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## DISCLAIMER

CROSSED BEAMS CHEMISTRY:

REACTIONS OF Ba, Sr, Ca, AND Mg WITH $Cl_2$ AND $Br_2$

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## ABSTRACT

Reactions of Ba, Sr, Ca, and Mg with $Cl_2$ and $Br_2$ have been studied in a crossed beam apparatus employing an electron bombardment ionizer-massfilter detector. Product center-of-mass (CM) recoil energy and angle distributions have been fit to the measured monohalide product (MX) laboratory (LAB) angular distributions by averaging the CM→LAB transformations over the measured (non-thermal) beam speed distributions. These experiments give no indications of a dihalide product ($MX_2$) and indicate that the formation of $MX_2$ (by a two-body radiative association) cannot account for more than a small fraction (< ∿ 5%) of the reactive collisions. All eight reactions favor forward product scattering (i.e., MX scattered in the direction defined by the incident M)

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with relatively low recoil energies ($\sim$10-20% of the reaction
exoergicity).  For reaction with either halogen molecule, the
fraction of the product scattered into the forward CM hemisphere
increases in the sequence:  Mg, Ca, Sr, Ba.  Similarities and
differences between the results of the present study and features
of the reactions of alkali atoms are discussed.

In recent years, crossed beam studies[1] have indicated that the reactions of the alkali atoms with halogen molecules are characterized by large reactive cross sections, $Q_R$, high internal excitation of the products, and a product alkali halide angular distribution which is sharply peaked forward (i.e., in the direction defined by the incoming alkali atom). Although it fails to account quantitatively for the magnitude of $Q_R$ in the $M + I_2$ reactions[2], these features have been rationalized qualitatively in terms of a simple electron transfer model. This model pictures a transfer of the alkali atom valence electron to the halogen molecule at a distance of reactant approach, $r_c$, estimated in terms of the atom ionization potential, $I(M)$, and halogen electron affinity, $E(X_2)$, by $r_c = e^2/(I(M) - E(X_2))$. The reaction is then pictured as proceeding via the breakup of the $X_2^-$ ion to give the ionically bound alkali halide product, i.e., $M + X_2 \rightarrow M^+ \text{---} X_2^- \rightarrow M^+ X^- + X$.

The introduction of the electron bombardment ionizer-mass spectrometer universal detector within the last few years has vastly extended the chemical scope of crossed beam studies of neutral reactions. This has prompted a number of studies[3,4] of the reactions of Group IIA alkaline earth atoms. This paper reports results on the reactions of Ba, Sr, Ca, and Mg with $Cl_2$ and $Br_2$.

The study of this family of reactions should complement and extend the evolving picture of the dynamics of alkali atom reactions because of interesting similarities and differences between the alkali and alkaline earth atoms. Thus, although Ba does not possess an unpaired spin, the electron transfer model suggests that it should react rapidly with halogen molecules because its ionization potential is actually less than that of the Li atom (5.2 vs. 5.4 ev.). The ionization potential of the Mg atom, on the other hand, is too large (7.6 ev.) to realistic picture its reactions as proceeding via an intermediate $Mg^+ - X_2^-$ ionic configuration. Another interesting difference between the two families of reactions arises because the stability of the alkaline earth dihalides gives rise to a deep chemical well in the potential hypersurface for the alkaline earth reactions which is not present in that for the alkali reactions. The presence of this well could result in longer collision lifetimes and a broadening of the product angular distribution; some indications of longer collision lifetimes are suggested by the recent observation[5] of the two-body radiative attachment of Ba and Sr to $Cl_2$.

## EXPERIMENTAL PROCEDURE

The apparatus is described in detail in Ref. 6. The detector, housed in a differentially-pumped UHV chamber and able to see the entire beam collision zone, may be rotated about the collision zone, in the plane defined by the two intersecting beams, so as to scan a range of laboratory (LAB) scattering angles, $\theta$, from

-15° to +115°; Fig. 1 illustrates that $\Theta = 0°$ is defined by the incident M direction, $\Theta = 90°$ by the incident $X_2$ direction. The scattered species are ionized by $\sim 150$ ev electrons, mass analyzed, and detected, via electron multiplier amplification, by means of a PAR HR-8 lock-in amplifier referenced (with negligible plase shift) to the halogen beam modulation frequency (typically 43 Hz square wave modulation). All of the product angular distribution measurements reported here were obtained with the mass spectrometer tuned to the $MX^+$ signal. Although the neutral precursor of this ion might be either MX or $MX_2$, arguments presented in a later section indicate that it arose predominately (if not exclusively) from ionization of MX. Although careful mass scans were made for some of the scattering partners (notably Ba and Mg with $Cl_2$ and $Br_2$), no scattered signals have been observed at the $MX_2^+$ mass peaks. The $Sr^+$ angular distribution of scattering of Sr off of $Br_2$ was also measured; its behavior was similar to that of the non-reactive scattering of alkali atoms from $Br_2$ at narrow angles, but it fell off less rapidly at larger scattering angles. However, some of this $Sr^+$ signal might have arisen from ionization of SrBr rather than Sr; this possibility precludes any inferences regarding the elastic scattering in the collisions studied here. This inability to study the elastic scattering as well as unknown detector response factors also precludes the determination of total reaction cross sections; order-of-magnitude estimates suggest $Q_R \sim 10\text{-}100$ Å$^2$ for Ba + $Br_2$ and $Q_R$ for Mg reactions about 25% of those for Ba reactions. Jonah and Zare[5] reported $Q_R = 60$ Å$^2$ for Ba + $Cl_2$.

