

Lawrence Berkeley National Laboratory

Recent Work

Title

CROSSED BEAMS REACTIONS OF Ba, Sr, AND Ca WITH SOME HALIDES OF METHANE

Permalink

<https://escholarship.org/uc/item/2190t80v>

Authors

Lin, Shen-Maw
Mims, Charles A.
Herm, Ronald R.

Publication Date

1972-12-01

Submitted to
Journal of Physical Chemistry

LBL-1175
Preprint

c.1

CROSSED BEAMS REACTIONS OF Ba, Sr, AND Ca
WITH SOME HALIDES OF METHANE

Shen-Maw Lin, Charles A. Mims,
and Ronald R. Herm

December 1972

Prepared for the U.S. Atomic Energy
Commission under Contract W-7405-ENG-48

For Reference

Not to be taken from this room



LBL-1175

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

-iii-

CROSSED BEAMS REACTIONS OF Ba, Sr, AND Ca
WITH SOME HALIDES OF METHANE

Shen-Maw Lin[†], Charles A. Mims^{††}, and Ronald R. Herm^{*}
Inorganic Materials Research Division, Lawrence Berkeley
Laboratory and Department of Chemistry, University of
California, Berkeley, California 94720

ABSTRACT

A crossed beams apparatus, equipped with an electron bombardment ionizer-massfilter detector unit, has been employed to measure scattered angular distributions of: MI^+ from Ba, Sr, and Ca + CH_3I and CH_2I_2 ; BaI^+ from Ba + CF_3I ; and $BaCl^+$ from Ba + CCl_4 . Product center-of-mass (CM) recoil angle and energy distributions have been fit to the measured laboratory (LAB) data by averaging the CM \rightarrow LAB transformation over the (non-thermal) beam speed distributions. The $MI + CH_3$ products from $M + CH_3I$ scatter predominately backward

[†]Present address: Department of Theoretical Chemistry,
Cambridge University, Cambridge, CB2 1EW, England.

^{††}Present address: Department of Chemistry, Massachusetts
Institute of Technology, Cambridge, Massachusetts.

in the CM system (i.e., MI scatters in the direction defined by the CH_3I reactant) with substantial recoil energy (average value $\approx 10\text{-}15$ kcal/mole); the BaI product angular distribution is broader than is that of SrI or CaI. All of the other reactions preferentially scatter products into the forward CM hemisphere. For these reactions, the MX^+ massfilter signals might arise from ionization of MX or MX_2 products. Features of the derived CM distributions, as well as other indirect evidence, suggest (but do not confirm) that MI and MI_2 are formed from $\text{M} + \text{CH}_2\text{I}_2$ and BaI and BaIF are formed from $\text{Ba} + \text{CF}_3\text{I}$.

This paper reports measurements of angular distributions of reactive scattering from crossed beams of alkaline earth atoms (M) and $\overline{\text{CH}_3\text{I}}$, $\overline{\text{CH}_2\text{I}_2}$, $\overline{\text{CF}_3\text{I}}$, and $\overline{\text{CCl}_4}$. The reactions of alkali atoms (A) with these halides of methane are known to span a wide range of dynamical behaviors, and this present study was undertaken in order to further compare the chemical behaviors of gaseous alkaline earth and alkali atoms. Reference 1 cites the variety of crossed beams studies of the A + $\overline{\text{CH}_3\text{I}}$ reactions. Studies with Li^2 , Na^3 , and K^{4-6} indicate that the A + $\overline{\text{CH}_3\text{I}}$ reactions provide classic examples of a "rebound" mechanism wherein the products scatter backward in the center-of-mass (CM) coordinate system (i.e., AI scatters preferentially in the direction defined by the $\overline{\text{CH}_3\text{I}}$ reactant) with a relatively large product recoil energy, E' . A recent study⁷ showed that the $\text{Cs} + \overline{\text{CH}_2\text{I}_2}$ reaction was an example of the opposite extreme direct reaction mechanism wherein the products recoil forward with a relatively small E' value; $\text{K} + \overline{\text{CH}_2\text{I}_2}$ also exhibited⁷ somewhat similar behavior, although the KI was less sharply forward peaked. The intermediate case between these extreme direct reaction mechanisms is provided by the A + $\overline{\text{CCl}_4}$ reactions^{2,5,8}; here, the product CM angular distributions peak at intermediate angles and are

especially sensitive to the identity of the alkali atom. There are no published product angular distributions for $A + CF_3I$. However, electric deflection experiments with spatially orientated CF_3I ⁹ and CH_3I ^{10,11} indicate quite different steric effects for reactions of these molecules with alkali atoms.

EXPERIMENTAL PROCEDURE

The apparatus is the same as that which was used to study the reactions of Ba, Sr, Ca, and Mg with Cl_2 and Br_2 ¹²; it is described in detail in Ref. 13. The two beams cross at right angles, resulting in a 1-5% attenuation of the M beam (beam 1) and negligible attenuation of the halide beam (beam 2). The laboratory (LAB) scattering angle, θ , is measured from the M beam; the halide beam direction defines $\theta = 90^\circ$. The number density speed probability distributions of beams 1 and 2 are non-thermal and are given by

$$\rho_i(v_i) = N_i (v_i - a_i)^2 \exp[-(v_i - a_i)^2 / \alpha_i^2] u(v_i - a_i). \quad (1)$$

Here, $u(t)$ is the unit step function ($u(t) = 0$ for $t \leq 0$, $u(t) = 1$ for $t > 0$); a_i and α_i are parameters which depend on the source temperature and pressure of beam i ; and $N_i = 4 \pi^{-1/2} \alpha_i^{-3}$. Table I gives beam operating conditions.

The scattered species are ionized by ~ 150 eV electrons and mass analyzed. The detector unit rotates about the beam collision zone in the plane defined by the two beams. The

speeds of the scattered species are not measured; only product LAB angular distributions are determined. All reactive scattering angular distributions which are reported here were measured with the massfilter tuned to the alkaline earth monohalide (MX) ion peak. Interference from fragment ions due to methyl halide reactants precluded angular distribution measurements of the methyl and halogenated methyl products. No alkaline earth dihalide signals were observed for scattering of M from CH_2I_2 , CF_3I , or CCl_4 . However, alkaline earth dihalides formed in these reactions would probably be vibrationally excited and would be expected to fragment into MX^+ upon electron bombardment ionization.

As Table II indicates, a number of reactions were examined in this study. Although uncertain and changing detector response factors precluded determinations of total reaction cross sections (Q_R), we estimate that our detection sensitivity is such that: $Q_R < \sim 1 \text{ \AA}^2$ for those reactions which failed to produce any detectable product (NR in Table II); $Q_R \approx 1-5 \text{ \AA}^2$ for those reactions which provided only a fragmentary product signal (F in Table II); and $Q_R > \sim 5 \text{ \AA}^2$ for the eight reactions for which product angular distributions are reported.

