Title

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Author

Valentini, James J.

Publication Date

1977-07-01

UC-22

Submitted to Journal of Chemical
Physics

LBL-5719 C-1
Preprint

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James J. Valentini, Yuan T. Lee, and Daniel J. Auerbach

July 1977

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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LBL-5719

A CROSSED MOLECULAR BEAM STUDY OF THE TRANSLATIONAL ENERGY DEPENDENCE OF Cl + $Br_2 \rightarrow BrCl + Br$ REACTION

James J. Valentini[†] and Yuan T. Lee

The James Franck Institute
and Department of Chemistry
The University of Chicago
Chicago, Illinois 60637

and

Materials and Molecular Research Division
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California, Berkeley, CA 94720

and

Daniel J. Auerbach[††]

The James Franck Institute
and Department of Chemistry
The University of Chicago
Chicago, Illinios 60637

JULY 1977

ABSTRACT

A crossed molecular beam study of the $Cl + Br_2 \rightarrow BrCl + Br$ reaction using supersonic nozzle beams of Cl and Br_2 has been carried out at collision energies of 6.8, 14.7 and 17.7 kcal/mole. At all three collision energies the BrCl product is quite strongly forward peaked, with a large fraction (80%-85%) of the energy in internal degrees of freedom. The results of the experiment indicate that the $Cl + Br_2$ reaction displays the characteristics of an exoergic reaction on an attractive surface with early energy release. Estimated total cross sections at 6.8 kcal/mole and 14.7 kcal/mole are 11 $\mathring{A}^2$ and 14 $\mathring{A}^2$ respectively.

INTRODUCTION

Among the first reactions successfully investigated using "universal" crossed molecular beam machines, i.e. those having very sensitive mass spectrometric detectors, were the halogen atom - halogen molecule exchange reactions, $X + YZ \rightarrow XY + Z$.

Reactions like

$$Cl + Br_2 \rightarrow BrCl + Br$$

$$Br + I_2 \rightarrow IBr + I$$

$$Cl + IBr \rightarrow ICl + Br$$

$$Cl + BrI \rightarrow BrCl + I$$

$$Br + ICl \rightarrow IBr + Cl$$

have been studied in crossed molecular beam experiments by three different groups.[1-3] However, these early studies always employed molecular effusion sources to produce the atom beam, generally also the molecule beam, with an attendant large spread in initial collision energy, and in most cases no velocity distribution data on the products was obtained. The conclusions that have been drawn, invoking possible complex formation, attractive potential energy surfaces with possible energy wells, and relatively small total cross sections, have as a result been somewhat tentative. Conclusions derived from such experiments using effusive beam sources are however expected to be quite reliable, if the reaction cross sections do not depend appreciably on collision energy.

A classical trajectory study of $Br + I_2$, $Cl + I_2$, and $Cl + Br_2$ using empirical surfaces having energy minima 0-10 kcal/mole deep with adjustable shapes and positions has been carried out by Borne and Bunker[4] in an attempt to exmplain the dynamics of these reactions. However, these authors found that no reasonable potential well for collinear reactant approach could explain the observed scattering.

A more complete crossed molecular beam study of one or more of these reactions with better defined initial conditions and product velocity analysis to allow complete unfolding of the center-of-mass distributions was obviously warranted. Investigation of these reactions at several collision energies in order to more completely probe the features of the X + YZ potential energy surface was also needed. For these reasons we began a study of the $Cl + Br_2 \rightarrow BrCl + Br$ reaction using crossed beams of Cl and Br_2 produced from supersonic nozzles, to allow us to study the reaction as a function of collision energy under well-defined initial conditions. Since the exothermicity of this reaction is only 6 kcal/mole,[5] it is not difficult to raise the collision energy as high as three times the exothermicity by using the seeded beam method.

EXPERIMENTAL

The crossed molecular beam apparatus used in studying this reaction is similar to the one which has been described in detail elsewhere.[6] The beam and detector arrangement is shown in Figure 1. Both the bromine molecule and chlorine atom beams were produced by supersonic nozzle sources. The bromine molecule beam source consisted of a glass nozzle connected by a glass feed line to a glass bulb immersed in a temperature regulated bath held at 300 K, which gives a Br_2 vapor pressure of 205 torr. The glass gas feed line from the bulb to the nozzle and the nozzle itself were heated to prevent condensation of the bromine. This heating was provided by passing AC current through a heating "tape" wrapped around the feed line and nozzle. The nozzle temperature was monitored by a chromel:alumel thermocouple firmly attached to the nozzle tip. The nozzle temperature was maintained at about 360 K.

The chlorine atom beam was produced by thermal dissociation of Cl_2 in a graphite nozzle.[7] Mixtures of 10% Cl_2 in argon, 5% Cl_2 in helium, and 1% Cl_2 in helium were used as seeded gas mixtures for these experiments. These chlorine mixtures were obtained commerically. For these experiments the nozzle was operated with a nozzle tip temperature of about 1900 K. Measurements of the velocity distributions of the Cl and Br_2 beams by the time-of-flight method indicated collision energies of 6.8, 14.7, and 17.7 kcal/mole for the three gas mixtures used, with a spread in energy of approximately ±35%.

Measurement of the angular distribution of the BrCl product in the plane of the reactant beams was made using the rotatable quadrupole mass spectrometer detector shown in Figure 1. These data were obtained using counting times of 60 to 120 seconds for each point, periodically returning to a reference angle to provide long-term normalization. Plotted angular distributions represent the average of several separate scans.

Product velocity distributions at selected angles were determined using a simple time-of-flight technique. These spectra of product intensity as a function of flight time were recorded using a 40 channel multiscaler which had adjustable channel time width and delay time. For these measurements the BrCl product was modulated at the detector entrance aperture by a rotating, 17.8 cm diameter aluminum wheel with four slots of .30 cm width cut out at equally spaced points along the periphery. The wheel was rotated at a frequency of about 400 Hz. This gave a shutter function FWHM of about 13 μsec, about 7% of the average flight time of a BrCl molecule to the ionizer of the mass spectrometer. The effective length of the ionizer is ~1.5 cm, and the average flight length is 17.3 cm. Hence the total system resolution was approximately 12%. Time-of-flight data were recorded for 60 to 180 minutes depending on the signal level.

RESULTS

The angular distributions of the BrCl product at three different collision energies are shown in Figure 2. At all three collision energies the interhalogen product is quite strongly forward peaked, i.e., peaked toward the initial Cl atom velocity. As the collision energy is raised the product peaks more sharply in the forward direction. At the lowest collision energy some BrCl product does appear in the backward direction while at the high collision energies the BrCl product is almost exclusively forward peaked.

From the angular distributions shown and from time-of-flight velocity analysis of the products, center-of-mass contour maps of product flux have been constructed. These are shown in Figures 3, 4, and 5 for the contours higher than 10% of peak product flux. The signal levels at wide angles and in the backward hemisphere are too low to provide meaningful information. These contour maps of $I_{c.m.}(\theta, u)$, the center of mass doubly differential reactive scattering cross section, were constructed by iterative deconvolution of the measured $\bar{I}_{LAB}(\Theta, v)$ cross section data. The deconvolution technique[8,9] solves the equation:

$$\bar{I}_{LAB}(\Theta, v) = \sum_i f_i \frac{v^2}{u_i^2} I_{c.m.}(\theta_i, u_i)$$

iteratively for $I_{c.m.}(\theta, u)$. This summation is taken over the range of transformation Newton diagrams generated by the finite widths of the beam velocity distributions and angular spreads, and f_i is the weighting factor for the i^{th} Newton diagram.