The halogen molecule beam emerges from a "crinkly-foil" many-channel source, 0.16 cm wide×0.7 cm high, prepared by stacking alternate layers of flat and corrugated (0.01 cm corrugation width) stainless steel foil (0.0025 cm thick×0.7 cm high×0.5 cm wide). Although this beam source is situated in the collision chamber, background pressures were $\leq 10^{-6}$ Torr (uncorrected ion gauge reading). Measurements of the halogen beam number density probability speed distributions showed them to be appreciably non-thermal and well fit by the empirical function

$$\rho_2(v_2) = N_2(v_2-a_2)^2 \exp[-(v_2-a_2)^2/\alpha_2^2]u(v_2-a_2). \tag{1}$$

Here, $u(t)$ is the unit step function ($u(t)=0$ for $t \leq 0$, $u(t)=1$ for $t > 0$); $\alpha_2$ is the most probable thermal speed in the source ($\alpha_2=(2kT_2/M_2)^{1/2}$); $N_2 = 4\pi^{-1/2}\alpha_2^{-3}$; and $a_2$ is a "flow speed" which increases with increasing source pressure.

The alkaline earth atoms emerge from a knife-edge slit (0.05 cm wide×0.5 cm high) in a resistively-heated, single chamber stainless steel oven. After collimations, the two beams intersect at right angles resulting in a 1-5% attenuation of the M beam and negligible attenuation of the $X_2$ beam. Measurements of the Ba beam speed distribution showed far less deviation from thermal behavior than was found for the halogen beams, although the low speed tail of the thermal distribution was appreciably attenuated. The approximate theory of deviations from thermal speed distributions due to intrabeam collisions which is developed in Ref. 7 predicts the same percent deviation as a function of reduced speed

(true speed divided by most probable thermal source speed) for two gases with the same collision cross section. Consequently, the thermal attenuation factors measured for the Ba beam were applied to the Sr, Ca, and Mg beam speed distributions. This procedure should adequately estimate[6a] the unmeasured Sr, Ca, and Mg speed distributions, although it may slightly overestimate the non-thermal behaviors due to decreasing collision cross sections. Empirically, the alkaline earth number density probability speed distributions, $\rho_1(v_1)$, are also well fit by Eq.(1); in this case, however, both $a_1$ and $\alpha_1$ are functions of the source pressure.

Figure 1 shows the angular profiles of the two beams and Table I lists beam operating conditions. All of the data analysis which is presented in the following section included averages over the actual beam speed distributions. Auxiliary calculations for thermal beams indicated that the derived center-of-mass (CM) cross section results could be considerably in error if the true halogen beam speed distributions had not been used; on the other hand, recognition of the smaller deviations from thermal behavior of the alkaline earth beams had much less influence on the derived CM cross sections.

## DATA ANALYSIS AND RESULTS

Figure 1 shows a diagram of the LAB↔CM transformation for the Ba + Cl$_2$ → BaCl + Cl reaction; the CM scattering angle, $\boldsymbol{\theta}$, is defined as 0° when the BaCl CM recoil velocity, $\vec{u}$, lies along the initial relative velocity vector, $\vec{V}$, in the direction defined

by the incident Ba; the LAB velocity of the center-of-mass of
the collision partners, $\vec{C}$, is also shown. Figures 1-3 show that
the measured LAB product angular distributions all peak at smaller
LAB angles than do the distributions in $\vec{C}$ (calculated[3] assuming
an energy independent collision cross section); furthermore, the
data points fall off smoothly with angle through the angular
regions of the peaks in the $\vec{C}$ distributions. Since any $MX_2$ product
formed must recoil in the LAB along $\vec{C}$, these comparisons show
that the $MX^+$ measured signal must arise primarily from ionization
of an MX product which has scattered predominately forward in the
CM coordinate system. Jonah and Zare[5] estimate that the two-body
radiative association of Ba to $Cl_2$ which they observe accounts
for only a small fraction of reactive encounters for these collision
partners. The present experiment should be especially sensitive to
any $MX_2$ which formed because it would be solely confined to the
detector-scan plane. A simple calculation, based on the smooth
fall-off of the measured data through the angular ranges of the
peaks of the $\vec{C}$ distributions, indicates that $MX_2$ formation cannot
account for as much as 1-5% of the reactive encounters for the
collision partners studied in this work.

