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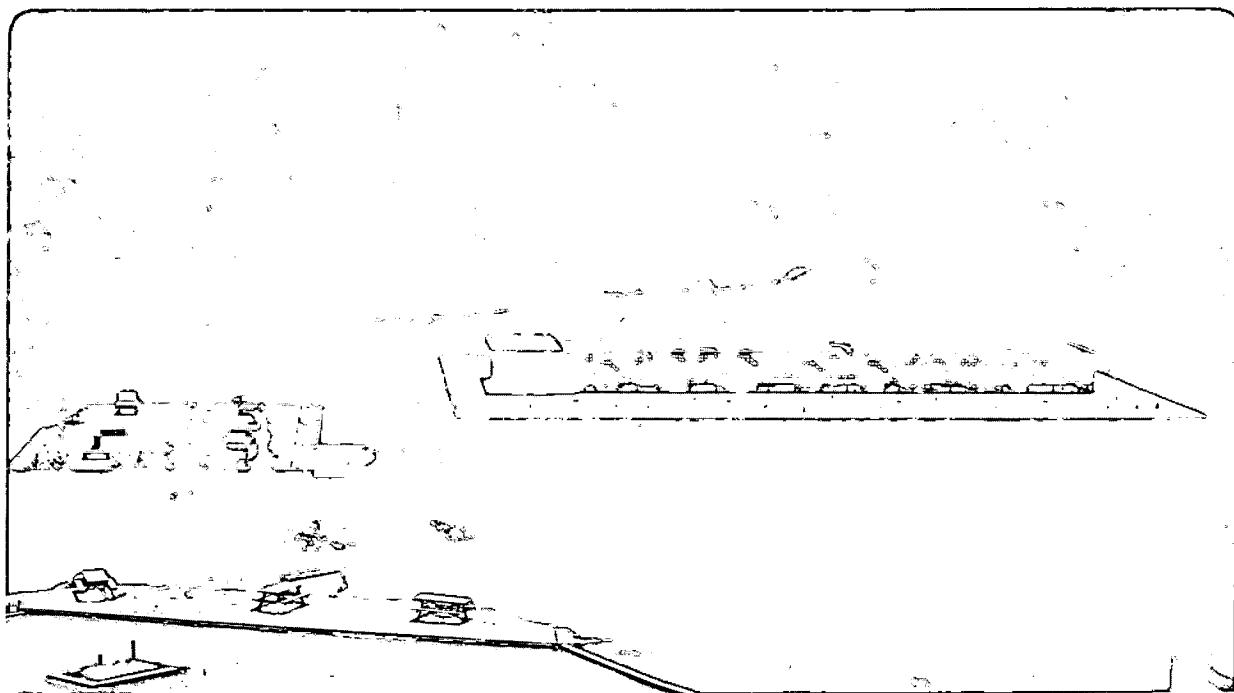
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**REACTION DYNAMICS FROM ORBITAL ALIGNMENT DEPENDENCE
AND ANGULAR DISTRIBUTIONS OF IONS PRODUCED IN COLLISION OF
Ba(¹P) WITH NO₂ AND O₃**

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**Reaction Dynamics from Orbital Alignment Dependence
and Angular Distributions of Ions Produced in Collision of
Ba(¹P) with NO₂ and O₃**

Abstract

Angular distributions, orbital alignment dependence and energy dependence of the relative cross sections of various ions produced in crossed beams collisions of electronically excited barium with O₃ and NO₂ were used to explore the dynamics of these reactions. The Ba⁺ product from both reactions showed strong dependence on alignment of the Ba(¹P) p orbital with respect to the relative velocity vector. The Ba⁺ was generally forward or forward-sideways scattered, with the latter favored by the dominant perpendicular orbital alignment. Similar results for Ba⁺ from both O₃ and NO₂ suggest that electron transfer is favored for large impact parameter collisions in which the Ba p orbital is directed toward the molecule at the critical configuration, regardless of the symmetry of the available orbital in the isolated molecule. BaO₂⁺ from the O₃ reaction exhibited angular distributions and energy dependences which were reminiscent of the Ba⁺ albeit two orders of magnitude lower in intensity, indicating a close relationship between these two channels. Important differences in the dynamics for the BaO⁺ channel were suggested in the angular distributions, which show a substantial backscattered component, as well as the alignment effects and energy dependence. These indicate that the BaO⁺ probably derives from neutral BaO^{*} which is sufficiently internally excited to undergo vibrational autoionization.

I. Introduction

The reactions of ground state barium with ozone and NO_2 are substantially exothermic process yielding both ground state and electronically excited products.¹⁻³ Owing to the high yield of chemiluminescent BaO^* , the reactions were extensively studied in the early 70's as possible media for a visible-wavelength laser.⁴⁻⁷ Although the predominance of ground state products eventually dissolved the dreams of a barium chemical laser, these reactions have proved to be a fruitful source of insight into the reaction dynamics of divalent systems.

Studies of the neutral products from reaction of $\text{Ba}(^1\text{S}_0)$ with O_3 and NO_2 in our laboratory^{8,9} have shown that, despite the large exoergicity (> 4 eV), the ground state reaction involves a long-lived (several rotational periods) collision complex. A direct reaction, probably responsible for the electronically excited states of BaO , is also observed.⁸ In addition, from the ozone reaction we reported the first gas phase observation of BaO_2 , which appeared to result exclusively from long-lived Ba-O_3 complexes. The maximum BaO_2 translational energy release yielded a lower bound of 120 kcal/mole for the Ba-O_2 bond energy, implying very large reaction exoergicities (-4.42 eV) for this channel as well.⁸ The existence of a long-lived complex despite the presence of these exoergic product channels implies a substantial barrier to its decay. This is also suggested by the translational energy distributions which are observed to peak away from zero. At higher translational energy the novel product BaNO was

observed from the NO_2 reaction, though its forward-sideways scattered angular distribution indicated a direct reaction in that case. These reactions, aside from the formation of BaNO , are initiated by long-range electron transfer yielding the singly ionic complexes Ba^+-O_3^- or $\text{Ba}^+-\text{NO}_2^-$. However, both ground state BaO and BaO_2 are thought to be well represented as doubly ionic species⁸⁻¹⁰. The production of ground state products from the initially formed complex requires substantial electronic rearrangement. The long lived complexes thus probably result from a barrier to the transfer of the second electron. The structure of these complexes and the dynamics of their decay have been the topics of discussion in our recent crossed molecular beam investigation.

Excitation to the $\text{Ba}(^1\text{P}_1)$ electronic state adds an additional 2.1 eV to the system. This results in the occurrence of the first intersection of the ionic and covalent potential energy surfaces at very long range. The vertical electron affinity of O_3 is 2.1 eV¹¹, implying an outer crossing distance of 14.8 Å. The inner crossing, corresponding to the transfer of the barium s electron, occurs at just 4.0 Å. At the outer crossing, the coupling between the diabatic surfaces is considerably weakened¹²⁻²¹ so that nonadiabatic transitions become increasingly important. Furthermore, the symmetries of the initially prepared covalent molecular state may be defined by the relation of the laser polarization with the relative velocity vector and the collision plane.^{22,23} This can result in profound dependence of the electron transfer probability on initial orbital alignment. Studies of alignment effects in atom-atom collisions has proceeded rapidly with the development of tunable narrow band lasers, and there now exist several clearly

understood examples. Only in a few cases have alignment effects been reported for reactive systems, but in those few examples the insight afforded into the details of the collision process has been remarkable. Recently we reported strong dependence of chemiionization cross sections and angular distributions on alignment of the barium p orbital in crossed beams collision of $\text{Ba}(^1\text{P}_1)$ with halogen molecules.^{24,25} The reaction with Br_2 revealed the importance of perpendicular alignment of the orbital with respect to the relative velocity vector. Different dependence observed for out-of-plane and in-plane orbital alignment showed that the reaction was dominated by large impact parameter collisions which achieved a Σ configuration at the crossing point. In addition, the change of the peak of the alignment dependence with scattering angle directly revealed the impact parameter dependence of the scattering distributions. The strong alignment dependence observed in the Br_2 reaction was understood in terms of the increasing importance of nonadiabatic behavior at crossings in the 10-15 Å range, and the sensitivity of the observed ion channels to these nonadiabatic transitions. The Br_2 results suggested that ion production in other systems with curve crossings in the 10-15 Å range might show similarly strong alignment effects, allowing for some generalization of those conclusions.

For O_3 and NO_2 , the additional energy and increased complexity of the system allow for a range of ionic product channels, and these can provide considerable insight into reaction dynamics involving several electronic potential energy surfaces and possible product channels. Despite the reduced symmetry of these systems, again very strong alignment were observed for various ion products. In addition to alignment dependences

and angular distributions, the energy dependence of the relative cross sections were used to gain insight into the broad range of dynamic behavior exhibited by these reactions. Some of the results can shed light on the direct components of the neutral reaction channels as well.

Values for several thermodynamic quantities result directly or indirectly from these studies. For example, appearance thresholds may be used in conjunction with known bond energies to obtain lower limits for ionization potentials. In addition to reaction with ozone, the associative ionization reaction with O_2 was studied to obtain a threshold for BaO_2^+ formation. This value is of some importance in considering the fate of Ba^+ in the atmosphere,²⁶ as well as having direct bearing on the energetics of the O_3 reaction.

The chemiion channels in reaction of $Ba(^1P_1)$ with O_3 and NO_2 show many remarkable similarities; in fact the results are almost identical except where the different thermodynamics dictate obvious differences. As a result, we have chosen to focus our study on O_3 , where the extra exoergicity affords stronger ion signal. We will present some results for NO_2 , however, to illustrate the parallel behavior and to facilitate a discussion of this somewhat surprising result.