The experimental laboratory angular and velocity distributions and those calculated from the deconvoluted center-of-mass flux distributions are compared in Figures 6 and 7. The fit to the lab angular distributions and the velocity distributions at E_{COLL} = 14.7 kcal/mole is quite good. The fit to the velocity distributions at E_{COLL} = 6.8 kcal/mole is slightly better, while the fit to the velocity distributions at the highest collision energy is about the same as that at the intermediate collision energy shown.

The contour maps of Figures 3, 4, and 5 show quite clearly that the BrCl product does peak almost exclusively in the forward hemisphere, even at the lowest collision energy. The BrCl which appears in the backward hemisphere in the lab angular distribution at a collision energy of 6.8 kcal/mole is mostly due to smearing of the lab angular distribution due to the range of Newton diagrams which effect the center-of-mass to lab transformation.

The contour maps show that the c.m. angular spread of the BrCl product does not change very much even when the collision energy increases from 6.8 kcal/mole to 17.7 kcal/mole. However, as the collision energy is increased the spread of the BrCl product in recoil velocity decreases quite sharply. It is this decrease in the range of recoil velocity that gives rise to the increased sharpness of the product lab angular distributions as the collision energy increases.

The change in the form of the recoil energy distribution is shown in detail in Figure 8. This figure gives plots of the relative intensity, $P\ (E_T'/E_{TOT})$, as a function of the fraction of the total available energy, E_{TOT}, which appears in translational energy of the products, E_T'. $P(f) = P(E_T'/E_{TOT}) = \sum_\theta I_{c.m.}(\theta,\ E_T') = \sum_\theta I_{c.m.}(\theta,\ u)/u$, where $I_{c.m.}(\theta,\ u)$ is the center-of-mass flux distribution as shown in Figure 3, 4, or 5. These distributions show that when averaged over recoil angle, the recoil energy distributions do not peak at energies which are very different. In all cases the distributions peak at approximately .14 - .18, i.e., 14% - 18% of the total available energy. However, these recoil energy distributions do show a pronounced change as the collision energy is increased. At the lowest collision energy the recoil energy distribution is quite broad, extending to the nominal kinematic limit, $E_T'/E_{TOT} = 1$. As the collision energy is increased the recoil energy distribution becomes sharper, and the amount of product which appears with a large amount of translational energy decreases dramatically.

The fact that the reocil energy distribution for the lowest collision energy does not become exactly 0 at $E_T'/E_{TOT} = 1$ is a consequence of the imperfect deconvolution of the laboratory data. This means that the actual distribution probably decreases more sharply as $f \to 1$. For the high collision energies the data are not plotted to $f = 1.0$, since the data are not as accurate at high values of f. Clearly, however, at the higher collision energies there is negligible probability of having translational recoil energies of greater than about 60% of the total available energy.

The <u>average</u> product translational energy,

$$\langle E_T' \rangle = \frac{\sum\limits_{E_T'} P(E_T')\cdot E_T'}{\sum\limits_{E_T'} P(E_T')} ,$$

is, however, a considerably larger fraction of the total energy, ~38%, for the lowest collision energy, than for the higher collision energies, ~22%. This is mainly due to the much greater spread of the recoil energy distribution, extending out toward a larger fraction in translational energy, for the lowest collision energy, even though the peak recoil energy is about the same fraction of the total energy for each case.

It is clear that the increased sharpness of the BrCl lab angular distributions at higher energy is a consequence of the narrower recoil energy (velocity) distributions at higher energies, and not an increasingly sharp center-of-mass angular distribution. As can be seen in Figure 9 the center-of-mass angular distributions, $I(\theta) = \sum_{E_T'} I_{c.m.}(\theta, E_T')$, are nearly identical at all three collision energies.

We have also made an attempt to determine the total reactive cross section, σ_R, for the Cl + Br_2 reaction at these collision energies. This was done by comparing the integrated intensity of reactive scattering to the observed intensity of small angle elastic scattering of chlorine atoms from bromine, which was normalized to the theoretical small angle elastic scattering intensity from theoretical van der Waals force constants.[10]

The integrated reactive scattering intensity, in arbitrary units, is given by:

$$\sigma_R' = 2\pi \int_0^\infty \int_0^\pi \bar{I}_{c.m.}(\theta, u) \sin\theta \, d\theta \, du,$$

where $\bar{I}_{c.m.}(\theta, u)$ is derived from a single ("canonical") Newton diagram transformation of the measured $\bar{I}_{LAB}(\Theta, v)$ data. This "canonical" Newton diagram was taken as the one which maximizes the quantity $(v_1^2 + v_2^2)^{1/2} \cdot f(v_1) \cdot f(v_2) \cdot f(\gamma)$, where $f(v_1)$, $f(v_2)$ are the velocity distribution functions of the two reactant beams and $f(\gamma)$ is the intersection angle distribution. This total cross section is related to the "true" total cross section by two constants, C_1 and C_2:

$$\sigma_R = \sigma_R' \cdot C_1 \cdot C_2 \ .$$

C_1 gives the ratio of detection efficiency for chlorine atoms (m = 35) to detection efficiency for BrCl (m = 116). C_2 gives the ratio of the theoretical small angle chlorine atom elastic scattering intensity in absolute units to the observed elastic scattering in arbitrary laboratory units.

The theoretical small angle elastic scattering intensity is given by:

$$I_{Cl}(\Theta) = \frac{v}{\mu^2 \cos\delta} \cdot .239\,(C_6/\bar{E})^{1/3}\,\theta^{-7/3},$$

where the first factor is the c.m. to lab transformation Jacobian, v and u are the lab and center of mass chlorine velocities, and δ is the angle between the $\bar{u}$ and $\bar{v}$ vectors. C_6 is the van der Waals constant and $\bar{E}$ is the most probable ("canonical") collision energy. C_6 was estimated to be 290 x 10^{-60} erg cm^6 using the combination rule[11]

$$C_{ab} = \frac{2C_{aa}C_{bb}}{[(\alpha_b/\alpha_a)C_{aa} + (\alpha_a/\alpha_b)C_{bb}]}$$

for C_6, and the Slater-Kirkwood approximation[12]

$$C_{ii} = 12.6 \times 10^{-60}\ \text{erg-cm}^6\ \alpha_i^{\,2}\ (N_i/\alpha_i)^{1/2}$$

for C_{aa}, C_{bb}. Here α_a, α_b are the static dipole polarizabilities, in Å^3, of Cl and Br_2, and N_a, N_b are the number of electrons in the outer shells of Cl and Br_2, 7 and 14 respectively. The Cl and Br_2 polarizabilities, 2.2 Å^3 and 6.4 Å^3 respectively, were approximated from the values[13] for HX and H_2 by $\alpha(X) = \alpha(HX) - 1/2\alpha(H_2)$ and $\alpha(X_2) = 2\alpha(X)$.

The result of this calculation at collision energies of 6.8 kcal/mole and 14.7 kcal/mole gives σ_R = 11 $\AA^2$ and σ_R = 14 $\AA^2$ respectively. The absolute magnitude of these numbers are probably only accurate to within a factor of three due to uncertainties attendant to the calculation of the total cross section in this manner. Namely, the cross sections may lie in the range of 4 - 33 $\AA^2$ and 5 - 42 $\AA^2$ at collision energies of 6.8 and 14.7 kcal/mole.