The measured MX LAB number density angular distribution is
related (in arbitrary units) to the CM reactive cross section,
$\sigma(\theta,u)$, by

$$I_{LAB}(\theta) = \int_0^\infty \int_0^\infty \int_0^\infty V\sigma(\theta,u)(v/u^2)\rho_1(v_1)\rho_2(v_2)dv_1 dv_2 dv \qquad (2)$$

where v and u are the LAB and CM recoil speeds of MX. In analyzing

the data by means of Eq. (2), it is assumed that $\sigma(\theta,u)$ is independent of relative velocity, V. Although Whitehead, Hardin, and Grice[8] have recently reported some differences between their higher energy ($\sim$5 kcal/mole) results on the K + $Br_2$ reaction and earlier thermal energy studies, the validity of this assumption is strongly supported by recent very careful measurements on the K + $I_2$ reaction.[9] These measurements indicated that an increase in collision energy from 1.9 to 3.6 kcal/mole produces only slight changes in the magnitude and shape of the K + $I_2$ CM reactive cross section. A second assumption of the data analysis procedure employed here is the separability of the CM recoil energy and angle distributions, i.e.

$$\sigma(\theta,u) = T(\theta)\ U(u). \tag{3}$$

Here again, this assumption is supported by the careful study[9] of the K + $I_2$ reaction which indicated only a weak coupling of these two distributions.

The actual data analysis procedure consist in assuming a form for $T(\theta)$ and $U(u)$ and calculating the resultant LAB angular distribution for comparison with the experimental data; this is repeated until a good fit to the data is achieved. Owing to the inability of the present experiments to measure the distribution in LAB recoil velocities and the resultant integration over v indicated in Eq. (2), a number of $T(\theta)$ and $U(u)$ combinations will often fit the data measured for a given reaction. In order to provide insight into the $T(\theta)$ and $U(u)$ functions compatible with the data, two different extreme data analyses are presented for

each reaction. The first, denoted the "stochastic" result,
employs $T(\theta)$ and $U(u)$ functions of the form[10]

$$T(\theta) = (1-C_1) \exp\{-\ell n2((\theta-\theta_1)/H_1)^2\} + C_1, \text{ and} \quad (4a)$$

$$U(u) = (u/u_1)^{n_1} \exp\{(n_1/m_1)(1-(u/u_1)^{m_1})\}, \quad u<u_1$$

$$U(u) = 1, \quad u_1 \le u \le u_2, \text{ and} \quad (4b)$$

$$U(u) = (u/u_2)^{n_2} \exp\{(n_2/m_2)(1-(u/u_2)^{m_2})\}, \quad u>u_2$$

where all subscripted variables serve as adjustable parameters.
The stochastic procedure employed here uses these functions to
obtain the $T(\theta)$ function with the narrowest breadth of the forward
scattered component (i.e., smallest $H_1$ value) which will provide
a good fit (i.e., within the estimated uncertainty of the data
points) over the entire angular range of the measured data.
Figures 1-3 indicate that this procedure provided good fits for
all eight reactions studied here; these fits were all obtained
with $u_1=u_2$ and $n_1=n_2=m_1=m_2=2$ in Eq.(4b). The $T(\theta)$ functions
which provided these good fits are shown in Figures 1, 4, and 5,
and Table II lists the parameters of the $T(\theta)$ and $U(u)$ functions.
Figure 1 also shows the distribution in translational recoil energy,
$E'$, with which the BaCl and Cl products of the Ba + $Cl_2$ reaction
separate; this is obtained from the $U(u)$ function by $P(E')dE' = U(u)du$.

The second data analysis extreme, denoted the "Single Recoil
Energy" (SRE) result, proceeds by assuming that the MX product
is scattered with a single, fixed CM recoil speed. Since this

procedure removes the flexibility in the U(u) function of Eq.(4b),
the $T(\theta)$ function has not been restricted to the form of Eq.(4a)
in seeking fits to the measured LAB data.  Because the full
breadth of the measured LAB angular distribution must be accounted
for by the $T(\theta)$ function, the SRE result should provide an upper
limit to the overall breadth of the true CM angular distribution.
Derived SRE CM angular distributions are shown in Figs. 1, 4, and
5 and Table II lists the derived single product recoil  energies.
Figures 1-3 indicate that the SRE procedure failed to provide a
good fit to the measured data for some of the reactions.

In general, data on any reactions which are adequately fit
by the SRE analysis could also be fit by a family of $T(\theta)$
functions bounded by the extremes presented in Figs. 4 or 5.
In practice, however, the true CM angular distribution should be
closer in shape to the stochastic extreme because product velocity
measurements on the analogous $K + I_2$[9] and $K + Br_2$[12] reactions
indicate product recoil energy distributions which are of
quantitatively similar shape to the stochastic results presented
here.  Results of calculations for a variety of $T(\theta)$ functions
in combination with the flexible U(u) function given in Eqs.(4a)
and (4b) have also provided the following further constraints on
the form of the true CM angular distribution for all of the reactions
studied here:  (1)  any $T(\theta)$ symmetric about $\theta = 90°$ is incompatible
with the data; (2)  $T(\theta)$ must peak at $\theta \leq 20°$; (3)   there is
substantial MX scattered intensity beyond 90°, arbitrarily provided
here, in the stochastic analysis, by an isotropic component; and
(4)  $T(\theta)$ might actual have a secondary peak at 180°, but it cannot

