+$ ,  $\text{O}^+$ ,  $\text{CO}^+$  and  $\text{O}_2^+$ . The energetics of the reactions which lead to these products are given in Table I. The only exoergic channels are those in which  $\text{HCO}_2^+$  or  $\text{HCO}^+$  are products, but all the other channels are accessible at energies that can easily be reached in ion beam experiments. Mass spectrometric<sup>7,8</sup> and flowing afterglow<sup>9</sup> experiments indicate that the  $\text{HCO}_2^+$  product channel is of exclusive importance for very low energy collisions, even though formation of  $\text{HCO}^+$  and  $\text{OH}$  has essentially the same overall energetics. It was of interest to determine whether any products besides  $\text{HCO}_2^+$  become important at higher energies, and to ascertain whether all such products are formed by the same reaction mechanism.

## Experimental

The instrument used in this work has been described in detail previously.<sup>2</sup> It consists of a magnetic mass spectrometer for preparation of a collimated beam of primary ions of known energy, a scattering cell to contain the target gas, and an ion detection train made up of an electrostatic energy analyzer, a quadrupole mass spectrometer, and an ion counter. The detector components and the exit aperture of the scattering cell are mounted on a rotatable lid, which permits the intensity of scattered ions to be measured at various angles and energies.

Primary ions were extracted from a microwave discharge through carbon dioxide-helium mixtures. As has been noted previously,<sup>4,5</sup> the effective electron temperature in such a discharge is approximately 5 eV. Thus there are relatively few high energy electrons, and  $\text{CO}_2^+$  should be produced predominantly in its ground  $^2\Pi_g$  electronic state, rather than its excited electronic states which lie at least 3.5 eV higher in energy. The Franck-Condon factors<sup>10</sup> for vertical ionization indicate that over 80% of  $\text{CO}_2^+$  will be formed in its lowest vibrational state.

Most of our experimental results are presented in the form of contour maps of the specific intensity<sup>2</sup>  $\bar{I}(\theta, u)$ , the intensity of ions per unit velocity space volume normalized to unit beam strength, scattering gas density, and collision volume. A polar coordinate system is used, with the radial coordinate  $u$  representing the speed of the ion relative to the center of mass of the target-projectile system, and the

angular coordinate  $\theta$  measured with respect to the original direction of the projectile ion beam. The specific intensity is normalized such that

$$\bar{\sigma} = 2\pi \int_0^{\pi} \sin\theta d\theta \int_0^{\infty} u^2 \bar{I}(\theta, u) du$$

is always proportional to the true cross section  $\sigma$ . Each contour map is generated from 10-20 scans of the laboratory angular distribution at different energies. In each scan, 10-20 measurements of the product intensity are made.

### Results

A total of 23 complete intensity contour maps of the product velocity vector distributions were determined. In addition, many one-dimensional scans of product speed at a fixed angle were performed. The data presented here are representative of these various experiments, and have been chosen to illustrate the most important features of the dynamics.

Nonreactive Scattering. Figure 1 shows the distribution of  $\text{CO}_2^+$  scattered non-reactively by  $\text{D}_2$  in an experiment performed at 1.88 eV initial relative energy. It is to be compared with Fig. 2, which shows  $\text{CO}_2^+$  scattered from He at the same initial relative energy. The intensities at very small scattering angles are very similar in the two experiments. However, the scattering at angles larger than  $60^\circ$  is of considerably smaller intensity in the  $\text{D}_2$  experiment. In addition, the nonreactive scattering from  $\text{D}_2$  appears to be somewhat more inelastic than is that from He.

The inelastic scattering of  $\text{CO}_2^+$  by  $\text{D}_2$  becomes particularly obvious as the initial relative energy is increased. Figure 3 shows the results of an experiment performed at 3.0 eV initial relative energy. In the small angle inelastic region, there is a prominent ridge of intensity. A similar inelastic ridge was found<sup>4</sup> in the nonreactive scattering of  $\text{O}_2^+$  by  $\text{D}_2$ . The inelastic feature persists in  $\text{CO}_2^+ - \text{D}_2$  experiments carried out in the relative energy range 3 - 12.3 eV, and seems to become more concentrated at the smaller angles as the initial relative energy is increased. Such a very inelastic small angle feature does not have a ready explanation in terms of impulsive models of collisions, but does seem to suggest the type of strong interaction associated with a chemically bound intermediate, which, while transient, exists for many vibrational periods. As we shall see, the appearance of the  $\text{DCO}^+$  product distribution provides additional evidence in support of such a persistent intermediate.

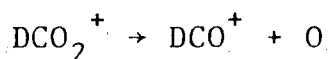
Formation of  $\text{DCO}_2^+$ . Figure 4 shows the velocity vector distribution of  $\text{DCO}_2^+$  formed from  $\text{CO}_2^+ - \text{D}_2$  collisions at an initial relative energy of 2.03 eV. The distribution is asymmetric about the  $\pm 90^\circ$  axis, which clearly indicates that  $\text{DCO}_2^+$  is formed predominantly by a direct interaction mechanism at this relative energy. The maximum product intensity occurs very close to the velocity predicted by the spectator stripping mechanism. The asymmetry persists in  $\text{HCO}_2^+$  and  $\text{DCO}_2^+$  product distributions obtained at an initial relative kinetic energy of 1.5 eV, although at this lower kinetic energy, resolution and target motion effects tend to broaden and symmetrize the product distributions.



Figure 5 shows the  $\text{DCO}_2^+$  product distribution obtained from  $\text{CO}_2^+ - \text{D}_2$  collisions at an initial relative kinetic energy of 5.0 eV. The asymmetry of the distribution is even more pronounced at this higher energy, and the peak at the spectator stripping velocity is more obvious. However, the  $\text{DCO}_2^+$  distribution is not as sharply peaked as are the product distributions from the  $\text{N}_2^+(\text{D}_2, \text{D})\text{N}_2\text{D}^+$  and  $\text{Ar}^+(\text{D}_2, \text{D})\text{ArD}^+$  reactions<sup>2,11</sup> at comparable initial kinetic energies. The  $\text{DCO}_2^+$  intensity in the very large angle region near  $\theta = 180^\circ$  is rather small in Fig. 5, particularly at the larger allowed values of the product speed. In the  $\text{Ar}^+ - \text{D}_2$  system,<sup>11</sup> much more prominent product backscattering is observed. Figure 5 suggests that the head-on collisions between  $\text{CO}_2^+$  and  $\text{D}_2$  frequently lead to some product other than  $\text{DCO}_2^+$ .

In Fig. 5, there is a considerable product intensity very close to the center of mass velocity. Any  $\text{DCO}_2^+$  formed with values of  $Q$ , the relative translational energy change, more negative than -4.5 eV is unstable with respect to dissociation to  $\text{CO}_2^+$  and  $\text{D}$  or to  $\text{CO}_2$  and  $\text{D}^+$ . Thus Fig. 5 indicates that a considerable fraction of the  $\text{DCO}_2^+$  is formed with nearly enough internal energy to dissociate. At comparable initial relative energies in the  $\text{Ar}^+ - \text{D}_2$  system,<sup>11</sup> the  $\text{ArD}^+$  product tends to be notably less excited internally. The increased complexity of the  $\text{CO}_2^+ - \text{D}_2$  system and the change in geometry of  $\text{CO}_2^+$  as it forms  $\text{DCO}_2^+$  evidently permit a more facile accommodation of the initial relative energy as internal energy of the product.

As the initial relative energy is raised,  $\text{DCO}_2^+$  product formed with the spectator stripping velocity becomes increasingly excited internally. When the energy of the  $\text{CO}_2^+$  projectile relative to one deuterium atom exceeds 4.5 eV, the product formed by the stripping mechanism is unstable with respect to dissociation to  $\text{D}^+$  and  $\text{CO}_2$ , or  $\text{D}$  and  $\text{CO}_2^+$ . This critical situation occurs at a laboratory energy of 101 eV, or at a relative energy of 8.4 eV. At higher projectile energies,  $\text{DCO}_2^+$  scattered at small angles must either disappear entirely, or move to velocities greater than that predicted by the spectator stripping model. If the incipient  $\text{DCO}_2^+$  formed by spectator stripping survives long enough for its internal energy to be spread throughout the molecule, there is another, more favorable dissociation path. The reaction



requires only 4.6 eV, and if the  $\text{DCO}_2^+$  is formed by spectator stripping, dissociation should start to occur at a laboratory energy of 86 eV, or at a relative energy of 7.15 eV. Figure 6 shows that at 10.4 eV initial relative energy, the  $\text{DCO}_2^+$  intensity still reaches a peak at a scattering angle of zero degrees, but this peak is considerably diminished in intensity, and lies at a velocity greater than the spectator stripping value. A similar result was found in a brief investigation of this system reported by Ding,<sup>12</sup> although an inconsistent labeling of the product energy scale makes his data hard to interpret. The data available does not reveal whether the spectator stripping intensity is lost at precisely the threshold

for dissociation to  $\text{DCO}^+$ , but one of our experiments performed at 8.3 eV relative energy does show a slight forward recoil and a diminished intensity for  $\text{DCO}_2^+$ . Thus the  $\text{CO}_2^+ - \text{D}_2$  reaction resembles other exoergic deuterium atom transfer reactions in that direct forward recoil of the product scattered at small angles is observed when spectator stripping can not lead to stable product. In the thermoneutral reactions<sup>3,13</sup>  $\text{O}^+(\text{D}_2, \text{D})\text{OD}^+$  and  $\text{N}^+(\text{H}_2, \text{H})\text{NH}^+$ , direct forward product recoil does not occur, and the small angle scattering is lost at high initial energies.

