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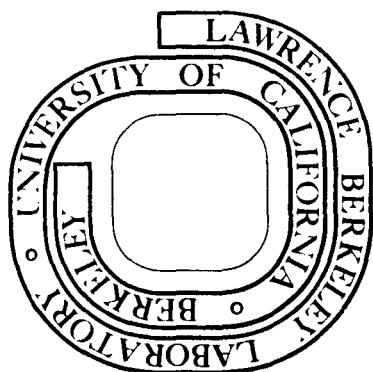
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CROSSED BEAMS CHEMISTRY: REACTIONS OF
Ba, Sr, AND Ca

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ABSTRACT

This paper constitutes the final report from our laboratory on crossed beams exploratory studies of the chemistry of gaseous alkaline earth atoms (M). Measured product laboratory angular distributions and derived center-of-mass (CM) recoil distributions are presented for Ba + SF₆, Ba and Sr + PCl₃, Sr and Ca + NO₂, Ba and Sr + (CH₃)₂CHNO₂, and Ca + CCl₃NO₂; in addition, qualitative results are presented for Ba, Sr, and Ca + SnCl₄ and Ba + SO₂. All derived CM product angular distributions are asymmetric, favoring scattering into the forward hemisphere (i.e., 0° < θ < 90°, where θ = 0° is defined by the initial M velocity), except for Ba + SF₆, where the CM distribution is approximately symmetric about θ = 90°. This suggests that the Ba + SF₆ reaction proceeds via formation of an BaSF₆ complex with a lifetime (τ_c) greater than its rotational period (τ_r), whereas the PCl₃, NO₂, (CH₃)₂CHNO₂, and CCl₃NO₂ reactions proceed via direct mechanisms with τ_c < τ_r. For SF₆, PCl₃, and NO₂, the qualitative behavior of the alkaline earth reaction parallels that previously reported for the analogous alkali (A) reaction. However, no evidence of an MSnCl₃ product from M + SnCl₄ is observed here, whereas ASnCl₃ is thought to be an important product of K, Rb, or Cs + SnCl₄. Also, MO is apparently the product of Ba or Sr + (CH₃)₂CHNO₂ in contrast to the CsNO₂ product formation reported for Cs + CH₃NO₂.

Earlier papers in this series reported results of crossed beams studies of reactions of alkaline earth atoms with HI^{la} , halogen molecules^{lb,c}, and some halides of methane^{ld}. The present paper reports on the remainder of our exploratory studies of gaseous alkaline earth atom chemistry; results are presented for reaction of Ba, Sr, and/or Ca with some inorganic halides (SF_6 , PCl_3 , and SnCl_4) as well as some oxygen containing compounds (NO_2 , SO_2 , $(\text{CH}_3)_2\text{CHNO}_2$, and CCl_3NO_2). Here again, reactive cross section are characterized only semi-quantitatively, the primary intention being to compare the chemical behavior of alkaline earth atoms (M) with that previously reported for alkali atoms (A).

APPARATUS AND DATA ANALYSIS PROCEDURE

The apparatus is described elsewhere^{1,2}. Table I gives conditions of the two beams which intersect at a right angle, resulting in a 1-5% attenuation of the M beam (beam 1) and negligible attenuation of the cross beam (beam 2). Scattered species are ionized by ~ 150 eV electrons and mass analyzed in a detector unit which rotates about the beam collision zone, in

the plane defined by the two intersecting beams, so as to measure the laboratory (LAB) product angular distribution. Table II lists the reactive systems which were examined and provides estimates (based on the approximate apparatus sensitivity) of their total reactive cross sections, Q_R .

The data analysis procedure consists^{1b-d,2} in assuming that the dependence of the center-of-mass (CM) reactive cross section on CM scattering angle, θ , and product relative translational recoil energy, E' , is factorable, i.e.,

$$\sigma(\theta, E') = T(\theta)P(E'). \tag{1}$$

By convention, 0° scattering angle in either the LAB or CM coordinate system corresponds to a reactive event wherein the product alkaline earth halide or oxide is scattered in the direction defined by the initial M velocity. Having assumed a form of $\sigma(\theta, E')$ given by Eq. (1), the corresponding LAB product angular distribution is computed numerically by averaging over the beam speed distributions and integrating over the unmeasured LAB product recoil speed distribution. This calculated LAB product angular distribution is compared with experimental measurements that, by trial and error, a $T(\theta)$ - $P(E')$ combination which provides a good fit to the data is obtained. In general, the data is of limited information content and can be fit by more than one $T(\theta)$ - $P(E')$ combination so that the quantitative forms of $T(\theta)$ and $P(E')$

are not uniquely determined.^{1b-d,2} Nevertheless, it does unequivocally determine the qualitative form of the product angular distribution (e.g., whether $T(\theta)$ is symmetric or sharply peaked forward or backward). Moreover, it is emphasized in earlier papers of this series^{1b-d} that the data also characterize the CM distributions quantitatively to lowest order because Q_F , the fraction of the products scattered into the forward CM hemisphere (i.e., $0^\circ < \theta < 90^\circ$), and \bar{E}' , the most probable relative product recoil energy, are approximate invariants of the data analysis.

RESULTS AND DISCUSSION

Reactions with Halides

In reactions with polyhalides, the experiments are unable to distinguish between alkaline earth monohalide (MX) and dihalide (MX₂) products because both species yield exclusively MX⁺ upon electron bombardment ionization. Signal strengths were too weak to distinguish between these two channels by means of appearance potential measurements. Interference from reactant mass peaks also precluded the observation of mass peaks corresponding to the other product. The measured LAB product angular distributions may be fit to CM distributions by assuming either product channel. Since the CM → LAB transformation is dependent only on the CM recoil velocity, \bar{u}_3 , of the species detected, the

derived CM $T(\theta)$ is not dependent on the assumed product identity. This is not true for $P(E')$, however, because E' is given by

$$E' = \gamma u_3^2, \quad (2)$$

$$\gamma = (m_3 + m_4)m_3 / 2m_4,$$

where m_3 and m_4 are the masses of the two recoiling products. In a previous study^{1d} of $M + \text{CH}_2\text{I}_2$, γ was quite different for the $\text{MI} + \text{CH}_2\text{I}$ versus the $\text{MI}_2 + \text{CH}_2$ product channels so that it was possible to draw inferences from the data regarding the likely product identity. For the reactions studied here, however, values of γ for formation of MX versus MX_2 are comparable. In general, E' values derived assuming an MX_2 product are shown in parentheses, E' values derived for an MX product are shown without parentheses.