be larger than ∿30% of the forward peak intensity. Figure 1
illustrates points (2) and (4) for the Ba + Cl$_2$ reaction. A
recent study of the Ba + Cl$_2$ reaction reported[4] a BaCl angular
distribution spanning a range of LAB angles from -25° to ∿60°;
this was fit to CM cross sections which are qualitatively quite
similar to the stochastic results shown in Fig. 1. Quantitatively,
however, the CM cross sections reported in Ref. 4 do not fit the
data points shown in Fig. 1 as well as the stochastic or SRE fits
obtained here, especially at wide LAB angles where they predict
insufficient scattered intensity.

Owing to the Jacobian factor in Eq. (2), the measured LAB
data is relatively insensitive to the form of U(u) at high recoil
speeds so that not too much significance should be assigned to
the stochastic forms of U(u) given in Fig. 1 and Table II. However,
the most probable product recoil energies, derived from the peaks
in the P(E') functions, should be approximately true because, as
Table II indicates, these derived values are approximately constant
for very different assumptions (stochastic vs. SRE) regarding the
form of P(E').

## DISCUSSION

Table III lists the fraction of the MX product scattered
into the forward hemisphere,

$$Q_F = \int_0^{\pi/2} T(\theta)\, \sin\theta d\theta \Big/ \int_0^{\pi} T(\theta)\, \sin\theta d\theta.$$

Although present to some extent in the SRE results as well, the
following trends in $Q_F$ evaluated from the more reliable stochastic

results are apparent:  (1)  for a given alkaline earth atom, the $Cl_2$ reaction produces somewhat more forward scattering than does the $Br_2$ reaction; (2)  for a given $X_2$, the forward MX scattered component increases in the sequence Mg, Ca, Sr, Ba; and (3)  Sr + $Br_2$ more closely resembles Ca + $Br_2$ whereas Sr + $Cl_2$ more closely resembles Ba + $Cl_2$.  The first two trends are also observed in the reactions of the alkali atoms with halogen molecules.[1]  The third trend correlates with the geometries (linear vs. bent) of the ground electronic states of the alkaline earth dihalides, although it is not clear how much significance should be assigned to this correlation because of the many other uncertain parameters associated with these reactions (e.g., precise forms of $T(\theta)$, reliable values for $D_o(MBr)$, and the absence of trajectory studies).

Quantitative comparisons of the present results with published results for the alkali atom reaction could be misleading because (1)  the study reported here has not uniquely determined the forms of the CM cross sections and (2)  results for most of the alkali reactions have been analyzed by a procedure, similar to the SRE procedure employed here, which assumed thermal beam speed distributions.  The similarity of the present stochastic results for Ba + $Br_2$ to the accurate CM cross sections for K + $Br_2$[12] was pointed out in the previous section.  It is also clear from the data presented here that the Ba atom reactive cross sections are qualitatively much more similar to those of the Cs reactions[13,14] rather than the Li reactions.[15]  This observation is somewhat surprising because the electron transfer model would suggest that Li and Ba are likely to react within a similar range of impact

parameters; it may indicate a high sensitivity of the product
angular distributions in these electron transfer reactions to
the mass of the attacking atom. Existing trajectory calculations[16,17]
do not support this conjecture, although these calculations have
not extensively studied the influence of changing reactant masses.

In view of the deep chemical wells in the potential hypersurfaces
for the alkaline earth reactions which are associated with the
stability of the alkaline earth dihalides, this similarity between
the reactions of alkali atoms and the heavier alkaline earth atoms
(notably Ba) is striking. Studies of the reactions of alkali atoms
with alkali halides[18] clearly indicate that the presence of a
well corresponding to a stable intermediate can result in a
long-lived collision complex reaction mechanism; on  the other hand,
the direct product scattering observed in the Li + $NO_2$ reaction[19]
indicates that this need not always be true. Co-linear trajectories
of attack of the Ba atom on the halogen molecule might be expected
to lead to reaction without assuming intermediate configurations
which felt the presence of this well; in terms of the electron
transfer model, these reactive trajectories, at least, would be
expected to resemble those characteristic of alkali reactions.
Furthermore, the metal atom (alkali or alkaline earth) cannot
transfer its totally symmetric valence electron into the vacant
$\sigma_u$ orbital (the lowest unfilled orbital) of $X_2$ in the case of the
broadside approach along the $C_{2v}$ symmetry axis because these two
orbitals transform as different irreducible representations of
the $C_{2v}$ point group; this symmetry restriction is likely to
favor the co-linear approach trajectory in reactive collisions.[20]

Moreover, even if the $BaX_2$ well were sampled in a significant fraction of the reactive trajectories, a crude RRK estimate indicates that, owing to the large reaction exoergicity, the lifetime of the complex would probably not exceed its rotational period.