II. Experimental

The experiment was performed in a crossed molecular beams machine which has been described in detail elsewhere.^{27,28} A supersonic barium atomic beam²⁹ crossed a

molecular beam at 90° under single collision conditions in a scattering chamber, typically 10^{-7} Torr for the ion experiments described here. The $(2 \text{ mm})^3$ interaction region of the two beams was surrounded by a metal cage which was electrically floated at a positive potential with respect to ground and was viewed by a triply differentially pumped quadrupole mass spectrometer which could be rotated in the plane of the two beams. Positive ions formed in the interaction region of the two beams entered a set of ion optics and retarding field energy analyzer³⁰ mounted on the front of the rotatable detector (Figure 1) and were then focused into the entrance of the quadrupole mass spectrometer and detected by a Daly-type scintillation ion detector. The existing electron bombardment ionizer of the detector was either grounded or biased slightly above ground potential to act as a further focusing element. A narrow band cw laser was directed into the interaction region as illustrated in Figure 2. For most experiments the laser was directed perpendicular to the plane of the molecular and atomic beams, allowing for rotation of the p orbital in the collision plane (Figure 2a). In this geometry, the angle of the laser polarization with respect to the relative velocity vector is designated β , and the peak polarization angle β' . Alternatively, the laser was directed antiparallel to the molecular beam allowing for rotation of the p orbital out of the collision plane. The polarization angle, θ , is then defined with respect to a line perpendicular to the collision plane as shown in Figure 2b. The possible experimental measurements were thus angular distributions of mass selected ions as a function of laboratory scattering angle, collision energy and laser polarization.

The NO_2 and O_3 beams were seeded $\sim 10\%$ in helium and expanded through a 0.075 mm nozzle heated to 200 °C to inhibit cluster formation. Two different methods were used to generate the ozone beam: for most experiments, the ozone was trapped on silica gel as described elsewhere. This method inevitably results in residual O_2 contamination, typically about 10% of the O_3 concentration. The residual O_2 generally produced no interference in the ion experiments since the ion channels in the O_3 reaction are so much more exoergic than for O_2 . But at some collision energies, particularly for BaO_2^+ which is weak in the O_3 reaction, the O_2 contamination was intolerable. For the relative cross section measurements and the BaO_2^+ angular distributions, in which O_2 contamination was unacceptable, the beam of ozone was produced by bubbling He through liquid O_3 , giving an O_3 of $\sim 3\%$.³¹

III. Results

Positive ions resulting from reaction of $\text{Ba}(^1\text{S}_0)$ and $\text{Ba}(^1\text{P}_1)$ with ozone were studied as a function of scattering angle, orbital alignment and collision energy. At a nominal collision energy of 1.1 eV, only BaO_2^+ and BaO_3^+ were observed from the ground state reaction, and both were very weak. However, from the excited state reaction at this collision energy all barium containing positive ions were observed: Ba^+ , BaO^+ , BaO_2^+ , and BaO_3^+ . Laboratory angular distributions were measured for all of these products of the excited state reaction. In addition, for Ba^+ and BaO^+ , dependence of the cross sections on alignment on the barium p orbital was measured at several

laboratory angles. The signal intensity for BaO_2^+ and BaO_3^+ was too low to provide useful data for alignment dependence studies.

A. Thresholds for BaO_2^+ and BaO_3^+ formation

A threshold for the appearance of BaO_2^+ was obtained in studies of the ground state associative ionization reaction of barium with molecular oxygen. No BaO_2^+ was observed at a nominal collision energy of 0.9 eV. At 1.5 eV the reaction was observed, very weakly, at the center of mass angle. This threshold is substantially higher than the only previously reported value,³² 0.2 eV, and possible sources of the discrepancy will be considered in the discussion.

The threshold for associative ionization of ground state Ba with O_3 could be fixed at a collision energy of 1.2 ± 0.1 eV because at this nominal collision energy the BaO_3^+ signal appeared as the O_3 concentration of the O_3/He beam was lowered, i.e., as the O_3 beam velocity was increased slightly. This implies that the collision energy was very near threshold.

B. Orbital Alignment Dependence and Angular Distributions at 1.1 eV

1. Ba⁺

The Newton diagram for collision of Ba with O₃ at 1.2 eV collision energy is shown in Figure 3. The analogous Newton diagram for NO₂, not shown, is almost identical. Angular distributions of Ba⁺ from reaction of Ba(¹P₁) + O₃ are shown in Figure 4. The two scans were performed with the Ba p orbital aligned in the collision plane and either along or perpendicular to the relative velocity vector. These angular distributions are quite reminiscent of the those obtained for Ba⁺ from reaction with Br₂ reported previously.²⁵ Both distributions in Figure 4 are largely forward of the center of mass, and the result for perpendicular alignment is substantially higher in intensity. In addition, the perpendicular distribution shows a larger contribution from angles behind the center of mass.

The dependence of scattered Ba⁺ signal on alignment of the Ba p orbital is shown in Figure 5 for in-plane rotation of the laser polarization for reaction with O₃. These polarization scans are shown along with a typical example of the fluorescence intensity which was recorded simultaneously. Both are fit by the expression:³³

$$I(\beta) = \frac{(I_{\max} + I_{\min})}{2} + \frac{(I_{\max} - I_{\min})}{2} \cos 2(\beta - \beta').$$

This yields values for $(I_{\max} - I_{\min})/I_{\min}$ and β' , which are presented in Table 1 for the data of Figure 5. A definite trend is evident in β' , which ranges from 47° at the rearmost angles to $\sim 110^\circ$ for the most forward scattered Ba^+ . The ratio $(I_{\max} - I_{\min})/I_{\min}$ shows a trend as well, reaching a value of 2.2 at the back angles and dropping to .14 at 7.5° . In-plane alignment dependence for Ba^+ from reaction with NO_2 is shown at laboratory angles of 15° and 20° , along with the corresponding O_3 results, in Figure 6. Although the polarization effect appears weaker in the NO_2 case, the experiments were performed under somewhat different conditions so that it would be difficult to draw conclusions from the relative magnitude of the effect. But the location of the alignment peak, β' , is nearly identical for the two molecules at both angles.

2. BaO^+

The angular distribution of BaO^+ from the reaction of $\text{Ba}(^1\text{P}_1)$ with O_3 is shown in Figure 7 for in-plane ($\beta = 35^\circ$) and out-of-plane alignment of the p orbital. These distributions show several important differences from the Ba^+ result. The out-of-plane orbital alignment is somewhat favored at most angles, quite the reverse of what is observed for Ba^+ . In addition, although the BaO^+ is seen to peak somewhat forward of

the center of mass angle, nearly 50% of the distribution appeared at angles behind the center of mass.

Figure 8 shows the orbital alignment dependence recorded for BaO^+ for out-of-plane rotation of the p orbital at laboratory angles 10 and 15 degrees. The BaO^+ appears somewhat favored by out-of-plane alignment of the orbital, with little difference on going from 10° to 15° . The angular distributions of Figure 7 further imply little change in this behavior with laboratory scattering angle.

3. BaO_2^+ , BaO_3^+

The laboratory angular distribution of BaO_3^+ from reaction of $\text{Ba}(^1\text{P}_1)$ with O_3 is presented in Figure 9. Because the associative ionization product BaO_3^+ is recoiling from an electron, with less than $1/10^5$ its mass, conservation of momentum requires that it appear in the vicinity of the direction of the center of mass in the laboratory coordinate system.

Associative ionization of Ba with O_2 contamination of the O_3 beam was found to yield an unacceptable background BaO_2^+ signal, so the BaO_2^+ channel from the ozone reaction was studied using purified O_3 as described in the experimental section. These conditions resulted in a slightly higher collision energy (1.23 vs. 1.1 eV) and a shift in the location of the center of mass from $\sim 15^\circ$ to $\sim 17^\circ$. Figure 10 shows the BaO_2^+ angular distribution which is slightly forward scattered, with none of the tail which was associated with the BaO^+ distribution.

B. Energy dependence of the relative cross sections.

Angular distributions were obtained for Ba^+ , BaO^+ , BaO_2^+ and BaO_3^+ products at 4 collision energies: 0.7, 0.9, 1.2 and 1.9 eV. The angular distributions were integrated and scaled by the relative barium beam flux (obtained from the fluorescence intensity and beam velocities) to explore the energy dependence of the relative cross sections. These angular distributions were all performed using purified liquid ozone, so that O_2 contamination was minimal. No attempt was made to obtain center of mass distributions, so the integrated intensities are uncorrected for the LAB \rightarrow CM transformation Jacobian or out-of-plane scattering of products. In cases in which a portion of the forward distribution was too close to the barium beam to be measured, its contribution was estimated and included. This results in relative cross sections accurate to within perhaps a factor of three between ions and significantly better for the energy dependence of a given ion channel. Figure 11 shows the trends which emerge from these measurements. In Figure 11a, the integrated intensities are all plotted on the same scale so that their relative magnitudes may be estimated. In Figure 11b, the same data is rescaled as indicated so that the nature of the energy dependence of the weaker channels may be discerned.

The most striking feature of Figure 11 is the obvious parallel between the behavior of Ba^+ and BaO_2^+ , despite the fact that the cross sections differ by nearly two orders of magnitude. The strong increase with collision energy is analogous to the

behavior of ion pair production in alkali atom-halogen molecule collisions, so it is not surprising for Ba^+ . But the similarities indicate that Ba^+ and BaO_2^+ are indeed very closely related channels.

The BaO^+ results, however, clearly imply a different origin. The energy dependence suggests a barrier with little change in cross section at energies beyond the threshold region. This is similar to the behavior seen for BaO_3^+ , but for the latter, the barrier probably represents simply the endoergicity of the associative ionization process.