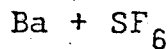


Figure 1 shows that the measured LAB angular distribution of the BaF^+ mass peak signal from the $\text{Ba} + \text{SF}_6$ reaction is broad and of comparable intensities on both sides of the calculated^{1a} LAB angular distribution (assuming an energy independent collision cross section) of center-of-mass velocity vectors, \vec{C} . This LAB distribution is well fit by CM product angular distributions, given in Fig. 1 and Table III, which are broad and almost

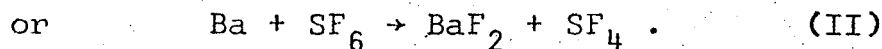
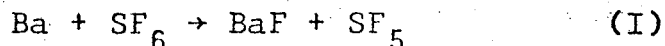
symmetric about $\theta = 90^\circ$, typical³ of the behavior expected if the lifetime of the complex (τ_c) is at least as long as its rotational period (τ_r). Indeed, product velocity analysis measurements⁴ on the K, Rb, and Cs + SF₆ reactions show symmetric CM product angular distributions, indicating that the reactions proceed via a long-lived complex with τ_c greater than several rotational periods⁵. The Q_P entries in Table III indicate that, even for the $T(\theta)$ curves shown in Fig. 1, the product scattering is almost evenly divided between the forward and backward CM hemispheres. Moreover, uncertainties in the data analysis suggest that the results presented here on Ba + SF₆ are consistent with a long-lived complex mechanism. For example, auxiliary calculations with a slightly altered SF₆ beam speed distribution (1.0 rather than the "best estimate" of 1.4 for the a_2 parameter of Table I) can fit the data by reflecting the 0° - 90° $T(\theta)$ functions shown in Fig. 1 through $\theta = 90^\circ$. The uncertainties in the form of $T(\theta)$ shown in Fig. 1 prevent an analysis^{3a,4} of the product angular distribution in terms of the statistical break up of an intermediate complex so as to extract information on its moments of inertia.

Product energy distributions produced by break up of a long-lived complex might be expected to partition the available energy statistically. Indeed, both $P(E')$ from K, Rb, and Cs + SF₆⁴ as well as the vibrational distribution in the product CsF₆ are consistent with a transition state formulation of this energy

randomization.⁷ For comparison with the results reported here, this theory⁷ would predict that the average product recoil energy is given by

$$\langle E' \rangle = (E + W + \Delta D_0)/(n + 2), \quad (3)$$

where centrifugal barriers in the exit channel, which would only increase somewhat the $\langle E' \rangle$ estimate, have been neglected. Here, E, the reactant translational energy, is estimated in Table I, W, the SF₆ internal energy, has a thermal average value of 3.4 kcal/mole, and n should be 14.5^{4,8} for break up of a "loose" BaSF₆ complex. The exoergicities, ΔD_0 , are listed in Table III for two possible product channels,



Equation (3) provides $\langle E' \rangle$ estimates of 4.1 and 7.9 kcal/mole for channels (I) and (II), respectively, and the experimental values are in reasonable agreement with this prediction⁹ if the data are analyzed assuming channel (I) (see Table III). Although channel (II) would be favored over (I) on a purely statistical basis, its larger exoergicity might lead to shorter interaction times and a non-statistical energy

randomization.¹⁰ Thus, the low resolution measurements reported here provide no basis for inferring the likely product identity because either reaction might proceed via initial formation of a one-electron transfer Ba^+SF_6^- intermediate which, in analogy to the K, Rb, and Cs reactions, would statistically distribute the energy associated with reaction (I).

Ba and Sr + PCl_3

Measured LAB angular distributions of MCl^+ signal from the Ba and Sr + PCl_3 reactions are shown in Fig. 2. In contrast to the BaF^+ from $\text{Ba} + \text{SF}_6$, the BaCl^+ from $\text{Ba} + \text{PCl}_3$ is mainly confined to smaller LAB angles than the calculated \bar{C} distribution, indicating that scattering into the forward CM hemisphere is favored. Figure 2 also shows CM product angular distributions derived for reasonable assumed forms of $P(E')$ which are specified in Table III. Auxiliary calculations reported in Ref. 2b which managed to fit the measurements using other assumed forms of $P(E')$ (including an unrealistic delta function referred to as the SRE analysis in Refs. 1b-1d) further indicate that: (1) $T(\theta)$ need not peak at 0° for either reaction, but the qualitative behavior of a more sharply forward peaked $T(\theta)$ for the Ba reaction which is exhibited in Fig. 2 appears valid; (2) Q_F is in the range

of 0.64 - 0.72 and 0.55 - 0.60 for the Ba and Sr reactions, respectively; and (3) $\langle E' \rangle$ for the Ba and Sr reactions are in the range of 3-5 and 2-4 kcal/mole if $\text{MX} + \text{PCl}_2$ is formed, 5-9 and 4-8 if $\text{MX}_2 + \text{PCl}$ is formed.

Thus, in contrast to the $\text{Ba} + \text{SF}_6$ reaction, the Ba and Sr + PCl_3 reactions proceed via a direct mechanism ($\tau_c \lesssim \tau_r$) wherein the products recoil preferentially into the forward CM hemisphere with only a modest fraction ($\sim 20\%$) of the reaction energy appearing as product recoil. Moreover, the observed SrCl^+ signal was appreciably weaker than the BaCl^+ signal. This observation as well as the observations on the Ca and Mg reactions shown in Table II indicate a particularly clear trend of decreasing Q_R in the $\text{M} + \text{PCl}_3$ family as M becomes less easily ionizable. In this regard, the MCl (or MCl_2) product CM angular distributions in Fig. 2 follow the expected trend for direct reaction mechanisms of increasing forward scattering with increasing impact parameters leading to reaction. Product velocity analysis measurements are not available on the $\text{A} + \text{PCl}_3$ reactions. Primitive product angular distribution measurements indicate that Li^{11} , K^{12} , and $\text{Rb}^{13} + \text{PCl}_3$ exhibit the same qualitative behavior as that found here, with reaction proceeding via a direct mechanism, although sideways rather than forward product scattering seems to be favored in the Li reaction.