DISCUSSION

The fact that the center of mass angular distributions of the BrCl product are essentially identical and peaking sharply forward at collision energies of 6.8 kcal/mole, 14.7 kcal/mole, and 17.7 kcal/mole seems to indicate that the Cl + Br_2 interaction is indeed one without an appreciable activation energy or barrier.[3] The lack of an energy barrier is also indicated by the fact that the total reactive cross section does not seem to be strongly dependent on the collision energy. The total cross section at 14.7 kcal/mole (5-42 $\AA^2$) is nearly the same as that at 6.8 kcal/mole (4-33 $\AA^2$). If the reaction had an appreciable barrier, a few kcal/mole, the total reactive cross section should increase rather sharply as the collision energy increases from 6.8 kcal/mole to 14.7 kcal/mole. The magnitude of the total cross section determined here is not much different from that measured previously for the Cl + Br_2 reaction at even lower collision energy, ~3.0 kcal/mole by Blais and Cross[2] and by Lee et al.[3a] Here the cross section was estimated to be about 1 $\AA^2$ to 20 $\AA^2$.

Thus, although the forward peaking of the ClBr product at all energies would seem to indicate that the dominant interaction between the reactants is attractive, the estimated total reactive cross sections are much smaller than hard sphere values. This is the basis of a conclusion drawn earlier that although the interaction is attractive is it short range in nature.[3a] It also might mean that reaction may take place for a wide range of impact parameters, but with low probability. Such a situation could arise if the reaction demonstrated a stereochemical constraint, i.e., a strong preference for a particular Cl-Br-Br geometry. As discussed in several previous works,[14,3c,15] these species may have a bent geometry. Thus, the forward peaking and small cross sections may be due to a preference for a bent Cl-Br-Br geometry.

Although the center-of-mass angular distributions and reaction cross sections seem to show little or no variation as the collision energy is increased, the recoil energy distributions at the three collision energies studied show dramatic differences. These differences are indicative of a change in the dynamics of the reaction as the collision energy increases.

The sharp recoil energy distribution at the highest collision energy, peaking at a small fraction (.14) of the total available energy, seems to indicate that the reaction is approaching the spectator stripping model. This highly simplified model assumes that the nonreacting Br atom in Br_2 acts as a fully disinterested spectator of the reaction. When the internal energy of Br_2 is ignored, or is insignificant, as is the case when the Br_2 beam is produced by supersonic expansion, the spectator stripping model predicts all products to be scattered exactly forward in the c.m. system. This model also gives a unique recoil translational energy $E'_{T,S.S.}$, which is simply related by a mass factor to the collision energy E_{COLL}:

$$E'_{T,S.S.} = \frac{m_{Cl}\, m_{Br}}{m_{Br_2} m_{BrCl}} E_{COLL} = .15\, E_{COLL} .$$

for E_{COLL} = 17.7 kcal/mole, $E'_{T,S.S.}$ = 2.7 kcal/mole, or 11% of the total available energy. The recoil energy distribution at E_{COLL} = 17.7 kcal/mole peaks at 14% of the total available energy, it is very narrow, and is quite close to the spectator stripping limit.

For E_{COLL} = 14.7 kcal/mole the recoil energy distribution is less sharp than at the highest collision energy, and peaks at 15% of E_{TOT}' while the spectator stripping model predicts a peak at 11%. Even so, this recoil energy distribution at 14.7 kcal/mole collision energy more closely resembles that at 17.7 kcal/mole collision energy than that at 6.8 kcal/mole collision energy, as might be expected from the relative magnitudes of the collision energies. The recoil energy distribution at the intermediate energy represents a transition from the clearly nonstripping behavior at the lowest collision energy to the nearly stripping limit behavior at the highest collision energy. A summary of the features of the product energy distributions are given in Table I.

The spectator stripping model assumes a pure two body collision in which Cl and a Br combine with negligible momentum transfer to the nonreacting Br atom of Br_2. The recoil energy distribution at the lowest collision energy clearly indicates substantial momentum transfer. This recoil energy distribution at the lowest collision energy is quite similar to the one obtained by LeBreton[3c] at a mean collision energy of 5 kcal/mole.

Analysis of the data by LeBreton[3c] has shown that an osculating complex model, assuming a complex lifetime of approximately one rotational period, and randomization of the total available energy into all accessible modes of the reaction intermediate, will fairly accurately reproduce his observed recoil energy and c.m. angular distributions. However, such an osculating complex model might not be a good description for the higher collision energies, and it will probably not be able to give the sharply forward peaked distribution for BrCl at 6.8 kcal/mole collision energy observed in our work. Our results would seem to indicate that if the Cl + Br_2 potential surface possesses an energy well, corresponding to a stable Cl-Br-Br complex, it must not be more than a few kcal/mole deep.

The results do strongly support the conclusion that the Cl + Br_2 potential energy surface is an attractive one, giving forward peaking and a large fraction of the available energy in internal degrees of freedom, as expected for an exoergic reaction on an attractive surface with early energy release.[3] The reaction dynamics will probably not be adequately explained by either a simple spectator stripping model or a simple osculating complex model, but it seems that as the collision energy is increased the reaction changes from a three body to more like a two body process.

As can be seen in the recoil energy distributions shown in Figure 8 and the data of Table I the reaction channels reagant translational energy into product internal energy with very high efficiency. At $E_{COLL} = 6.8$ kcal/mole the average internal energy is about 7.9 kcal/mole, while at collision energies of 14.7 kcal/mole and 17.7 kcal/mole this value increases to 16.2 kcal/mole and 18.4 kcal/mole. Thus, one expects that the BrCl product will be highly vibrationally and rotationally excited as the collision energy is increased.

It is possible that more than one electronic state is important in the dynamics of this reaction. The thermal dissociation chlorine atom source produces both the $^2P_{3/2}$ and $^2P_{1/2}$ (~15-20%) states of chlorine, and the reaction dynamics of these two states may be somewhat different. Since the spin orbit splitting in chlorine is 2 kcal/mole, these differences may only be important at low collision energies. Airey, Pacey, and Polanyi[16] have detected Br ($^2P_{1/2}$) in infrared chemiluminescence studies, observing the excited electronic state in the H + HBr → H_2 + Br reaction. Since the spin-orbit splitting in bromine is quite large, about 8 kcal/mole, we should observe a bimodel recoil energy distribution if both the $^2P_{1/2}$ and $^2P_{3/2}$ states were produced in the Cl + Br_2 reaction. The recoil energy distributions do not give a clear indication that such is the case, However, if the partitioning of the excess energy were drastically different for the channel producing Br ($^2P_{1/2}$) or if only a small fraction of products are produced in this channel, such a bimodel distribution might be obscured.

It is important to note that many conclusions derived from previous lower resolution experiments using effusive beam sources are consistent with the results of the lowest energy experiment of this work. In analyzing the results of effusive beam experiments, if information on the energy dependence of reaction cross sections is not available, one often makes an assumption that the reaction cross sections do not depend on collision energy. Apparently, this is a good assumption in the $Cl + Br_2 \rightarrow BrCl + Br$ reaction, as evidenced by the present work.

ACKNOWLEDGMENT

This work was done with support from the U. S. Energy Research and Development Administration. The valuable comments made by Dr. K. Shobatake are gratefully acknowledged.

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† National Science Foundation Predoctoral Fellow, 1972-1975. Present address: Department of Chemistry, Harvard University, Cambridge, Mass. 02138.

†† Present address: Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218.

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Table I. Energy Distributions of Product Molecules for $Cl + Br_2 \rightarrow BrCl + Br$ at Various Collision Energies.