RESULTS AND DATA ANALYSIS

The data analysis procedure, described in more detail in Refs. 12 and 13, consists in assuming a form for the CM cross section, $\sigma(\theta, u)$, and calculating the resultant LAB number density angular distribution by

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

the procedure is repeated until the calculated $I_{\text{LAB}}(\theta)$ fits the measured data. In Eq. (2), \bar{V} is the initial relative velocity, and \bar{u} and \bar{v} are, respectively, the CM and LAB recoil velocities of the species which is detected; the CM scattering angle, θ , is defined as 0° when \bar{u} lies along \bar{V} in the direction defined by the M velocity; v^* , the upper limit on v , is calculated from the reaction exoergicity, ΔD_0 . Table III lists values of ΔD_0 as well as the relative collision energy, E , and average thermal reactant internal excitation, W .

The derived CM cross sections which are presented here are of the simple functional form

$$\sigma(\theta, u) = T(\theta) U(u); \quad (3)$$

the limited information content of the data do not warrant use of a more sophisticated form. For convenience, $T(\theta)$ and $U(u)$ are also often expressed as:

$$T(\theta) = (1-C_1) \exp\left[-\ln 2 \left((\theta-\theta_1)/H_1\right)^2\right] + C_1, \quad \theta > \theta_1,$$

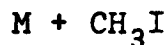
$$T(\theta) = 1 \quad \theta_1 > \theta > \theta_2, \quad (4a)$$

$$T(\theta) = (1-C_2) \exp\left[-\ln 2 \left((\theta-\theta_2)/H_2\right)^2\right] + C_2, \quad \theta < \theta_2, \text{ and}$$

$$U(u) = (u/u_1)^{n_1} \exp\left[(n_1/m_1)\left(1 - (u/u_1)^{m_1}\right)\right], \quad u < u_1, \quad (4b)$$

$$U(u) = (u/u_1)^{n_2} \exp\left[(n_2/m_2)\left(1 - (u/u_1)^{m_2}\right)\right], \quad u > u_1$$

where all subscripted variables serve as adjustable parameters. Three $T(\theta) - U(u)$ functions are presented for each CH_3I reaction in order to provide insight into the range of possible CM cross sections which will provide fits to the measured LAB data. One of these, termed the "single recoil energy" (SRE) result, should provide an upper limit on the breadth of the true CM product angular distribution because it unrealistically treats the product recoil speed distribution as a delta function.



Figures 1-3 show that the measured MI^+ angular distributions from $\text{M} + \text{CH}_3\text{I}$ all peak at larger LAB scattering angles than do the calculated (assuming an energy independent collision cross section) angular distributions of the LAB velocity of the center-of-mass, \bar{C} , indicating that the MI

products rebound predominately into the backward CM hemisphere (i.e., $90^\circ \leq \theta \leq 180^\circ$). Examples of CM cross sections, of the form of Eq. (3), which provide fits to the data for each reaction are given in Figs. 1-3 as well as Table IV; the product recoil energy distributions plotted in these figures are calculated from $P(E') dE' = U(u) du$. The fits to the data which were provided by the A CM cross sections are also shown in Figs. 1-3; the SRE and B CM cross sections provided fits of comparable or only slightly poorer quality. A recent study¹ of the $K + CH_3I$ reaction indicated that $Q_R(E)$ exhibits a maximum for $E = 4$ kcal/mole. In order to investigate the significance of this to the data analysis presented here, LAB MI angular distributions were calculated for the Ba, Sr, and Ca + CH_3I reactions using a CM cross section of the form: $\sigma(\theta, u) = T(\theta) U(u) Q_R(E)$. Here, $T(\theta)$ and $U(u)$ were taken as the A functions given in Table IV. Although the true form of $Q_R(E)$ for CH_3I reactions is undoubtedly dependent on the metal atom reactant¹⁴, the form of $Q_R(E)$ reported¹ for $K + CH_3I$ was employed in the calculation. The resulting calculated MI LAB angular distributions were practically indistinguishable from those shown in Figs. 1-3. Thus, although the true form of $\sigma(\theta, u)$ for these reactions is undoubtedly more complex, this calculation supports the reliability of the product angle and energy distributions which are derived here by use of Eq. (3).

The rather wide range of CM cross sections which can be fit to the data presented for any one reaction prevents a

detailed comparison of the features of the Ba, Sr, and Ca + CH₃I reactions; however, some features are clearly established. The CM MI product angular distributions clearly peak in the backward direction, at or near 180°. Moreover, the Ba reaction leads to a broader product angular distribution than do the Sr and Ca reactions; this is shown in Figs. 1-3 and in the entries in Table IV for the fraction of the products which scatter backwards:

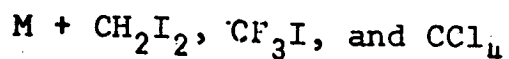
$$Q_B = \int_{\pi/2}^{\pi} T(\theta) \sin \theta d\theta / \int_0^{\pi} T(\theta) \sin \theta d\theta. \quad (5)$$

Figures 1-3 also show that, for a given reaction, the derived form of the product angular distribution is relatively insensitive to the assumed form of the recoil energy distribution (except for fit B for the Ca reaction). The approximate constancy of the average product recoil energy,

$$\langle E' \rangle = \int_0^{\Delta D_0} E' P(E') dE' / \int_0^{\Delta D_0} P(E') dE', \quad (6)$$

for very different assumed forms of $P(E')$ which is shown in Table IV also clearly establishes that the products separate with a recoil energy which is relatively large and is rather insensitive to the identity of the attacking atom. The SRE and B fits represent two extremes for the breadth of the true $P(E')$ function; thus, the true $T(\theta)$ and $P(E')$ should lie

within the ranges provided by these fits. The A fits are obtained for a more likely form of $P(E')$ and are likely to closely approximate the true CM cross sections. Recent product velocity measurements of the KI scattered from a beam of CH_3I crossed by a velocity selected K beam have determined⁶ a $P(E')$ function for this reaction which is of roughly the same breadth (although peaking at a somewhat higher E') as the $P(E')$ A fits shown in Figs. 1-3.