Ba, Sr, and Ca + SnCl₄

LAB angular distributions of MCl⁺ (corresponding to MCl and/or MCl₂) from the Ba, Sr, and Ca + SnCl₄ reactions were measured in Ref. 2b to peak sharply near $\theta = 0^\circ$. In subsequent experiments^{2b} measuring the SnCl₄ speed distribution, however, it was discovered that the SnCl₄ beam profile was unaccountedly broadened, rendering an analysis of the measured LAB product angular distributions useless because of possible severe distortion by an unknown viewing factor (Refs. 2b and 11 discuss this possible mechanism of distortion). Nevertheless, the measured MCl⁺ signals were quite strong, indicating large cross sections for reactions of Ba, Sr, and Ca with SnCl₄ (but not Mg; see Table II).

There is indirect evidence^{4,12,14} that the K, Rb, and Cs + SnCl₄ reactions yield a heavier alkali product in addition to ACl, presumably the ionically bound alkali chlorostannite, A⁺SnCl₃⁻. If a similar product formed in the alkaline earth reactions, evidence of it should appear in the product mass spectrum because ionization of an ionically bound M⁺SnCl₃⁻ might be expected to involve removal of a non-bonding electron^{1b} from M⁺ with little rearrangement of the molecular geometry. Despite careful mass scans at various angles for the Ba, Sr, and Ca + SnCl₄ reactions, however, no evidence of an MSnCl_n⁺ mass peak, for n = 0,1,2,3, or 4, was observed. It is possible that any MSnCl₃ formed might

decompose before reaching the detector. This is probably not a consideration in the alkali reactions¹⁵ because decomposition into MCl (or ACl) + $SnCl_2$ would be endoergic even allowing for excitation of the initial chlorostannite product. In contrast, however, decomposition of any alkaline earth chlorostannite into MCl_2 + $SnCl$ might take place because $M + SnCl_4 \rightarrow MCl_2 + SnCl + Cl$ is exoergic¹⁶ by 5-10 kcal/mole. However, if $MSnCl_3$ formed in yields comparable to $ASnCl_3$, the absence of observable $MSnCl_n^+$ mass peaks would require that most of it ($> \sim 95\%$) decompose before reaching the detector. Since this seems unlikely in view of the energetics, these observations suggest that, in contrast to $A + SnCl_4$, $MSnCl_3$ is not a significant product of the $M + SnCl_4$ reactions.

Reactions with Oxides

Reactions producing alkaline earth monohalide products are especially suited to crossed beams studies^{1b} because electron bombardment ionization of MX is expected to produce MX^+ almost exclusively. However, the situation is less favorable for ionization of MO because a bonding, as opposed to non-bonding, electron is lost. If the fragmentation ratio, M^+/MO^+ , were strongly dependent on the internal excitation of MO , it could hamper the interpretation of the experiments reported here where only the MO^+ product ion signal is

analyzed. In the usual case (expected here), the M^+/MO^+ ratio should increase with increasing MO internal excitation, so that the product recoil energy distribution derived from the measured MO^+ LAB angular distribution would be distorted, indicating too low a probability for low recoil energy (and high product internal excitation) reactive events. For example, this fragmentation ratio is very strongly dependent on internal excitation for ionization of alkali halides,¹⁷ because of the weak ion-induced dipole bond in AX^+ , so that it would be impractical to measure product AX scattering with the apparatus employed here.

However, this fragmentation ratio should be far less sensitive to internal excitation for ionization of MO because the MO^+ molecules should have appreciable bond dissociation energies (data in Ref. 18 suggest $D_0(BaO^+) \approx 70$ kcal/mole). Mass spectral data are not available for the M^+/MO^+ fragmentation ratio of thermal CaO or SrO because the solid oxides vaporize with appreciable decomposition; data for BaO indicate¹⁸ a Ba^+/BaO^+ ratio less than one. Furthermore, data on the $Sr + NO_2$ scattering reported in Ref. 2b indicate that, for LAB scattering angles greater than $\sim 25^\circ$: (1) the Sr^+ and SrO^+ LAB angular distributions are of roughly the same shape; and (2) the SrO^+ intensity exceeds that of Sr^+ (by ~ 1.4). Feature (1) suggests that the Sr^+ signal arises largely from ionization of product SrO. Since the apparatus sensitivity for parent

and daughter ions is approximately the same,^{2b} feature (2) then indicates that the Sr^+/SrO^+ fragmentation ratio is less than one and is independent of LAB scattering angle.¹⁹ Thus, these arguments indicate that the CM product distributions, which are derived in this section by fitting measured LAB MO^+ product angular distributions, cannot be significantly in error, although they could overestimate, somewhat, the fraction of the reaction energy which appears as product recoil.

Ba + SO₂

A strong BaO^+ signal was observed for scattering of Ba from SO_2 . However, owing to the limited pumping capacity for SO_2 in the collision chamber, the background pressure was rather high ($\sim 6 \times 10^{-6}$ torr) during this experiment. Since the Ba beam path is rather long, this could have produced significant pressure broadening of the Ba beam, thereby introducing a possible viewing factor distortion of the measured LAB product angular distribution.²⁰ Nevertheless, the strong BaO^+ signal observed indicates a large reactive cross section so that $D_0(\text{BaO}) \geq D_0(\text{OS-O}) = 129$ kcal/mole,²¹ in agreement with the lower bound of 131.5 kcal/mole for $D_0(\text{BaO})$ determined from a crossed-beam chemiluminescence study²² of the $\text{Ba} + \text{NO}_2$ reaction.

Sr and Ca + NO₂

The fact that most of the wide angle scattering of Sr from NO₂ is due to reactive events indicates qualitatively that the cross section for this reaction is large, in agreement with the large Q_R value measured in Ref. 22. The LAB product distributions from Sr and Ca + NO₂ shown in Fig. 3 can be fit to a rather wide range of T(θ) - P(E') combinations. Figure 3 illustrates the range of T(θ) which can be fit to the Sr or Ca + NO₂ data for reasonable breadths in P(E'); less reasonable breadths (e.g., a delta function) leads to broader T(θ) estimates. Nevertheless, the data, and further data analysis reported in Ref. 2b, clearly establish important qualitative reaction features. The Sr and Ca + NO₂ reactions show quite similar features; this is illustrated by the examples of CM distributions given in Table III. The average product recoil energy, <E'>, is not well determined because of uncertainties in ΔD₀ as well as the insensitivity of the data at higher E' values; however, the dominate E' value, \bar{E}' , is relatively well characterized (~3-7 kcal/mole). Most importantly, T(θ) must definitely peak forward (although not necessarily precisely at 0°) with Q_F > 0.50 and asymmetry about θ = 90° so that the reactions proceed via a direct mechanism.