Collision Energy $\bar{E}_{COLL}$ (kcal/mole)	Total Energy $\bar{E}_{TOT}^{a}$ (kcal/mole)	Product Translational Energy $<E_T'>$ (kcal/mole)	Product Internal Energy $<E_{V,R}'>$ (kcal/mole)	Peak of Products Translational Energy $E_{T, peak}'$ (kcal/mole)	Spectator Stripping Model $E_{T,S.S.}'$ (kcal/mole)
6.8	12.8	4.9	7.9	2.3	1.0
14.7	20.7	4.5	16.2	3.1	2.3
17.7	23.7	5.3	18.4	3.3	2.7

[a] $\bar{E}_{TOT} = \bar{E}_{COLL}$ + 6 kcal/mole[5]

FIGURE CAPTIONS

Fig. 1. Schematic diagram of the crossed molecular beam apparatus used in the study of the Cl + Br_2 reaction.

Fig. 2. Experimental laboratory angular distributions of BrCl produced in the reaction Cl + Br_2 at collision energies of 6.8 kcal/mole, 14.7 kcal/mole, and 17.7 kcal/mole.

Fig. 3. Contour map of BrCl flux density in the center-of-mass coordinate system produced in the reaction Cl + Br_2 at a collision energy of 6.8 kcal/mole.

Fig. 4. Contour map of BrCl flux density in the center-of-mass coordinate system produced in the reaction Cl + Br_2 at a collision energy of 14.7 kcal/mole.

Fig. 5. Contour map of BrCl flux density in the center-of-mass coordinate system produced in the reaction Cl + Br_2 at a collision energy of 17.7 kcal/mole.

Fig. 6. — Experimental laboratory angular distributions of BrCl produced in the Cl + Br_2 reaction at collision energies of 6.8 kcal/mole, 14.7 kcal/mole, and 17.7 kcal/mole; ○ laboratory angular distributions calculated by transforming $I_{c.m.}(\theta, u)$ (Figures 3-5) to the laboratory frame using a full range of Newton diagrams, and then summing over laboratory velocities.

Fig. 7. □ Experimental laboratory velocity distribution of BrCl produced in the Cl + Br_2 reaction at a collision energy of 14.7 kcal/mole at four laboratory angles; — laboratory velocity distributions derived from the center-of-mass product distribution shown in Figure 4.

Fig. 8. ● Product recoil energy distributions for the Cl + Br_2 reaction at collision energies of 6.8 kcal/mole, 14.7 kcal/mole, and 17.7 kcal/mole, as a function of the fraction of the total available energy, obtained by angle averaging $I_{c.m.}(\theta, E_T')$, see text.

Fig. 9. ○ Center-of-mass angular distributions of BrCl produced in the Cl + Br_2 reaction at collision energies of 6.8 kcal/mole, 14.7 kcal/mole, and 17.7 kcal/mole, obtained by averaging $I_{c.m.}(\theta, E_T')$ over recoil energy.