IV. Discussion

A. Thresholds for BaO_2^+ and BaO_3^+ formation

The thermodynamic quantities obtained above are presented in Figure 12, along with established values for a variety of the reactions considered. The previously reported value³² of 0.2 eV for the threshold for BaO_2^+ formation in Ba- O_2 collisions was obtained in an experiment in which a sputtered Ba beam, containing kinetic energies in the range from thermal to >100 eV, was crossed by a supersonic O_2 beam. The threshold was obtained from the maximum scattering angle observed, which was assumed to correspond to the center of mass angle of the slowest reacting Ba atoms. The O_2 beam velocity was not measured, and its angular and velocity spreads were neglected in obtaining the threshold. Although a number of the assumptions employed are somewhat crude, they are not sufficient to account for the discrepancy between their 0.2 eV and our 1.3 eV

thresholds. The most likely explanation is the production of electronically excited metastable Ba($^1,^3D$) atoms, containing an additional 1.1 eV of energy, in the sputtering process. This would reconcile the two measurements quite well. Alternatively, the question of O₂ dimers was not discussed in the previous work, and this could also lead to underestimation of the Ba-O₂ associative ionization threshold. The O₂ velocity given (740 m/s) implies a room temperature nozzle, which would certainly result in the formation of dimers. If dimers were responsible for the maximum scattering angle (taken to be 8°) this would imply a threshold for Ba + (O₂)₂ → BaO₂⁺ + O₂⁻ or BaO₂⁺ + O₂ + e⁻ of 1.48 eV, more in line with our result. Further support for the higher value comes when considering the implications for the ionization potential of BaO₂. We previously obtained a value of 5.2 ± 0.5 eV for D₀(Ba-O₂).⁸ Assuming that the thresholds derive from the fastest components of our beams, a 10% spread in beam velocity suggests an appearance energy for Ba + O₂ → BaO₂⁺ + e⁻:

$$1.0 < E_{\text{th}} < 1.7 \text{ eV} .$$

When combined with the value for the bond energy given above, this implies

$$6.2 \pm 0.5 \text{ eV} < \text{I.P. BaO}_2 < 6.9 \pm 0.5 \text{ eV} .$$

The corresponding value given the previously reported BaO₂⁺ threshold is only 5.4 eV, only slightly higher than the ionization potential of atomic barium. The ionization potential of BaO has been fixed in several experiments at 6.9 ± 0.2 eV. It seems reasonable, particularly given the strong BaO₂ bond, that the ionization potentials of the two species, BaO and BaO₂, should be comparable. Owing to the weakness of the BaO₂⁺ signal observed from ground state reaction with O₂ even at 1.5 eV collision energy, we

suggest that the actual threshold is nearer the higher energy, and recommend a value of 6.7 ± 0.5 eV for the ionization potential of BaO_2 .

The threshold obtained for BaO_3^+ from ground state Ba reaction with O_3 may be used to estimate the Ba- O_3 binding energy. BaO_3 has not been directly observed in the gas phase before, but the existence of long-lived complexes in Ba- O_3 reactions implies a substantial bond energy. If Ba- O_3 is assumed to be a single electron ionic bond, then the ionization potential of BaO_3 should, like BaBr, be somewhat lower than that of atomic barium (5.1 eV); for BaBr the value is 4.8 eV. This yields a value for the bond energy of Ba- O_3 :

$$\begin{aligned} D_0(\text{Ba-O}_3) &= \text{IP}_{\text{BaO}_3} - E_{\text{thr}} \\ &= 4.8 \pm 0.2 - 1.2 \pm 0.1 = 3.6 \pm 0.3 \text{ eV} \\ &= 82 \pm 7 \text{ kcal/mole.} \end{aligned}$$

This provides the estimated location of the neutral BaO_3 shown in Figure 12.

B. Ba^+

The angular distributions and in-plane orbital alignment dependence for Ba^+ shown in Figures 4 and 5 are quite reminiscent of the Br_2 results described previously. In the bromine reaction two configurations were thought to be favorable for electron transfer owing to a conical intersection^{34,35} of the potential energy surfaces: for collisions which attain C_{2v} symmetry, charge transfer is favored by alignment in which the p orbital is perpendicular to the symmetry axis and lies in the plane of the body-fixed frame, while for collisions which attain $C_{\infty v}$ symmetry, parallel alignment favors electron transfer. A

strong dependence of electron transfer probability on orbital alignment and internuclear geometry thus results. The tendency to forward scattering exhibited by the parallel orbital alignment was ascribed to the importance of the covalent trajectories for low impact parameter collisions. These are the trajectories which avoid electron transfer at the first crossing and in which the ion pair is produced in electron transfer on exit. Small impact parameter collisions which transfer the electron at the first crossing on approach were thought to favor the formation of neutral BaBr and Br, or the chemiion channel yielding BaBr^+ and Br^- when the collision is strictly collinear. The sideways- or less forward-scattered distributions associated with the dominant perpendicular orbital alignment revealed the overall importance of large impact parameter collisions. The sideways scattering is anticipated for large impact parameter collisions yielding ion pairs since the strong Coulombic attraction may produce substantial deflection. The overall importance of perpendicular alignment is a consequence of the greater statistical weight associated with the range of impact parameters in such collisions as well as the increased likelihood for electron transfer resulting from the prolonged excursion through the crossing region for these trajectories. The strong dependence of peak alignment angle on laboratory scattering angle directly revealed the impact parameter dependence of the scattering distributions, as suggested by the schematic illustration in figure 3. The results for out-of-plane polarization rotation were interpreted assuming that initial and final orbital angular momenta were roughly equal. The fact that Ba^+ was favored by alignment of the orbital in the scattering plane independent of scattering angle further indicated that large impact parameter collisions were dominant. Large impact parameter

collisions in which the orbital is aligned perpendicular to the plane will only reach a collinear configuration when the bromine molecule lies perpendicular to the plane. In this case, the orbital angular momentum of reactants lies in the plane of the detector and beams, so the products are generally scattered out of the plane of the detector. Even though these collisions favor ion production, the resulting ions are not detected. The evidence thus indicated that at large impact parameters the initially prepared π orbital alignment (the p orbital perpendicular to the relative velocity vector) corresponded to a Σ configuration (in the molecular frame) at the crossing seam, and the result of electron transfer is the formation of Ba^+ and Br_2^- ion pairs.

For $\text{Ba}(^1\text{P}_1)$ collision with O_3 and NO_2 the problem is considerably more complex, yet similarities between the alignment results for all three systems indicate that the solution may actually be quite simple. Analogy with the Br_2 result suggests that here, too, Ba^+ production is favored from large impact parameter collisions in which the orbital is directed in toward the molecule at the crossing point. Considering C_{2v} geometry, in the case of NO_2 electron transfer from the barium atom fills the $6a_1$ orbital, resulting in a $\text{Ba}^+-\text{NO}_2^-$ complex of overall A_1 symmetry. This orbital is already filled in the case of O_3 , so the first electron must enter the $2b_1$ orbital. In both O_3 and NO_2 there exist excited states of the anion, but these are considerably higher in energy hence are less likely to be important here. Nevertheless at first it might seem puzzling that, although the symmetries of the relevant orbitals of the isolated molecules are entirely different, O_3 and NO_2 show quite similar behavior. But in fact the overall symmetry of the problem has been greatly reduced: genuine C_{2v} collisions are exceedingly rare. The

similarities between O_3 and NO_2 indicate that the dominant geometries favoring electron transfer do not achieve C_{2v} configuration, otherwise some distinction between them would be expected to appear. It seems reasonable to suggest that the importance of the Σ orbital alignment (in the body-fixed frame) may derive largely from the fact that the electron density is closer to the molecule and effective interaction can occur even when internuclear geometries are not optimal.

C. BaO_2^+

Ozone exhibits two resonances in dissociative electron attachment: at zero energy there is a resonance producing O^- and O_2 , and at 0.4 eV another resonance yielding O_2^- and O .³⁶ The zero energy resonance implies that the electron affinity exceeds the O^-O_2 binding energy, and a number of measurements bear this out.^{11,37,38} The electron affinity of O_3 is well established at 2.1 eV, while several measurements have placed the O^-O_2 bond energy at 1.8 eV. The higher threshold for the appearance of O_2^- is a consequence of the lower electron affinity of O_2 (0.43 eV) versus O (1.45 eV).³⁹ The existence of the zero energy resonance indicates that electron transfer is likely to produce highly excited O_3^- . Electron transfer from a barium atom to ozone will not result in this 2.1 eV being available for dissociation of the ozonide ion since, in effect, it has been harnessed to ionize the barium atom in the first place. Nevertheless, the O_3^- will be formed in a repulsive region of the potential energy surface, and dissociation in the field of the barium ion will occur quite readily. The resulting fragments may subsequently interact

with the departing Ba^+ . For low impact parameter collisions, this will generally result in the formation of neutral products BaO and O_2 , since the ion pairs will exhibit a strong attraction for each other. For certain favorable collision geometries and large impact parameter collisions, however, the departing Ba^+ may encounter the neutral O_2 fragment from the dissociating O_3^- . Our value for the BaO_2^+ appearance threshold implies a substantial 90 kcal/mol Ba^+-O_2 bond energy, and the R^{-4} ion-induced dipole potential allows for fairly long range Ba^+-O_2 interaction. This picture is suggested by the strong parallels which appear in the Ba^+ and BaO_2^+ channels. Although the BaO_2^+ shows some tendency to forward scattering reminiscent of the Ba^+ , the remarkably similar energy dependences shown by these two channels provides the most convincing evidence. The relative weakness of the BaO_2^+ signal, lower in intensity than Ba^+ by a factor of 100, is not surprising given the expected rarity of effective secondary encounters. Secondary interaction between Ba^+ and O^- is much more likely owing to the Coulomb attraction between them, but the result of this will be a contribution to the neutral BaO signal which would be very difficult to detect against the large BaO background from the ground state reaction. The BaO_2^+ thus can be thought of as deriving directly from the dominant Ba^+ channel through those relatively rare collisions in which the departing Ba^+ encounters an O_2 fragment from the dissociating O_3^- . In fact, this BaO_2^+ represents additional evidence for the importance of large impact parameter collisions in the Ba^+ channel, its parent. For low impact parameter collisions, the neutral products would certainly dominate and no BaO_2^+ would be expected.

