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Dynamic Consequences of the Divalent Nature of Barium

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REACTION OF Ba ATOMS WITH NO₂, O₃ AND Cl₂:
DYNAMIC CONSEQUENCES OF THE DIVALENT NATURE OF BARIUM

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ABSTRACT

The role of the divalent nature of barium atoms in chemical reactivity was explored using crossed molecular beams. Angular and velocity distributions of products from reactions of Ba(¹S) with NO₂ and O₃ indicate the existence of long lived collision intermediates despite very large reaction exothermicities. The existence of these intermediates results from barriers to transfer of the second electron necessary to form ground state products. Although BaO was the dominant product in both reactions, two previously unknown channels were observed: Ba + NO₂ → BaON + O and Ba + O₃ → BaO₂ + O. We obtained bond dissociation energies of D₀(Ba-ON)=65±20 kcal/mole and D₀(Ba-O₂)=120±20 kcal/mole for these molecules. The dependence of the cross sections for the ion channels, Ba(¹P) + Cl₂⁺ → Ba⁺ + Cl₂ and Ba(¹P) + Cl₂ → BaCl⁺ + Cl on Ba(¹P) orbital alignment and collision energy was used to probe the course of the reaction through intersections between the ionic and covalent potential energy surfaces.

Although the electron transfer at a long distance is an important and often dominating process involving alkali atoms with molecules of appreciable electron affinity, the long range electron transfer does not always lead to the formation of reaction products, especially when the negative ions formed in the electron transfer process are strongly bound. For example, in our recent experiment⁵ to promote the endothermic reaction of $\text{Na} + \text{O}_2 \rightarrow \text{NaO} + \text{O}$ through electronic excitation of Na atoms, long range electron transfer yielding the $\text{Na}^+ \text{O}_2^-$ reaction intermediate does not lead to formation of NaO product. The ground state O_2^- molecule formed by the attachment of an electron to O_2 is strongly bound, and the $\text{Na}^+ \text{O}_2^-$ formed by long range electron transfer is found to result in quenching of electronic excitation. The formation of NaO is only observed at sufficient translational energy and when Na(4D) is aligned with d-orbital perpendicular to the relative velocity vector. Apparently, for the formation of NaO, the electron transfer must take place at short Na- O_2 distances, and the electron is likely to be transferred to an excited repulsive state of O_2^- . For this to occur, the long range electron transfer from Na to O_2 has to be avoided.

Reactions of heavier alkaline earth atoms with halogen containing molecules have many similarities to those involving alkali atoms. The low ionization potentials and the dissociative electron attachment are again the reason

why the electron transfer in the approach channel plays an important role in these systems. However, since there are two valence electrons in alkaline earth atoms, when they react with molecules containing divalent oxygen atoms or molecules containing two halogen atoms, the transfer of a second electron from the Ba atom becomes feasible. In this investigation, through the use of the crossed molecular beams method, combined with orbital alignment of the excited Ba atom, the complex behavior in the reactions of Ba + O₃, NO₂ and Cl₂ are unraveled. The role of the second electron in chemical reactivity and the dynamic consequences of the divalent nature of barium atoms are the focus of this work.

Chemi-ionization reaction forming BaCl⁺ and Cl⁻ from the ground state Ba with Cl₂ was investigated by Ross et al.,⁶ using the crossed molecular beams method. The angular and velocity distributions of BaCl⁺ and Cl⁻ products suggest strongly coupled collisions which contrast with the dynamics of the neutral product channel BaCl + Cl.

Experimental

A seeded supersonic barium atomic beam was formed by expanding the mixtures of Ba and rare gas from the nozzle located at the end of a resistively heated molybdenum tube which was connected to a Ba reservoir surrounded by a graphite radiation heater as shown in figure 1.3. The barium beam was skimmed by a heated molybdenum skimmer prior to

former configuration. The chlorine beam was seeded in helium and the nozzle heated to 190°C to inhibit cluster formation.

RESULTS AND DISCUSSION

Barium + NO₂ and O₃

The reactions of ground state barium atoms with NO₂ and O₃ were studied at several collision energies between 9 kcal/mole and 67 kcal/mole. The relevant energies for these systems are summarized in figure 3. Two product channels were observed for reaction of each molecule. In addition to formation of BaO, reaction with NO₂ at high collision energies led to formation of BaON; in the reaction with O₃, BaO₂ was observed as a secondary channel.

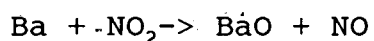


Figure 4 shows the laboratory angular distribution of the BaO products obtained at a collision energy of 16 kcal/mole. Although the strongest signal lies in the forward hemisphere, a second maximum was seen in the backward direction with respect to the barium beam. Two explanations are consistent with this forward-backward peaking in the product intensity. One possible model involves the formation of an "osculating" BaNO₂ complex with a lifetime comparable to one rotational period. Alternatively, the observed angular distributions may be

interpreted as arising from the superposition of a long lived component exhibiting forward-backward symmetry in the CM frame with a second component peaking in the forward direction. Two observations indicate that the latter explanation is correct. First, upon raising the collision energy from 9 to 40 kcal/mole, no shift to forward scattering was observed. If osculating complexes were involved, such a large increase in collision energy should result in a substantial decrease in the lifetime of the complex, leading to a shift toward forward scattering. Such behavior has been observed for the reaction $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$.¹⁰ Second, the decay of osculating complexes would result in product translational energy distributions essentially independent of CM scattering angle. Product time of flight measurements (figure 5) indicate a smaller average release of translational energy in the forward direction than for backward scattered products. The translational energy distributions and center of mass angular distributions are shown in figure 6. The forward scattered BaO (channel 1) was formed with low translational energy. The P(E) peaked at only 12 kcal/mole, corresponding to less than 20% of the total available energy. Decay of collision complexes led to the forward-backward symmetric CM angular distribution shown for channel 2. In contrast to the direct reaction, a much larger release of translational energy was observed.

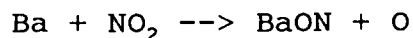
Although reaction via collision complexes often results in low product translational energies due randomization of energy before dissociation,¹¹ in this case, more translational energy is released from decay of complexes than from the direct reaction. Two factors are responsible for this rather unusual behavior. A large potential energy barrier for decay of BaNO_2 to ground state $\text{BaO} + \text{NO}$, followed by strong repulsive forces in the exit channel leads to large translational energy release. In contrast, the direct reaction mechanism involves a much smaller potential barrier. The existence of a low potential barrier, combined with the smaller product translational energy in the forward direction strongly suggests that in the direct reaction the Ba atom picks up an O atom from the NO_2 molecule leading to formation of electronically excited BaO products.