00004607802

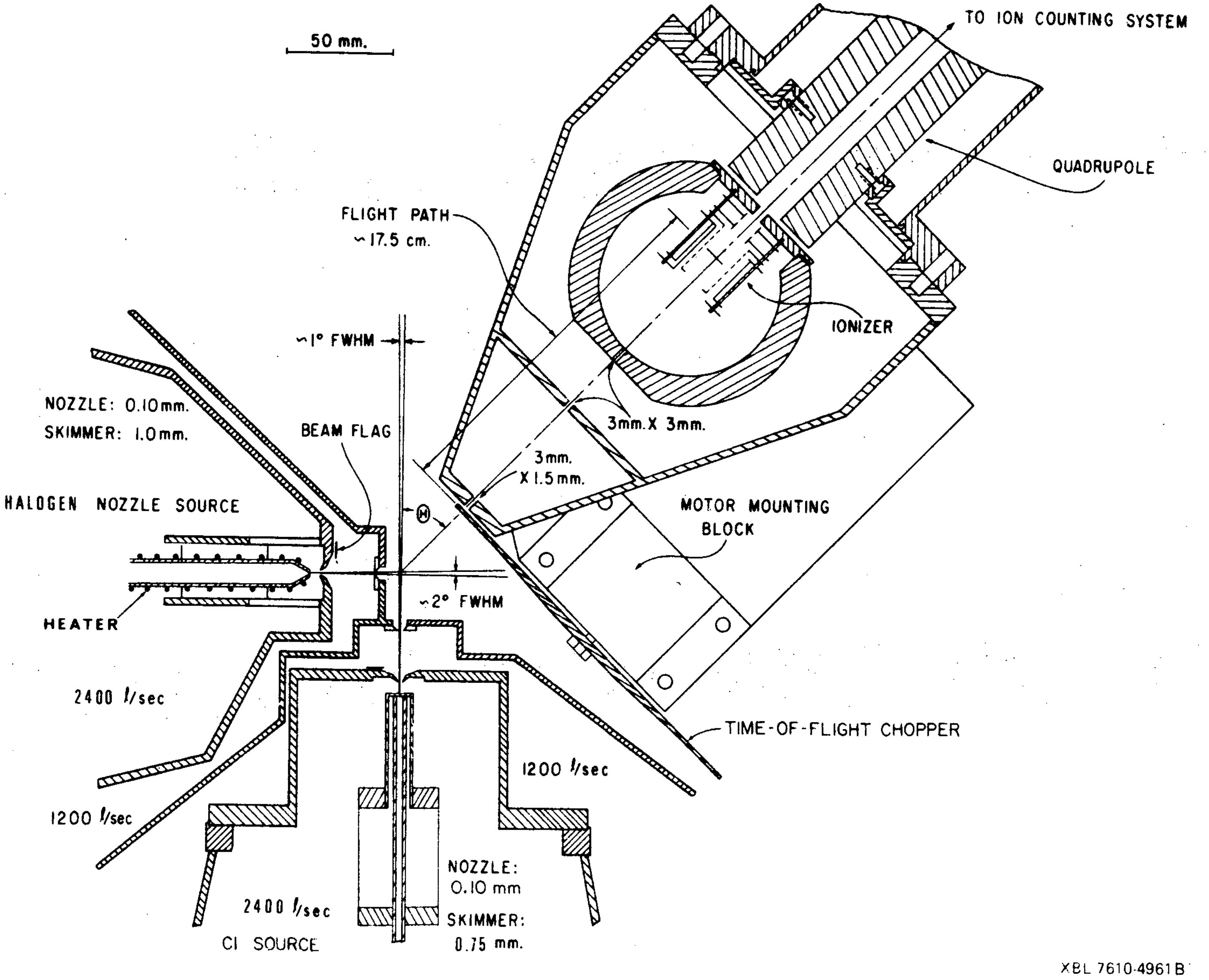


Fig. 1

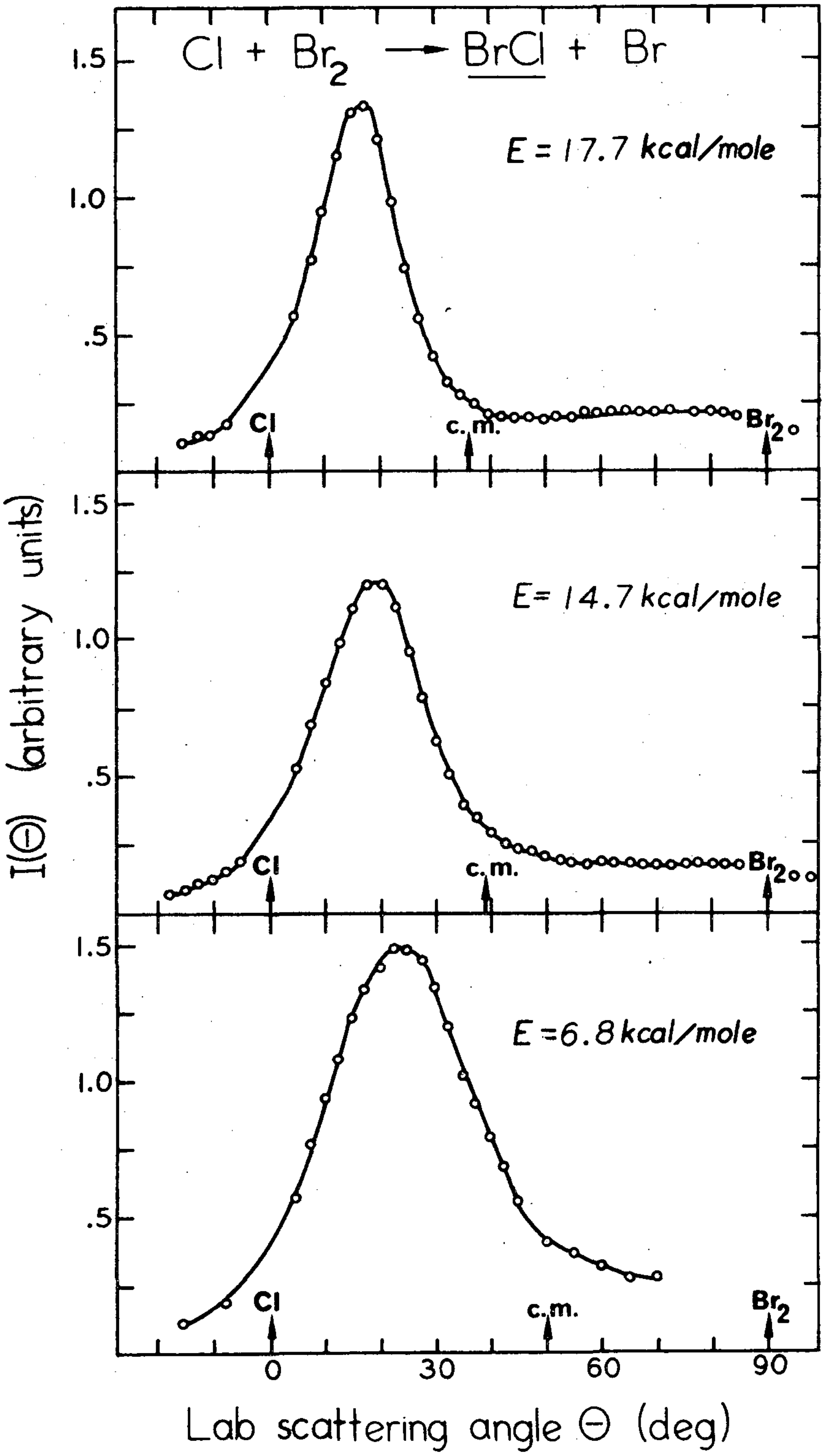
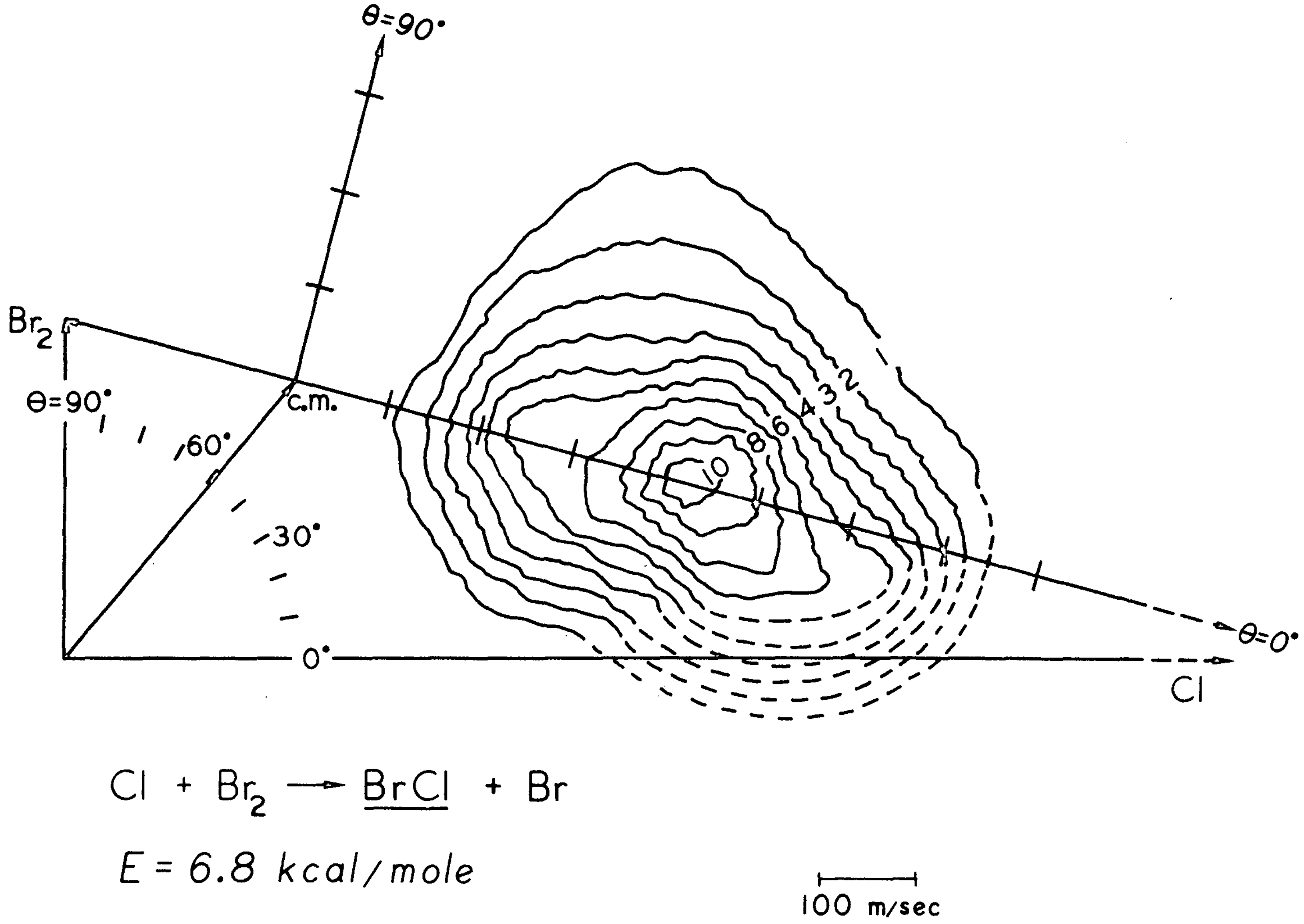