All of these features are in agreement with a previous crossed beams study of the Ba + NO₂ reaction.^{23,24} These are also the same qualitative features reported for the Li + NO₂ reaction.²⁵ As pointed out in Ref. 25, the potential hypersurfaces for these reactions are expected to exhibit an inner well corresponding to formation of the MNO₂ intermediate,²⁶ a feature which a priori might have been expected to lead to a long-lived complex rather than direct reaction mechanism. The large reaction cross sections and forward product scattering which are observed suggest a reaction mechanism wherein the incoming M transfers an electron to the NO₂, and the NO₂⁻ which is formed immediately breaks up in the force field provided by the M⁺ to form the MO + NO products.

Ba and Sr + (CH₃)₂CHNO₂

The K + CH₃NO₂ reaction proceeds with a large reactive cross section to give a practically isotropic product angular distribution;²⁷ electric deflection experiments on Cs + CH₃NO₂ have established that the products are CsNO₂ + CH₃.²⁸ Similar results have been reported for Li + CH₃NO₂,^{25,29} although the product angular distribution, while still very broad, appears to favor forward scattering. Thus, it seemed of special interest to examine the reaction of Ba with a nitroalkane, as this reaction should provide an opportunity for the alkaline earth to directly assert its potential divalency, forming

BaO rather than the BaNO_2 which would presumably form if Ba reacts via the mechanism characteristic of the analogous Cs reaction.

Figure 4 shows the data measured for the reactions of Ba and Sr with 2-nitropropane.³⁰ For both reactions, MO^+ is the only alkaline earth containing product ion observed, although the signal-to-noise was such that MNO_2^+ (or MNO^+) should have been observed had it been present at as little as 5% of the MO^+ signal. Since MNO_2 would presumably involve a single ionic bond, its ionization should proceed via the removal of a non-bonding electron on the alkaline earth, suggesting that it wouldn't be expected to fragment exclusively into MO^+ . Thus, we feel that the most reasonable interpretation of the observed MO^+ product signal is that MO , rather than MNO_2 , is formed via a direct reaction mechanism different from that characteristic of the alkali reactions.

Further support for this conclusion is provided by the shapes of the measured product angular distributions. Table III lists particular examples of CM distributions which will fit the data. Qualitatively, the product CM angular distributions resemble those shown for the NO_2 reaction in Fig. 3, and other remarks regarding the CM distributions from the NO_2 reactions are generally applicable here. The data do support the general conclusion, however, that the BaO product is more

sharply forward scattered (i.e., larger Q_F value) than the SrO product. As for the NO_2 reactions, \bar{E}' is a more reliable indication of the energy partitioning than is $\langle E' \rangle$. This is especially true for the Sr reaction because of uncertainties in ΔD_0 . Indeed, the rather large cross section indicated by the data for this reaction would suggest that either $D_0(\text{SrO})$ in Ref. 31 is too low or that the $\Delta H_f^\circ(\text{R-NO}) - \Delta H_f^\circ(\text{R-NO}_2)$ estimate from Ref. 32 is too high. At any rate, the outstanding qualitative feature of these reactions is their close similarity (especially for Ba) to the behavior of the $\text{M} + \text{NO}_2$ reactions. This suggests that they proceed via the same direct, electron-transfer intermediate mechanism.³³

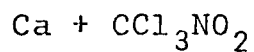


Table II indicates that, although a weak CaO^+ signal was seen as well, the predominate product signal observed for scattering of Ca from CCl_3NO_2 was CaCl^+ . The measured LAB CaCl^+ angular distribution is shown in Fig. 4, and Table III provides an example of a CM distribution which adequately fits the data. In general, the CM distributions which will fit this data are similar to those found for the $\text{M} + \text{NO}_2$ and $(\text{CH}_3)_2\text{CHNO}_2$ reactions, so that this reaction presumably proceeds via a direct, electron-transfer intermediate mechanism. Comments presented on the likely shape of the true CM

distributions for the NO_2 and R-NO_2 reactions are generally applicable to this reaction as well. Calculations reported in Ref. 2a indicate that the CM product angular distribution for $\text{Ca} + \text{CCl}_3\text{NO}_2$ does appear to be somewhat more sharply peaked in the forward directions than is that for $\text{Ca} + \text{CCl}_4$,^{1d} suggesting that CCl_3NO_2 is a better electron acceptor than CCl_4 . Although the nature of the molecular orbital in CCl_3NO_2 which accepts the donated electron is not known, the observation that CaCl (or CaCl_2) is the predominate product is not surprising since the $\text{CCl}_3\text{NO}_2^-$ intermediate would be expected to correlate asymptotically with Cl^- and CCl_2NO_2 by virtue of the large electron affinity of Cl . A similar effect is observed in the $\text{M} + \text{ICl}$ reactions where MCl is the dominate product despite the fact that the donated electron initially enters a molecular orbital which is located primarily on the I side of the ICl molecule.^{1b}

CONCLUSIONS

It seems natural to conclude these exploratory studies with some general comments on the contrasting gas-phase, single-encounter chemistry of alkaline earth and alkali atoms. One obvious possible cause of different behavior is the potential divalency of the alkaline earths. In this regard, it is gratifying that the M and $\text{Li} + \text{NO}_2$ reactions are quite similar, as these are the reactions for which the potential

hypersurfaces are expected to be most similar. Results for the homonuclear diatomic halogens^{1c} and methyl iodide^{1d} also indicate that A and M atoms exhibit quite similar chemical behaviors when steric effects are likely to inhibit the potential attractive interactions between products which are expected for M, but not A, reactions. For some other reactions, on the other hand, A and M atoms show different chemical behaviors. There is some evidence for this contrasting behavior in the ICl reactions,^{1b} and it is quite apparent in the CH_2I_2 ^{1d} and R-NO₂ reactions.