In order to understand our observations, it is useful to compare divalent barium with monovalent cesium. The Ba-O binding energy is 133 kcal/mole, nearly twice that of Cs-O (70 kcal/mole).^{12a} This large difference, attributable to strong coulombic attraction possible in the $\text{Ba}^{2+}\text{O}^{2-}$ configuration,¹³ leads to a large exothermicity for reaction of Ba with NO_2 ($\Delta H = -62$ kcal/mole) whereas the reaction of Cs is slightly endothermic ($\Delta H = +2$ kcal/mole). Considerable similarity, however, is expected between the two M^+NO_2^- intermediates. Empirical correlations indicate the well

depth should be approximately 100 kcal/mole.¹⁴ The known involvement of collision complex intermediates for Cs + NO₂ has been satisfactorily explained solely on thermodynamic grounds- a slight endothermicity combined with a deep potential well. A similar thermodynamic analysis, employing the large exothermicity for the Ba + NO₂ reaction would require that BaNO₂ be unreasonably strongly bound (>250 kcal/mole) for complex lifetimes to approach one rotational period (1 psec). Formation of long lived BaNO₂ collision complexes cannot be explained from the stability of BaNO₂ and the exothermicity alone.

The BaNO₂ singly ionic surface correlates directly with electronically excited BaO product states, best described as Ba⁺O⁻. Formation of ground state BaO requires a crossing to another electronic surface, corresponding to transfer of the second electron. Transfer of the second electron to the two lowest unoccupied orbitals of NO₂⁻ is symmetry forbidden; successful transfer likely involves excited states resulting in a substantial potential barrier. The very existence of long lived collision complexes, and the rather large translational energy released from their decay are attributable to this exit barrier. The potential energy surface involving two-electron transfer is not accessed in the small fraction of collisions resulting in formation of BaO*. Because no difference in CM product angular distributions was seen on varying the collision energy from

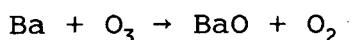
6 to 40 kcal/mole, the relative yield of electronically excited BaO appears to be insensitive to collision energy.



Formation of BaON was only observed at collision energies above 35 kcal/mole. Even at the highest collision energy, it does not account for more than 1% of the total reactive cross section. The angular distribution peaked over a narrow range of CM angles, away from the relative velocity vector (Fig 7). This indicates that the reaction is direct, and only occurs for a very limited range of impact parameters. These observations suggest that unlike formation of BaO and BaO*, BaON results from collisions which do not involve long range electron transfer. Product translational energy distributions and the high threshold energy for product formation indicate that the reaction is slightly endothermic and with substantial entrance barrier. From the maximum translational energy release of products, the Ba-ON binding energy was found to be 65 ± 20 kcal/mole.

This appears to be the first observation of BaON; although its structure is not readily apparent, likely structures may be derived by comparison with similar molecules. Li⁺ON⁻ has been observed in rare gas matrices; a linear or slightly bent structure involving a metal-oxygen bond was postulated.¹⁵ Bernath and coworkers¹⁶ have studied

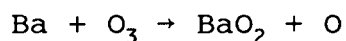
the spectroscopy of a range of radicals involving alkaline earth atoms. They concluded that CaOCN and CaOCH_3 involve Ca-O bonding with substantial Ca^+OR^- character. By analogy, considerable ionic character is expected for BaON ; interaction with the oxygen atom appears most likely but a non-symmetrical triangular structure could also be possible.



Although some backscattered BaO product is noticeable in the product angular distributions, considerably more forward scattering is observed than in the reaction with NO_2 (Fig 7). The electron affinity of O_3 is 2.1 eV, close to that of NO_2 (2.3 eV).^{12b} Based on this, we also expect long range electron transfer, in this case leading to formation of a Ba^+O_3^- reaction intermediate.

It is known that a substantial fraction of BaO reaction products are formed in electronically excited states.¹⁷ Ba^+O_3^- is a bound molecule with considerable ionic character. As in the case of BaNO_2 , we expect formation of electronically excited BaO to result from immediate decomposition of the ion pair, whereas decay to ground state BaO involves a surface crossing with substantial potential barrier. In contrast to the reaction with NO_2 , formation of ground state products does not conserve spin. The results in the NO_2 case, where spin is conserved, indicate that conservation of spin may be irrelevant to the existence of

long lived complexes. The low translational energy in the backscattered BaO products suggests that the barrier for decay of BaO₃ is lower than for BaNO₂. The forward peaking in the BaO angular distribution as shown in figure 8 indicates that most reactions are direct, similar to the famous harpoon mechanism¹ in the reaction of an alkali atom with a halogen molecule, and occur on a timescale faster than one rotational period. The dotted line shows the maximum calculated velocity for ground state BaO products. The product flux contour diagram shows that all products are formed with a much lower average translational energy release, suggesting that a large fraction of the products are internally excited.



Although a long lived BaO₂ complex intermediate has been thought to exist in reactions of Ba with O₂,^{19,20} this appears to be the first direct observation of BaO₂ in the gas phase. This product channel amounted to less than 10% of the total reaction cross section. The large translational energy observed for the recoiling BaO₂ products indicates a very large exothermicity for Ba + O₃ --> BaO₂ + O. The maximum translational energy release indicates that the binding energy of Ba-O₂ is 120±10 kcal/mole. This is nearly as great as Ba-O, suggesting that it is a true peroxide with substantial Ba²⁺O₂²⁻ character.

The best fits of the product angular and time of flight spectra exhibit forward-backward symmetry in the CM frame (fig 7), indicating that BaO_2 results exclusively from decay of long lived Ba^+O_3^- collision complexes.

Involvement of complex intermediates in such a highly exothermic reaction is unexpected and remarkable. Their existence, together with the large product translational energy release leads to a mechanism very similar to that for formation of ground state BaO . Like ground state BaO , the BaO_2 molecule formed in the reaction must correlate to a surface involving transfer of the second valence electron away from barium; as before, a substantial barrier has to be surmounted to access this decay channel.