D. BaO⁺

The results for BaO⁺ from reaction of Ba(¹P₁) with O₃ are unlike the other ion channels in every respect. The out-of-plane orbital rotation scans of Figure 8 favored perpendicular alignment apparently independent of scattering angle. Furthermore, this was the only ion channel in these studies to feature a significant backscattered contribution in its laboratory angular distribution. Finally, the energy dependence showed a threshold at about 0.9 eV, and little change in cross section was observed at energies above this. Both the angular distributions and the insensitivity of the out-of-plane alignment results to scattering angle suggest a larger role for low impact parameter collisions in this case. However, the nature of the alignment dependence indicates that the BaO⁺ results preferentially from collisions which avoid electron transfer at the outer crossing. We have argued that in general low impact parameter collisions will favor the formation of neutrals, owing to the opportunity for strong interaction between nascent ions and the fact that the neutral channels are far more exoergic. These considerations hint that the BaO⁺ may in fact derive from the neutral BaO channel. This suggests the following model for the formation of BaO⁺ in Ba(¹P₁)-O₃ collisions: for those collisions which avoid electron transfer at the outer crossing, electron transfer at the second crossing results in the formation of electronically excited BaO^{*} and O₂.^{8,9} A substantial fraction of the BaO may be formed with sufficient internal energy to undergo vibrational autoionization yielding BaO⁺ + e⁻. Results for neutral BaO from the ground state reaction showed translational energy distributions peaking at only ~0.5 eV despite 6 eV

available energy. Much of this is probably tied up in electronic and rotational energy of the products, but the BaO is likely to be highly vibrationally excited as well. Although low impact parameter collisions may be more important for BaO⁺ formation, probably a consequence of the increased likelihood for nonadiabaticity at the outer crossing, the angular distributions nevertheless indicate substantial forward scattering as well. Large impact parameter collisions may result in neutrals from a stripping mechanism⁹ yielding highly vibrationally excited BaO and BaO^{*}, so these collisions may also be important in BaO⁺ formation.

V. Conclusions

Angular distributions, energy dependence of the relative cross sections and orbital alignment effects have been used to explore the reaction dynamics for chemiion channels in collisions of electronically excited barium with O₃ and NO₂. The general features for the Ba⁺ from collision with both triatomics resembles that from the Ba(¹P₁)-Br₂ reaction reported previously: the product is generally forward or forward-sideways scattered, with the latter favored by the dominant perpendicular alignment of the p orbital with respect to the relative velocity vector. The parallels between the results for Ba⁺ from O₃ and NO₂ suggest that the symmetry of the available orbital in the isolated molecule is not important in determining the probability for electron transfer at the outer crossing of the potential energy surfaces. Rather electron transfer appears simply to be favored for large impact parameter collisions in which the orbital is directed toward the molecule.

The BaO_2^+ from the O_3 reaction exhibits angular distributions and energy dependences which are quite reminiscent of the Ba^+ albeit two orders of magnitude lower in intensity. This, in conjunction with the threshold for BaO_2^+ formation, indicate that it derives from the Ba^+ channel as a consequence of those collisions in which the departing Ba^+ encounters a dissociating O_2 fragment.

Important differences in the dynamics for the BaO^+ channel are suggested in the angular distributions, which show a substantial backscattered component, as well as the alignment effects and energy dependence. These are used to suggest that the BaO^+ probably derives from neutral BaO^* which is sufficiently internally excited to undergo vibrational autoionization.

The profound sensitivity of these nonadiabatic channels to the factors governing electron transfer probability at intersections of the electronic potential energy surfaces allow for detailed insight into the underlying reaction dynamics. Thus, despite the complexity of the atom-triatom collision and the tremendous energies available in these reactions, the use of orbital alignment dependences in combination with the traditional crossed beam measurements of angular distributions and energy dependences, allows the complete picture of the reaction to emerge.

Acknowledgement

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Table 1: Ba⁺ In-Plane Alignment Dependence

Lab Angle	$(I_{\max}-I_{\min})/I_{\min}$	β'
10.0°	.14	108°
12.5°	.79	106°
15.0°	.71	97°
17.5°	2.4	64°
20.0°	2.0	60°
22.5°	2.2	53°
25.0°	.6	47°

Table 1: In-plane alignment dependence for Ba⁺ from collision of Ba(¹P₁) with O₃ at 1.1 eV. Values for $(I_{\max}-I_{\min})/I_{\min}$ and β' were obtained from the fits shown in Figure 5.

Figure Captions

- Figure 1. Schematic view of crossed beams apparatus at interaction region.
- Figure 2. Illustration of experimental geometry for a) in-plane and b) out-of-plane rotation of the Ba(1P) orbital alignment.
- Figure 3. Newton diagram for collision of Ba with O₃ at 1.1 eV shown with schematic illustration of ionic trajectories for $\beta = \pm 45^\circ$ illustrating negative correlation between impact parameter and deflection angle.
- Figure 4. Laboratory angular distributions of Ba⁺ from Ba(1P_1)-O₃ collision at 1.1 eV for perpendicular (diamonds) and parallel (squares) alignment of the p orbital with respect to the relative velocity vector. Lines are drawn to guide the eye.
- Figure 5. Orbital alignment dependence of Ba⁺ from Ba(1P_1)-O₃ reaction for in-plane alignment of the p orbital. Laboratory angles are indicated. Also shown is a representative record of the Ba(1P_1) fluorescence monitored simultaneously.
- Figure 6. Orbital alignment dependence of Ba⁺ from Ba(1P_1) reaction with O₃ (A and B) and NO₂ (C and D) at the indicated laboratory angles for in-plane polarization rotation.

- Figure 7. BaO^+ laboratory angular distributions for in-plane ($\beta = 35^\circ$) and out-of-plane ($\theta = 0^\circ$) alignment of the p orbital, from reaction with O_3 at 1.1 eV.
- Figure 8. Orbital alignment dependence of BaO^+ from $\text{Ba}(^1\text{P}_1)\text{-O}_3$ reaction for out-of-plane rotation of the p orbital. Laboratory angles are indicated.
- Figure 9. Laboratory angular distribution of BaO_3^+ from reaction of $\text{Ba}(^1\text{P}_1)$ with O_3 at 1.1 eV.
- Figure 10. Laboratory angular distribution of BaO_2^+ from reaction of $\text{Ba}(^1\text{P}_1)$ with O_3 at 1.2 eV.
- Figure 11. A) Energy dependence of integrated angular distributions for Ba^+ (asterisks), BaO^+ (circles), BaO_2^+ (squares) and BaO_3^+ (triangles). B) The same data as A rescaled: $\text{Ba}^+ (/100)$ (asterisks), $\text{BaO}^+ (/50)$ (circles), $\text{BaO}_2^+ (\times 5)$ (squares) and $\text{BaO}_3^+ (\times 5)$ (triangles). Lines are drawn to guide the eye.
- Figure 12. Relative energies for electronic ground states of ion and neutral channels for Ba-O_3 reaction.