The ionization potentials of Ba, Sr, Ca, and Mg are 5.2, 5.7, 6.1, and 7.6 ev. respectively. Thus, reactions of this family of atoms should show the transition from a reaction forming an ionic bond, where the potential surface exhibits long-ranged reactant attraction due to an electron transfer, to a reaction forming a covalent (more precisely, less ionic) bond, where the potential surface leading from reactants to products is more short-ranged and is, presumably, traversed more quickly. In view of this, it is perhaps surprising that the CM reactive cross sections given in Table II and Figs. 1,4, and 5 don't exhibit more variation for changing reactants. The stochastic MgCl angular distribution from Mg + $Cl_2$ which is shown in Fig. 4 is striking; this reaction especially warrants further study, with product velocity measurements, to quantitatively determine the CM cross section. While the wide-angle isotropic product scattering is likely to arise from small impact parameter collisions, the sharp forward spike in the product angular distribution for this reaction is suggestive of a spectator stripping mechanism. Although the true reaction trajectories are unlikely to be quite this simple, the spectator stripping model might approximate them because of rapidly acting forces in the reaction. Similar ideas have been advanced[21] in discussion of the forward product scattering seen in the Cl + $Br_2$ reaction.

## ACKNOWLEDGEMENT

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Table I. Experimental beam conditions.[a]

| Collision partners | Alkaline earth atom beam | | | | Halogen molecule beam | | |
| | source conditions[b] | | speed distribution[c] | | source conditions | | "flow speed"[c] |
| | temperature | pressure | $\alpha_1$ | $a_1$ | temperature | pressure | $a_2$ |
|---|---|---|---|---|---|---|---|
| $Br_2$ + Ba | 1060 | 0.3 | 3.1 | 1.1 | 340 | 4-5 | 1.4 |
| $Br_2$ + Sr | 960 | 0.4 | 3.7 | 1.3 | 340 | 2.5-3.3 | 1.4 |
| $Br_2$ + Ca | 1020 | 0.3 | 5.8 | 1.9 | 350 | 3-4 | 1.4 |
| $Br_2$ + Mg | 820 | 0.3 | 6.7 | 2.2 | 340 | ~4 | 1.4 |
| $Cl_2$ + Ba | 1050 | 0.3 | 3.1 | 1.1 | 340 | 2 | 1.7 |
| $Cl_2$ + Sr | 960 | 0.4 | 3.7 | 1.3 | 330 | ~4 | 2.0 |
| $Cl_2$ + Ca | 1010 | 0.3 | 5.8 | 1.9 | 360 | 3.0-3.5 | 2.0 |
| $Cl_2$ + Mg | 820 | 0.3 | 6.7 | 2.2 | 340 | 2-4 | 1.7-2.0 |

[a] Temperatures are given in °K, pressures in Torr, and speeds in 100 m/sec.

[b] Obtained from vapor pressures of the alkaline earths given in: J.L. Margrave, Characterization of High Temperature Vapor, John Wiley and Sons, Inc., New York, 1967.

[c] Taken from data given in Ref. 6a; symbols refer to parameters in Eq.(1).

Table II. Results of data analysis of the M + $X_2$ → MX + X reactions.[a]

| Reactants | Energetics | | | Stochastic Analysis[e] | | | | SRE Analysis |
|---|---|---|---|---|---|---|---|---|
| | $E^b$ | $W^c$ | $\Delta D_o^d$ | $H_1$ | $C_1$ | $u_1$ | $\bar{E}'^f$ | $\bar{E}'^f$ |
| $Br_2$ + Ba | 2.5 | 1.1 | 55 | 20° | .08 | 3.2 | 4.8 | 5.5 |
| $Br_2$ + Sr | 2.4 | 1.1 | 35 | 27° | .20 | 4.3 | 5.6 | 5.0 |
| $Br_2$ + Ca | 2.7 | 1.1 | 45 | 20° | .12 | 6.0 | 6.3 | 6.5 |
| $Br_2$ + Mg[g] | 2.3 | 1.1 | 29 | 15° | .15 | 5.0 | 3.5 | 4.8 |
| $Cl_2$ + Ba | 2.1 | 0.9 | 48 | 35° | .15 | 2.3 | 3.1 | 3.5 |
| $Cl_2$ + Sr | 2.2 | 0.9 | 39 | 35° | .15 | 3.5 | 3.5 | 3.5 |
| $Cl_2$ + Ca | 2.6 | 0.9 | 37 | 35° | .25 | 5.5 | 4.2 | 4.0 |
| $Cl_2$ + Mg[g] | 2.2 | 0.9 | 17 | 10° | .06 | 4.5 | 1.9 | 3.5 |

[a] Energies are given in kcal/mole and speeds in 100 m/sec.

[b] E is the characteristic initial relative kinetic energy, calculated for the most probable (number density distribution) beam speed.

[c] W is the internal (rotational and vibrational) energy of the halogen molecule. This could be an overestimate if the internal degrees of freedom relax in the beam expansion.

Table II Cont'd.