Barium + Chlorine

The observation of chemiluminescence from the reaction of barium with chlorine stimulated a great deal of work in the early seventies, as it was initially considered a possible medium for an electronic transition chemical laser.²¹ Such hopes faded, however, when it became apparent that the dominant channel in this reaction at thermal energies is the formation of neutral, ground state BaCl , with electronically excited products accounting for only about 10% of the total reactive cross section.²² In addition to the chemiluminescent channels, early work revealed the presence of a chemi-ionization channel,

$\text{BaCl}^+ + \text{Cl}^-$,²³ which is exoergic from ground state reactants. The chemi-ionization cross section was found to be roughly an order of magnitude smaller than the chemiluminescence cross section. Because the dominant products of this reaction are radical pairs, $\text{BaCl} + \text{Cl}$, in a variety of electronic states (the ion pair is the only closed-shell product channel), low-lying electronically excited states of the collision complex exist which participate in determining the course of the reaction.

Figure 9 shows a family of diabatic potential curves for collinear approach of barium + chlorine estimated by empirical correlations. The covalent curves are based on alkali metal-rare gas potentials determined by scattering,²⁴ while the ionic curves are calculated using a Rittner potential²⁵ with the repulsive term adjusted to give the correct energy minima and bond lengths. A "reactive" electron affinity of 1 eV was used for Cl_2 ²⁶ to scale the $\text{Ba}^+ + \text{Cl}_2^-$ curves relative to the covalent curves. Laser excitation of the Ba ($^1\text{P} \leftarrow ^1\text{S}$) transition corresponds to an additional 2.2 eV of available energy, and the use of crossed, seeded beams of barium and chlorine allow one to select collision energies anywhere in the range 0.2-3.0 eV. In the Landau-Zener model, the probability of a non-adiabatic transition increases with radial velocity, so the initial collision energy can be used to modulate the likelihood of long-range electron transfer. Electronic

excitation of the barium atom lowers its ionization potential, so the initial crossing point is moved to a greater distance for electronically excited versus ground state reactants (1 and 1^* in figure 9). Furthermore, electronic excitation changes the symmetry of the reactants' electronic configuration, resulting in a conical intersection at 1^* (and 3^*). The probability of charge transfer there is thus expected to be sensitive to the alignment of the p-orbital, which can be chosen in the laboratory by means of the polarization of the laser. As can be seen from figure 9, the chemi-ion products, $\text{BaCl}^+ + \text{Cl}^-$, correlate to the doubly ionic surface: both barium valence electrons must be transferred to chlorine. This is the adiabatic path, and the chemi-ion cross section is thus a sensitive measure of access to this doubly ionic surface. The angular distributions of products and their dependence on collision energy, electronic state and orbital alignment can be used to probe the interaction of these factors in determining the reaction dynamics for collisions involving several electronic potential energy surfaces.

Figure 10 shows a laboratory angular distribution for BaCl^+ from the reaction of Ba with Cl_2 at a collision energy of 0.75 eV. The BaCl^+ product was clearly backscattered, indicating that collinear low impact parameter collisions dominate the reactant geometries leading to this channel. This is in marked contrast to the neutral BaCl product which

is largely forward scattered and analogous to the alkali metal halogen reactions. Angular distributions for the neutral BaCl approached this spectator stripping limit.²⁷ As noted above, the BaCl⁺ chemi-ion product requires that the second electron be transferred from the barium atom (on which it will be localized even in the Ba⁺Cl₂⁻ intermediate) to the departing chlorine atom. This second electron transfer thus occurs only at very short BaCl-Cl bond distances. But it is only for low impact parameter collisions and collinear geometries that this will occur, since otherwise prompt dissociation to neutrals will follow the first electron transfer. This is also consistent with measurements of the chemi-ionization cross section (1.4 Å²)²³ and estimates of total reactive cross section (ca. 60 Å²).²²

Figure 10 also shows an angular distribution for BaCl⁺ obtained under the same conditions but with a laser saturating the Ba(¹P) ← Ba(¹S) transition at the interaction region. We observed a 35% depletion of intensity independent of laboratory angle. We estimate that under these conditions the barium beam contained about 25% Ba(¹P), 25% Ba(^{1,3}D) and the remainder Ba(¹S); thus, most of this signal represents residual ground state reaction. Laser excitation of the D states alone was slightly less effective at depleting the BaCl⁺ signal, so we conclude that excitation to the (¹P) state resulted in almost complete

extinction of the BaCl^+ channel. Yet at this collision energy the yield of neutral BaCl is virtually unaffected by laser excitation.

These observations can be reconciled by a consideration of the dynamics of the low impact parameter collisions which we infer are responsible for the BaCl^+ product. Laser excitation moves the crossing point to a greater Ba-Cl_2 distance and reduces the coupling matrix element. These factors compete in determining the overall effect on the cross section for neutral products. But for ion formation, which requires an intimate Ba-Cl-Cl interaction, the consequences are much more dramatic. The longer range electron transfer results in stretching of the Cl-Cl bond before the barium atom can approach close enough for the second electron transfer to occur, precluding the intimate interaction unless the barium approach happens to be in phase with the Cl_2 vibration. The distance between the first and second crossing points, in other words, is crucially important in determining the branching onto the doubly ionic surface.

At higher collision energies we observed the same laser induced depletion of the BaCl^+ channel, but another ion channel began to appear. At a collision energy of 3 eV we are just over the threshold for formation of Ba^+ and Cl_2^- from ground state reactants. We indeed observed Ba^+ near the center of mass angle from the ground state Ba reaction,

but excitation to the (1P) state resulted in greater than 20-fold enhancement in Ba^+ intensity. In addition, this Ba^+ signal, measured in the backward direction, shows a remarkable dependence on the initial alignment of the barium p-orbital. Figure 11 shows the Ba^+ intensity at a laboratory angle of 15 degrees measured as a function of laser polarization for in-plane and out-of-plane rotation of the p-orbital. The fluorescence intensity monitored simultaneously confirmed that the p-orbitals were well aligned. The Ba^+ signal was enhanced roughly two-fold when the laser polarization was in the plane (20 degrees from the relative velocity vector) over that seen when the polarization was perpendicular to the plane (90 degrees from the relative velocity vector). The fits are given by

$$I(\theta_E) = \frac{I^{\max} + I^{\min}}{2} + \frac{I^{\max} - I^{\min}}{2} \cos 2\theta_E$$

where θ_E is the angle between the electric vector of the laser and the collision plane (fig 3b) or the relative velocity vector (3a).²⁸ The polarization dependence was precisely that expected from the nature of the conical intersection at the outer crossing (1^* in figure 9): collision geometries for which the p-orbital is aligned along the relative velocity vector result in a covalent surface of Σ symmetry (in the collinear case), which can then interact with the Σ ionic surface. This geometry favors electron transfer, leading to the ground state ionic