Formation of  $\text{DCO}^+$ . Figure 7 shows the velocity vector distribution of  $\text{DCO}^+$  formed by  $\text{CO}_2^+ - \text{D}_2$  collisions at an initial relative energy of 4.36 eV. The product distribution is rather broad, and shows considerable symmetry about the  $\pm 90^\circ$  axis. A map, which we do not show here, of the  $\text{HCO}^+$  intensity obtained from  $\text{CO}_2^+ - \text{H}_2$  collisions at the same initial relative energy is even more symmetric. This type of symmetric distribution suggests that  $\text{DCO}^+$  is formed by a collision mechanism which involves a persistent intermediate complex  $\text{D}_2\text{CO}_2^+$ . The ground state of this ion of formic acid is in fact bound by 2.56 eV with respect to  $\text{CO}_2^+$  and  $\text{D}_2$ , and by 1.8 eV with respect to  $\text{DCO}^+$  and  $\text{OD}$ , or  $\text{DCO}_2^+$  and  $\text{D}$ . Thus the occurrence of a persistent complex at low initial relative energies would not be unreasonable.

While the symmetry of the  $\text{DCO}^+$  and  $\text{HCO}^+$  distributions obtained from collisions of  $\text{CO}_2^+$  with  $\text{D}_2$  and  $\text{H}_2$  suggests a persistent complex mechanism, it is not impossible that the reaction goes by a direct interaction process which fortuitously

products a symmetric product distribution. Strong evidence in favor of the persistent complex mechanism at low relative energies comes from the  $\text{DCO}^+$  and  $\text{HCO}^+$  product distributions from collisions of  $\text{CO}_2^+$  with HD. Exemplary results appear in Fig. 8, where product intensity profiles along the  $0 - 180^\circ$  axis are shown. Both the  $\text{DCO}^+$  and  $\text{HCO}^+$  intensities peak at, and are symmetric about, the center of mass velocity. It has been demonstrated a number of times<sup>3,5</sup> that protonated and deuterated products of abstraction reactions from HD have qualitatively different angular distributions when the reaction proceeds by direct interaction, and similar distributions when a persistent complex is involved. The similarity of the  $\text{DCO}^+$  and  $\text{HCO}^+$  distributions in Fig. 8 reinforce the conclusion that product is formed in this channel by a persistent complex mechanism.

Approximate calculations using the RRKM semiclassical model of unimolecular reactions suggest that the lifetime with respect to dissociation of  $\text{D}_2\text{CO}_2^+$  formed from  $\text{CO}_2^+ - \text{D}_2$  collisions at initial relative energies below 4 eV should be  $10^{-12}$  sec or greater. The rotational period of the intermediate varies with its angular momentum, but typical impact parameters (1-2 Å) and velocities lead to rotational periods of approximately  $10^{-13}$  sec. Use of a statistical theory to predict lifetimes of such sort duration is a questionable procedure. However, the results suggest that the lifetime of the intermediate complex will be several times the rotational period in the regime of low initial relative energies. This is consistent with the appearance of the distributions in Figs. 7 and 8.

As the initial relative energy is increased, the lifetime of the collision complex is expected to decrease more rapidly than the rotational period. As a result, asymmetric product distributions typical of direct interaction mechanisms are anticipated from experiments performed at high initial relative kinetic energies. Figure 9 shows the velocity vector distribution of  $\text{DCO}^+$  from  $\text{CO}_2^+ - \text{D}_2$  collisions at an initial relative energy of 10.4 eV. Even though the distribution is broad, the anticipated asymmetry about the  $\pm 90^\circ$  axis is apparent.

In order to explore the mechanism of  $\text{DCO}^+$  formation more thoroughly, we measured product intensity profiles along the  $0 - 180^\circ$  axis at several initial relative energies in the range 1.89 - 20.8 eV. The results are shown in Fig. 10. The asymmetry about the center of mass speed is first evident in the experiment conducted at an initial relative energy of 8.33 eV, and increases with increasing kinetic energy. At an initial relative energy of 16.67 eV, there is a dramatic decrease in the overall intensity of  $\text{DCO}^+$ , which suggests that near and above this energy, formation of  $\text{DCO}^+$  is controlled by product stability considerations.

In this connection, it is of interest to explore two simple models for  $\text{DCO}^+$  formation in the high energy regime. In the first model, the  $\text{CO}^+$  and O which constitute  $\text{CO}_2^+$  are assumed to behave completely independently as they each pick up deuterium atoms from  $\text{D}_2$ . This mechanism might be termed double stripping. Since in this model the momenta of the D -  $\text{CO}^+$  and D-O systems are conserved separately, the laboratory velocities of  $\text{DCO}^+$  and OD are predicted to be

$$v(\text{DCO}^+) = \frac{28}{30} v(\text{CO}_2^+) = 0.933 v(\text{CO}_2^+)$$

and

$$v(\text{OD}) = \frac{16}{18} v(\text{CO}_2^+) = 0.889 v(\text{CO}_2^+).$$

Consequently,  $\text{DCO}^+$  is expected to appear in the forward scattered or small angle region, while OD (if it were detected) would be back scattered. Also, according to this double stripping model, the minimum internal excitation energy of  $\text{DCO}^+$  would be equal to the energy associated with the  $\text{CO}^+$  fragment of the  $\text{CO}_2^+$  projectile, relative to one deuterium atom. To this minimum internal excitation energy might be added some unknown fraction  $f$  of the reaction exoergicity (0.9 eV), so we have

$$\frac{28}{44} \times \frac{2}{30} E_L \leq U(\text{DCO}^+) \leq \frac{28}{44} \times \frac{2}{30} E_L + 0.9.$$

If the internal excitation energy  $U(\text{DCO}^+)$  exceeds 6.2 eV, the minimum dissociation energy of  $\text{DCO}^+$ , this product should be unstable, and undetectable. According to the above expression, this should occur at a projectile energy of  $135 \pm 10$  eV or at a relative energy of  $11.3 \pm 0.9$  eV. At higher energies, any  $\text{DCO}^+$  should appear at velocities greater than the double stripping value, if it appears at all.

In Fig. 10 the predictions of the double stripping model are compared with some of the experimental data on  $\text{DCO}^+$  formation. In both the experiments at 8.33 eV and 12.54 eV, where  $\text{DCO}^+$  formed by double stripping could be stable, the product intensity reaches a maximum at velocities greater than

that predicted by the model. Moreover, the breadth of the distributions indicate substantial recoil of the products from each other, and this is not at all consistent with the complete decoupling of the two fragments postulated in the double stripping model. On the other hand, there is a dramatic decrease in the  $\text{DCO}^+$  intensities in the experiments at 16.7 and 20.8 eV, where double stripping can not yield a stable product. Thus, some  $\text{DCO}^+$  may be formed by an impulsive process which is related to the double stripping model, but this model certainly does not provide a complete or adequate description of the reaction dynamics.

A second simple model for  $\text{DCO}^+$  formation at high energies involves a primary reaction to give  $\text{DCO}_2^+$  at its spectator stripping velocity, followed by a dissociation of this product to  $\text{DCO}^+$  and O. This process was discussed earlier as a possible loss mechanism for  $\text{DCO}_2^+$ . It is significant that the maximum internal energy of  $\text{DCO}^+$  formed by this process is

$$U(\text{DCO}^+) = -\Delta E_{\text{O}}^{\text{O}} + \frac{2}{46} E_{\text{L}} - D_{\text{O}}(\text{DCO}^+ - \text{O})$$

where  $\Delta E_{\text{O}}^{\text{O}}$  is the energy of reaction to form  $\text{DCO}_2^+$ ,  $E_{\text{L}}$  is the laboratory energy of the projectile, and  $D_{\text{O}}(\text{DCO}^+ - \text{O})$  is the dissociation energy of  $\text{DCO}_2^+$  to the  $\text{DCO}^+$  product. Making the appropriate substitutions we get

$$U(\text{DCO}^+) = -3.7 + 0.043 E_{\text{L}}$$

If the upper limit of  $U(\text{DCO}^+)$  is set by the proton affinity of CO, 6.2 eV,  $\text{DCO}^+$  formed by this mechanism should be stable

with respect to dissociation up to a projectile laboratory energy of 230 eV, or a relative energy of 19.2 eV. This constitutes a minimum upper limit for operation of the stripping plus dissociation model, for if there is any recoil of the  $\text{DCO}^+$  and O fragments upon dissociation of  $\text{DCO}_2^+$ , the  $\text{DCO}^+$  product could be still formed at projectile energies greater than 230 eV.