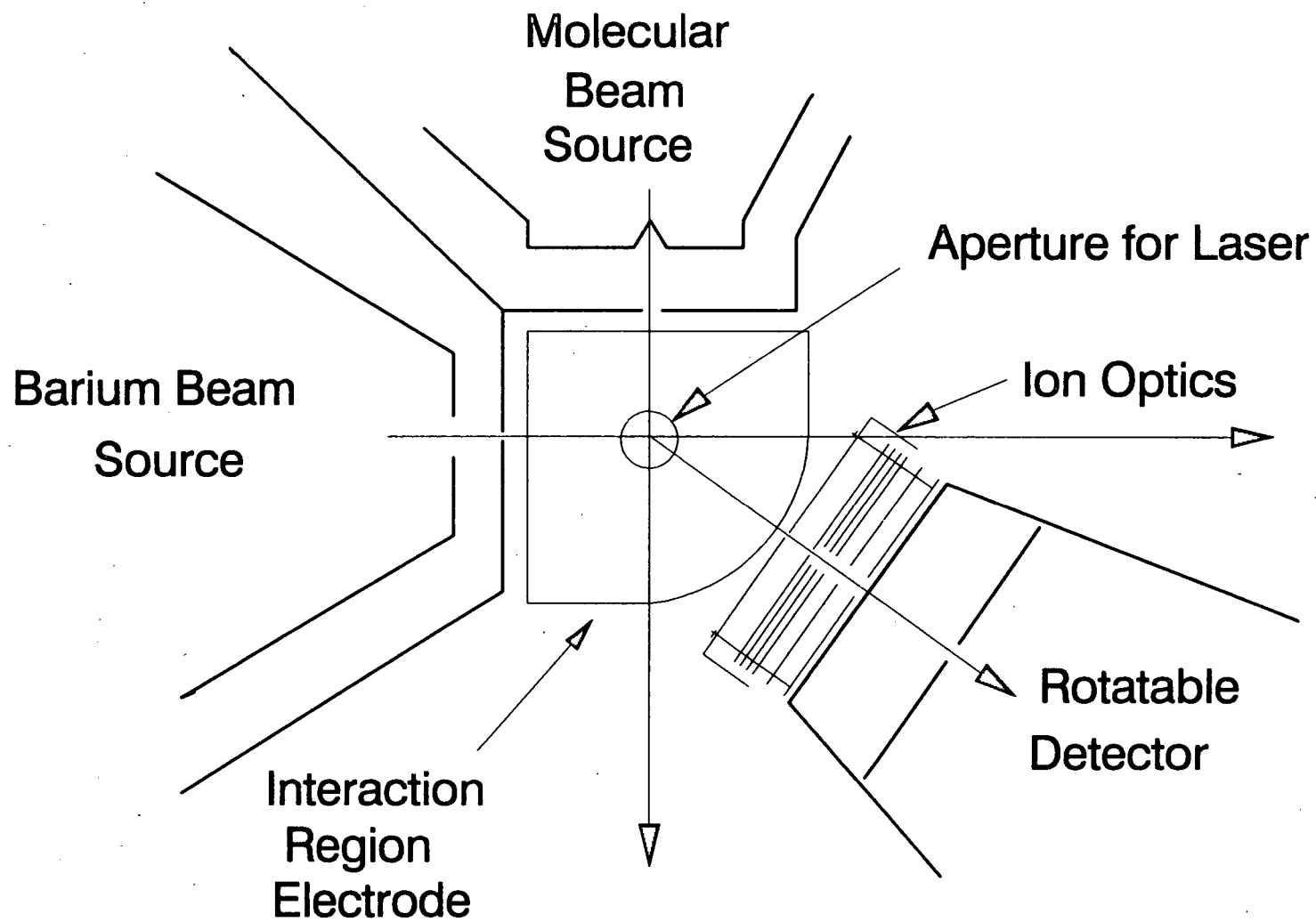


Figure 1

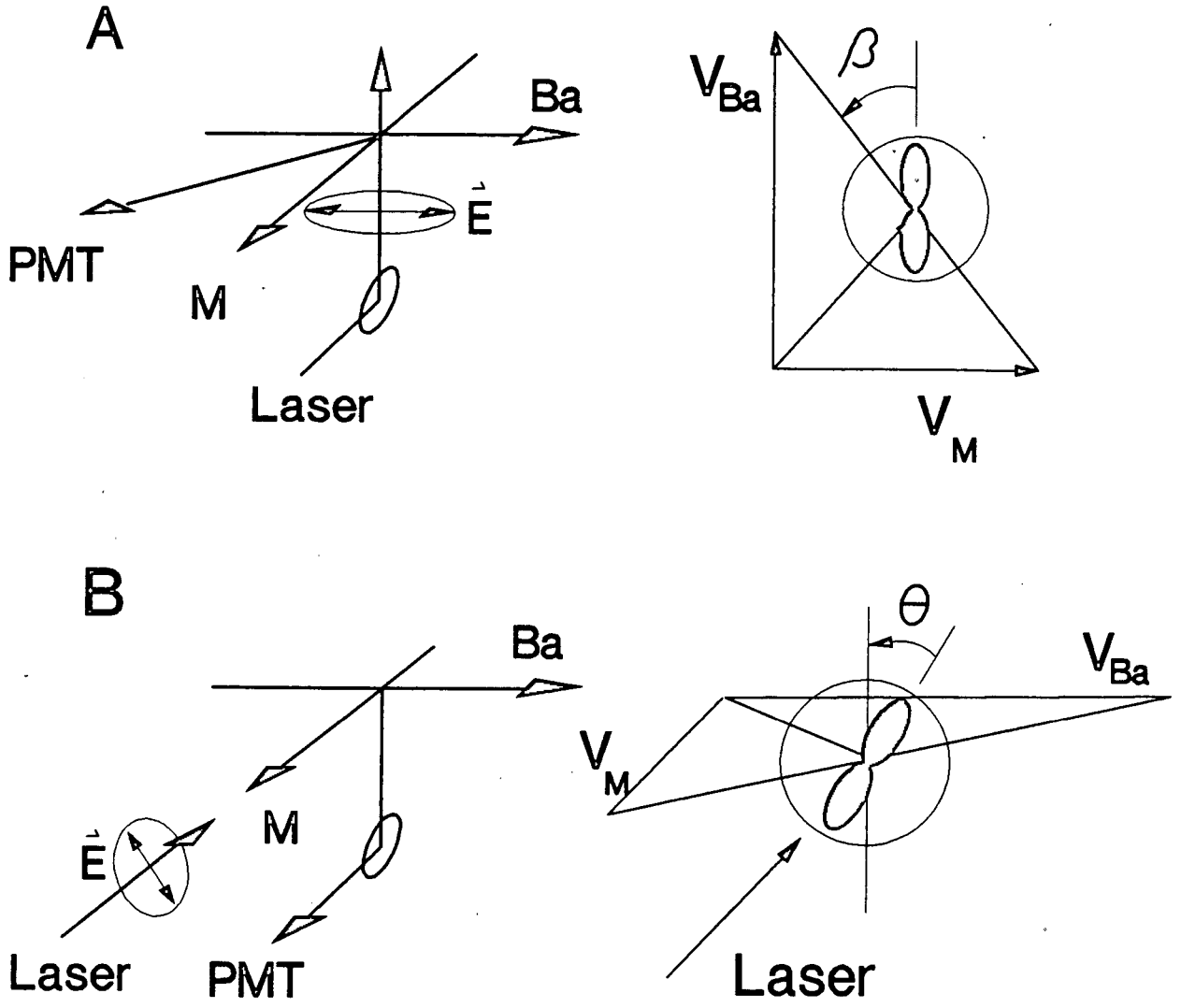


Figure 2

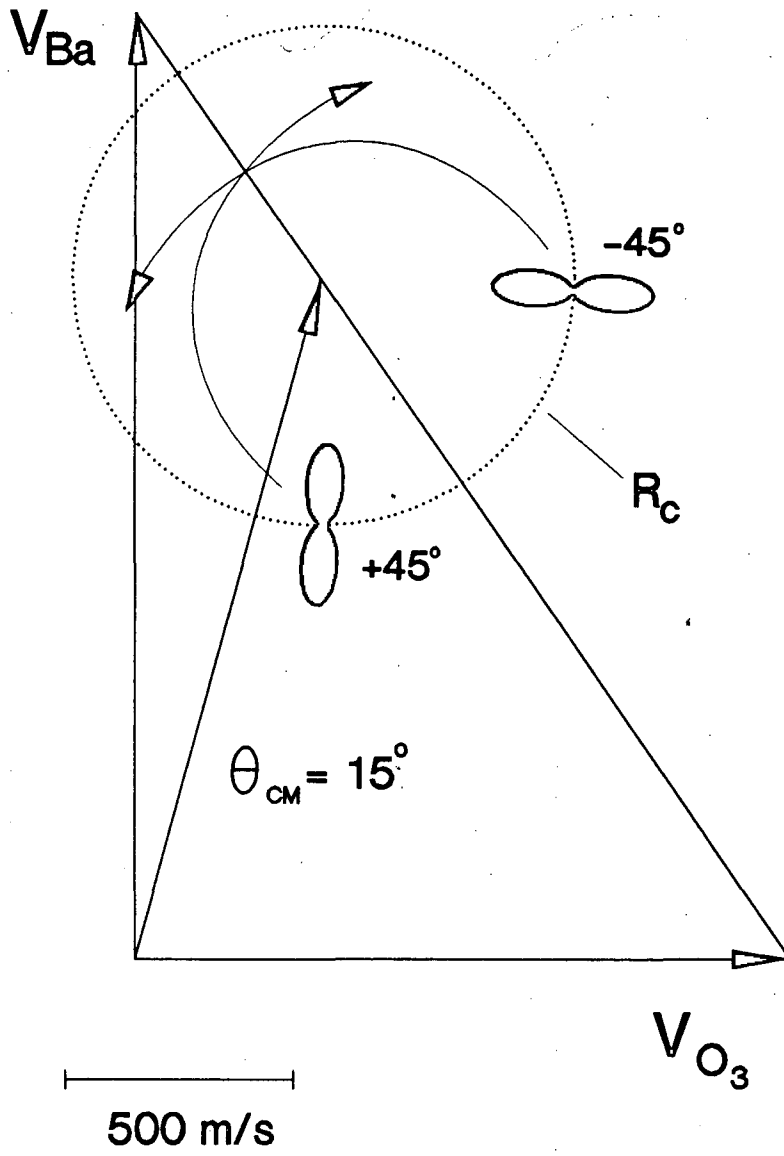


Figure 3