surface which correlates both to $\text{Ba}^+(^2\text{S})$ and to ground state BaCl . When the p-orbital is perpendicular, however, the diabatic curves are of different symmetry, so they cross without interaction. Laser excitation at this collision energy resulted in little change in intensity of the neutral BaCl or Ba scattering. If the alignment of the p-orbital were determining the branching at 1^* , then we might expect the same polarization dependence to appear for the neutral BaCl which arises from charge transfer there. But the fate of the reaction is not yet fully determined at the first crossing; following a non-adiabatic transition at 1^* , a second opportunity for escape to an exoergic product channel is presented at 2^* . This inner crossing is fully avoided rather than conical (the adiabatic path corresponds to transfer of the barium s-electron rather than the p-electron); most of the flux there appears as electronically excited BaCl . These results are complementary to those described by Rettner and Zare²⁹ for CaCl excited state production in the reaction of $\text{Ca}(^1\text{P})$ with Cl_2 . They reported a peak in chemiluminescence intensity for perpendicular p-orbital alignment, albeit much weaker than what we observed. At a laboratory angle of 15 degrees, the Ba^+ signal is probably dominated by backscattered product resulting from collinear ($\text{C}_{\infty\text{v}}$) geometries; the magnitude of the observed polarization dependence is likely the result of

our having selected, by means of scattering angle, the collision geometries which will show the strongest effect.

Conclusion

Reactions of barium atoms with NO_2 , O_3 and Cl_2 are like the analogous alkali metal reactions in that, owing to the low ionization potential of barium, these reactions are initiated by electron transfer in the entrance channel. Unlike the alkali metals, though, barium has a second valence electron; its presence has a profound effect on the reaction dynamics. In the reactions with NO_2 and O_3 , long-range electron transfer results in an ionic complex which does not correlate to ground state products, so it may survive many rotational periods despite the availability of highly exoergic product channels. When these complexes finally dissociate through transfer of the second electron, the large translational energy release bears witness to the barrier over which they have come. In addition, there are direct product channels: for BaO this implies electronically excited products while in the case of BaON , unusual chemistry from the covalent surface.

In the reaction of barium with Cl_2 the dynamics of the dominant product channel, BaCl and Cl , reveals little about the role of barium's second valence electron. But there exist ion channels which, because they correspond to the transfer of both electrons ($\text{BaCl}^+ + \text{Cl}^-$) or because they

clearly mark the events at a particular point on the potential energy surface ($\text{Ba}^+ + \text{Cl}_2^-$), can be used to trace the important moments in the collision. The backscattered angular distribution implies that collinear approach and low impact parameter collisions are necessary for BaCl^+ formation. Laser excitation results in a substantial separation between crossings onto the singly ionic and doubly ionic surfaces, resulting in reduction of access to the latter crossing and inhibition of BaCl^+ signal at all collision energies. At high collision energy a strong polarization dependence for Ba^+ was observed which can be attributed to non-adiabatic transitions at the conical intersection between the electronically excited covalent surface and the ground state ionic surface.

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References

1. J. H. Birely and D.R. Herschbach, *J. Chem. Phys.* **44**(4), 1690 (1966).
2. D. R. Herschbach, G. H. Kwei, J. A. Norris, *J. Chem. Phys.* **34**, 1842 (1961).
3. W. B. Miller, S. A. Safron, and D. R. Herschbach, *discuss. Faraday Soc.* **44**, 108 (1967).
4. R. Grice and D. R. Herschbach, *Molecular Physics*, **27**(10), 159 (1974).
5. H. Schmidt, P. S. Weiss, J. M. Mestdagh, M. H. Covinsky, Y. T. Lee, *Chem. Phys. Lett*, **118**(6), 539 (1985).
6. R.H. Burton, J.H. Brophy, C.A. Mims, and J. Ross, *J. Chem. Phys.* **73**, 1612 (1980).
7. Y. T. Lee, J. D. McDonald, P. R. LeBreton, and D. R. Herschbach, *Rev. Sci. Instrum.* **40**, 1402 (1969).
8. G. Comsa, R. David, and B.J. Schumacher, *Rev. Sci. Instrum.* **52**, 789 (1981).
9. D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden and Y. T. Lee, *J. Chem. Phys.*, **82**(7), 3045 (1985).
10. C. H. Becker, P. Casavecchia, P. W. Tiedemann, J. J. Valentini and Y. T. Lee, *J. Chem. Phys.*, **73**(6), 2833 (1980).
11. K. Shobatake, Y. T. Lee, and S. A. Rice, *J. Chem. Phys.* **59**(11), 6104 (1973).

12. a) J. Phys. Chem. Ref. Data, **12**(4), 982 (1983).
b) J. Phys. Chem. Ref. Data, **17**(1), 789 (1988).
13. L. Wharton and W. Klemperer, J. Chem. Phys., **38**, 2705 (1963).
14. R. R. Herm, D. R. Herschbach, J. Chem. Phys., **52**, (11) 5783 (1970).
15. a) W. L. S. Andrews and G. C. Pimentel, J. Chem. Phys., **44**, 2361 (1966).
b) D. E. Tevault and L. Andrews, J. Phys. Chem., **77**(13), 1640 (1973).
16. a) L. C. Ellingboe, A.M.R.P. Bopegedera, C. R. Brazier, P. F. Bernath, Chem. Phys. Lett., **126**(3,4) 285 (1986).
b) C. R. Brazier, L. C. Ellingboe, S. Kinsey-Nielsen, P. F. Bernath, J. Am. Chem. Soc. **108**, 2126 (1986).
17. J. W. Cox and P. J. Dagdigian, J. Chem. Phys., **79**(11), 5351 (1983).
18. L. Andrews and R. C. Spiker Jr., J. Chem. Phys., **59**(4), 1863 (1973).
19. T. P. Parr, A. Freedman, R. Behrens, Jr., R. R. Herm, J. Chem. Phys. **72**(9) 5163 (1980).
20. P. J. Dagdigian, H. W. Cruse, A. Schultz, R. N. Zare, J. Chem. Phys. **61**(11) 4450 (1974).
21. Michael Menzinger, The M + X₂ Reactions: A Case Study, in **Gas Phase Chemiluminescence and Chemi-Ionization**, A.