In Fig. 10 we see that a small amount of  $\text{DCO}^+$  product is observed in the experiments at 16.67 and 20.83 eV, energies well above the limit for the double stripping model. The 16.67 eV experiment is in the range where stripping followed by dissociation of  $\text{DCO}_2^+$  can give a stable product. However, the intensity maximum in this experiment does not occur at the stripping velocity of  $\text{DCO}_2^+$ . The same may be said about the experiment conducted at 20.83 eV. Thus neither the double stripping model nor the stripped  $\text{DCO}_2^+$  dissociation model alone provides a satisfactory explanation of the  $\text{DCO}^+$  distribution. It is likely that the operating dynamic process is some combination of variants of these primitive models.

Minor Products. The formation of  $\text{CO}^+$  was studied at several energies. When the initial relative energy was less than 8 eV, no significant amount of  $\text{CO}^+$  was detected. At higher energies,  $\text{CO}^+$  was found to have a distribution very similar to those of the products of collision induced dissociation which have been measured in our laboratory.<sup>14</sup> The distributions of  $\text{CO}^+$  from  $\text{CO}_2^+$  - He collisions were very similar to distributions obtained with  $\text{D}_2$  as the target. These findings suggest that  $\text{CO}^+$  appears only as a result of



an impulsive collisional dissociation mechanism in which formation of chemical products like  $D_2O$  or  $OD$  plays at most a minor role.

A search was made for  $D_2O^+$ , but none was detected. However, both  $OD^+$  and  $O^+$  were detected as minor products of  $CO_2^+ - D_2$  collisions at relative energies above 8.3 eV. The distributions of  $O^+$  resembled those of  $CO^+$ , which suggests that  $O^+$  is formed by a simple impulsive collisional dissociation of  $CO_2^+$ . The  $OD^+$  was clearly not the product of a double stripping process in which  $DCO$  was formed concomitantly. The  $OD^+$  appeared as a very broad distribution peaked in the forward scattering direction, with no intensity in the region predicted by the double stripping mechanism. It is possible that  $OD^+$  is formed as a dissociation product of highly excited  $DCO_2^+$ , although this is not the energetically favored path.

### Discussion

The experimental data indicate that at and above relative energies of 1.5 eV, the reaction  $CO_2^+(D_2,D)DCO_2^+$  proceeds predominantly by a direct interaction mechanism in which spectator stripping is prominent. In contrast, the  $CO_2^+(D_2,OD)DCO^+$  channel involves a persistent collision complex at initial relative energies at and below 4.3 eV, and proceeds by direct interaction only at relative energies above this value. This considerable difference in the dynamics associated with two channels which have nearly exactly the same thermochemistry is striking, and it is of interest to attempt

to rationalize this behavior in terms of the electronic structure of the system.

To begin, we consider the possibility of forming a collision intermediate  $D_2CO_2^+$  which is the vibrationally excited formic acid ion in its electronic ground state. As noted, the minimum energy of this ion lies 2.6 eV below that of the reactants, and approximately 1.7 eV below that of either product channel. The  $^2\Pi_g$  ground state of  $CO_2^+$  has one electron missing from a nonbonding  $\Pi_g$  orbital, and in the ground state of formic acid<sup>10</sup> one nonbonding electron is missing from an orbital concentrated on the carbonyl oxygen. From the point of view of conversion of orbitals, addition of  $D_2$  to  $CO_2^+$  is very much like the classic  $H_2 - C_2H_4$  addition problem. That is, the bonding-antibonding pair of  $\sigma$  orbitals on  $D_2$  and the bonding-antibonding pair of  $\Pi_u$  orbitals on  $CO_2$  are converted to CD and OD bonding and antibonding orbital pairs. For ground state reactants and products, such a process is "forbidden" by orbital symmetry in the  $H_2 - C_2H_4$  case.

The strict symmetry arguments do not apply in the  $D_2 - CO_2^+$  case, but the qualitative fact remains that the nodal properties of the occupied reactant orbitals and those of the ground state orbitals of  $D_2CO_2^+$  are sufficiently different to make it likely that formation of  $D_2CO_2^+$  involves passage over a potential energy barrier. It is difficult to estimate how high this barrier is. Nevertheless, the experimental results provide some guidance. We have observed  $HCO^+$  from  $CO_2^+ - H_2$  collisions at initial relative energies as low as 1 eV.

However,  $\text{HCO}^+$  has not been reported<sup>7-9</sup> as a product of thermal or very low energy  $\text{CO}_2^+ - \text{H}_2$  collisions. Our data indicate  $\text{HCO}^+$  or  $\text{DCO}^+$  is formed at low energies exclusively through a persistent collision complex, and we believe this complex is the formic acid ion. Consequently, we conclude that a barrier to formic acid ion exists, but that it is less than 1 eV high.

Once formed, the  $\text{D}_2\text{CO}_2^+$  complex might dissociate either to give  $\text{DCO}_2^+$  and D, or  $\text{DCO}^+$  and OD. There seems to be no reason to expect barriers in excess of the dissociation energy in either of these channels. We therefore consider the possibility that both the  $\text{DCO}_2^+$  and  $\text{DCO}^+$  products are formed exclusively from this common intermediate. By itself, this can not lead to an explanation of the data, since its most obvious consequence would be that both the  $\text{DCO}_2^+$  and  $\text{DCO}^+$  product distributions should be symmetric about the  $\pm 90^\circ$  axis at low initial relative energies. However, if one adds to this the possibility that  $\text{DCO}_2^+$  could also be formed by a direct interaction path, then the most obvious features of the data might be explained. This direct interaction path would lie on the same potential surface as the formic acid ion intermediate, but would involve  $\text{D}_2\text{CO}_2^+$  conformations which depart considerably from the equilibrium geometry of formic acid ion. That is, atom transfer by direct interaction might involve conformations which are approximately collinear, or T or L shaped. Thus most of the  $\text{DCO}_2^+$  could be formed by collisions in which the system avoids the region of the potential energy well. This would account for the asymmetry of this product distribution, and the prominence of spectator

stripping. Some smaller amount of the  $\text{DCO}_2^+$  might also be formed by decay of the  $\text{D}_2\text{CO}_2^+$  complex, and this could account for the highly excited  $\text{DCO}_2^+$  which is observed in the product intensity maps.

In contrast, it is difficult to imagine the formation of  $\text{DCO}^+$  in low energy experiments by any other path than through a collision complex with the approximate geometry of the formic acid ion  $\text{D}_2\text{CO}_2^+$ . This constraint on the formation of  $\text{DCO}^+$  would be consistent with the symmetry of the product distribution, and with the fact that the intensity of  $\text{DCO}^+$  is qualitatively less than that of  $\text{DCO}_2^+$ .

In summary, we conclude that a persistent  $\text{D}_2\text{CO}_2^+$  intermediate is accessible to the reactants at the energies of our experiment. At low energies,  $\text{DCO}^+$  is formed exclusively by dissociation of this intermediate. Some of the  $\text{DCO}_2^+$  comes from the dissociation of the persistent complex, but most is formed by direct interaction processes in which the system passes through conformations well removed from the potential energy minimum.

#### Acknowledgement

This work was done with support from the U. S. Energy Research and Development Administration.