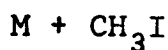


Figures 4 and 5 show that the measured angular distributions of MX^+ for the CH_2I_2 , CF_3I , and CCl_4 reactions are skewed to smaller LAB angles than the calculated angular distributions of \bar{C} , indicating that the products are preferentially scattered into the forward CM hemisphere. All of these reactions share the property that the MX^+ signal observed might have arisen from ionization of product MX , MX_2 (MIF for the CF_3I reaction), or a combination of the two. Indeed, if both MX and MX_2 products are formed, the data analysis provided here, using a cross section of the form of Eq. (3), could be misleading because the two products might scatter with quite different angle and recoil energy distributions. Because of this possibility, derived CM cross sections are not presented graphically. For each reaction, however, an example of a CM cross section of the form of Eq. (3) is given in Table IV, and Figs. 4 and 5 show the

corresponding fits to the measured data. A number of other calculations, also based on Eq. (3), which are discussed in Ref. 13a indicate that $T(\theta)$ must peak within the ranges of $0^\circ - \sim 70^\circ$ for $M + CH_2I_2$ and $Ba + CCl_4$ and $\sim 50^\circ - \sim 90^\circ$ for $Ba + CF_3I$.

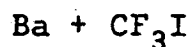
DISCUSSION

Reactions of metal atoms of the type studied here involve the rupture of a covalent reactant bond to form an ionic product bond. Since this involves the transfer of an electron from the metal atom, it is natural to discuss the observed dynamical features in terms of the reactant attraction and product repulsion which are suggested by the known (or estimated) electron attachment behavior of the halogen containing reactant.



Herschbach¹⁵ discusses the dynamics of the $A + CH_3I$ reactions in terms of the known electronic absorption spectrum of CH_3I and the likely structure of CH_3I^- ; he estimates the vertical electron affinity of CH_3I as $\sim -20 \pm 20$ kcal/mole. Thus, reaction of CH_3I with a metal atom is not expected to proceed via a long-range electron transfer and is likely to take place only for smaller impact parameters which permit appreciable overlap of the A (or M) and I electron distributions. This is consistent with the backward product

scattering which is observed with both the alkali and alkaline earth atoms. Moreover, the observation that both the A and M + CH₃I reactions channel a considerable fraction of ΔD_0 into product recoil energy is consistent with the picture¹⁵ of considerable C-I repulsion in CH₃I⁻. The M + CH₃I reaction dynamics might have differed somewhat from those of A + CH₃I because of a possible substantial attraction between the departing MI and CH₃ free radical products. However, the observed similarities of the A and M + CH₃I reactions indicate that this effect is not important, possibly because of an unfavorable combination of appreciable C-I repulsion, which leads to rapid product separation, and a steric effect which, for the K¹⁰ and Rb¹¹ reactions, has been shown to favor approach of the metal atom along the I end of the C-I bond. The trend towards narrower product angular distributions on proceeding to lighter and less readily ionizable atoms which is observed in this work runs counter to that observed for K, Na, and Li². However, this could simply be a consequence of decreasing ΔD_0 's in the alkaline earth family which might restrict reaction to a decreasing range of impact parameters¹⁶.

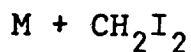


For the Ba + CF₃I reaction, four exothermic reaction channels are possible, corresponding to formation of BaI, BaF, BaIF, and BaF₂ products. Table IV indicates that the measured BaI⁺ angular distribution, which might arise from

ionization of BaI and/or BaIF, can be fit, using Eq. (3), to a CM angular distribution which peaks at $\theta = 70^\circ - 90^\circ$. However, the bimodal structure of this measured distribution is striking and is suggestive of contributions from two reaction mechanisms. Table II shows that a weak BaF^+ signal was observed as well, with a peak magnitude about 5-10% of that seen for BaI^+ ; this might arise from ionization of BaF, BaF_2 , or BaIF. Berkowitz and Marguart¹⁷ have reported that fragmentation into MgF^+ upon electron bombardment ionization of MgF_2 is much more likely than is fragmentation into MgI^+ upon ionization of MgI_2 . This suggests that ionization of BaIF would likely involve a vertical transition to a repulsive BaF bond in BaFI^+ , leading one to expect formation of BaI^+ to be favored over formation of BaF^+ . Thus, the magnitudes of the BaF^+ and BaI^+ signals which are observed here are consistent with formation of BaIF, and possibly some BaI as well.

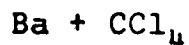
Diffusion flame studies^{18,19} of the reactions of Na with CF_3I , CF_3Br , and CF_3Cl have been analyzed in terms of primary reactions giving only $\text{NaX} + \text{CF}_3$. In his classic diffusion flame study, M. Polanyi²⁰ found that the rate constants for the $\text{Na} + \text{CH}_3\text{X}$ reactions followed the sequence $k_{\text{I}} > k_{\text{Br}} > k_{\text{Cl}} > k_{\text{F}}$, with $k_{\text{I}} > 10^6 k_{\text{F}}$. Presumably this trend arises because the Na atom must transfer an electron into the σ^* antibonding C-X orbital which becomes progressively more repulsive on

going from I to F. Although $D_0^{\circ}(\text{BaF}) > D_0^{\circ}(\text{NaF})$, these trends are likely to hold, at least qualitatively, for Ba reactions as well; evidence of this is provided by entries in Table II. This suggests that it is unlikely that the observed BaF^+ signal arose from ionization of BaF or BaF_2 . The reaction of CF_3 with a metal atom, on the other hand, might well be quite fast because the metal atom can initially transfer its electron into a non-bonding orbital on CF_3 . Moreover, BaI might react in much the same way as Ba because the ionization potentials of the two species are comparable²¹; thus, it is reasonable to expect some decomposition of a $\text{F}_3\text{C} - \text{IBa}$ reaction intermediate into BaIF and CF_2 . Although bimolecular reactions which involve the transfer of two groups are rare in conventional kinetics literature, these considerations suggest that the observed BaI^+ and BaF^+ signals indicate formation of BaIF , and possibly BaI , from $\text{Ba} + \text{CF}_3\text{I}$.



A previous study⁷ of K and $\text{Cs} + \text{CH}_2\text{I}_2$ indicated that the $\text{AI} + \text{CH}_2\text{I}$ products scattered, via a direct reaction mechanism, with SRE E' values of about 3 and 2 kcal/mole, respectively. The MI^+ signals observed in the present study might have arisen from ionization of product MI and/or MI_2 . However, analyses of the MI^+ data assuming no MI_2 product result in surprisingly small values for the product recoil energies.