- Fontijn, ed., Elsevier Science Publishers, B.V., 1985, pp.25-66.
22. C. D. Jonah and R. N. Zare, Chem. Phys. Lett. **9**, 65 (1971).
 23. G. J. Diebold, F. Engelke, H. U. Lee, J. C. Whitehead, and R. N. Zare, Chem. Phys. **30**, 265 (1977).
 24. D. Beck and H. J. Loesch, Zeitschrift fur Physik **195**, 444 (1966).
 25. Edmund S. Rittner, J. Chem. Phys. **19**, 1030 (1951).
 26. M. M. Hubers, A. W. Kleyn and J. Los, Chem. Phys. **17**, 303 (1976).
 27. Shen-Maw Lin, Charles A. Mins, and Ronald R. Herms, J. Chem. Phys. **58**, 327 (1973).
 28. W. Reiland, G. Jamison, U. Tites and I. V. Hertel, Z. Phys. A - Atoms and Nuclei **307**, 51 (1982).
 29. R. K. Janev, Adv. Atom. Mol. Phys. **12**, 1 (1976).

Figure Captions

- Figure 1. Schematic diagram of the crossed molecular beams apparatus showing the supersonic barium atom source.
- Figure 2. (A) Modifications of crossed molecular beams machine for detection of ionic products. Experimental geometry is shown for in-plane (B) and out-of-plane (C) polarization rotation.
- Figure 3. Energy level diagram for the reaction of Ba + NO₂ and Ba + O₃.
- Figure 4. Experimental BaO laboratory angular distribution for Ba NO₂ → BaO + NO at collision energy of 16 kcal/mole. The nominal newton diagram is shown with a limiting circle indicating the maximum center of mass velocity for BaO based on the known reaction exothermicity for formation of ground state products.
- Figure 5. BaO product time-of-flight spectra at indicated laboratory angles for Ba + NO₂ → BaO + NO at collision energy of 16 kcal/mole. Dotted lines show contributions from the two separate channels used in fitting the data. The points are experimentally measured, and

the sum of the two contributions are shown as a solid line.

- Figure 6. Best fit translational energy ($P(E)$) and center of mass angular distributions for the $\text{BaO} + \text{NO}$ products. Channel 1 represents the direct reaction and channel 2 is the channel involving long lived BaNO_2 collision complexes.
- Figure 7. Center of mass product flux contour map in velocity space for the BaON product from the $\text{Ba} + \text{NO}_2$ reaction.
- Figure 8. Center of mass product flux contour map in velocity space for the BaO and BaO_2 products from reaction of $\text{Ba} + \text{O}_3$. Dotted line indicates the maximum center of mass velocity for BaO based on the known reaction exothermicity for formation of ground state products.
- Figure 9. Sections of the important diabatic potential energy surfaces for collinear $\text{Ba} + \text{Cl}_2$. The energy is scaled relative to ground state reactants.
- Figure 10. Measured laboratory angular distributions for BaCl^+ at a collision energy of 0.75 eV shown with the nominal Newton diagram.

Figure 11. Measured polarization dependence of Ba^+ at a collision energy of 3.0 eV monitored at a laboratory angle of 15 degrees. (A) Ba^+ intensity for in-plane polarization rotation. The peak corresponds to the p-orbital aligned along the relative velocity vector. (B) Ba^+ intensity and (C) fluorescence for out-of-plane polarization rotation. The peak corresponds to the p-orbital in the collision plane.