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Table I  
Reaction Energetics

| Reaction         |  | $\Delta H^\circ$ (eV) |
|------------------|--|-----------------------|
| $\text{CO}_2^+$  | $\text{CO}_2^+ + \text{H}_2 \rightarrow \text{H}_2\text{CO}_2^+$             | -2.56                 |
|                  | $\text{CO}_2^+ + \text{H}_2 \rightarrow \text{H} + \text{HCO}_2^+$           | -0.9                  |
|                  | $\text{CO}_2^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{OH}$            | -0.8                  |
|                  | $\text{CO}_2^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H} + \text{O}$  | 3.66                  |
|                  | $\text{CO}_2^+ + \text{H}_2 \rightarrow \text{H} + \text{H} + \text{CO}_2^+$ | 4.5                   |
|                  | $\text{CO}_2^+ + \text{H}_2 \rightarrow \text{H} + \text{H}^+ + \text{CO}_2$ | 4.4                   |
|                  | $\text{CO}_2^+ + \text{H}_2 \rightarrow \text{HCO}_2^+$                      | 5.5                   |
| $\text{HCO}_2^+$ | $\text{HCO}_2^+ \rightarrow \text{H} + \text{CO}_2^+$                        | 5.5                   |
|                  | $\text{HCO}_2^+ \rightarrow \text{H}^+ + \text{CO}_2$                        | 5.3                   |
|                  | $\text{HCO}_2^+ \rightarrow \text{HCO}^+ + \text{O}$                         | 4.6                   |
|                  | $\text{HCO}_2^+ \rightarrow \text{CO} + \text{OH}^+$                         | 5.9                   |
|                  | $\text{HCO}_2^+ \rightarrow \text{CO}^+ + \text{OH}$                         | 6.8                   |
| $\text{HCO}^+$   | $\text{HCO}^+ \rightarrow \text{H}^+ + \text{CO}$                            | 6.2                   |
|                  | $\text{HCO}^+ \rightarrow \text{H} + \text{CO}^+$                            | 6.6                   |

## Figure Captions

Figure 1. A contour map of the specific intensity of  $\text{CO}_2^+$  scattered from  $\text{D}_2$  at an initial relative energy of 1.88 eV. The circle labeled  $Q=0$  is the locus of elastically scattered  $\text{CO}_2^+$ . Note the low intensity in the large angle region and the inelasticity of the features near  $\pm 90^\circ$ .

Figure 2. A contour map of the specific intensity of  $\text{CO}_2^+$  scattered from He at a relative energy of 1.89 eV. Note the crater-like distribution, with a distinct ridge in the inelastic region near  $180^\circ$ .

Figure 3. The distribution of  $\text{CO}_2^+$  scattered nonreactively by  $\text{D}_2$  at an initial relative energy of 3.0 eV. Note the high intensity in the inelastic region inside the elastic circle, and the distinct inelastic ridge in the small angle region.

Figure 4. The distribution of  $\text{DCO}_2^+$  from  $\text{CO}_2^+ - \text{D}_2$  collisions at an initial relative energy of 2.0 eV. The intensity reaches a maximum very close to the spectator stripping velocity, which is marked by a small cross. Note the breadth of the distribution, and the relatively high intensity near the center of mass velocity.

Figure 5. A contour map of the specific intensity of  $\text{DCO}_2^+$  from  $\text{CO}_2^+ - \text{D}_2$  collisions at an initial relative energy of 5.0 eV. The intensity maximum occurs at the spectator stripping velocity, which is marked by a small cross. Note the low intensity near  $180^\circ$ , and the absence of an intensity minimum near the center of mass velocity.



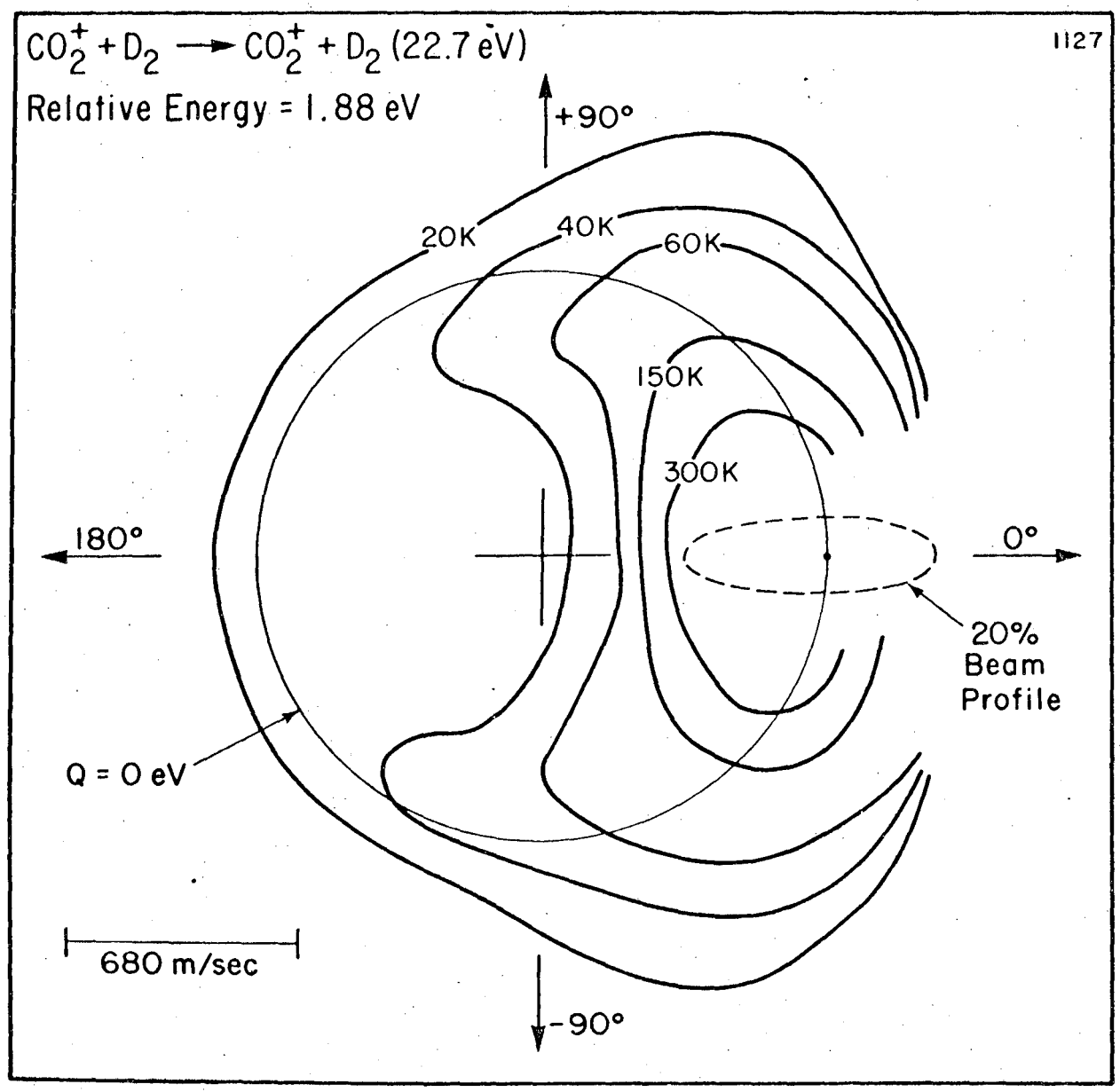
Figure 6. The distribution of  $\text{DCO}_2^+$  formed from  $\text{CO}_2^+-\text{D}_2$  collisions at 10.4 eV initial relative energy. Note that intensity maximum appears at a greater velocity than the spectator stripping point.

Figure 7. The distribution of  $\text{DCO}^+$  formed from  $\text{CO}_2^+-\text{D}_2$  collisions at an initial relative energy of 4.36 eV. Note the near symmetry of the distribution about the  $\pm 90^\circ$  axis.

Figure 8. Profiles of the intensities along the 0-180° axis of  $\text{HCO}^+$  and  $\text{DCO}^+$  from  $\text{CO}_2^+-\text{HD}$  collisions at 1.5 and 2.22 eV initial relative energy. The velocity of the  $\text{CO}_2^+$  beam, the system center of mass, and the elastically back scattered projectile ( $V_{\text{BS}}$ ) are shown. Note the symmetry of both isotopic products about the center of mass velocity.