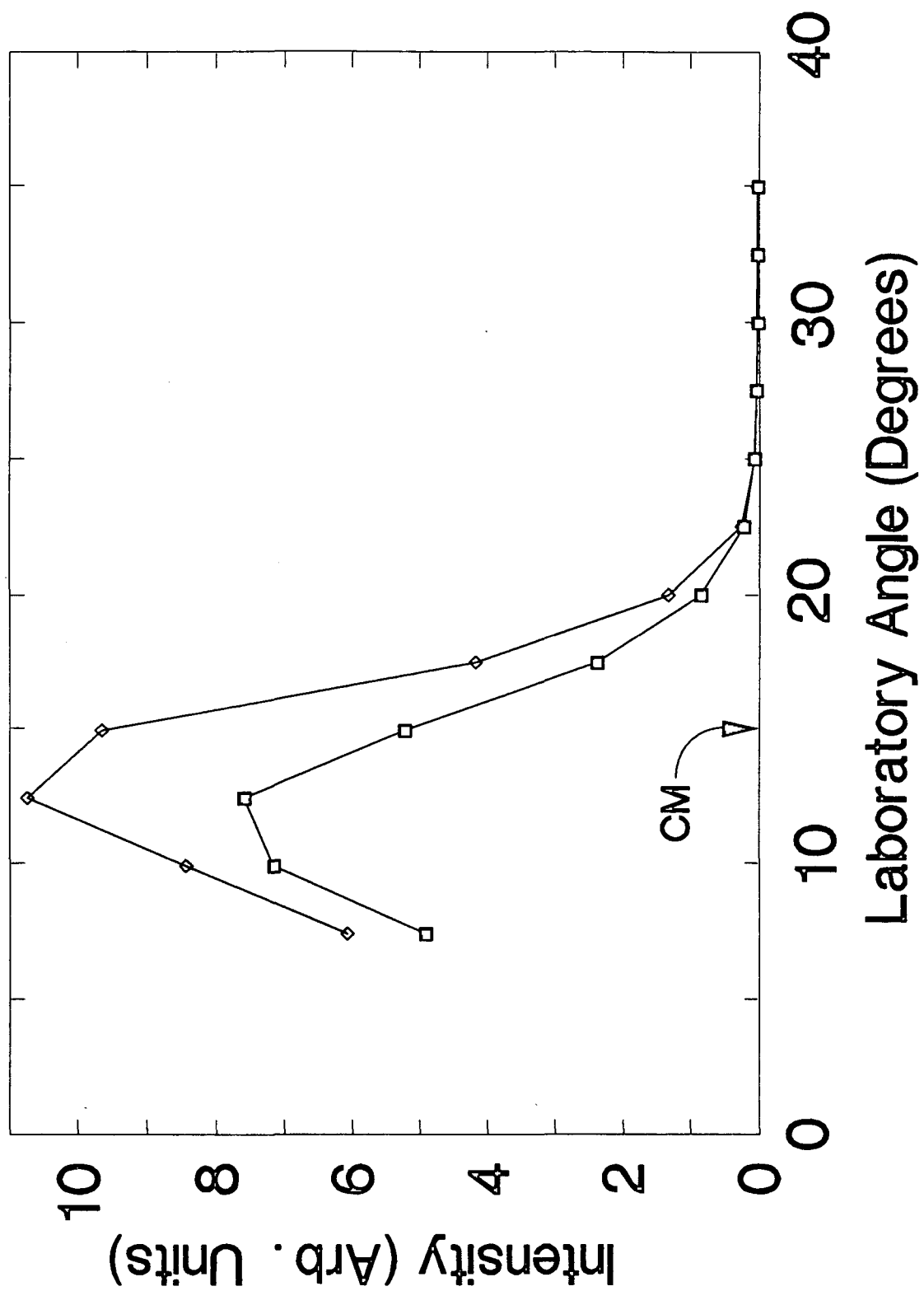


Figure 4

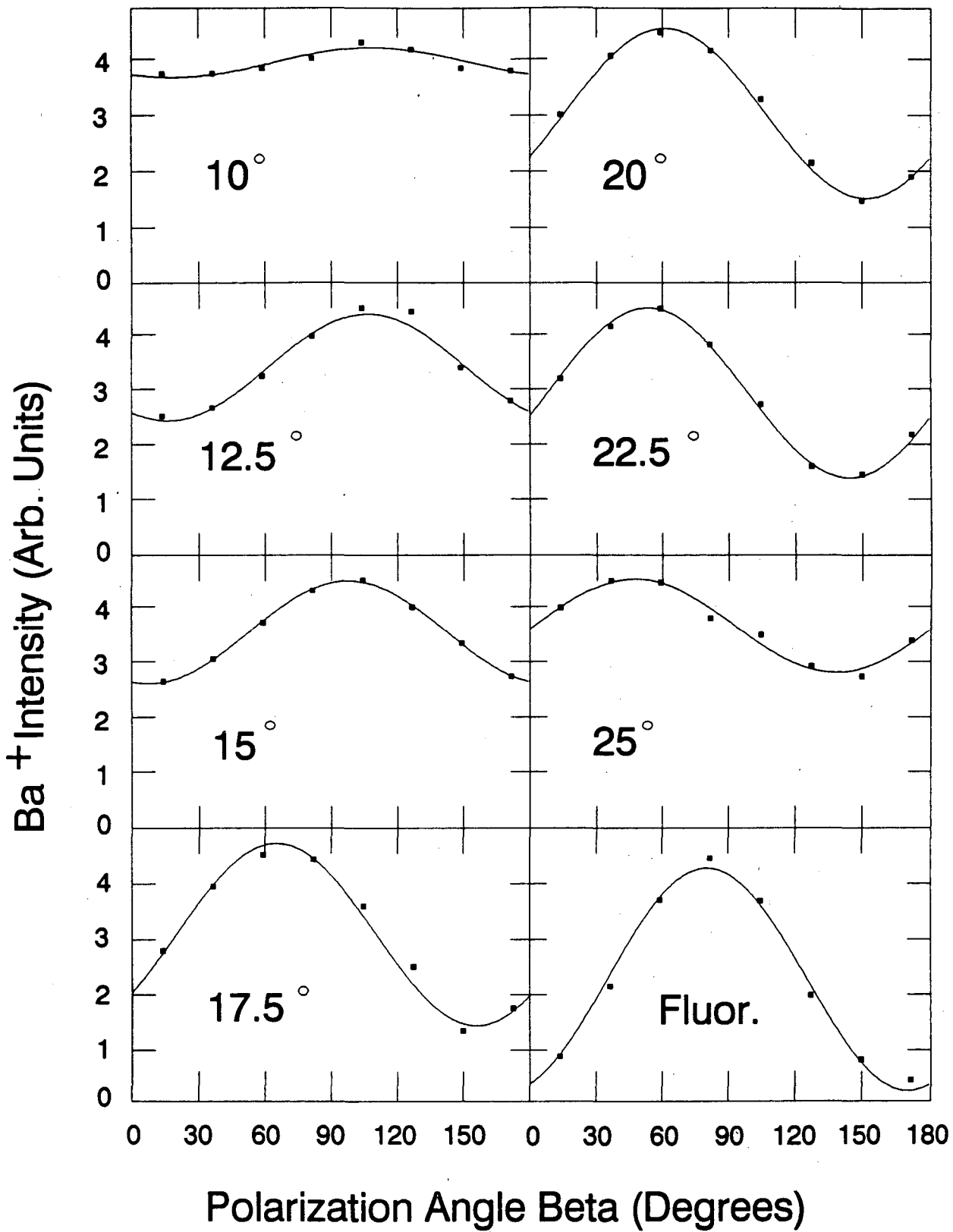


Figure 5

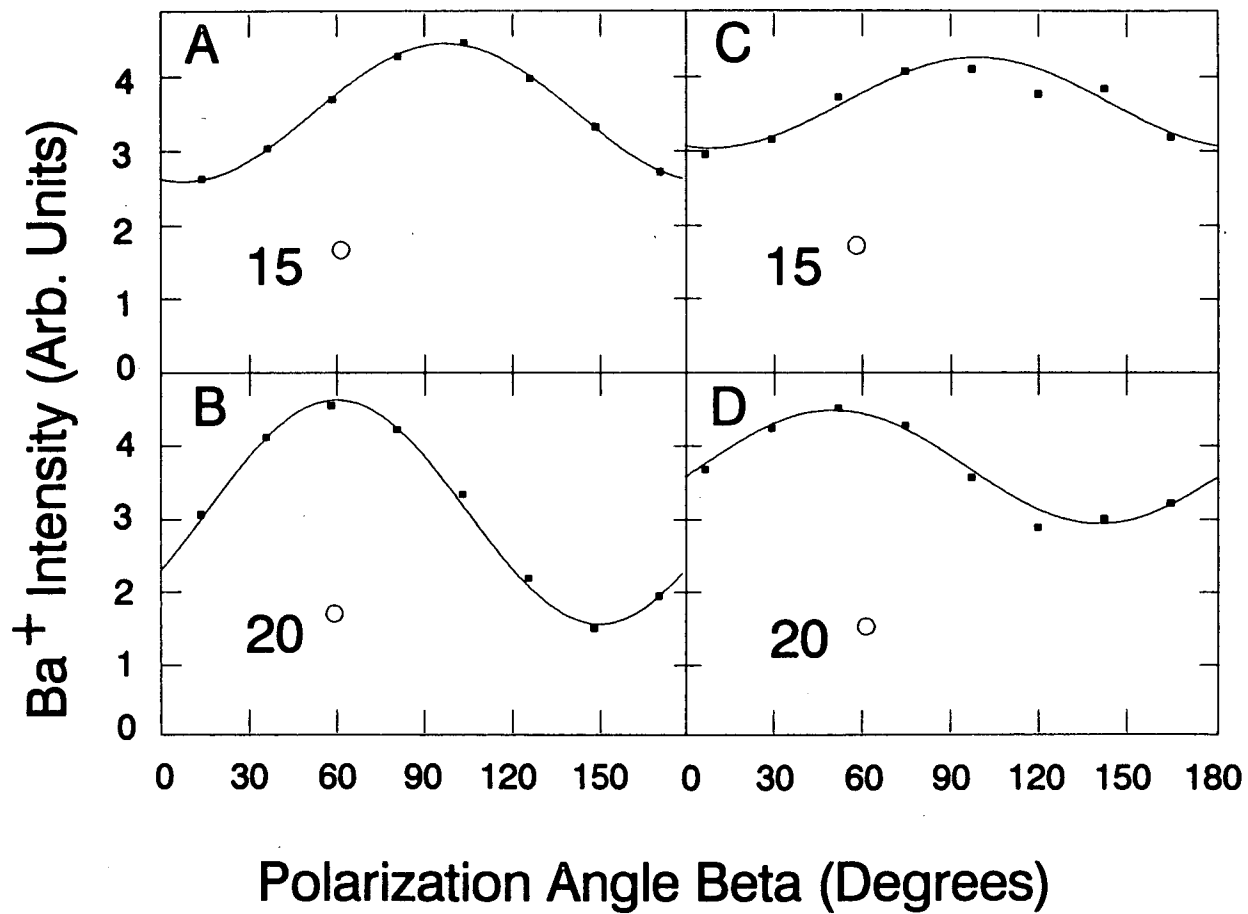


Figure 6