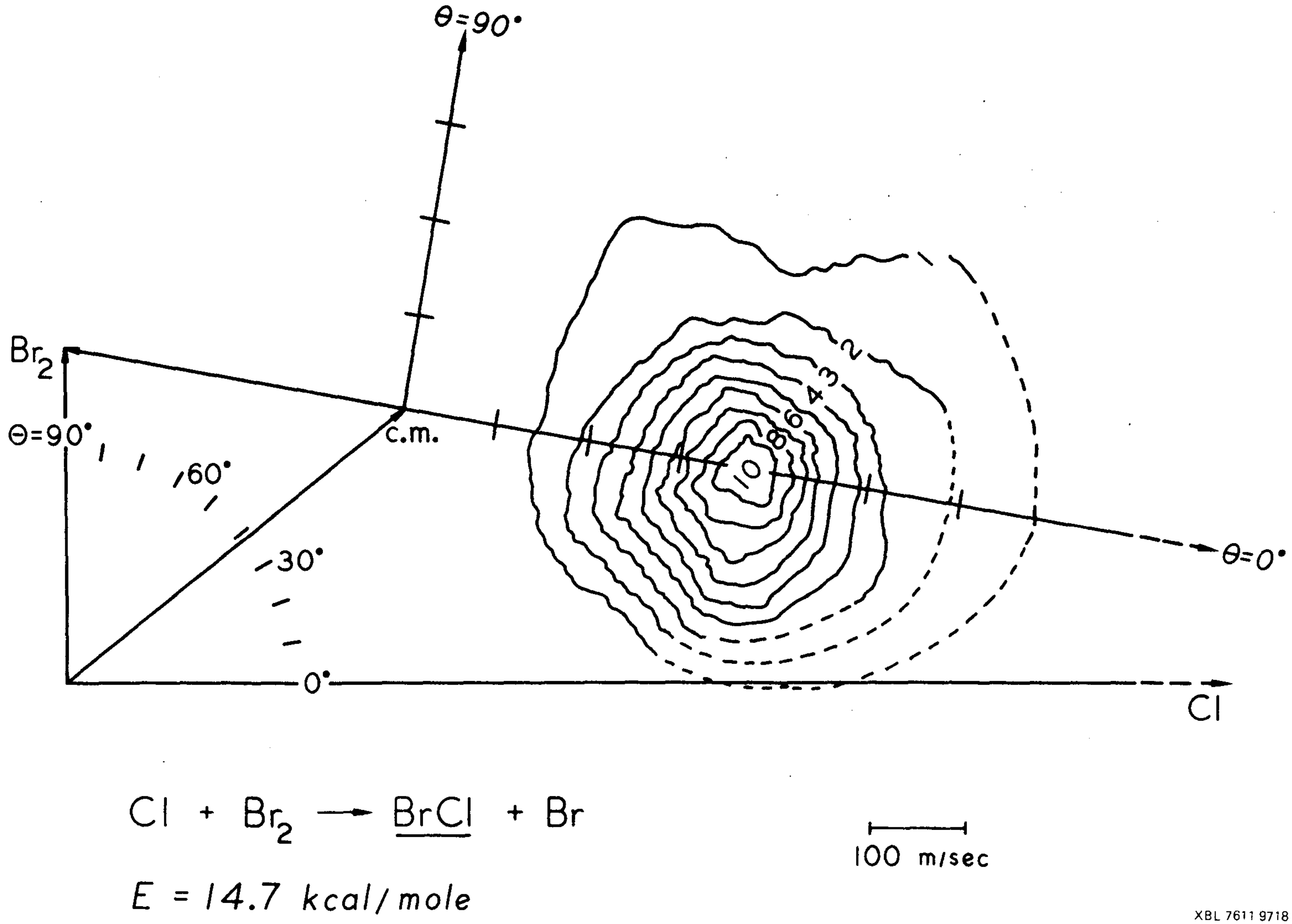
Fig. 2

XBL 7611-4782



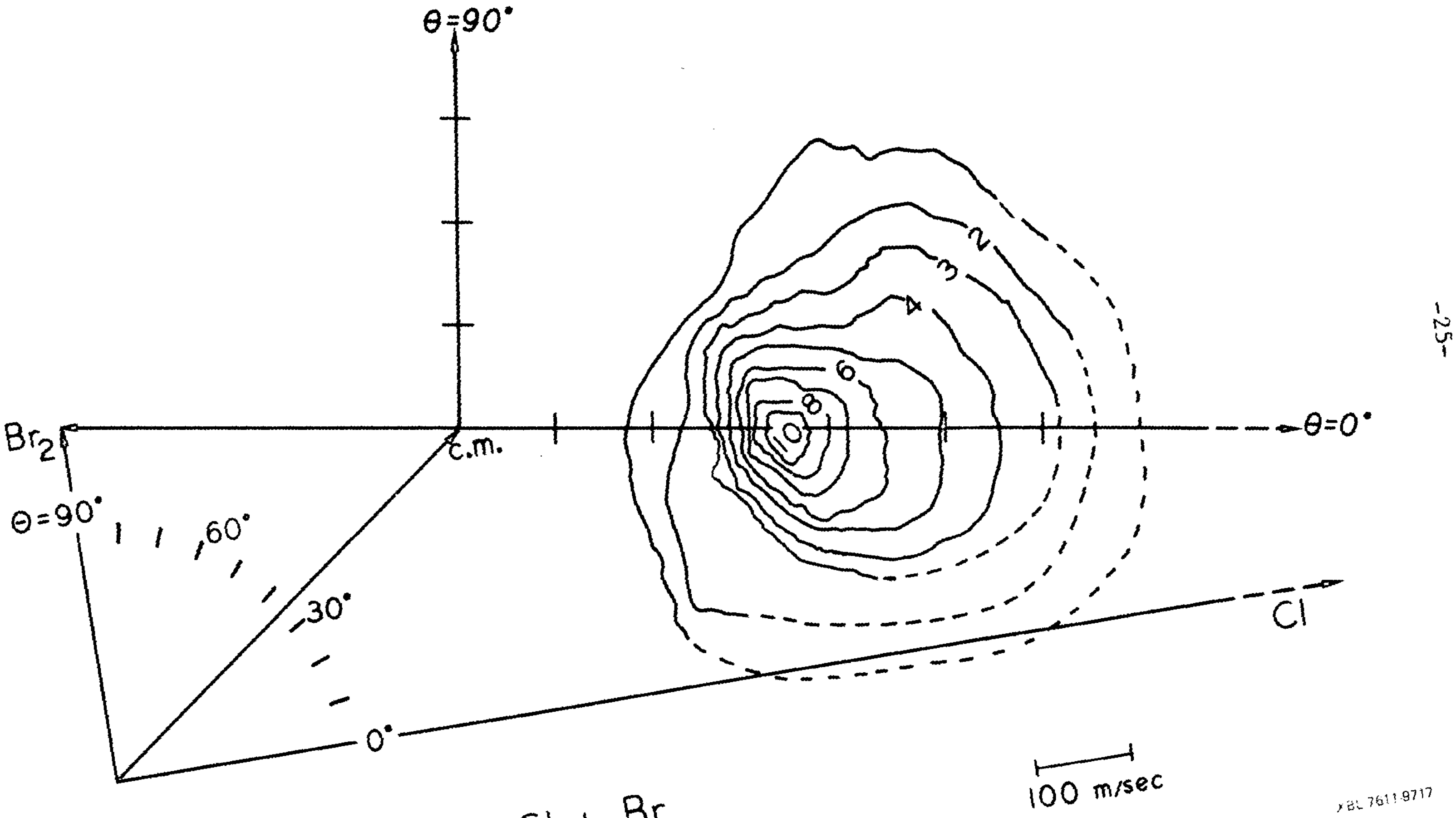
XBL 7611-9776

Fig. 3



XBL 7611 9718

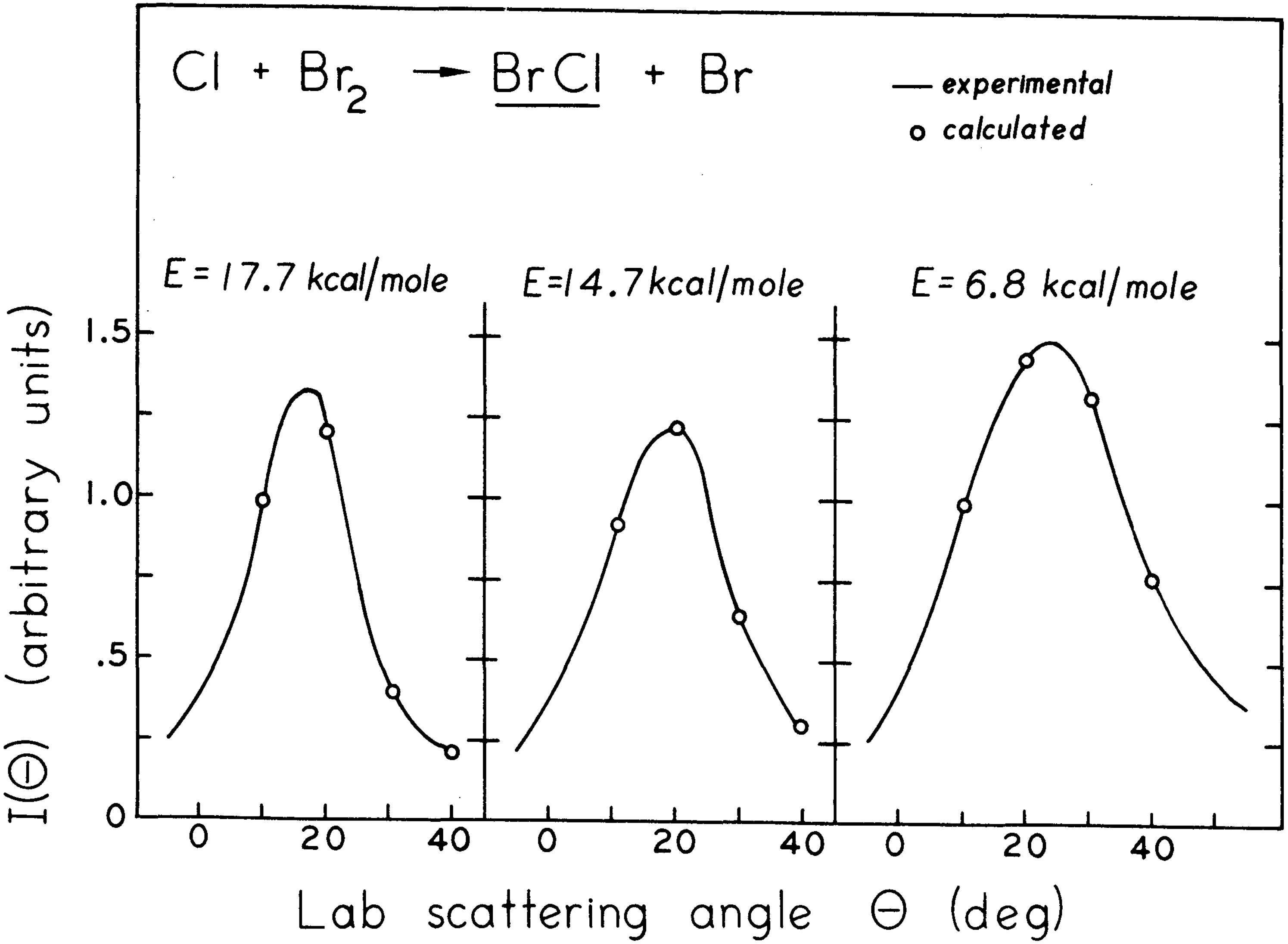
Fig. 4



$Cl + Br_2 \longrightarrow \underline{BrCl} + Br$

E = 17.7 kcal/mole