Another possible cause for differences is the paired versus unpaired valence structure of the reactant atoms. This would probably not be expected to be important for reactions proceeding via an electron-transfer intermediate which formed at large reactant separations. However, it suggests that the activation energies determined for the Ba, Sr, and Ca + HI reactions^{1a} are surprising small, since the A + HI reactions would probably not proceed via a long-range electron transfer. At any rate, this effect or the relatively rapid rise in ionization potential (and consequent trend towards the "non-metallic" regime) in the Ba → Mg sequence does give rise to contrasting reactivity trends in the two families of reactions. Thus, although total reaction cross sections haven't been determined, data reported here and in Ref. 1 indicate that Ba is as reactive as an alkali metal whereas

Mg is observed to react only with halogen molecules, and Sr and Ca exhibit intermediate reactivities.³⁴ This behavior may be contrasted to the alkali metals, where reaction cross sections show only a modest decrease in the Cs → Li sequence.^{35,36} It is interesting to note that vapor co-deposition of Mg atoms and organics has recently been used in synthesis.³⁷ The contrasting reactivities of the alkaline earths might prove of importance in this regard if this proves to be a useful synthetic technique.

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14. The product velocity analysis measurements reported in Ref. 4 provide especially strong indirect evidence.
15. Conclusions of the alkali experiments (Ref. 4 and 12) would probably be insensitive to any subsequent ASnCl_3 dissociation.
16. Bond strengths in the tin chlorides are discussed in: G. A. Oldershaw and K. Robinson, J. Chem. Soc. (A), 2963 (1971).
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20. Actually, estimates reported in Ref. 2b suggest that this pressure broadening should produce only negligible viewing factor distortion. If this is true, the data reported in Ref. 2b indicates that $\text{Ba} + \text{SO}_2 \rightarrow \text{BaO} + \text{SO}$ proceeds via a direct mechanism with a sharply forward peaked product CM angular distribution ($Q_F \sim 0.7 - 0.8$) and $\langle E' \rangle \sim 3-4$ kcal/mole.

21. G. Herzberg, Molecular Spectra and Molecular Structure III, Van Nostrand Reinhold Company, New York, 1966 recommends $D_0(\text{OS-O}) = 129$ kcal/mole but cautions that there are indications that it may be lower.
22. C. D. Jonah, R. N. Zare, and Ch. Ottinger, *J. Chem. Phys.*, 56, 263 (1972).
23. J. A. Haberman, K. G. Anlauf, R. B. Bernstein, and F. J. Van Itallie, *Chem. Phys. Letters*, 16, 442 (1972).
24. Our plans to study the $\text{Ba} + \text{NO}_2$ reaction as well so as to directly reproduce data reported by another laboratory were thwarted by an abrupt and (essentially) irreversible loss of apparatus sensitivity which brought these experiments to a premature end. However, Ref. 1c reports good agreement between our data on $\text{Ba} + \text{Cl}_2$ and that reported in Ref. 23.
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26. This is certainly true for Ca and $\text{Sr} + \text{NO}_2$. It is almost certainly true for $\text{Ba} + \text{NO}_2$ as well because an estimate of $D_0(\text{Ba} - \text{NO}_2)$, based on an empirical correlation between bond energy and length for ionic bonding (Ref. 27), suggests that $\text{BaNO}_2 \rightarrow \text{BaO} + \text{NO}$ is endoergic.
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29. Actually, the identity of the product (LiO versus LiNO_2) is not definitely established for this reaction.
30. Nitropropane, rather than nitromethane, was chosen for study here in order that the detected product not be unduly heavier than the undetected product.
31. L. Brewer and G. M. Rosenblatt, *Adv. High Temp. Chem.*, 2, 1 (1969).
32. S. W. Benson, *Thermochemical Kinetics*, John Wiley, New York, 1968.
33. Although negative ions of nitroalkanes are apparently unknown in the gas phase, CH_3NO_2^- has been observed as an intermediate in the reaction of CH_3NO_2 with the hydrated electron; see: A. Henglein, *Angew. Chem. Internat. Edit.*, 5, 256 (1966).
34. Part, but not all, of this decreasing reactivity might simply be due to decreasing reaction exoergicities.
35. Alkali metal studies are reviewed in: J. L. Kinsey, *MTP International Review of Science*, edited by J. C. Polanyi (Butterworths, London, 1972), *Phys. Chem. Ser. 1*, Vol. 9, Chap. 6.

36. Exceptions to this statement arise when the reactions are practically thermonentral (e.g., NO_2 or HCl).
37. P. S. Skell and J. E. Girard, J. Am. Chem. Soc., 94, 5518 (1972).

Table I. Experimental Beam Conditions^a

Collision partners	Alkaline earth atom beam			Cross beam				Relative Collision Energy,
	Source Temperature	Speed distribution ^{b,c}		Source conditions		Speed distribution ^{b,d}		
		α_1	a_1	Temperature	Pressure	α_2	a_2	
Ba+SF ₆	1060	3.2	1.1	340	2.2	2.0	1.4	2.5
Ba+PCl ₃	1040	3.2	1.1	360	3.5	2.2	2.0	2.9
Sr+PCl ₃	990	3.8	1.3	350	3.2	2.2	1.8	2.6
Ba+SO ₂	950	3.3	0.0	360	4.0	3.1	2.0	1.9
Sr+NO ₂	950	3.8	1.3	350	2.2	3.6	2.0	2.1
Ca+NO ₂	1050	5.9	2.0	360	4.0	3.6	2.3	2.5
Ba+(CH ₃) ₂ CHNO ₂	1020	3.1	1.1	390	2.6	2.7	1.8	2.4
Sr+(CH ₃) ₂ CHNO ₂	960	3.7	1.3	350	2.8	2.5	1.8	2.3
Ca+CCl ₃ NO ₂	1020	5.8	1.9	320	3.8	1.8	1.7	2.8

^aTemperatures are given in °K, pressures in Torr, speeds in 100 m/sec, and energies in kcal/mole.

^bThese are parameters of the functional representation of the beam number density speed distribution employed in Ref. 1b-d.

^cParameters for Ba from measurements reported in Ref. 2b; parameters for Sr and Ca from an extrapolation discussed in Ref. 2b.

^dParameters for PCl₃, NO₂, and (CH₃)₂CHNO₂ from measurements reported in Ref. 2b; parameters for SF₆, SO₂, and CCl₃NO₂ from an extrapolation reported in Ref. 2b.

^eE is a characteristic translational energy of reactant approach, calculated for the most probable (number density distribution) beam speeds. If no relaxation took place during beam formation, the cross beam also possess thermal rotational and vibrational energies.