This is illustrated by the \bar{E}' values listed in Table IV and by the fact that SRE fits (not shown here) are obtained^{13a} for E' values of 0.7 (Ba), 0.6 (Sr), and 0.3 (Ca) kcal/mole. Thus, these comparisons suggest that these alkaline earth reactions do not produce exclusively the MI + CH₂I products via the mechanism characteristic of the K and Cs reactions. These low \bar{E}' values might be understandable²² in terms of a mechanism which proceeded via an intermediate complex whose lifetime was long enough to statistically partition the reaction energy and still short enough to be consistent with the anisotropic angular distribution given in Table IV; the divalency of the alkaline earth atoms could give rise to such a difference in the M and A reactions. In view of the ideas developed in discussing the Ba + CF₃I reaction, however, it seems likely that such a statistical complex would produce some MI₂ product as well. Because of the mass differences, the measured angular distributions shown in Fig. 4 can be fit to CM cross sections with more reasonable E' values for MI₂ + CH₂ products; Table IV gives the recoil energies obtained in this case. Thus, as for Ba + CF₃I, the data are inconclusive, but suggest formation of MI₂ product, and possibly some MI as well. Interestingly, rupture of both C-I bonds has also been observed²³ in the UV photodissociation of CH₂I₂, yielding CH₂ and an electronically excited I₂.



Here again, the observed BaCl^+ signal might have arisen from ionization of product BaCl and/or BaCl_2 ; the measured BaCl^+ LAB distribution provides no basis for estimating which is formed. In analogy with CH_2I_2 and CF_3I , both products might form; this would also be consistent with dissociative electron attachment results for CCl_4 , where both Cl^- and Cl_2^- are observed²⁴.

ACKNOWLEDGMENT

This work was supported by the U.S. Atomic Energy Commission through the Lawrence Berkeley Laboratory. Partial support from the Committee on Research of the University of California at Berkeley is also gratefully acknowledged.

REFERENCES

1. M. E. Gersh and R. B. Bernstein, J. Chem. Phys. 56, 6131 (1972).
2. D. D. Parrish and R. R. Herm, J. Chem. Phys. 54, 2518 (1971).
3. J. H. Birely, E. A. Entemann, R. R. Herm, and K. R. Wilson, J. Chem. Phys. 51, 5461 (1969).
4. G. H. Kwei, J. A. Norris, and D. R. Herschbach, J. Chem. Phys. 52, 1317 (1970).
5. J. C. Whitehead, D. R. Hardin, and R. Grice, Mol. Phys. 23, 787 (1972).
6. A. M. Rulis and R. B. Bernstein, J. Chem. Phys. (to be published).
7. E. A. Entemann, J. Chem. Phys. 55, 4872 (1971).
8. K. R. Wilson and D. R. Herschbach, J. Chem. Phys. 49, 2676 (1968).
9. P. R. Brooks, J. Chem. Phys. 50, 5031 (1969).
10. P. R. Brooks and E. M. Jones, J. Chem. Phys. 45, 3449 (1966).
11. R. J. Beuhler, Jr., R. B. Bernstein, and K. H. Kramer, J. Amer. Chem. Soc. 88, 5331 (1966); R. J. Beuhler, Jr. and R. B. Bernstein, Chem. Phys. Letters 2, 166 (1968); 3, 118 (1969); J. Chem. Phys. 51, 5305 (1969).
12. S.-M. Lin, C. A. Mims, and R. R. Herm, J. Chem. Phys. (to be published).

13. (a) S.-M. Lin, Ph.D. thesis, University of California, Berkeley, California, 1972.
(b) C. A. Mims, Ph.D. thesis, University of California, Berkeley, California, 1972.
14. D. L. Bunker and E. A. Goring, Chem. Phys. Letters 15, 521 (1972).
15. D. R. Herschbach, Adv. Chem. Phys. 10, 319 (1966).
16. D. D. Parrish and R. R. Herm, J. Chem. Phys. 53, 2431 (1970).
17. J. Berkowitz and J. R. Marguart, J. Chem. Phys. 37, 1853 (1962).
18. J. W. Hodgins and R. L. Haines, Can. J. Chem. 30, 473 (1952).
19. E. D. Kaufman and J. F. Reed, J. Phys. Chem. 67, 896 (1963).
20. M. Polanyi, Atomic Reactions (Williams and Norgate, London, 1932).
21. D. L. Hildebrand, J. Chem. Phys. 52, 5751 (1970).
22. S. A. Safron, N. D. Weinstein, D. R. Herschbach, and J. C. Tully, Chem. Phys. Letters 12, 564 (1972).
23. D. W. G. Style and J. C. Ward, J. Chem. Soc. (London) 1952, 2125.
24. J. J. DeCorpo, D. A. Bafus, and J. L. Franklin, J. Chem. Phys. 54, 1592 (1971).

Table I. Experimental beam conditions.^a

collision partners	alkaline earth atom beam			halogenated methane beam		
	source conditions temperature	pressure	speed distribution ^b α_1	source conditions temperature	pressure	speed distribution ^c α_2
CH ₃ I + Ba	1030	0.3	3.1	360	3.6	2.1
CH ₃ I + Sr	980	0.6	3.7	330	3.3	2.0
CH ₃ I + Ca	1050	0.6	5.8	370	3.4	2.1
CH ₂ I ₂ + Ba	1050	0.3	3.1	330	0.6	1.4
CH ₂ I ₂ + Sr	970	0.5	3.7	340	0.5	1.5
CH ₂ I ₂ + Ca	1030	0.4	5.8	330	0.4	1.4
CF ₃ I + Ba	1060	0.4	3.1	330	3.8	1.7
CCl ₄ + Ba	1040	0.3	3.1	370	3.0	2.0

^aTemperatures are given in °K, pressures in torr, and speeds in 100 m/sec.

^bThese are parameters of Eq. (1). Parameters for Ba are from measurements reported in Ref. 13b; parameters for Sr and Ca are from an extrapolation discussed in Ref. 13b.

^cThese are parameters of Eq. (1). Parameters for CH₃I, CH₂I₂, and CCl₄ are from measurements reported in Ref. 13b; parameters for CF₃I are from an extrapolation discussed in Ref. 13b.

Note that this beam is much more "non-thermal" than is the alkaline earth atom beam.

Table II. Summary of reactions studied.^a

	alkaline earth atom				mass peak detected
	Ba	Sr	Ca	Mg	
CH ₃ I	R	R	R	NR	MI ⁺
CH ₂ I ₂	R	R	R	NS	MI ⁺
CF ₃ I	R	NS	NS	NS	MI ⁺
CF ₃ I	F	NS	NS	NS	MF ⁺
CH ₂ Br ₂	NS	NS	F	NS	MBr ⁺
CH ₂ ClBr	F	NS	NS	NS	MBr ⁺
CH ₂ ClBr	NR	NS	NS	NS	MCl ⁺
CCl ₃ Br	NS	NS	NR	NS	MCl ⁺ ; MBr ⁺
CCl ₄	R	I	NR	NS	MCl ⁺
(CH ₃) ₃ C-OH	NR	NS	NS	NS	MO ⁺ ; MOH ⁺ ; MOC(CH ₃) ₃ ⁺

^aR - Product angular distribution is reported here. NR - No product signal was observed. F - A product signal was observed which was too weak to permit measurement of a reliable angular distribution. I - It proved impossible to draw any conclusion about this reaction because of an interfering reactant mass peak. NS - This reaction was not studied.