Fig. 5



XBL 7611-4781

Fig. 6

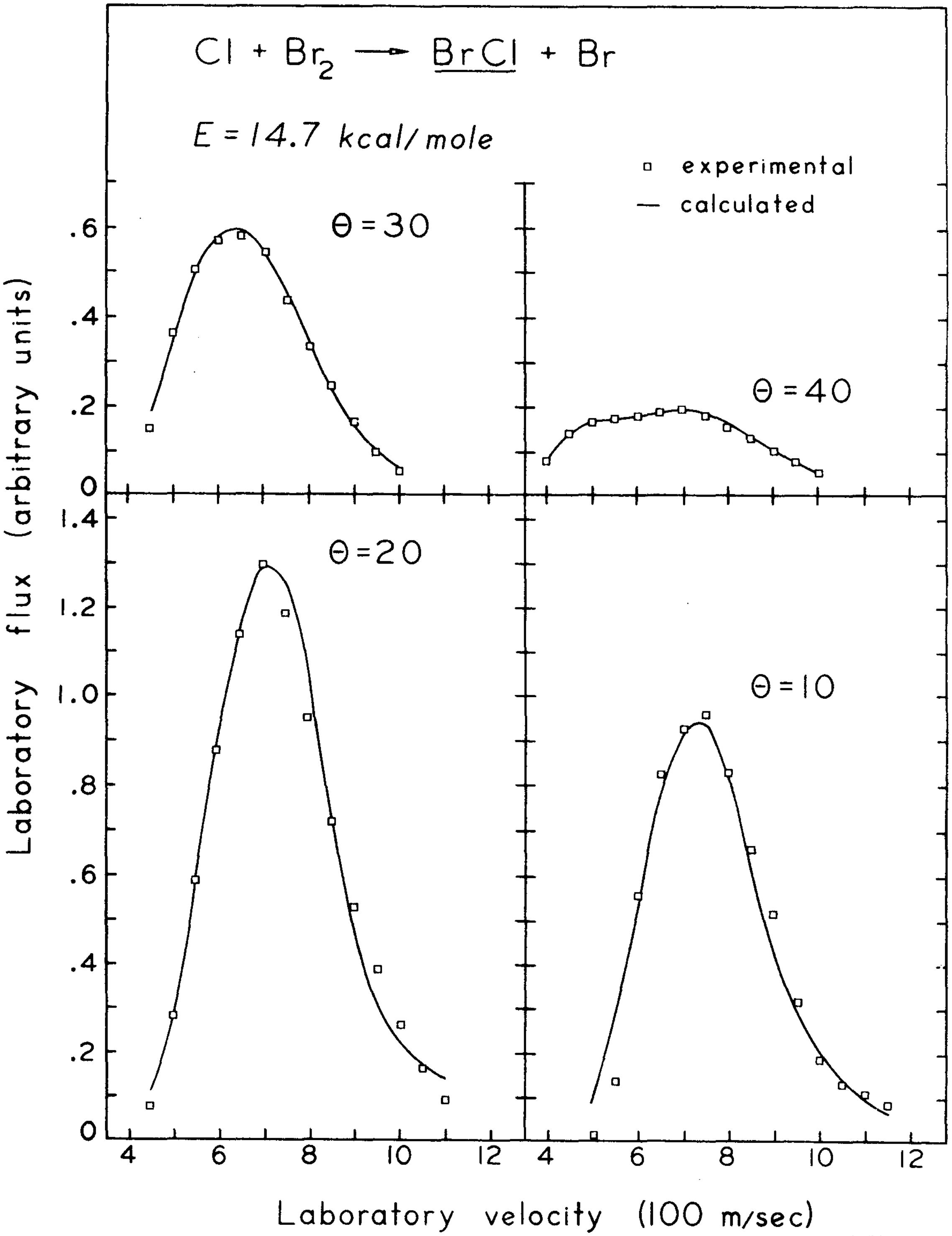


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Fig. 7

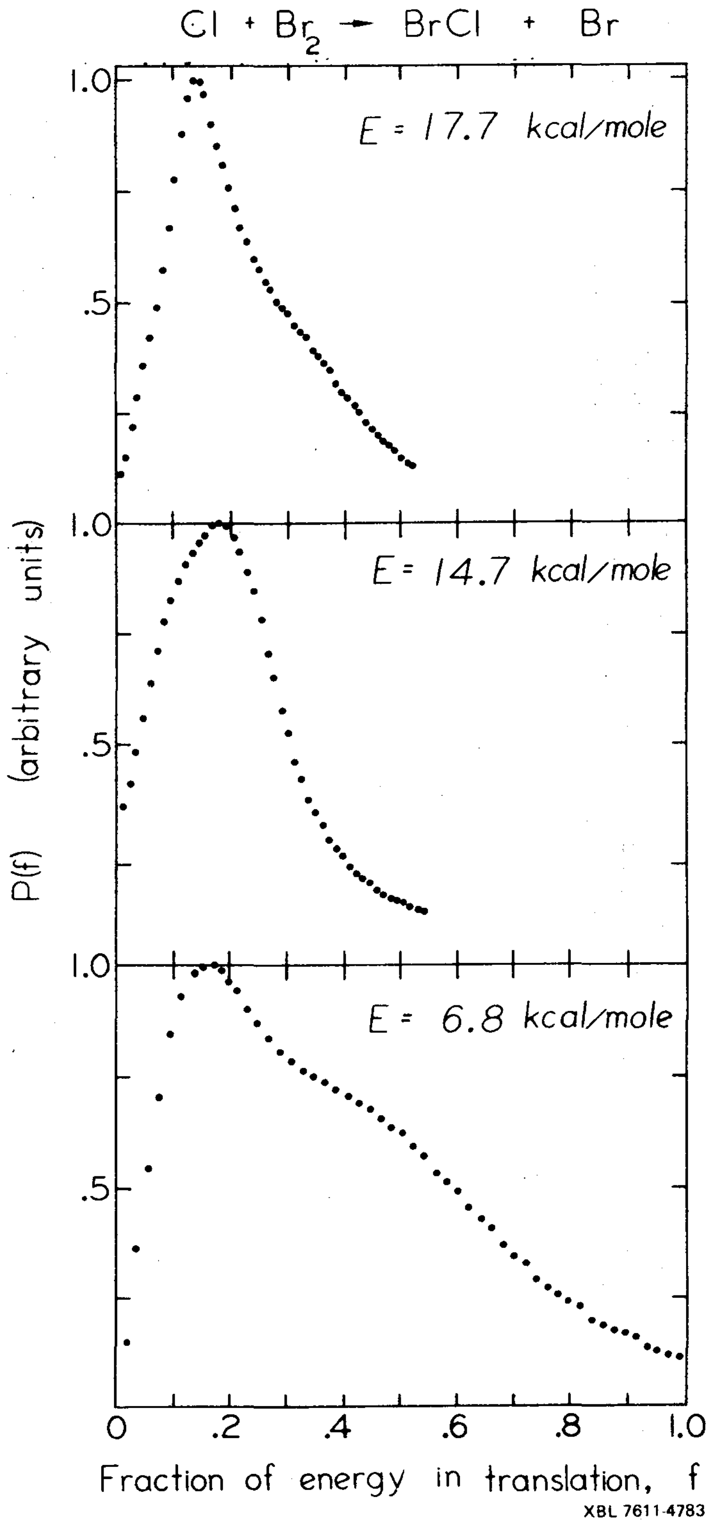
Cl + Br$_2$ → BrCl + Br
E = 17.7 kcal/mole
E = 14.7 kcal/mole
E = 6.8 kcal/mole
1.0
.5
1.0