Table II. Summary of Reactions Studied^a

	Alkaline earth atom (M)				Mass peak detected
	Ba	Sr	Ca	Mg	
SF ₆	R	I(SF ₄ ⁺)	NR	NR	MF ⁺
PCl ₃	R	R	F	NS	MCl ⁺
SnCl ₄	R	R	R	NR	MCl ⁺
SO ₂	R	NR	NR	NS	MO ⁺
NO ₂	NS	R	R	I(Ar ⁺)	MO ⁺
(CH ₃) ₂ CHNO ₂	R	R	NR	NS	MO ⁺
CCl ₃ NO ₂	NS	NS	R	NS	MCl ⁺
CCl ₃ NO ₂	NS	NS	F	NS	MO ⁺

^aNS - This reactive system was not studied; I (X⁺) - it proved impossible to draw any conclusion about this reaction because of interference from the X⁺ mass peak; NR - no product signal was observed, $Q_R < \sim 1 \text{ \AA}^2$; F - a product signal was observed which was too weak to permit measurement of a reliable angular distribution, $\sim 1 \text{ \AA}^2 < Q_R < \sim 5 \text{ \AA}^2$; R - a product angular distribution was measured, $Q_R > \sim 5 \text{ \AA}^2$.

Table III. $M + X - R \rightarrow MX + R$ Derived CM Reaction Cross Sections^a

Reaction	Legend	Angular distribution ^b			Speed distribution ^c					Energetics		ΔD_{OC}
		H_1	C_1	Q_F	u_1	n_1	m_1	n_2	m_2	\bar{E}'^d	$\langle E' \rangle^e$	
Ba+F-SF ₅	A	20°	0.40 ^g	0.51	3.0	2	1	2	2	1.0	3.4(4.5)	62(124)
	B	250°	0.00	0.53	2.3	4	2	2	4	1.6	2.1(2.8)	62(124)
Ba+Cl-PCl ₂		20°	0.10	0.64	3.2	2	1	2	2	1.4	4.8(8.7)	~25(60)
Sr+Cl-PCl ₂		20°	0.30	0.55	4.0	2	1	2	2	1.3	3.9(7.7)	~20(55)
Sr+O-NO		10°	0.12	0.54	4.5	2	1.5	2	2	4.4	~6	20
Ca+O-NO		10°	0.09	0.55	6.0	2	2	2	2	3.5	~5	11
Ba+O-ONC ₃ H ₇		30°	0.15	0.68	4.5	2	1	2	2	2.9	~15	~35
Sr+O-ONC ₃ H ₇		10°	0.15	0.56	4.3	2	1	2	2	1.4	~5	~0
Ca+Cl-CCl ₂ NO ₂		15°	0.20	0.57	7.0	2	1	2	2	1.8	8.5	~35

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

^bThese are parameters of the $T(\theta)$ function employed in Ref. 1d; $\theta_1 = \theta_2 = 0^\circ$ for all reactions except that $\theta_1 = 5^\circ$ for Sr + C₃H₇NO₂ and Ca+CCl₃NO₂.

^cThese are parameters of the distribution function employed in Ref. 1d for the recoil speed of the detected product.

^d \bar{E}' , the most probable recoil energy, is obtained from: $dP(E')/dE'|_{E' = \bar{E}'} = 0$.

$e\langle\bar{E}'\rangle$ is the average product recoil energy. Energies given in parentheses refer to formation of an alkaline earth dihalide product.

$f\Delta D = D(MX) - D(R-X)$; D taken from: for MF and MCl: D. L. Hildebrand, J. Chem. Phys., 48, 3657 (1968); 52, 5751 (1970); for MO: Ref. 31; for SF₆: D. L. Hildebrand, J. Phys. Chem., 77, 897 (1973); for NO₂: Ref. 21; for CCl₃NO₂, assumed same as CCl₄: Ref. 1d; for other bonds, estimates² from Ref. 32.

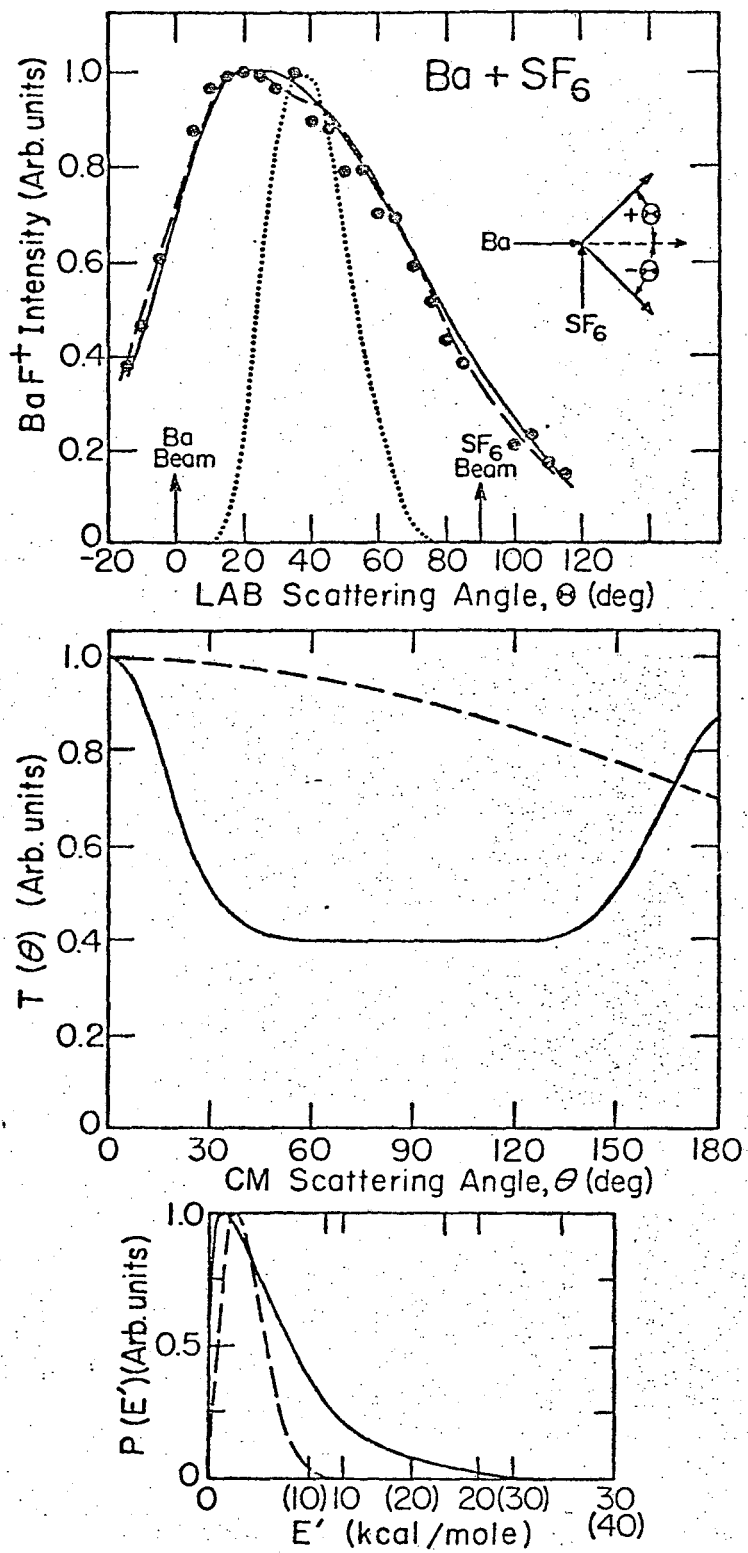
g Gaussian part of $T(\theta)$ reflected through 90° and multiplied by 0.75.