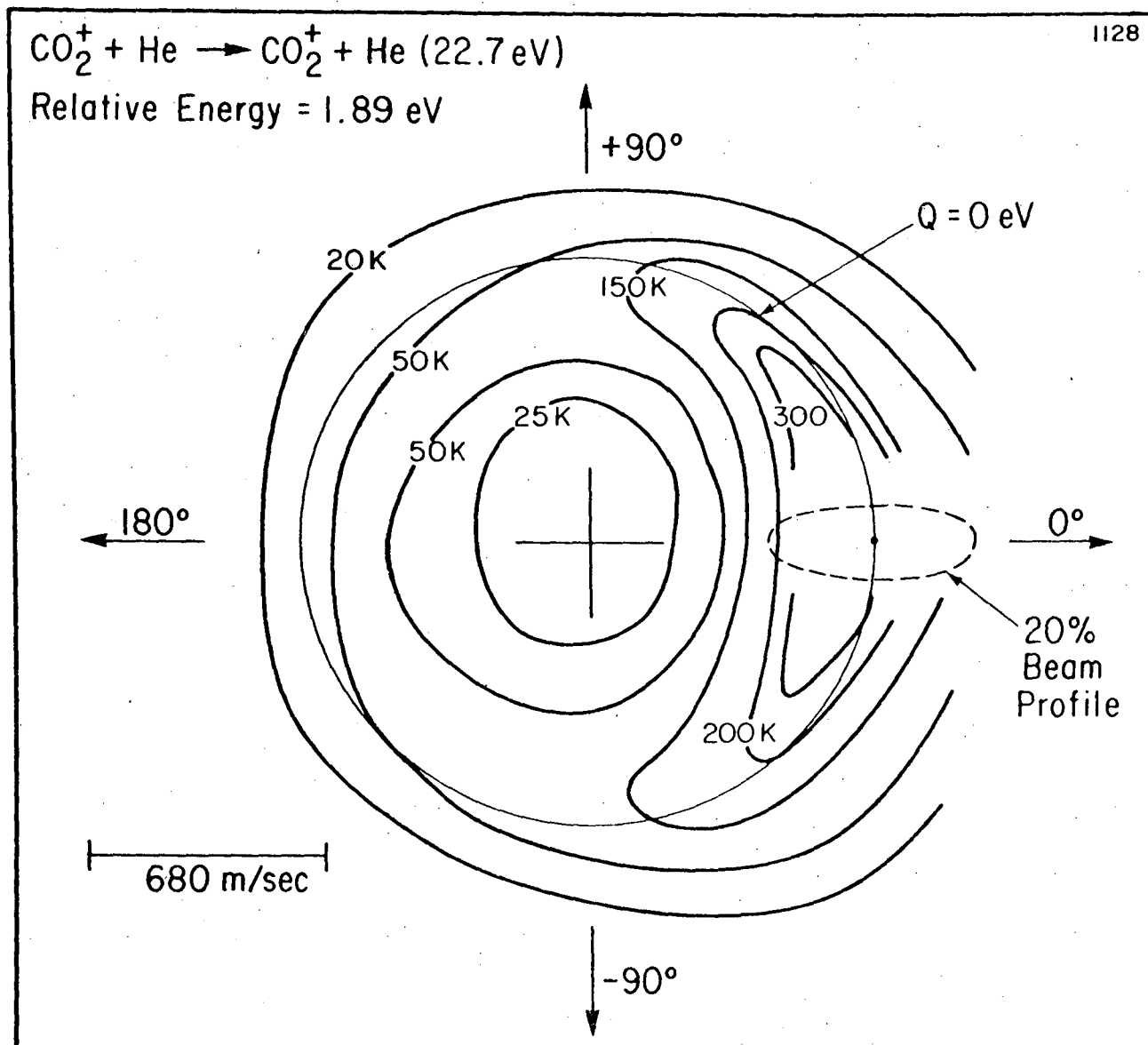
Figure 9. The distribution of  $\text{DCO}^+$  formed by  $\text{CO}_2^+-\text{D}_2$  collisions at an initial relative energy of 10.4 eV. Note the asymmetry of the distribution with respect to the  $\pm 90^\circ$  axis. The intensity maximum occurs at the spectator stripping velocity of  $\text{DCO}_2^+$  which is marked by a small cross.

Figure 10. Profiles of the intensity along the 0-180° axis of  $\text{DCO}^+$  formed from  $\text{CO}_2^+-\text{D}_2$  collisions at several different initial relative energies. The velocities which correspond to spectator stripping to form  $\text{DCO}_2^+$  and double stripping (see text) to form  $\text{DCO}^+$  are indicated, in addition to the beam, elastically back scattered beam, and center of mass velocities.