[d] $\Delta D_O = D_O(MX) - D_O(X_2)$. $D_O$ for $Cl_2$ and $Br_2$ taken from: R.J. Leroy and R.B. Bernstein, Chem. Phys. Letters 5, 42 (1970). $D_O$ for MCl taken from: D.L. Hildebrand, J. Chem. Phys. 52, 5751 (1970); ±3 estimated uncertainties. $D_O$ for MBr taken from: A.G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules (3rd Ed.) (Chapman and Hall, Ltd., London, 1968); ±15 estimated uncertainties.

[e] $H_1$, $C_1$, and $u_1$ are parameters in Eqs.(4a) and (4b). The $\theta_1$ parameter of Eq.(4a) was 0° for all reactions.

[f] $\bar{E}'$ is the most probable product recoil energy, obtained from the position of the peak in the P(E') function.

[g] The stochastic analysis can fit the Mg reactions data almost as well for even narrower T($\theta$) curves. For example, adequate fits are provided by: $H_1 = 5°$, $C_1 = .05$, $u_1 = 4.3$ for Mg + $Br_2$; and $H_1 = 5°$, $C_1 = .03$, $u_1 = 4.5$ for Mg + $Cl_2$.

Table III.  Fraction of product MX scattered into forward CM
            hemisphere, $Q_F$.

|  | Br$_2$ reactions | | | | Cl$_2$ reactions | | | |
|---|---|---|---|---|---|---|---|---|
|  | Mg | Ca | Sr | Ba | Mg | Ca | Sr | Ba |
| $Q_F$, stochastic | 0.56 | 0.62 | 0.62 | 0.67 | 0.58 | 0.64 | 0.71 | 0.71 |
| $Q_F$, SRE | 0.63 | 0.67 | 0.68 | 0.73 | 0.67 | 0.65 | 0.71 | 0.70 |
| MX$_2$ Geometry[a] | $\ell$ | $\ell$ | $\ell$ | b | $\ell$ | $\ell$ | b | b |

[a] MX$_2$ geometry; $\ell$ for linear and b for bent; data taken from
L. Wharton, R.A. Berg, and W. Klemperer, J. Chem. Phys. _39_,
2023 (1963).

FIGURE CAPTIONS

Fig. 1.   The data points show the measured LAB angular distribution

from the Ba + $Cl_2$ reaction.  The solid, short-dashed,

and dot-dashed CM angular distributions were combined

with the solid CM recoil energy distribution (all shown

in the upper panel) to calculate the corresponding BaCl

LAB angular distributions shown in the lower panel; note

that the dot-dashed and solid CM angular distributions

are identical for $\theta \leq 90°$.  Calculations for the short-

dashed and dot-dashed CM angular distributions with other

forms of P(E') are in equally poor agreement with the

data.  The long-dashed LAB BaCl angular distribution shown

in the lower panel was calculated from the corresponding

angular distribution in the upper panel by assuming a

single product recoil energy of 3.5 kcal/mole.  Also

shown are:   (1)   angular profiles of the two beams;

(2)   calculated distribution in $\vec{C}$ (dotted curve); and

(3)   a LAB↔CM transformation diagram drawn for the

most probable beam speeds.  The circles indicate the BaCl

recoil speed for some possible product recoil energies,

E' (kcal/mole).

Fig. 2.   The data points show the measured LAB angular distributions

from the Sr, Ca, and Mg + $Cl_2$ reactions; different data

symbols indicate experiments run on different apparatus

pumpdowns.  The solid and long-dashed curves are,

respectively, the stochastic and SRE fits provided by CM

angular distributions shown in Fig. 4 and recoil speed distributions given in Table II. The short-dashed curves show calculated distributions in $\vec{C}$.