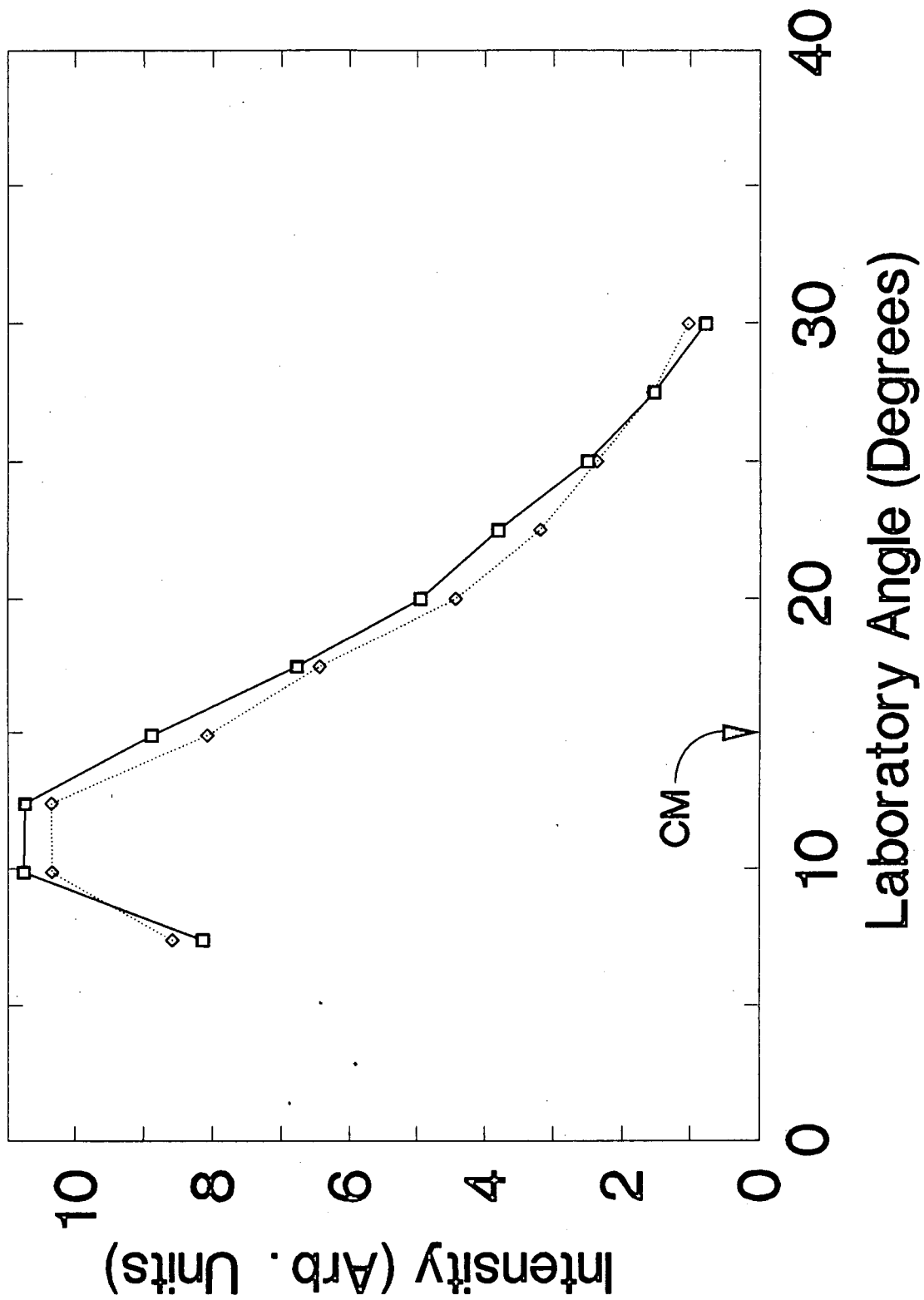


Figure 7

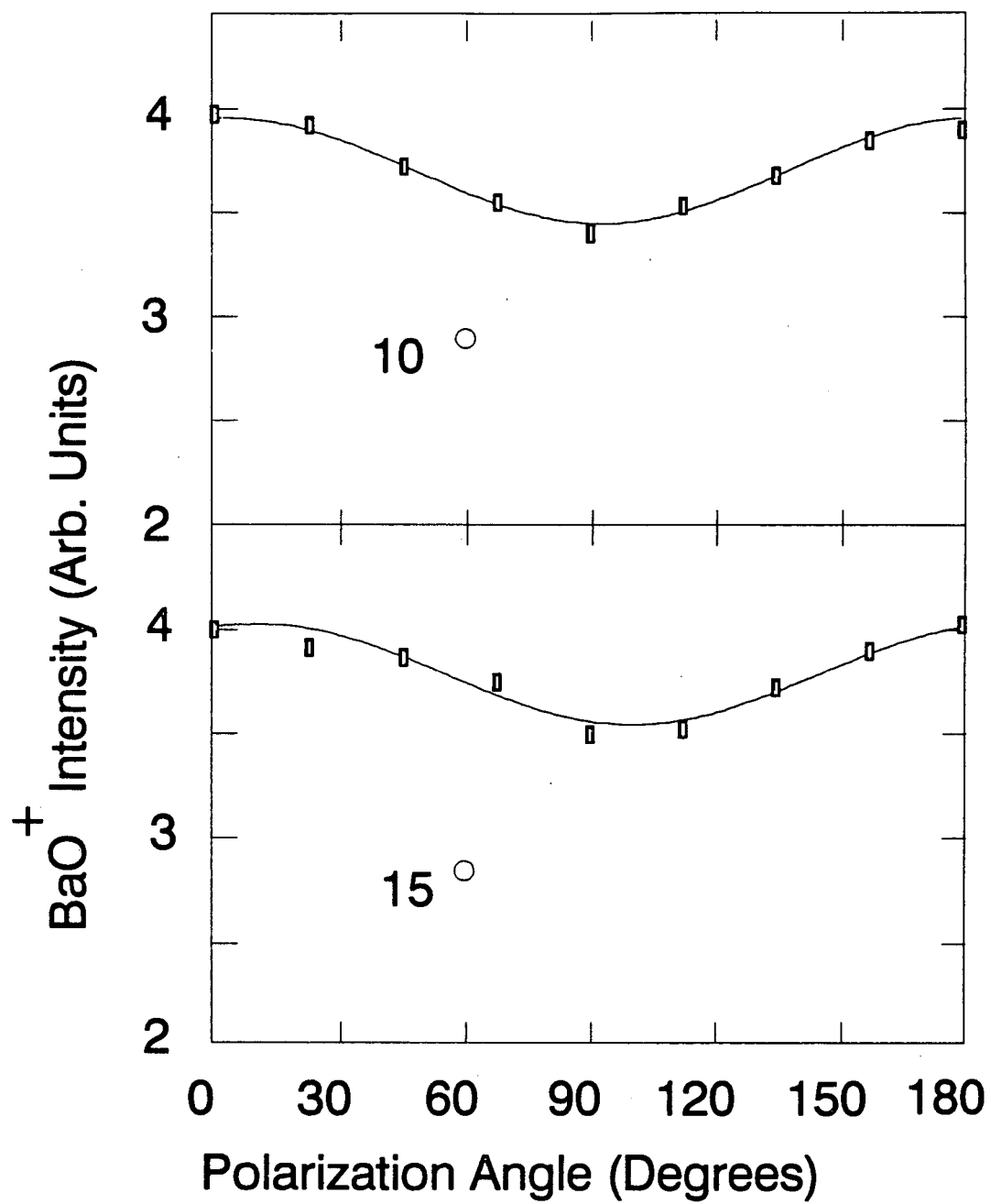
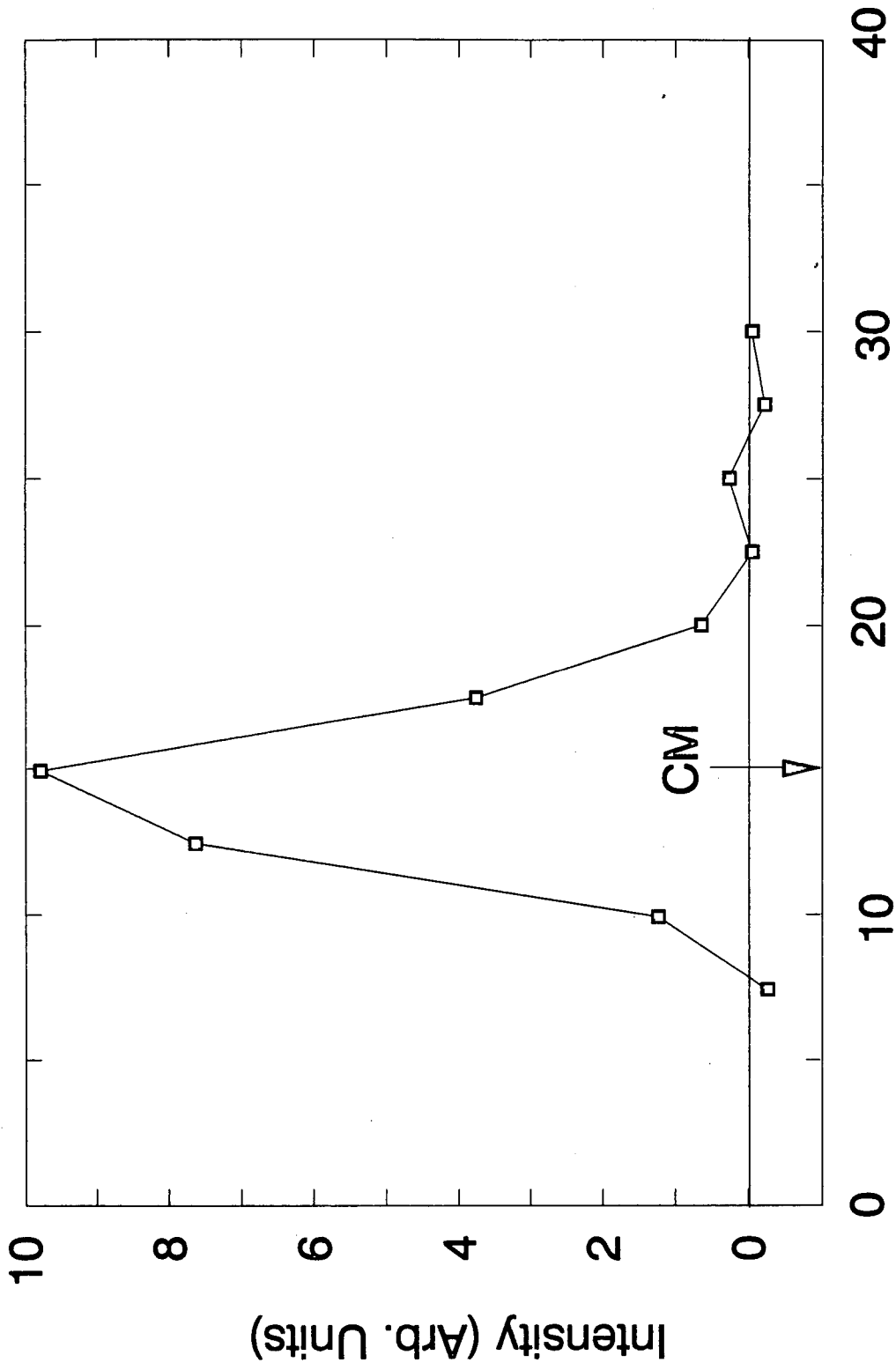


Figure 8



Laboratory Angle (Degrees)