XBL 748-7118

Fig. 1



XBL 748-7116

Fig. 2

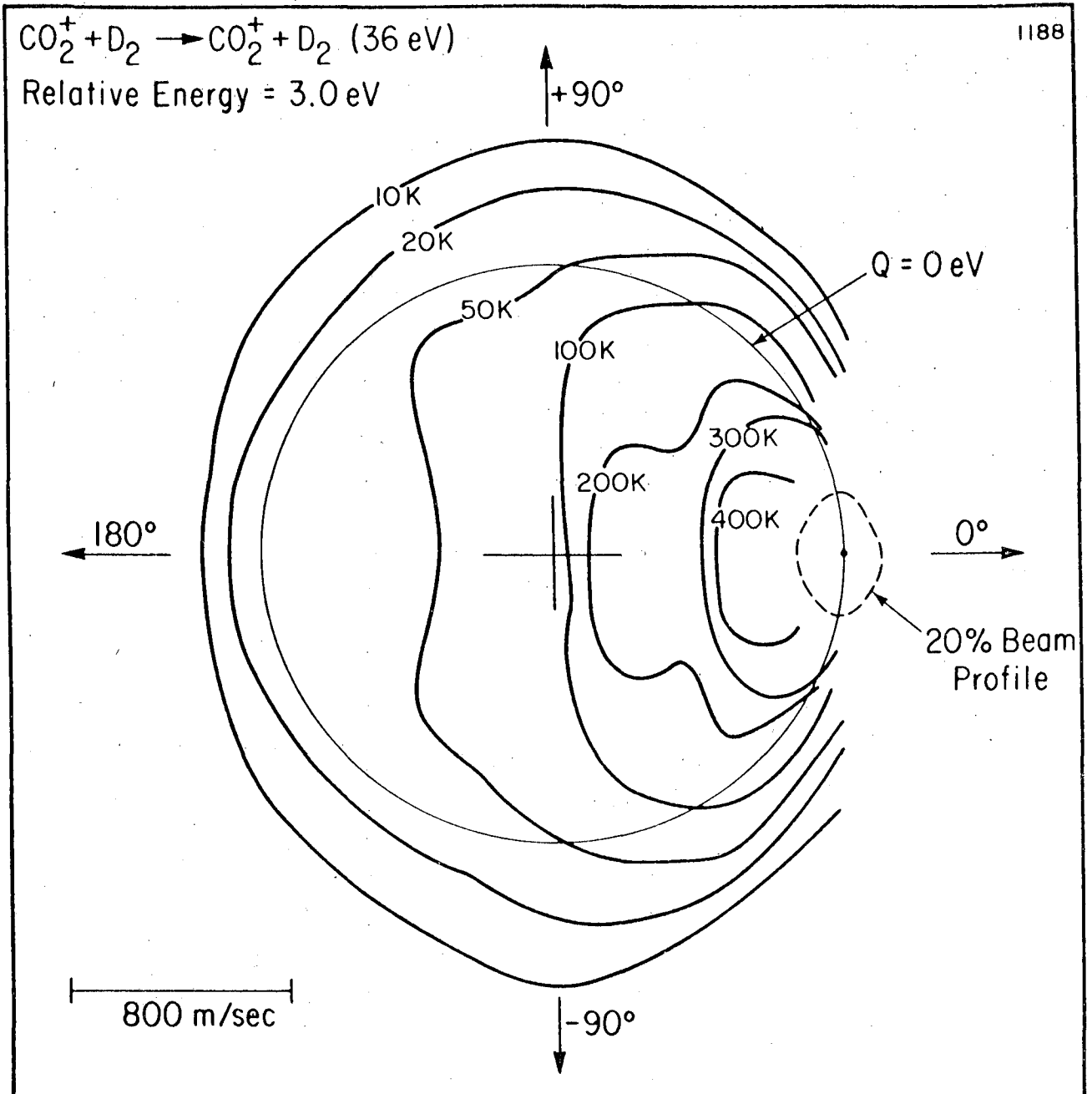


Fig. 3



1124

Relative Energy = 2.03 eV

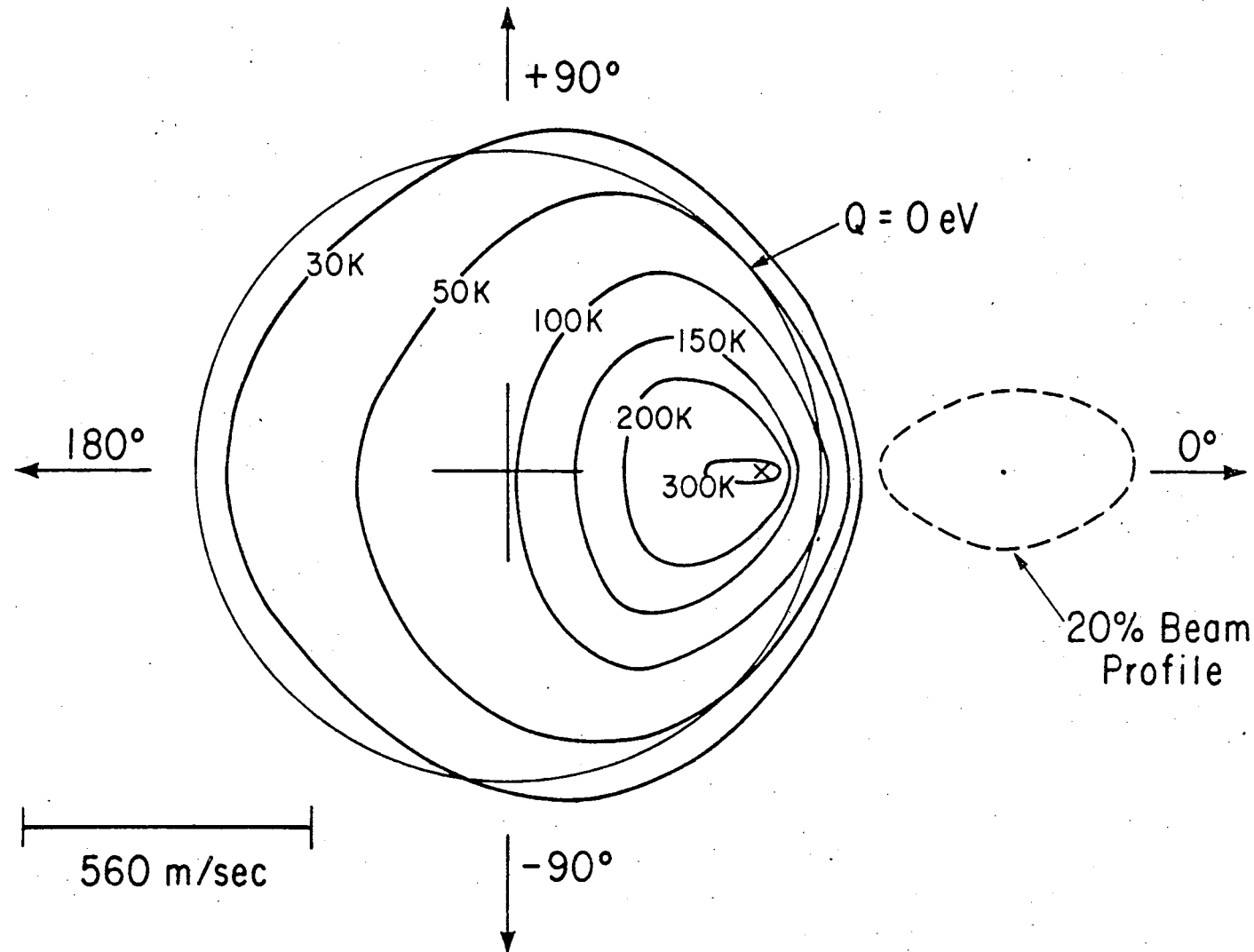
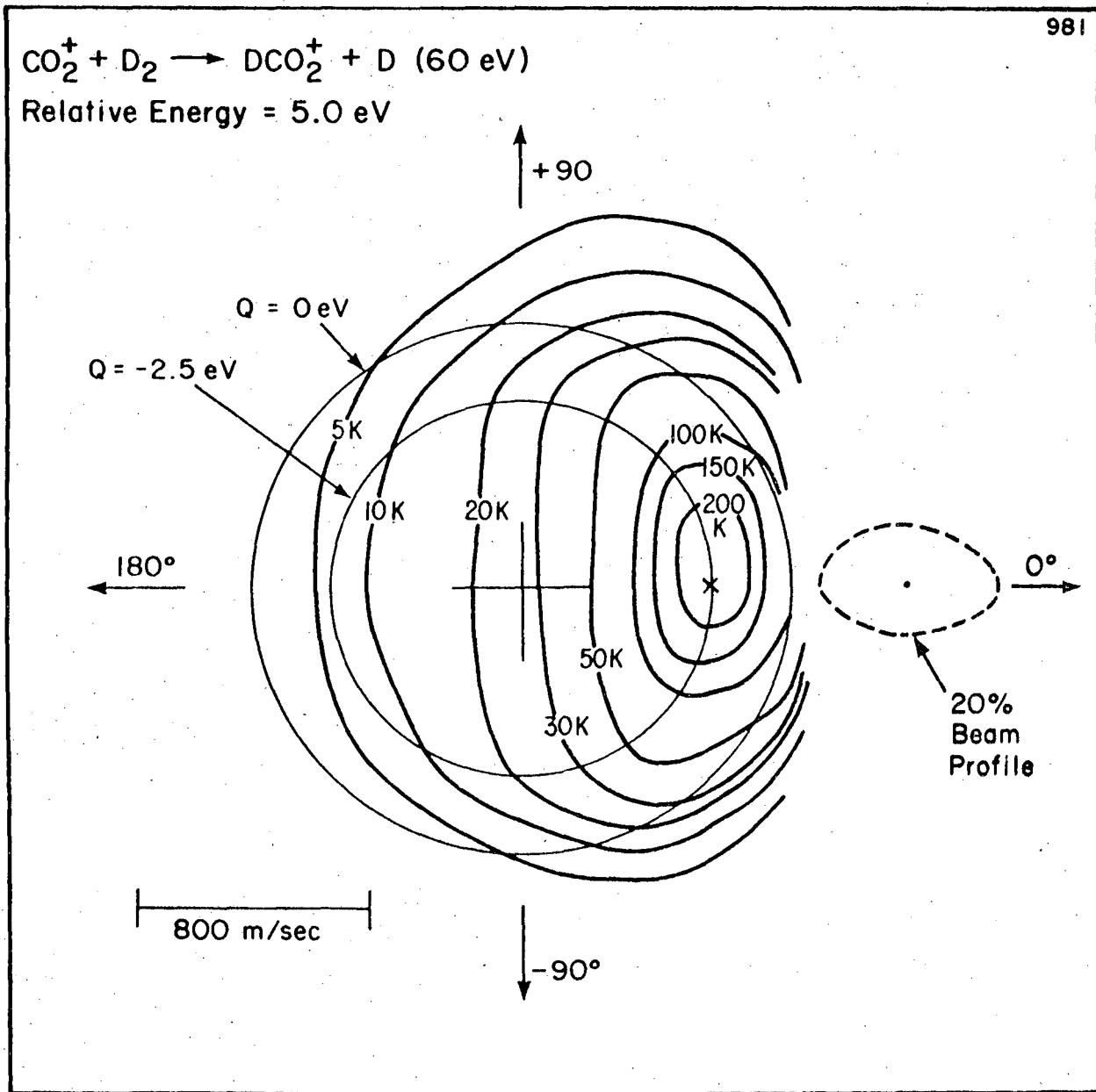