Fig. 3.  Fits to the measured data points, provided by CM cross sections given in Fig. 5 and Table II, for the Ba, Sr, Ca, and Mg + $Br_2$ reactions.  Conventions are as described for Fig. 2.
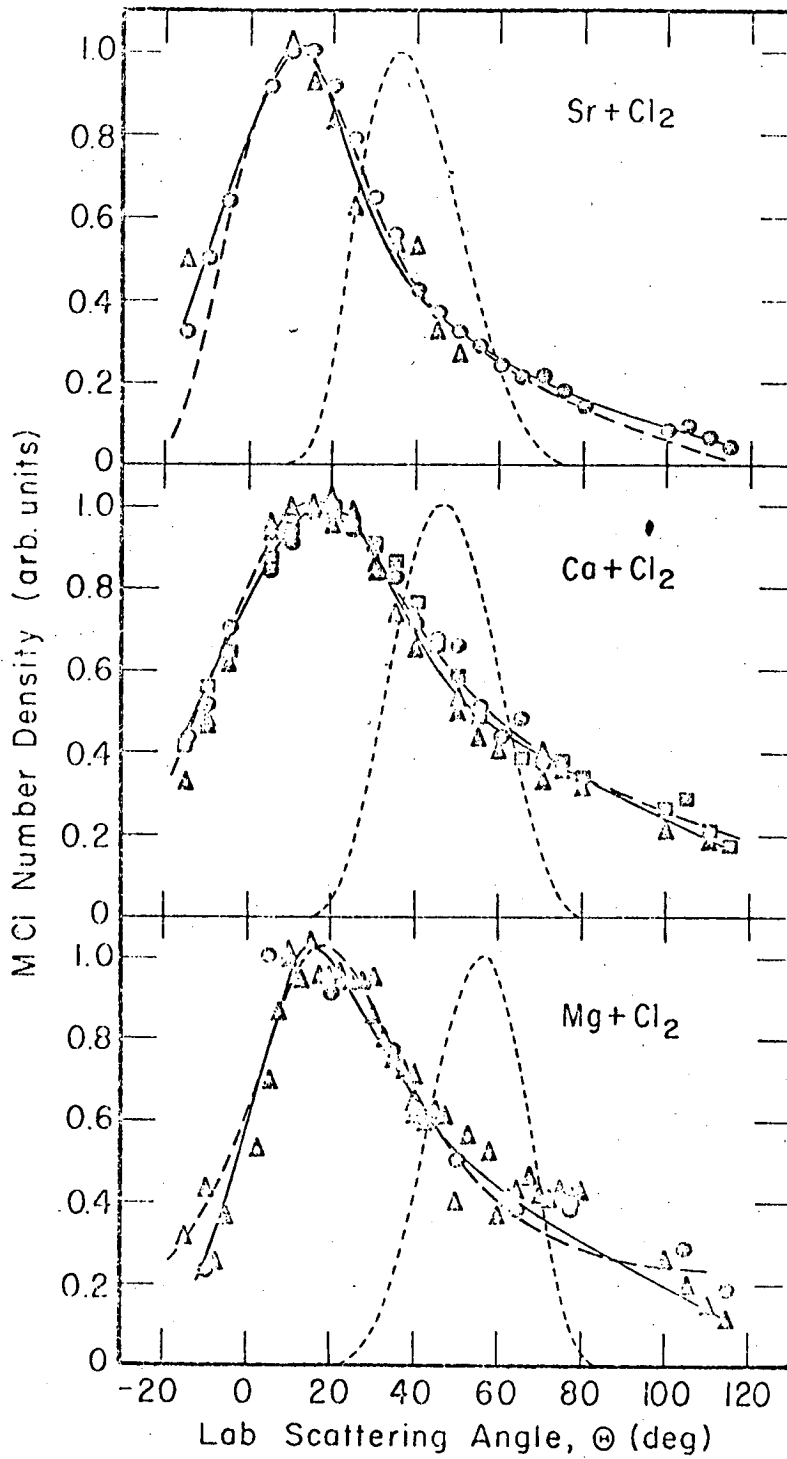
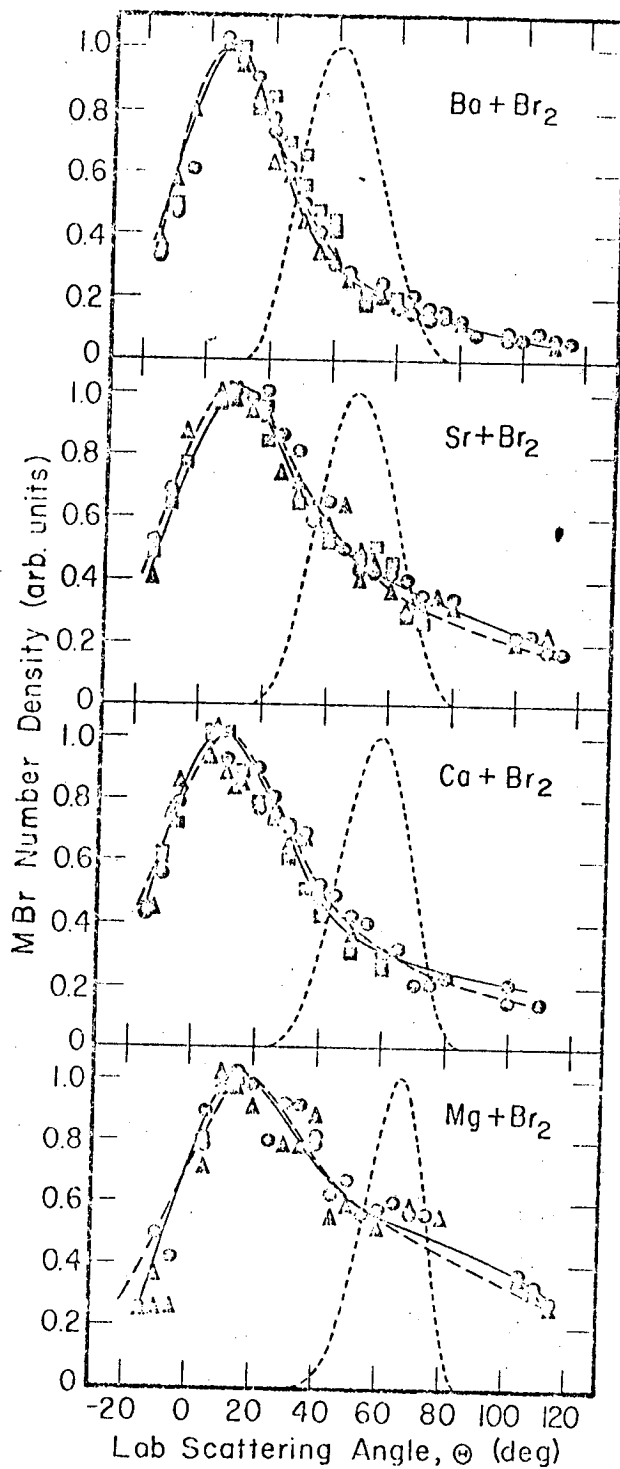Fig. 4.  Stochastic (solid curves) and SRE (dashed curves) MCl product CM angular distributions which provide the fits to the data shown in Fig. 2.