Table III. M + X - R + MX + R reaction energetics.^a

reaction	relative collision energy, E ^b	reactant internal excitation, W ^c	reactive exoergicity, $\Delta D_0^{d,e}$
Ba + I-CH ₃	2.6	1.4	34
Sr + I-CH ₃	2.5	1.4	26
Ca + I-CH ₃	2.8	1.4	23
Ba + I-ICH ₂	2.4	1.9	34
Sr + I-ICH ₂	2.3	1.9	26
Ca + I-ICH ₂	2.6	1.9	23
Ba + I-CF ₃	2.6	2.8	34
Ba + Cl-CCl ₃	2.7	3.5	37

^aAll energies are given in kcal/mole.

^bCalculated for the most probable (number density distributions) beam speeds.

^cThe average thermal rotational and vibrational reactant excitation which is given here will be too large if the internal degrees of freedom relax somewhat in the expansion process.

^d $\Delta D_0 = D_0(M-X) - D_0(R-X)$; D_0 taken from: for MCl, Ref. 21; for MI, A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, 3rd ed. (Chapman and Hall, London, 1968); for CH₃I and CCl₄, B. de B. Darwent, Bond Dissociation Energies in Simple Molecules, Nat'l. Bur. Std. U.S. Report NSRDS-NBS 31 (1970); for CH₂I₂ and CF₃I, value taken as the same as in CH₃I.

^eIn the event that two halogen atoms are transferred in the last five reactions, the estimated ΔD_0 values become: 70 (BaI₂ + CH₂); 59 (SrI₂ + CH₂); 54 (CaI₂ + CH₂); 46 (BaIF + CF₂); and 80 (BaCl₂ + CCl₂).

Table IV. $M + X - R \rightarrow MX + R$ derived CM reaction cross sections. ^a

reaction	legend	angular distribution ^b			speed distribution ^c			recoil energy ^d			
		θ_1, θ_2	H_1, H_2	C_1, C_2	Q_B	u_1, n_1, m_1, n_2, m_2	\bar{E}'	$\langle E' \rangle$			
Ba + I-CH ₃	SRE	-	-	-	0.58	-	10	10	10		
	A	180, 140,	80,	80, 0.3,	0.3	1.4, 6, 2,	6,	2	9.6		
	B	180, 180,	100,	100, 0.2,	0.2	2.0, 2, 1,	2,	2	5.9		
Sr + I-CH ₃	SRE	-	-	-	0.70	-	10	10	10		
	A	180, 180,	60,	60, 0.1,	0.1	1.6, 6, 2,	6,	2	8.3		
	B	180, 180,	40,	40, 0.1,	0.1	2.5, 2, 1,	2,	2	6.1		
Ca + I-CH ₃	SRE	-	-	-	0.74	-	8.0	8.0	8.0		
	A	180, 180,	40,	40, 0.1,	0.1	1.9, 6, 2,	6,	2	7.3		
	B	180, 180,	20,	20, 0.0,	0.0	2.5, 2, 1,	2,	2	3.8		
Ba + I-CH ₂ I		0,	0,	100, 100,	0.3,	0.3	0.39	1.2, 2, 2,	2	0.7	
Sr + I-CH ₂ I		0,	0,	100, 100,	0.3,	0.3	0.39	1.2, 2, 2,	2	0.5	
Ca + I-CH ₂ I		0,	0,	100, 100,	0.5,	0.5	0.43	1.0, 2, 2,	2	0.2	
Ba + I-CF ₃		90,	70,	45,	15,	0.0,	0.8	0.42	2.5, 6, 6,	6	9.0
Ba + Cl-CCl ₃		30,	30,	60,	30,	0.2,	0.5	0.31	4.0, 2, 2,	2	4.0

^aEnergies are given in kcal/mole, speeds in 100 m/sec, and angles in degrees.

^b $\theta_1, \theta_2, H_1, H_2, C_1, C_2$ are parameters of Eq. (4a); if no entries are given, $T(\theta)$ was not restricted to the form of Eq. (4a). Q_B is the fraction scattered backwards [Eq. (5)].

^cThese are parameters of Eq. (4b).

Table IV. Continued

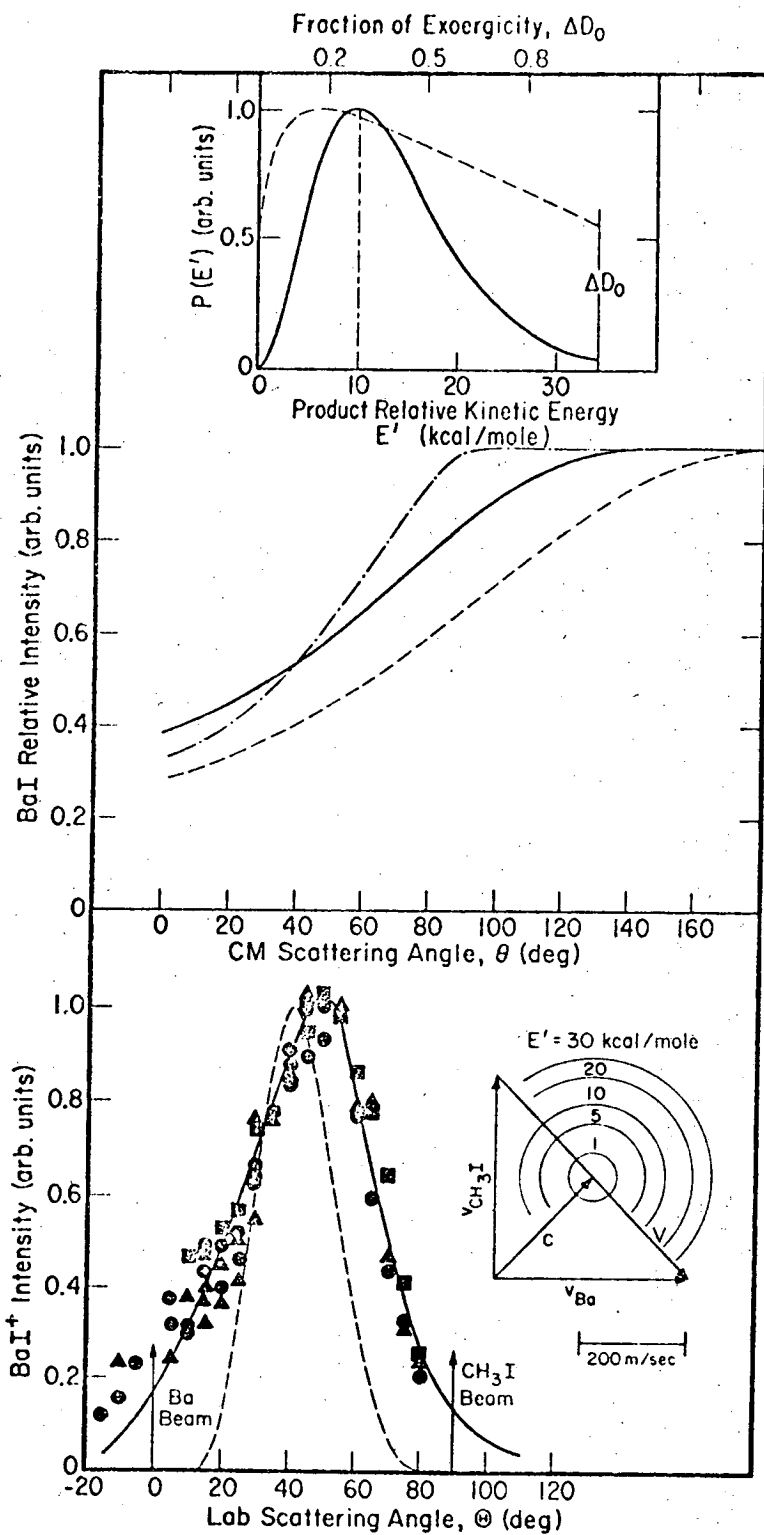
$d\langle E' \rangle$ is the average product recoil energy [Eq. (6)]; \bar{E}' , the most probable E' value, is obtained from $dP(E')/dE' |_{E' = \bar{E}'}$. Values are given for formation of an alkaline earth monohalide product. If the dihalide product were formed in the last five reactions, the corresponding \bar{E}' , $\langle E' \rangle$ entries would be: 9.7, 25 ($\text{BaI}_2 + \text{CH}_2$); 7.5, 20 ($\text{SrI}_2 + \text{CH}_2$); 3.8, 11 ($\text{CaI}_2 + \text{CH}_2$); 13, 13 ($\text{BaIF} + \text{CF}_2$); and 7.0, 20 ($\text{BaCl}_2 + \text{CCl}_2$).