Figure 9

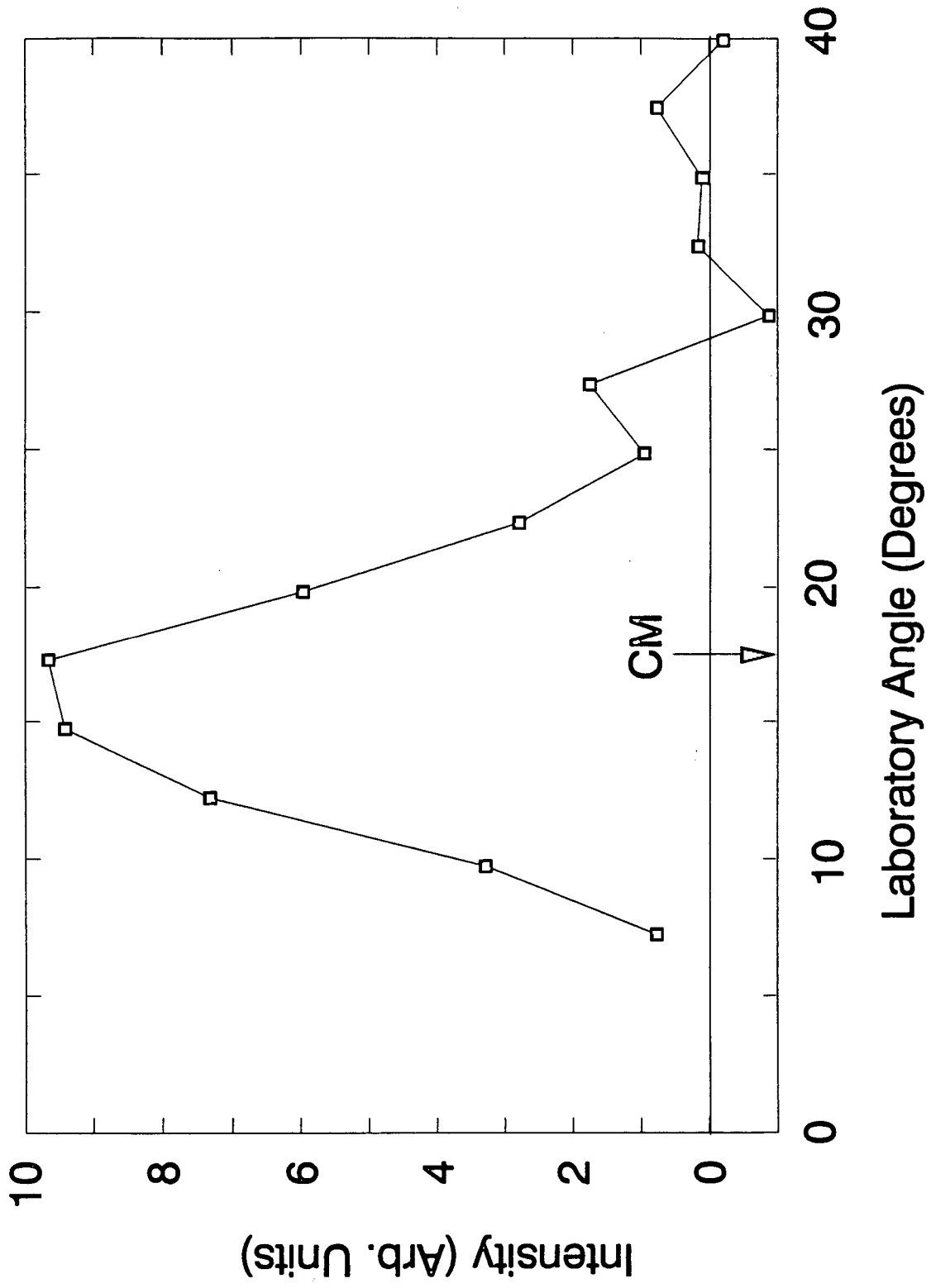


Figure 10

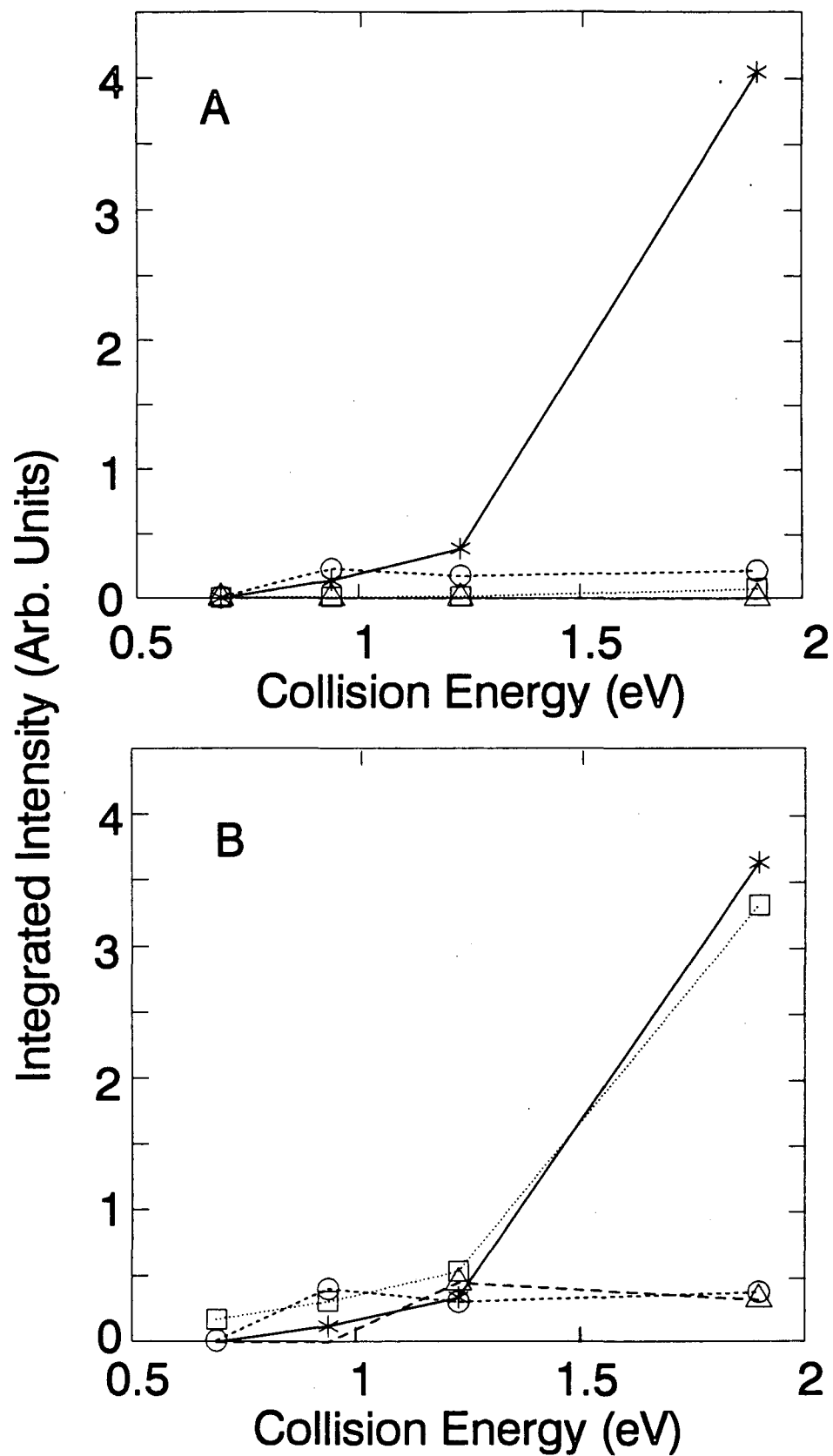


Figure 11

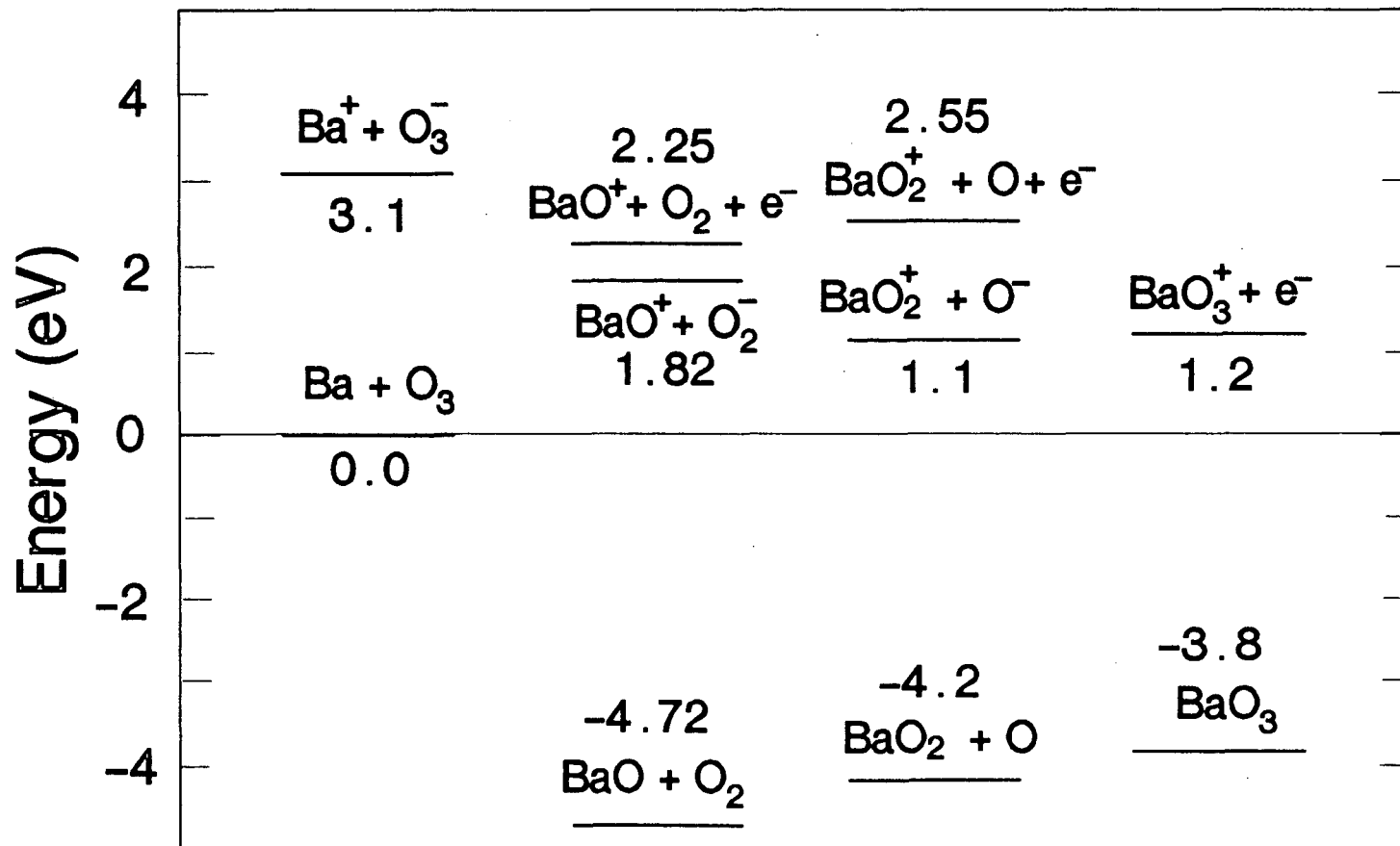


Figure 12

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