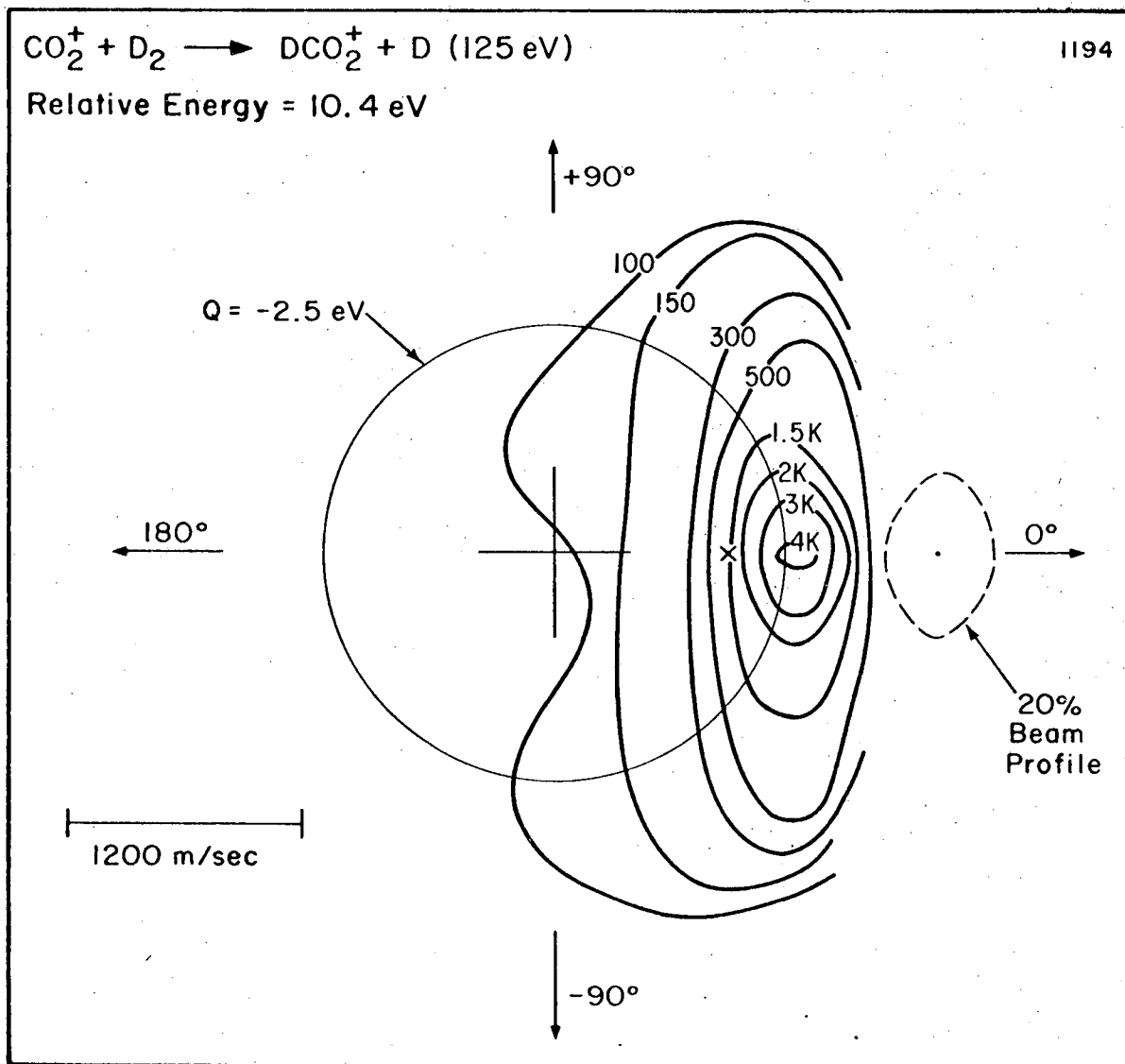
Fig. 4

XBL 749-7208



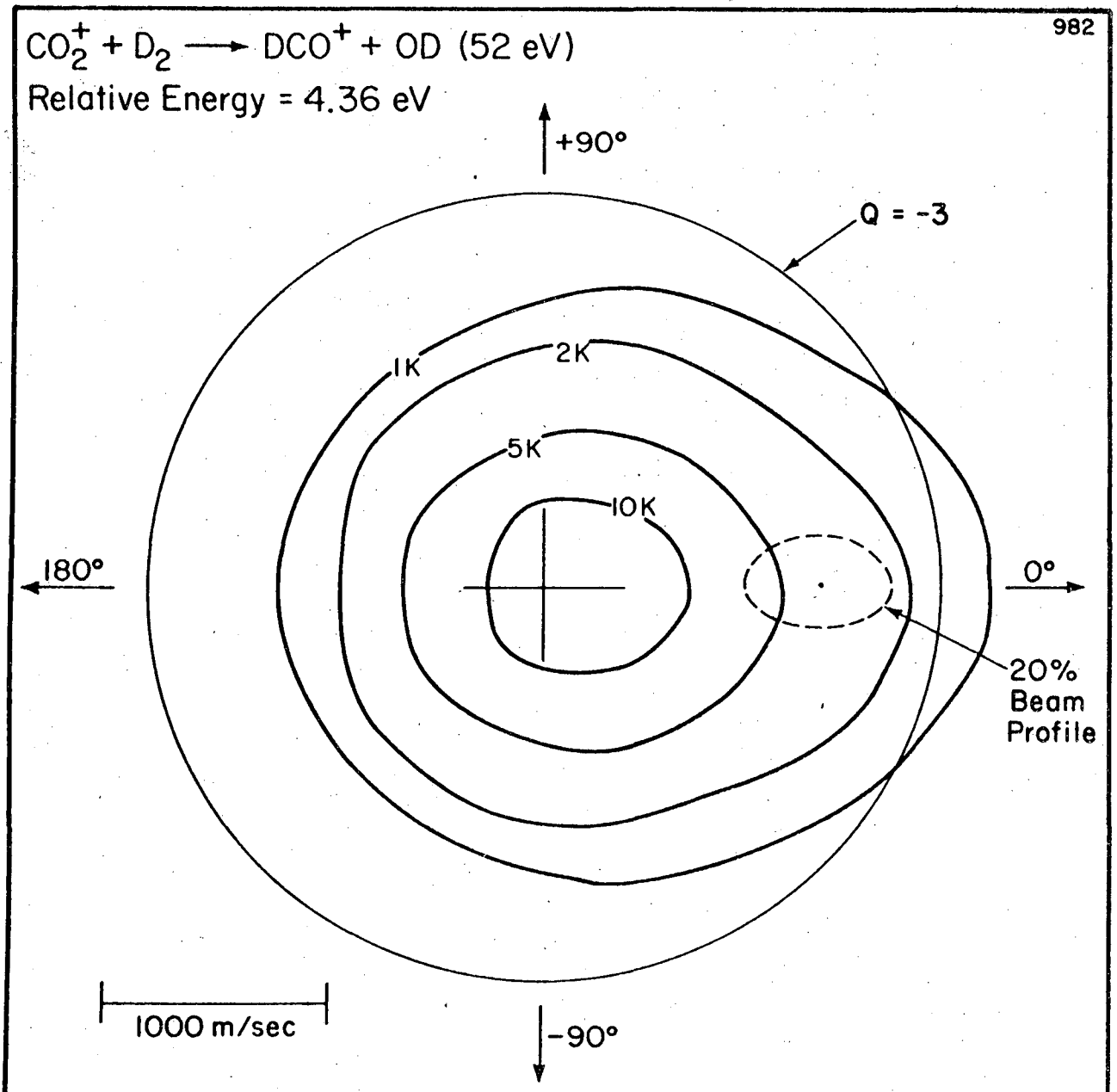
XBL 749-7207

Fig. 5



XBL 749-7237

Fig. 6



XBL 749-7206



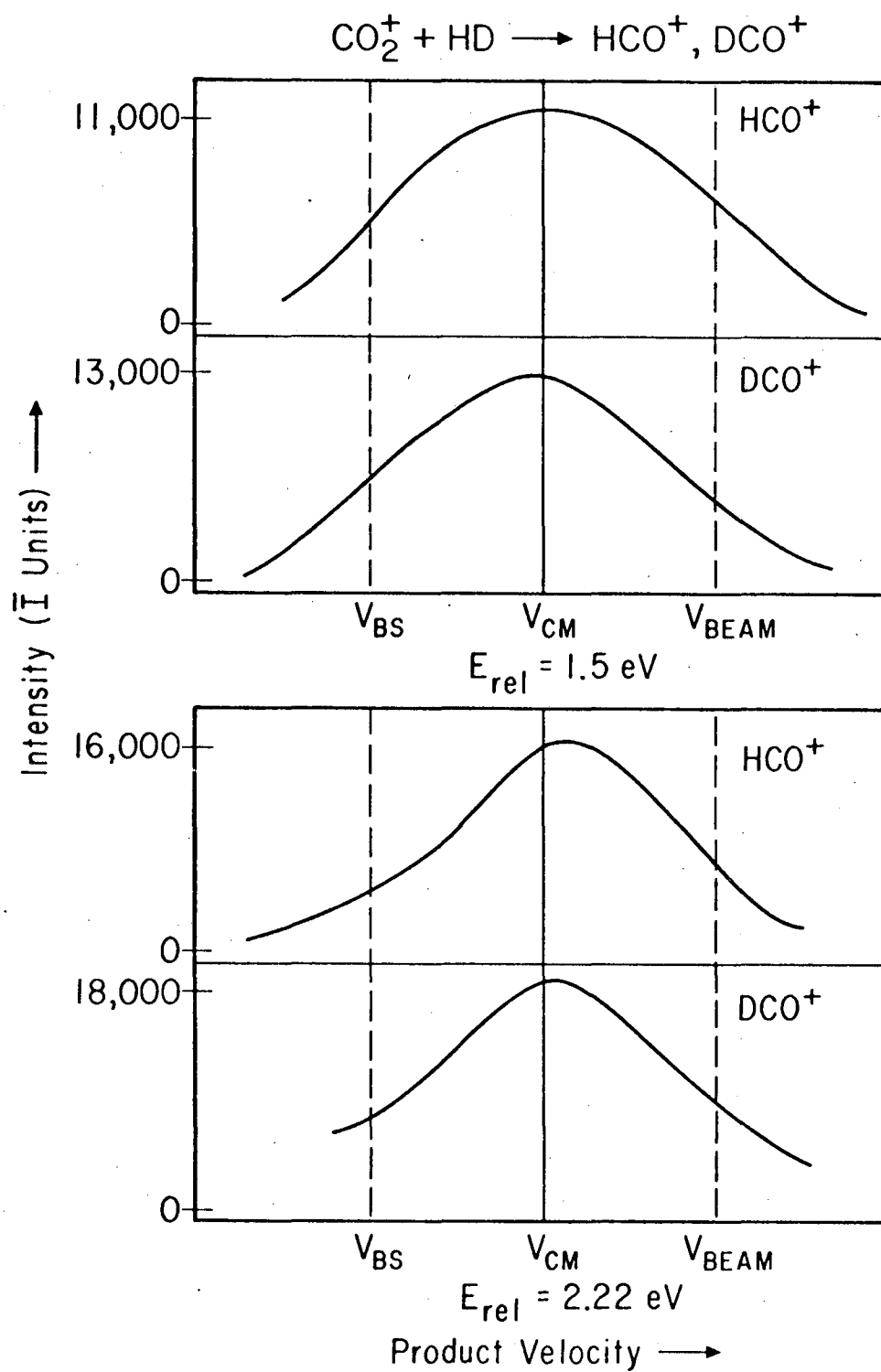
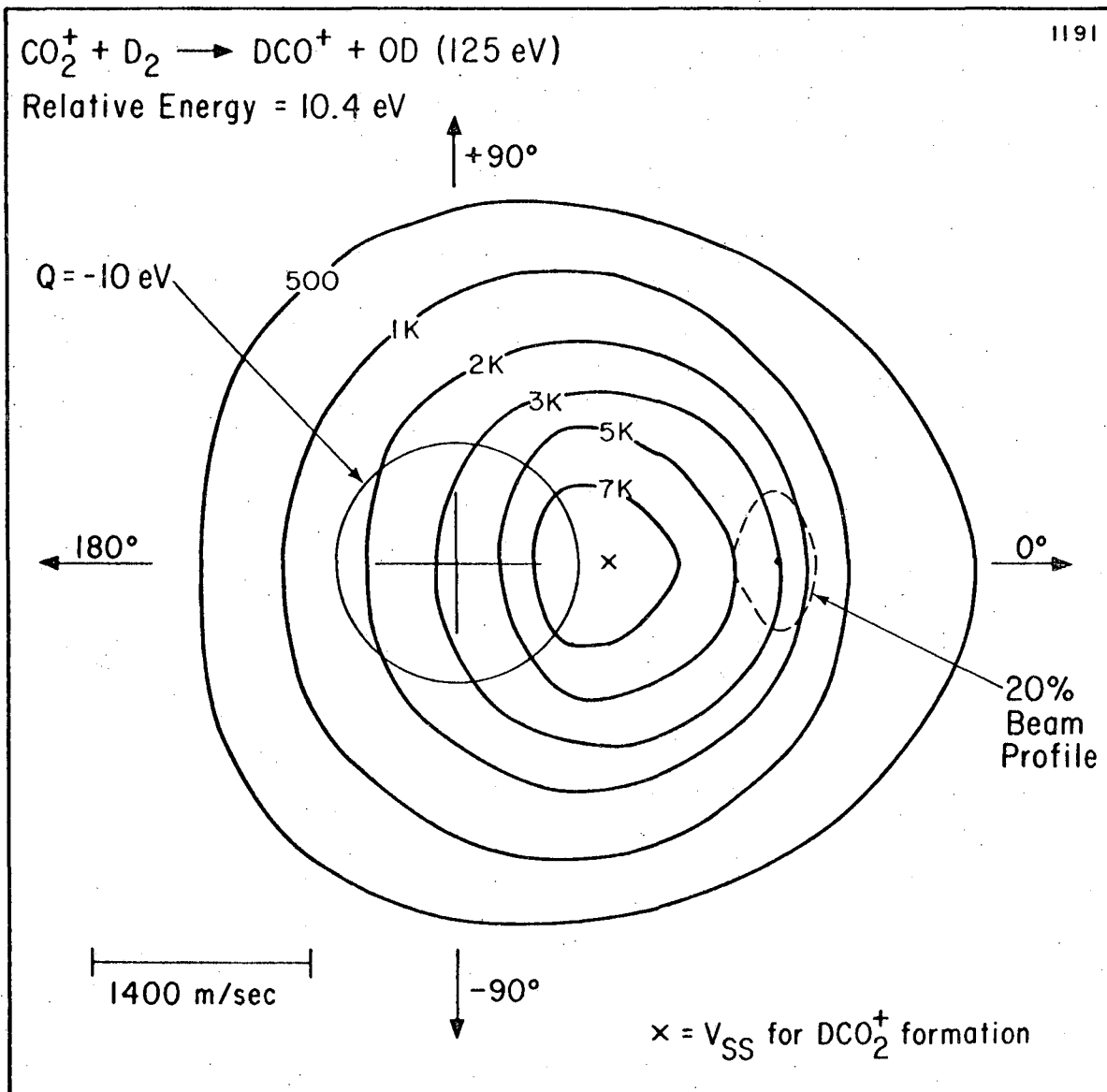