FIGURE CAPTIONS

- Fig. 1. Data points show measured BaI^+ LAB angular distribution from $\text{Ba} + \text{CH}_3\text{I}$; different data symbols show results measured on different apparatus pumpdowns. The upper panel shows three derived CM cross sections ($T(\theta)$ and associated $P(E')$); parameters for these are given in Table IV as SRE (dot-dashed), A (solid), and B (dashed); the corresponding fit to the LAB data provided by the A CM cross section is shown as the solid curve in the lower panel. Also shown in the lower panel are: (1) a calculated angular distribution for the LAB velocity of the center-of-mass, \vec{C} (dashed curve); and (2) a LAB \leftrightarrow CM transformation diagram for $\text{Ba} + \text{CH}_3\text{I} \rightarrow \text{BaI} + \text{CH}_3$. This latter was drawn for most probable beam speeds; the circles show loci of BaI CM recoil velocities for some possible product recoil energies, E' .
- Fig. 2. Measured SrI^+ LAB angular distribution and derived product CM cross sections for $\text{Sr} + \text{CH}_3\text{I} \rightarrow \text{SrI} + \text{CH}_3$. Conventions as described for Fig. 1.
- Fig. 3. Measured CaI^+ LAB angular distribution and derived product CM cross sections for $\text{Ca} + \text{CH}_3\text{I} \rightarrow \text{CaI} + \text{CH}_3$. Conventions as described for Fig. 1.

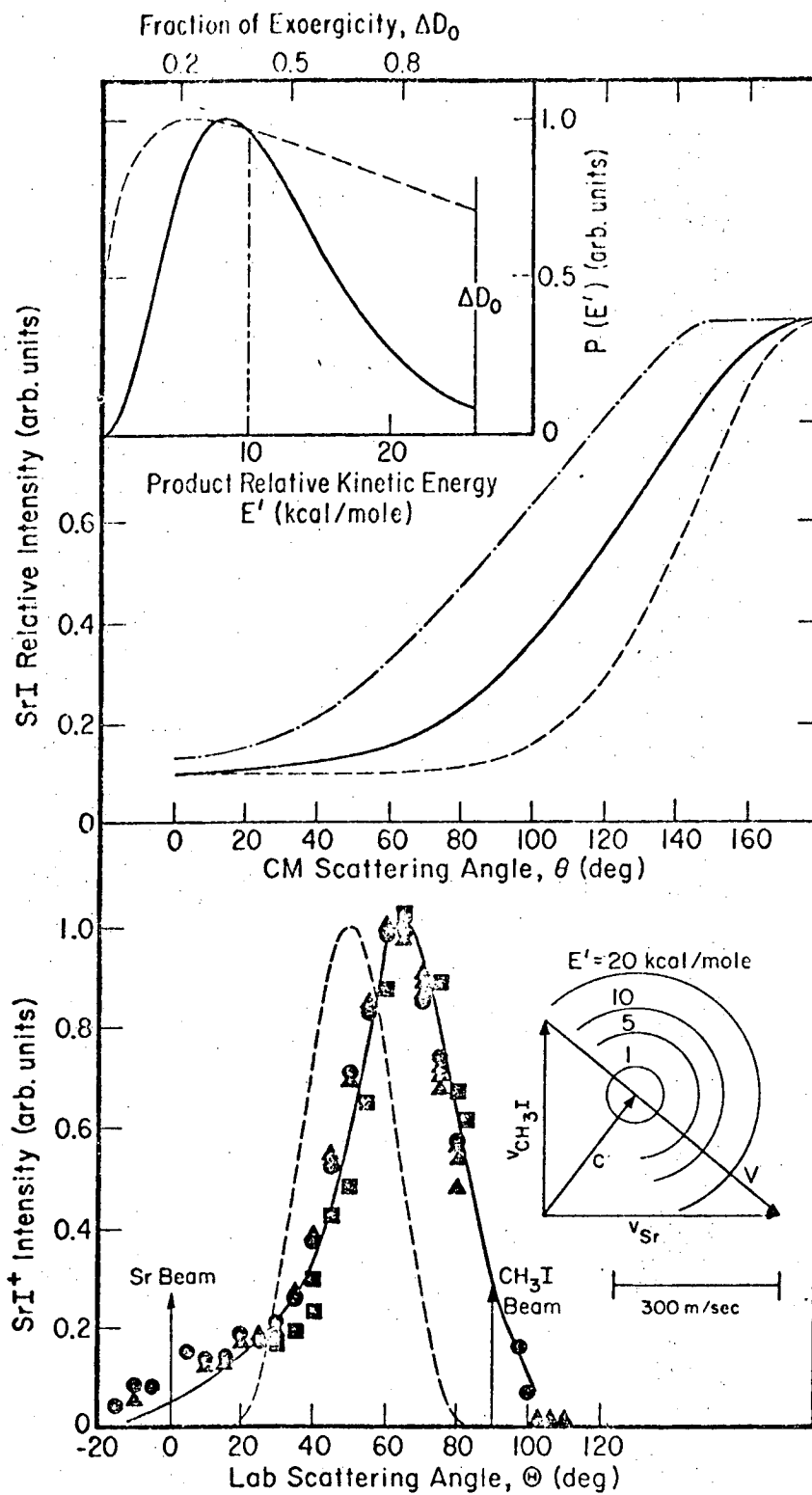
Fig. 4. Data points show measured MI^+ LAB angular distributions from the Ba, Sr, and Ca + CH_2I_2 reactions. Solid curves show fits to the data provided by CM cross section functions given in Table IV; dashed curves show calculated distributions in \bar{C} . On the LAB \leftrightarrow CM transformation diagram, solid circles correspond to BaI CM recoil velocities (for $E' = 0.3$ and 1) whereas dashed circles correspond to BaI_2 CM recoil velocities (for $E' = 10$ and 30).