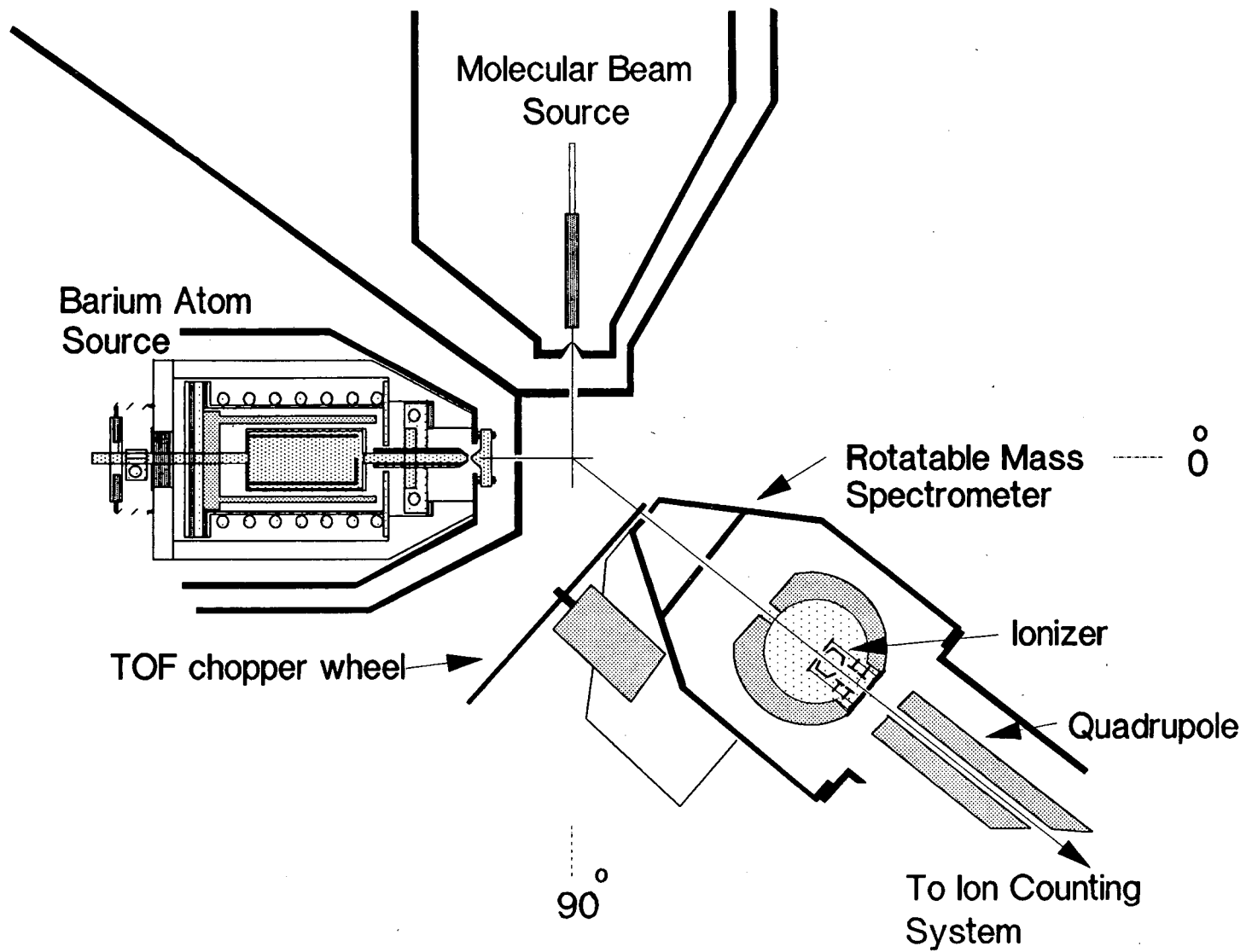


Fig. 1

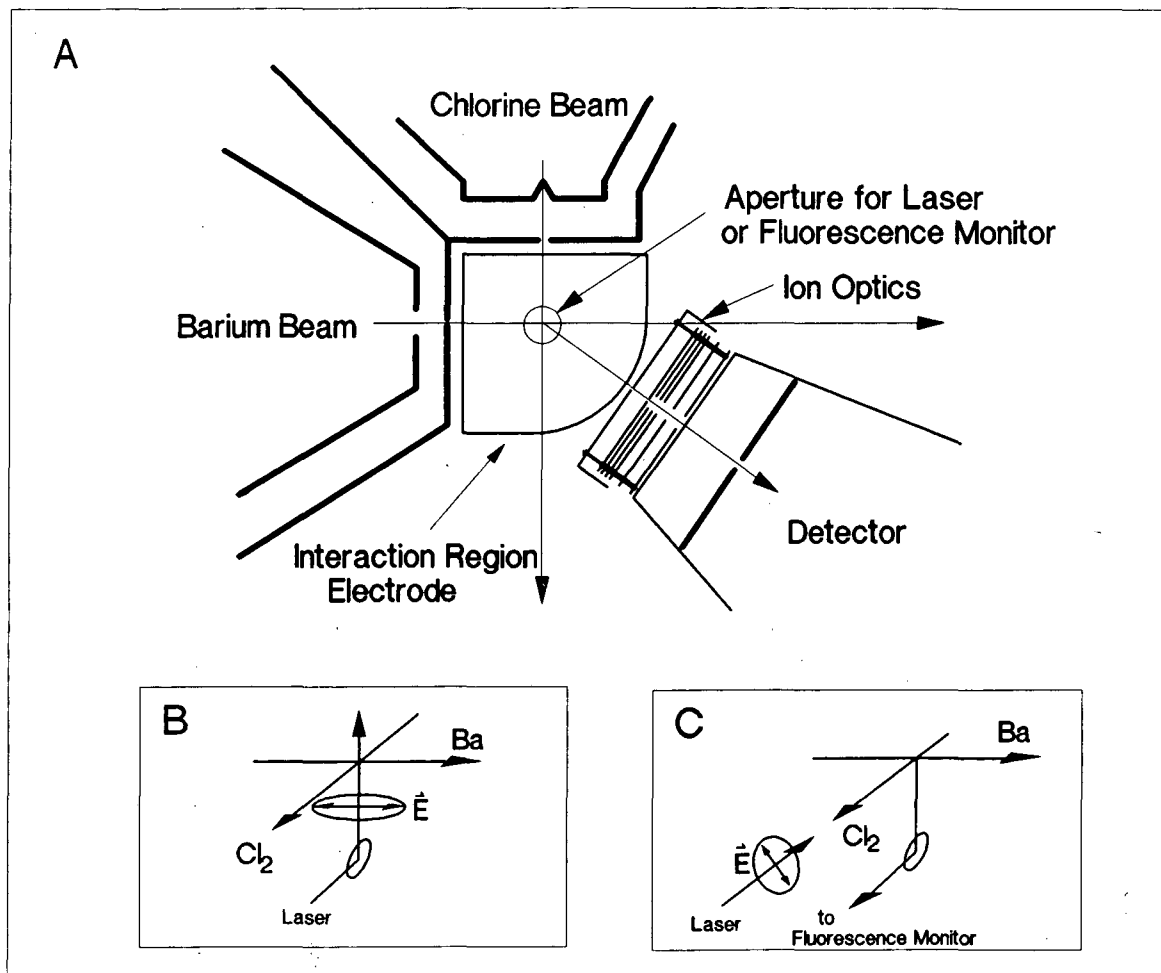


Fig. 2

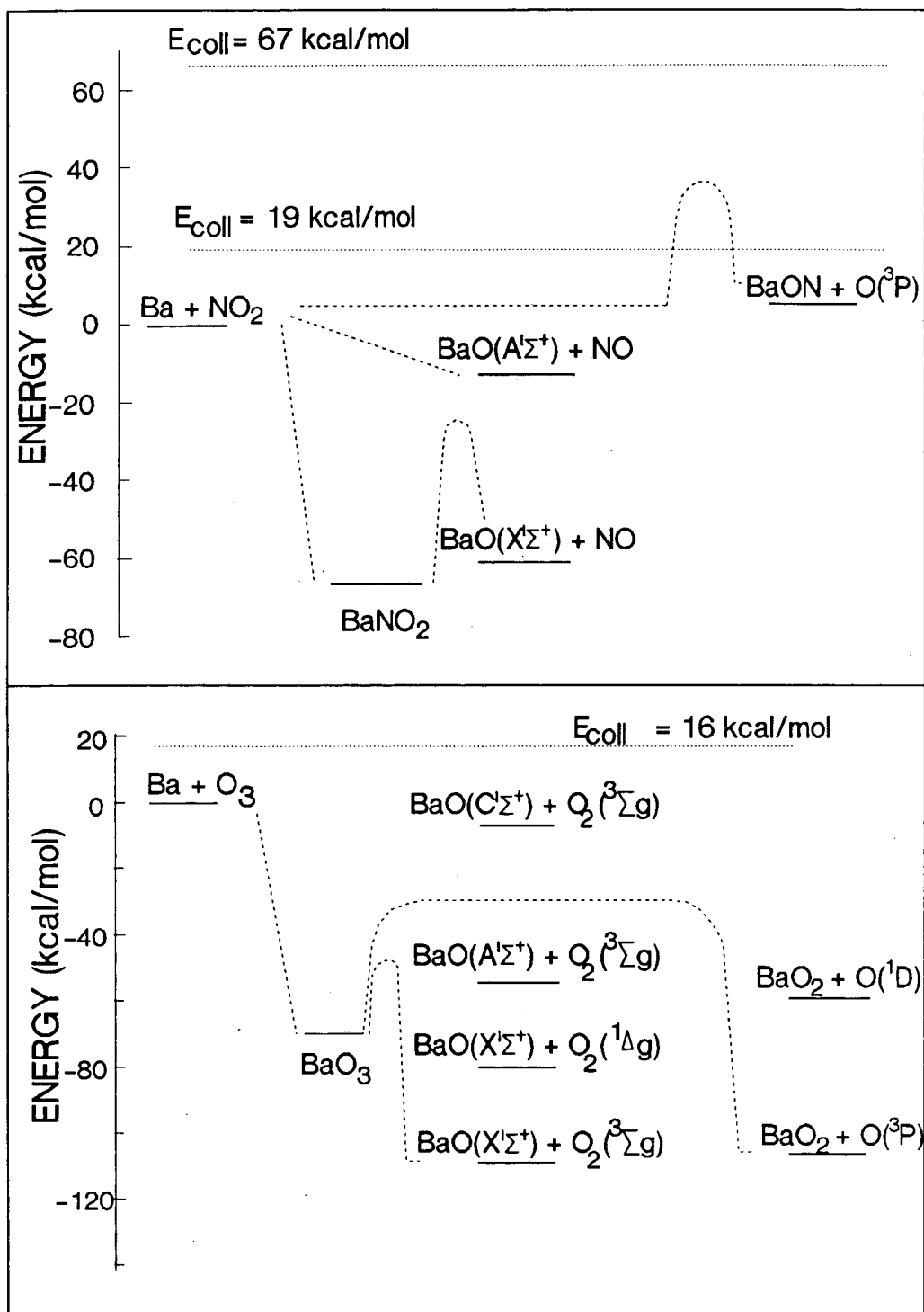