.5
1.0
.5
P(f) (arbitrary units)
0
.2
.4
.6
.8
1.0
Fraction of energy in translation, f
XBL 7611-4783

Fig. 8

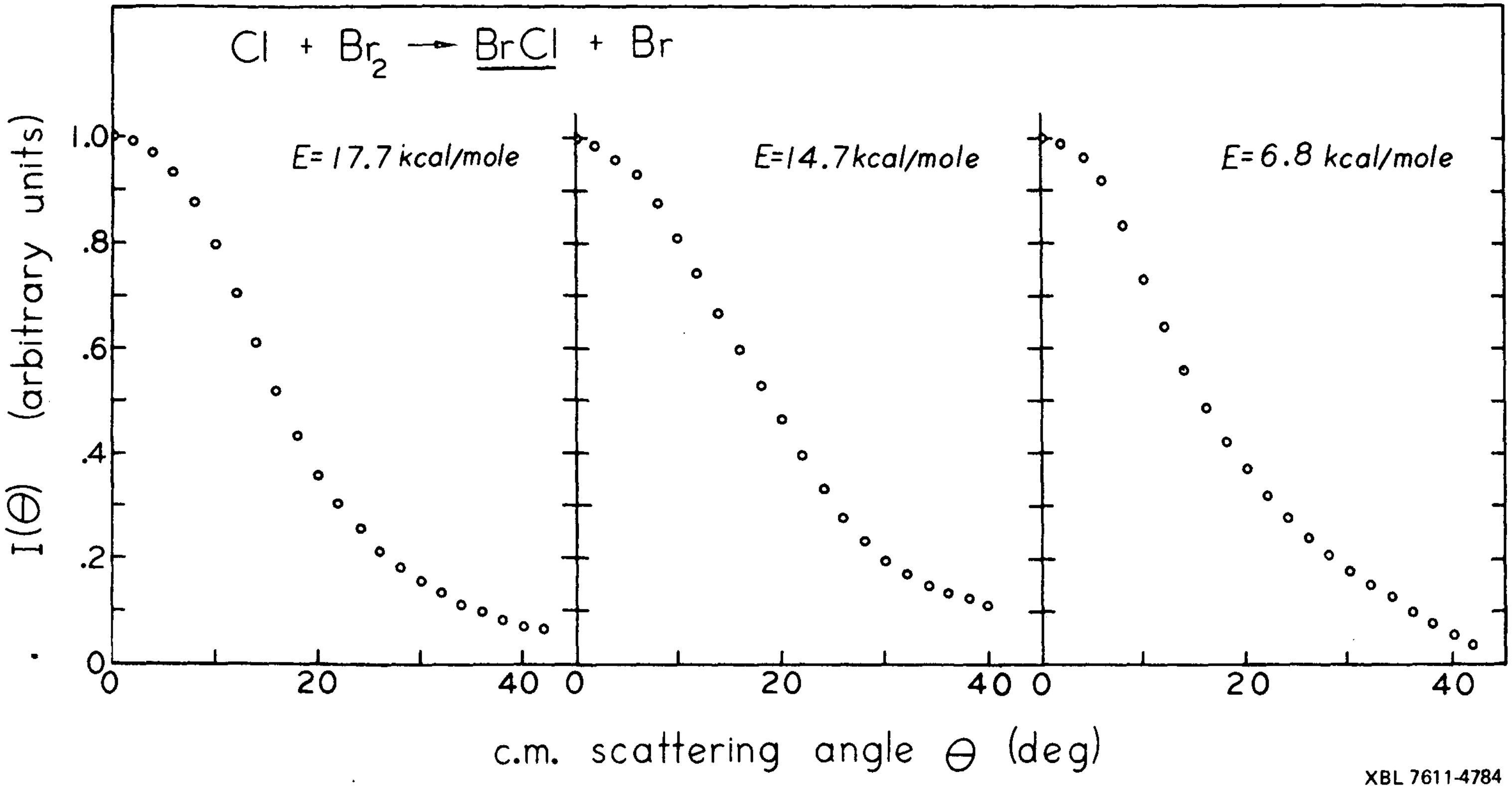

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Fig. 9

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720