FIGURE CAPTIONS

- Fig. 1. Data points in upper panel show measured LAB angular distribution of BaF^+ signal from $\text{Ba} + \text{SF}_6$. Lower panels show derived CM $T(\theta)$ and $P(E')$ distributions which are also given in Table III as A (solid curve) and B (dashed curve). On the $P(E')$ plot, abscissa numbers in parentheses refer to $\text{BaF}_2 + \text{SF}_4$ products, numbers without parentheses refer to $\text{BaF} + \text{SF}_5$ products. The convention followed is that the solid $T(\theta)$ must be used in combination with the solid $P(E')$ to produce the corresponding solid curve fit to the data shown in the upper panel. Also shown in the upper panel is a calculated angular distribution of \bar{C} (dotted curve).
- Fig. 2. Upper panel: Data points show measured LAB angular distribution of BaCl^+ signal from $\text{Ba} + \text{PCl}_3$ as well as the fit to the data provided by the CM $T(\theta)$ shown in the lower panel together with the $P(E')$ specified in Table III. Dotted curve shows the calculated angular distribution of \bar{C} . Middle panel: LAB results on the $\text{Sr} + \text{PCl}_3$ reaction; conventions are as in the upper panel. Lower panel: Comparison of derived CM product angular distributions for Ba (solid curve) and Sr (dashed curve) + PCl_3 .

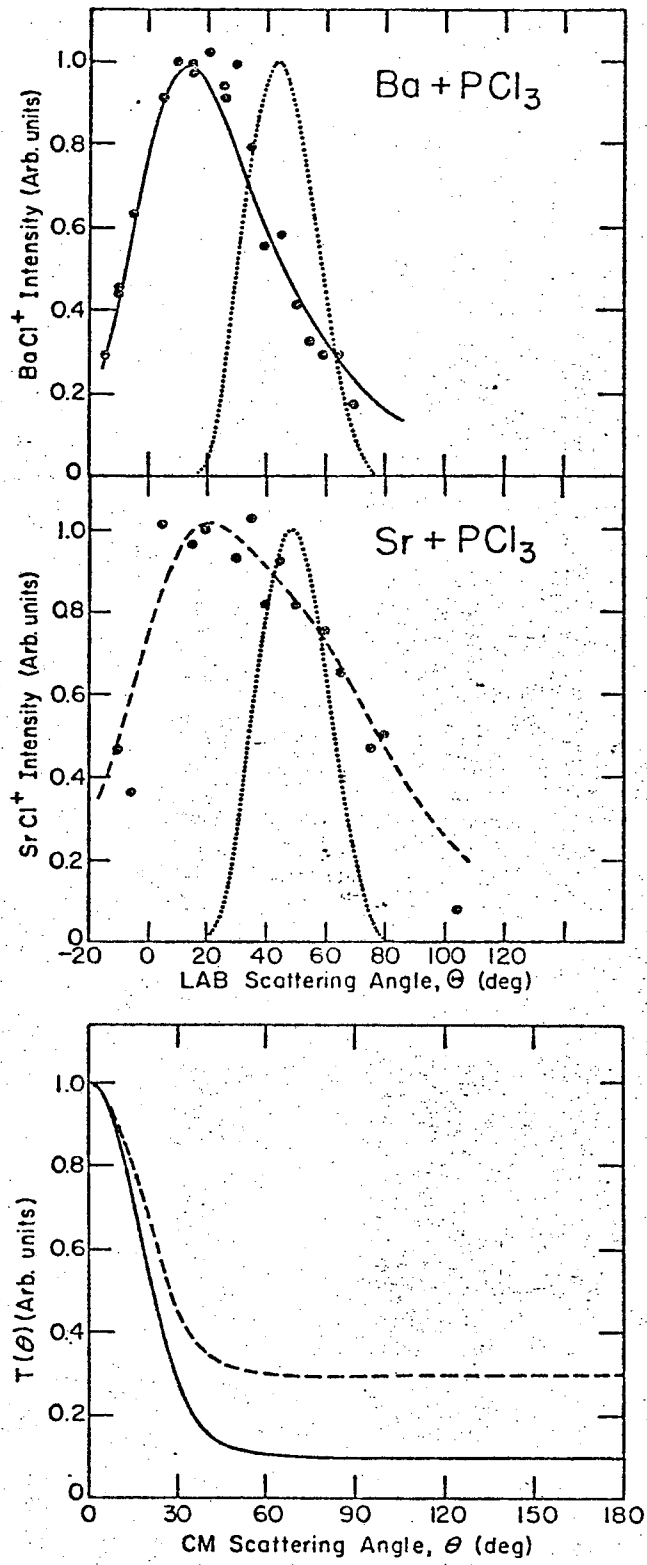
Fig. 3. Two upper panels: LAB product angular distributions from Sr and Ca + NO₂; solid curves through data points show fits provided by CM distributions given in Table III; dotted curves show calculated angular distributions of \bar{C} . Lower panel: Range of "likely" CM product angular distribution for these reactions.

Fig. 4. Measured LAB angular distributions from Ba and Sr + (CH₃)₂CHNO₂ and Ca + CCl₃NO₂; conventions as in Fig. 3.