Fig. 3

BaO⁺ Angular Distribution

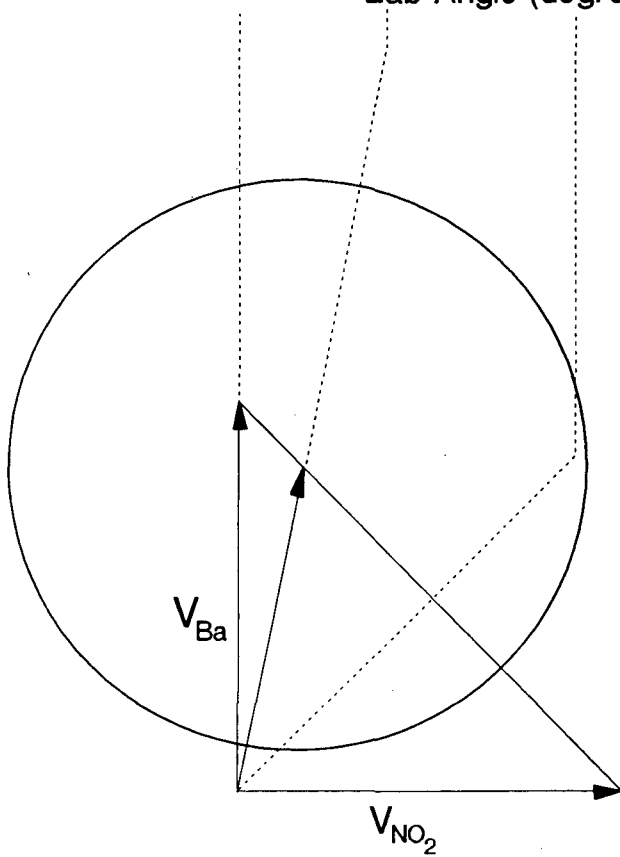
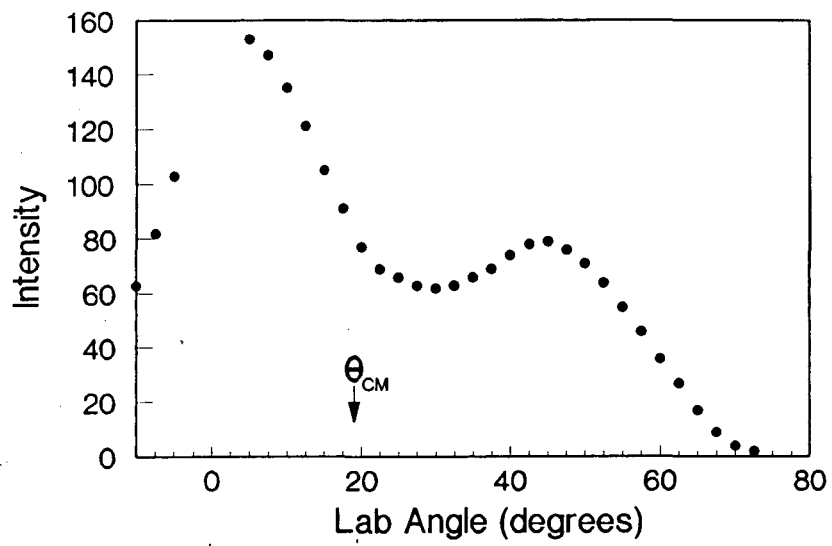