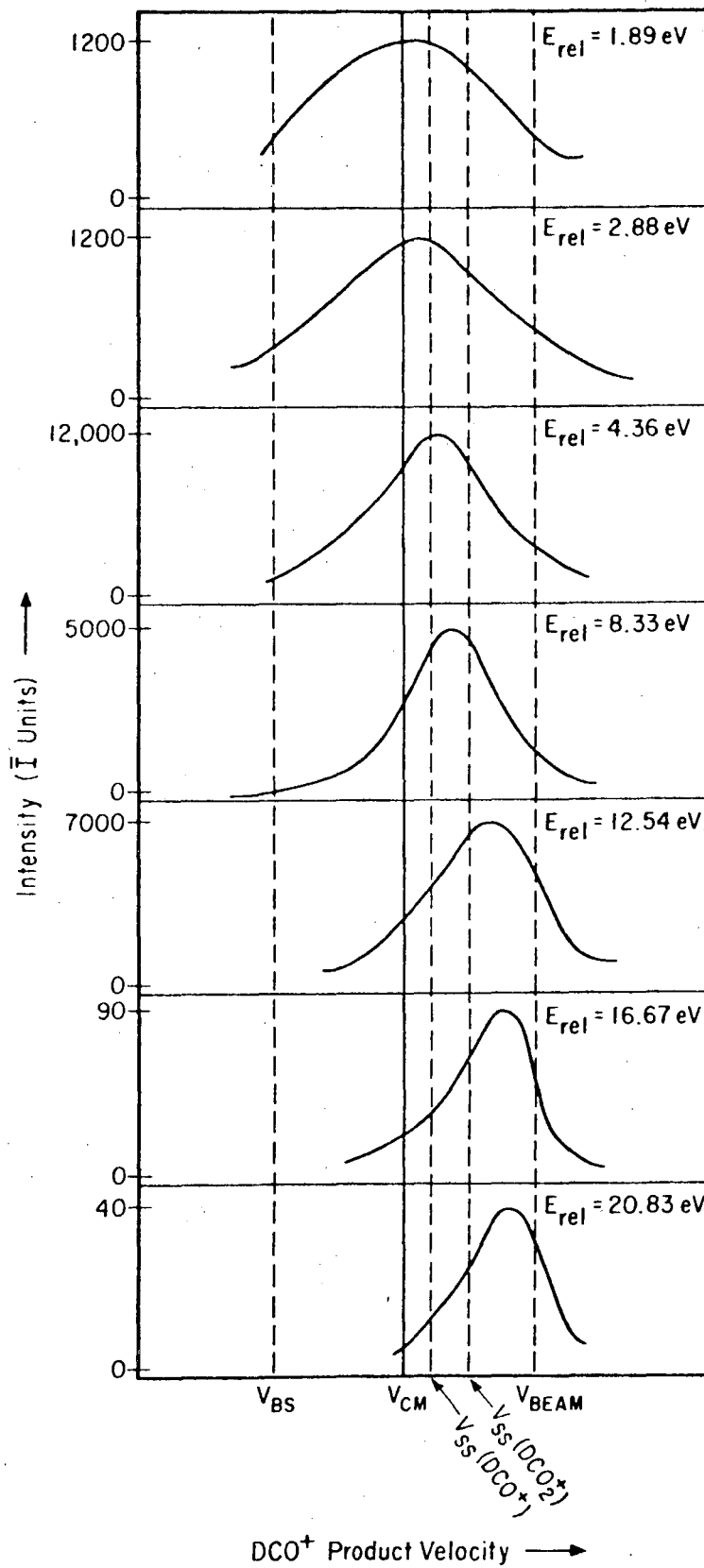
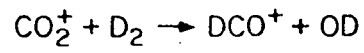


Fig. 8



XBL 749-7231

Fig. 9



XBL 749-7229.

Fig. 10

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

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