Fig. 5.  Stochastic (solid curves) and SRE (dashed curves) MBr product CM angular distributions which provide the fits to the data shown in Fig. 3.
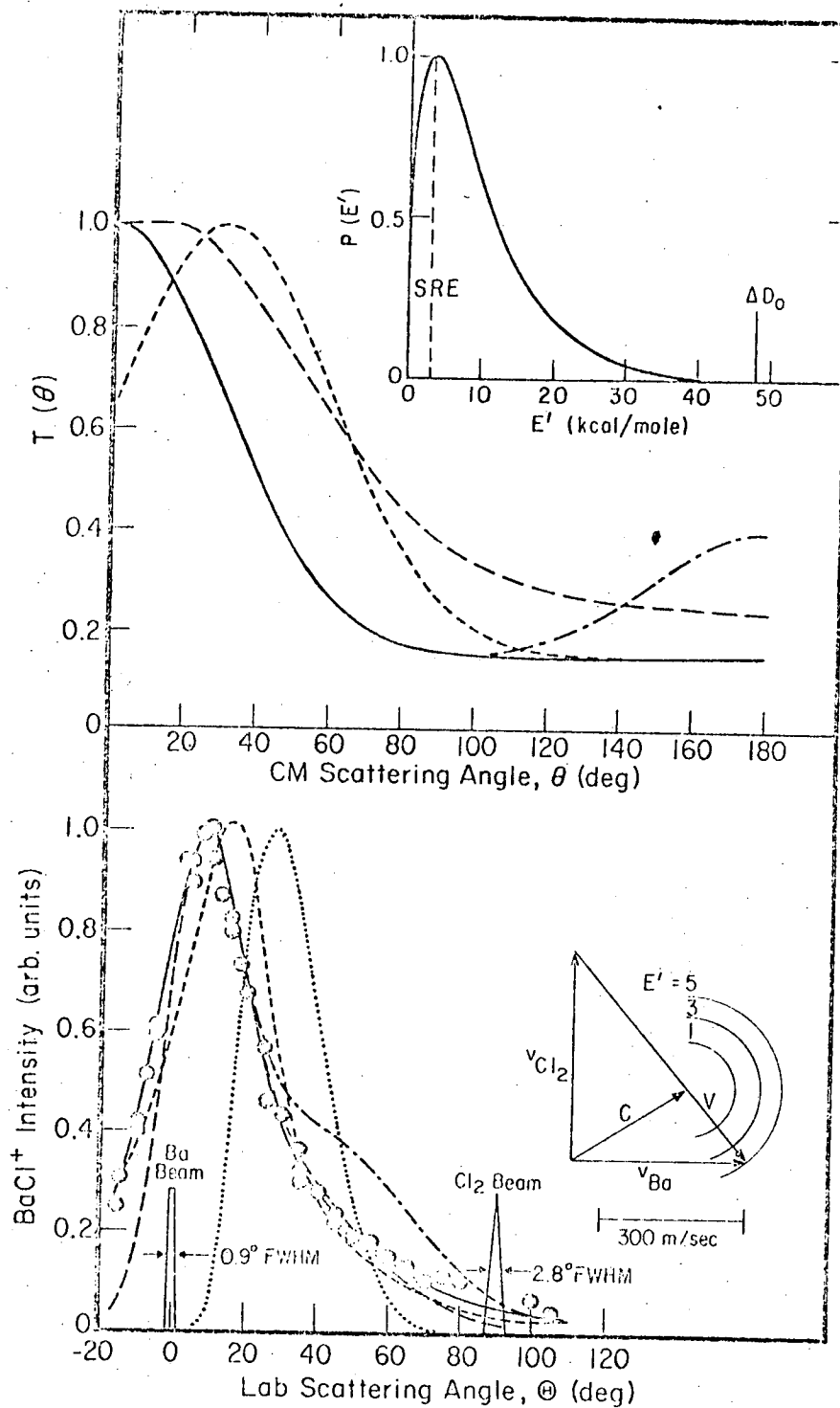
Fig. 1

XBL 727-6730

Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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