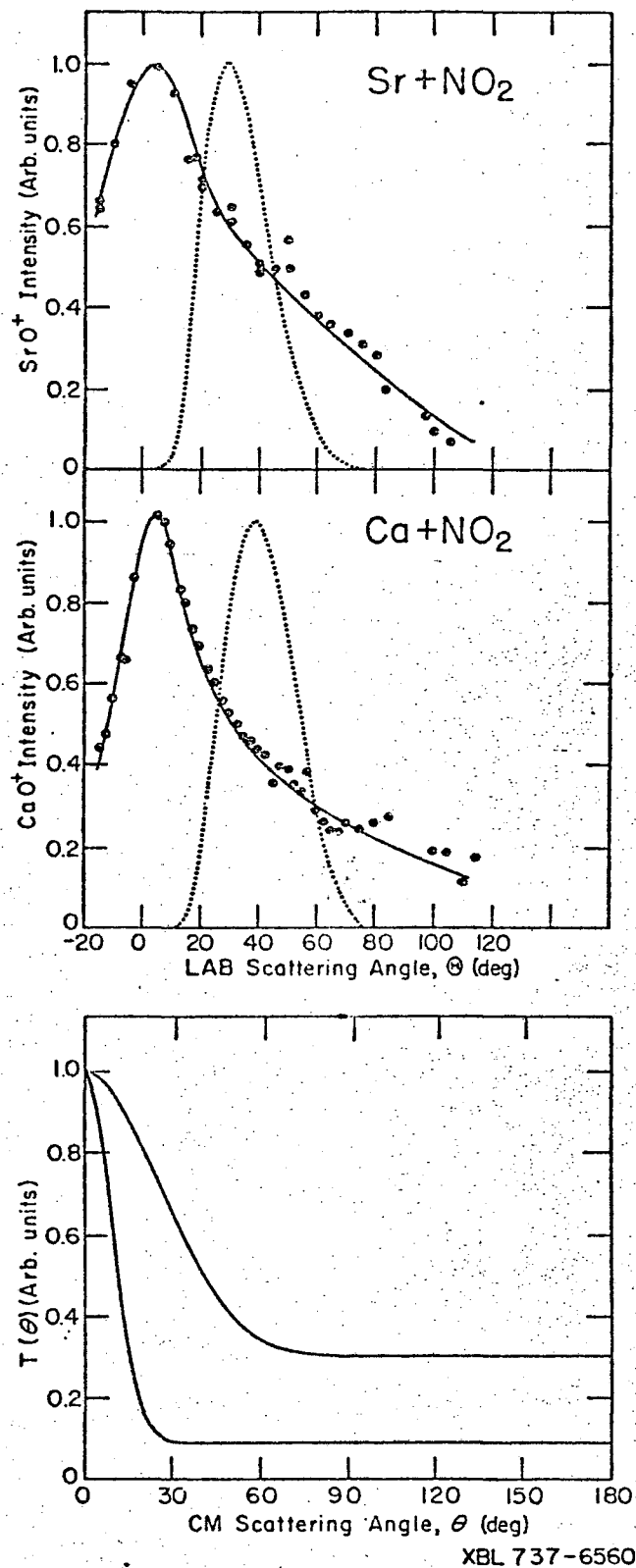
XBL 7210-7093b

Fig. 1



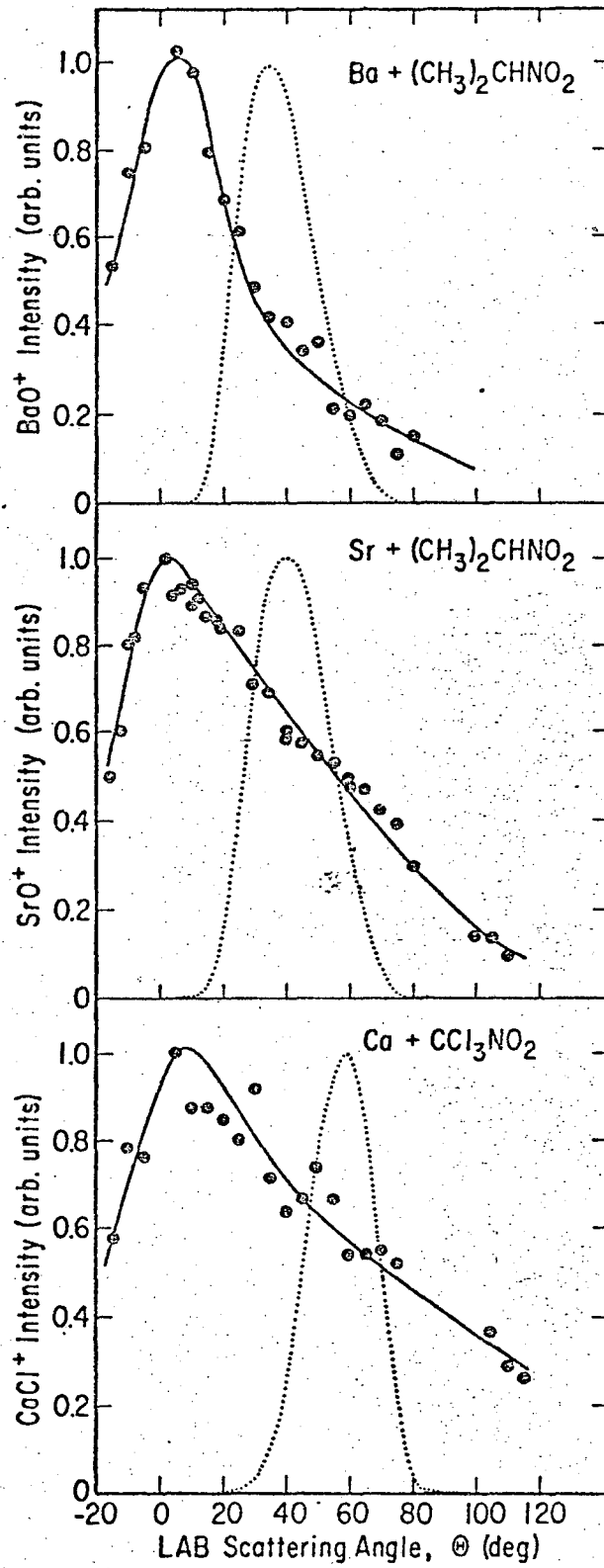
XBL737-6559

Fig. 2



XBL 737-6560

Fig. 3



XBL 737-6561

Fig. 4

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