Fig. 5. Data points show measured BaI^+ (from Ba + CF_3I) and $BaCl^+$ (from Ba + CCl_4) angular distributions. Solid curves show fits to the data provided by CM cross sections given in Table IV; dashed curves show calculated distributions in \bar{C} . Circles on the LAB \leftrightarrow CM transformation diagrams show loci of possible CM recoil velocities of alkaline earth monohalide products.



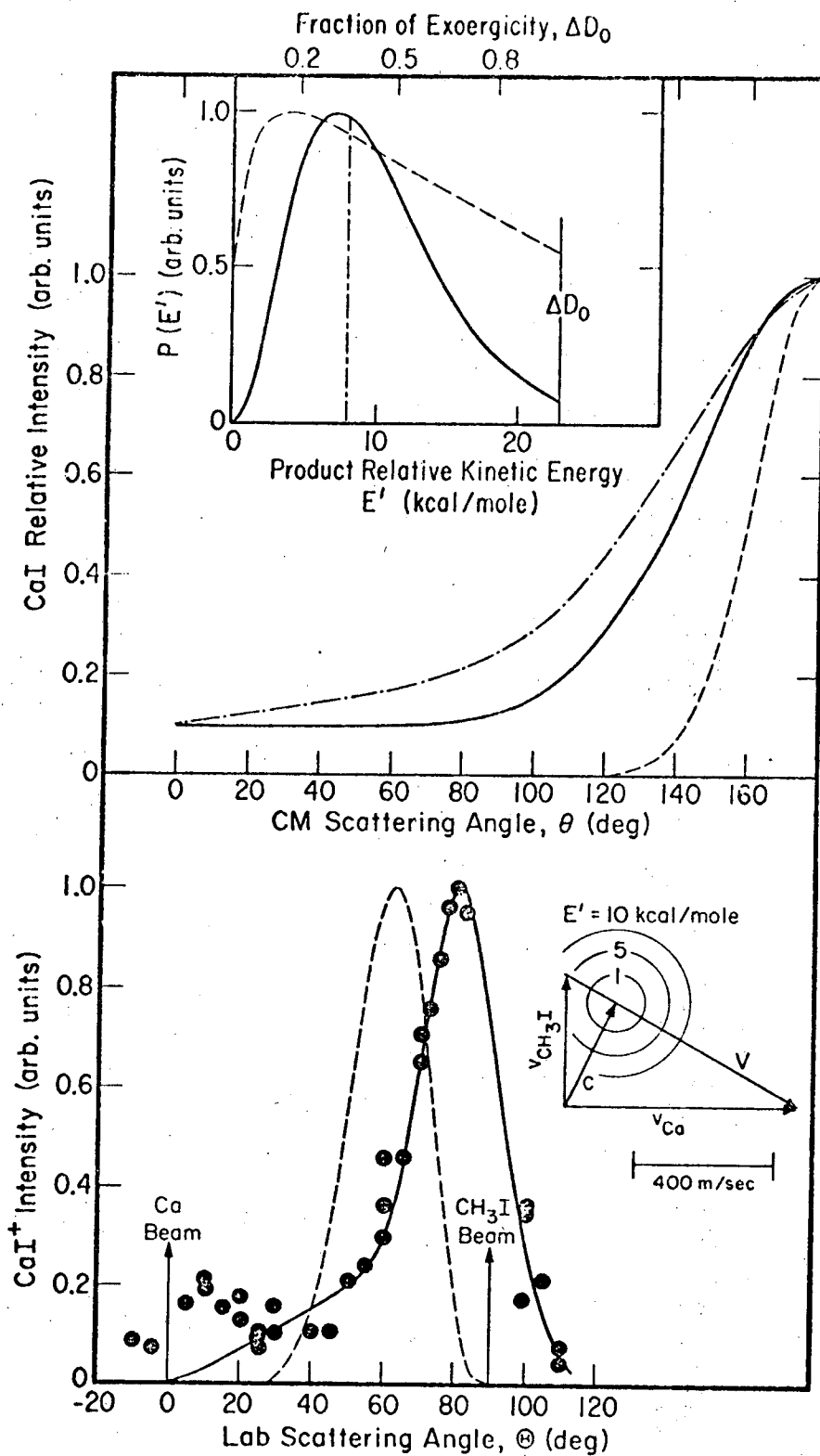
XBL 7210-7140

Fig. 1



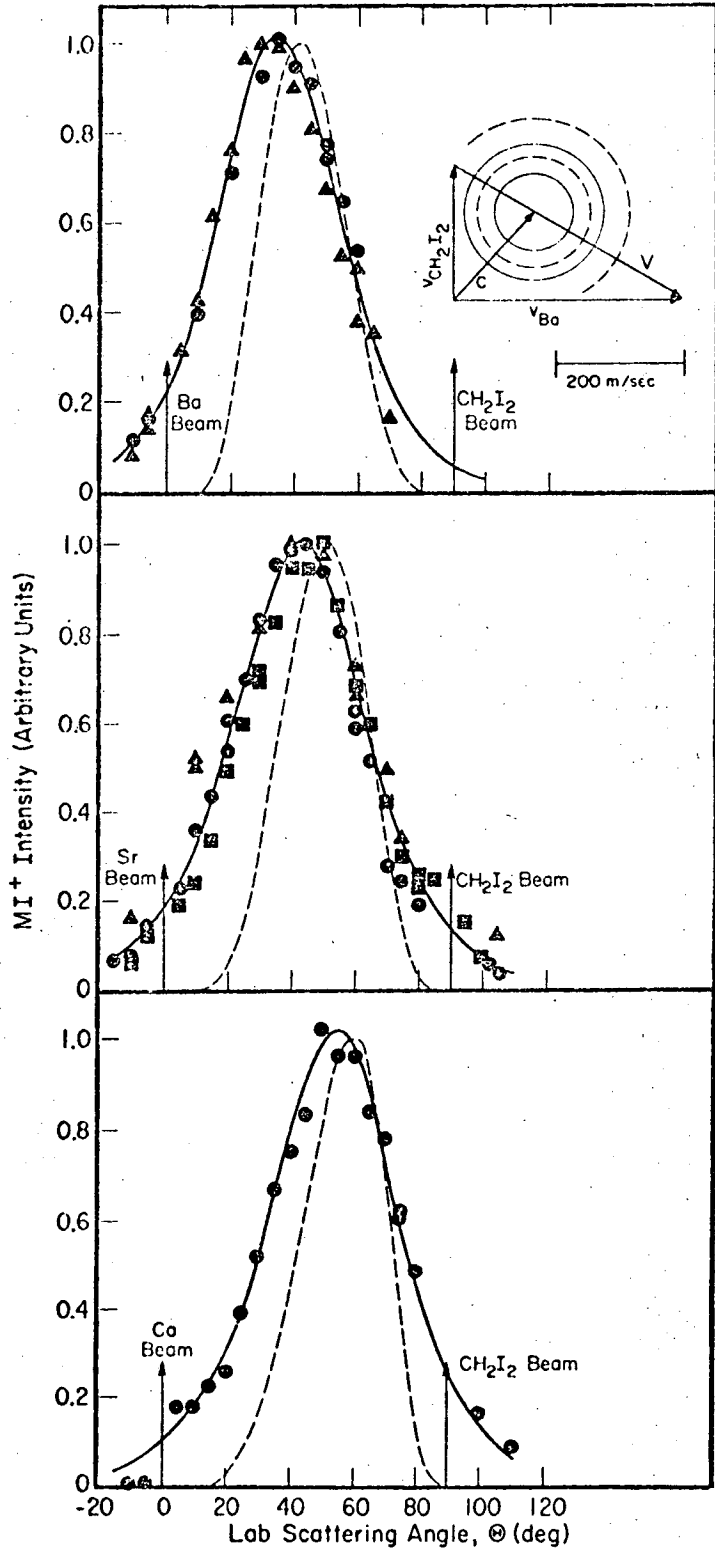
XBL 7210-7141

Fig. 2



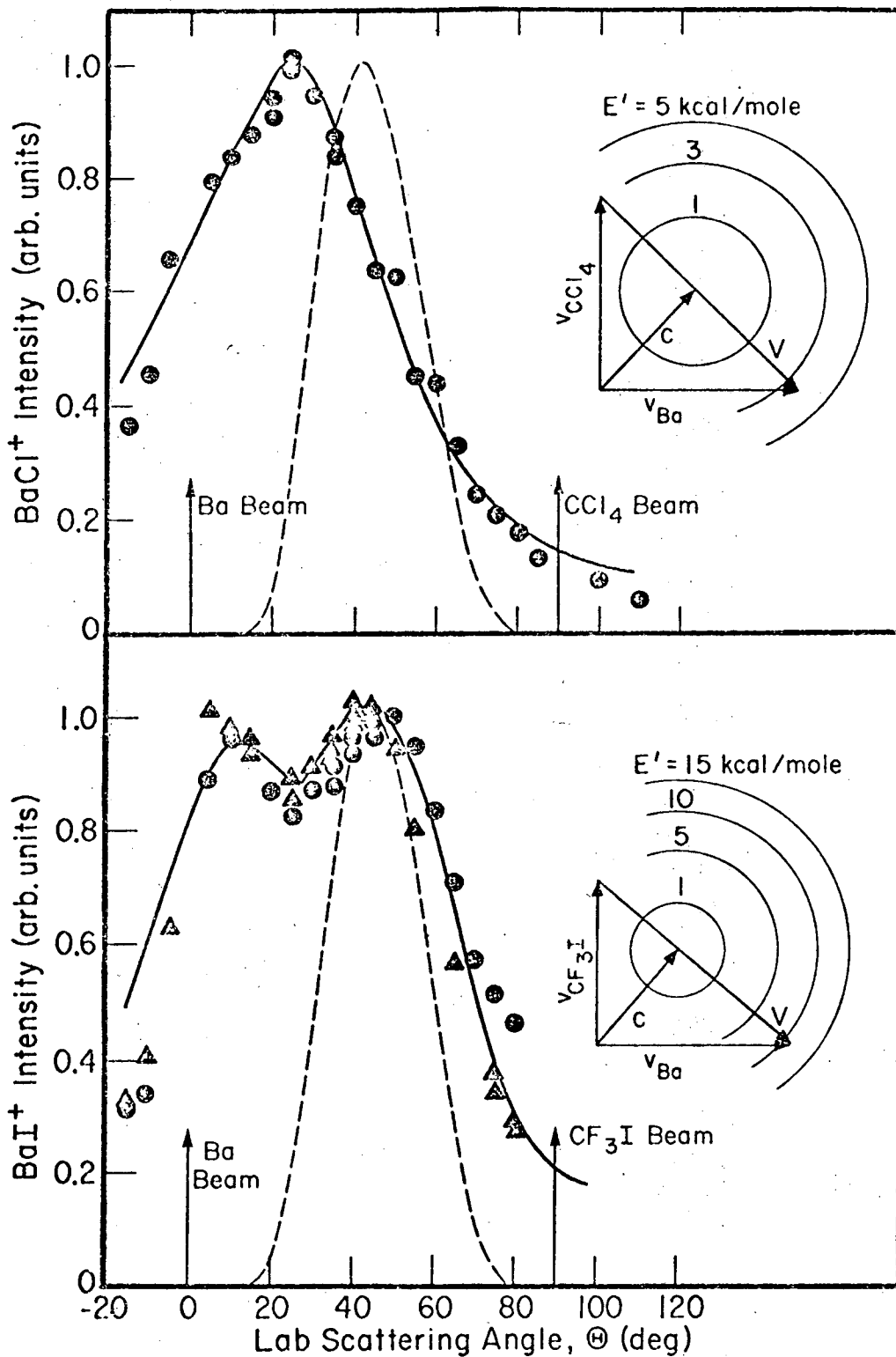
XBL 7210-7142

Fig. 3



XBL 7210-7143

Fig. 4



XBL 7210-7144

Fig. 5

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

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