Fig. 4

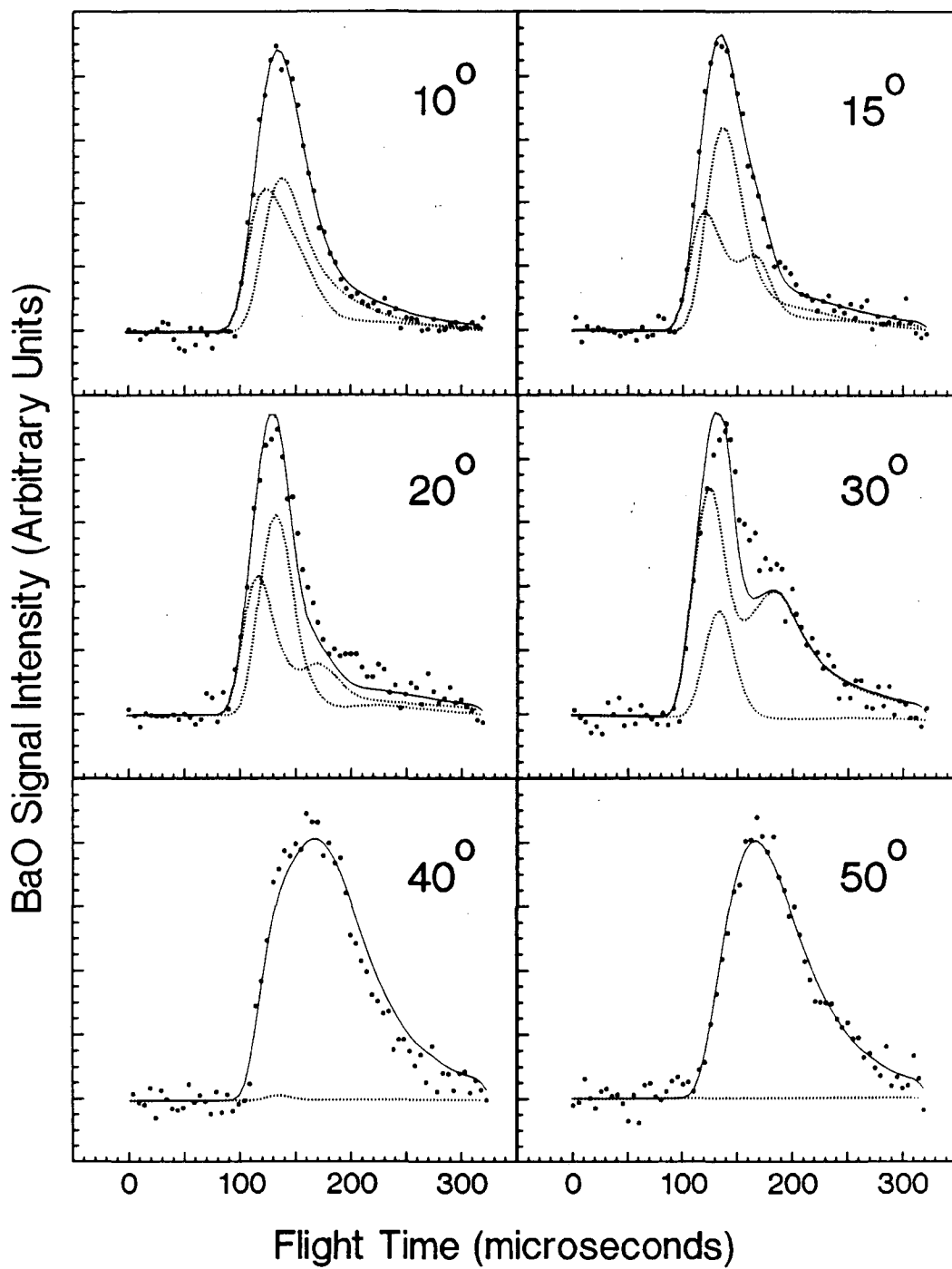
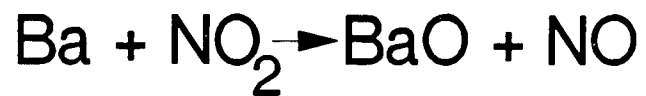


Fig. 5

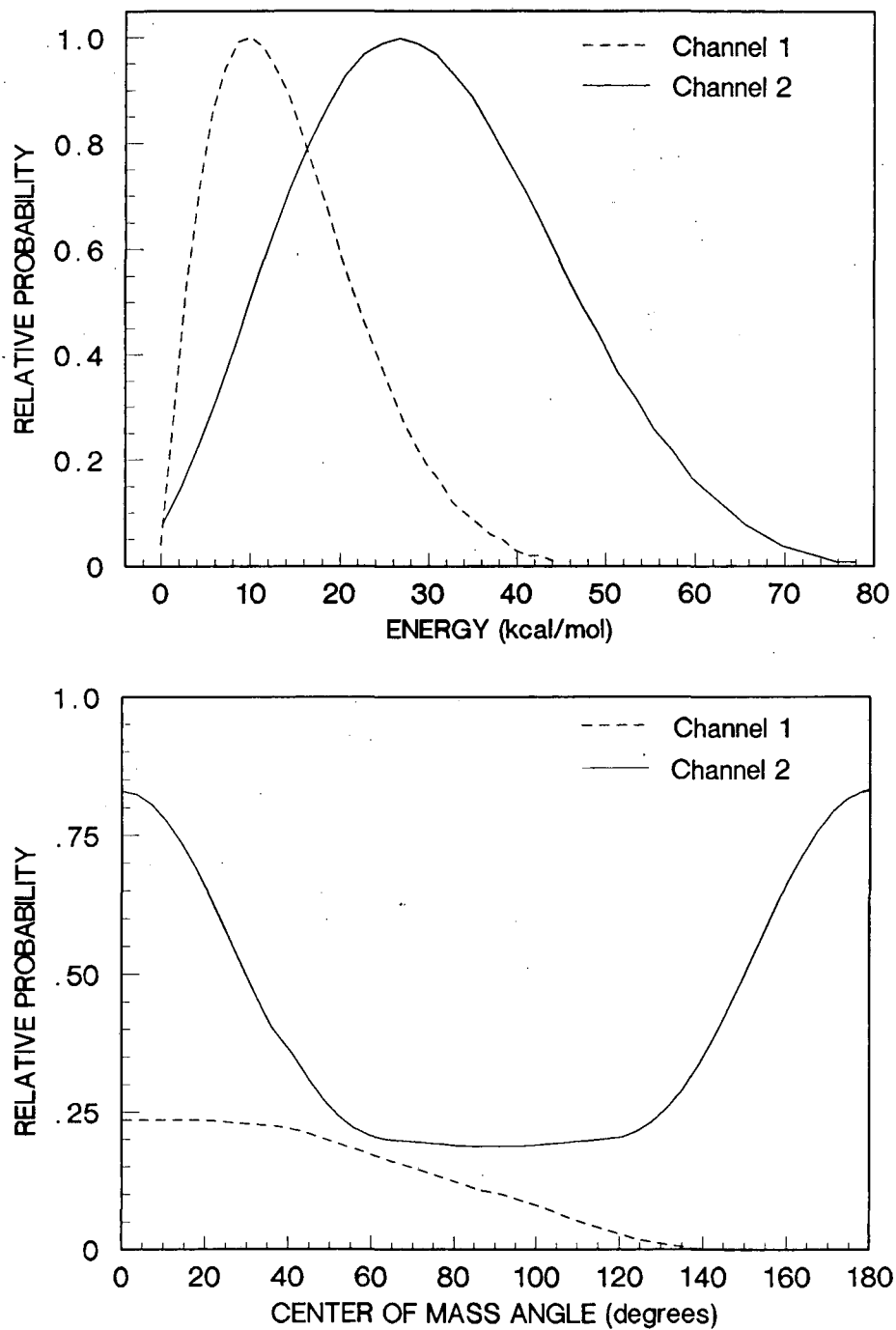
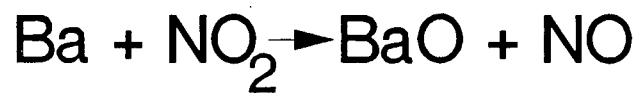


Fig. 6

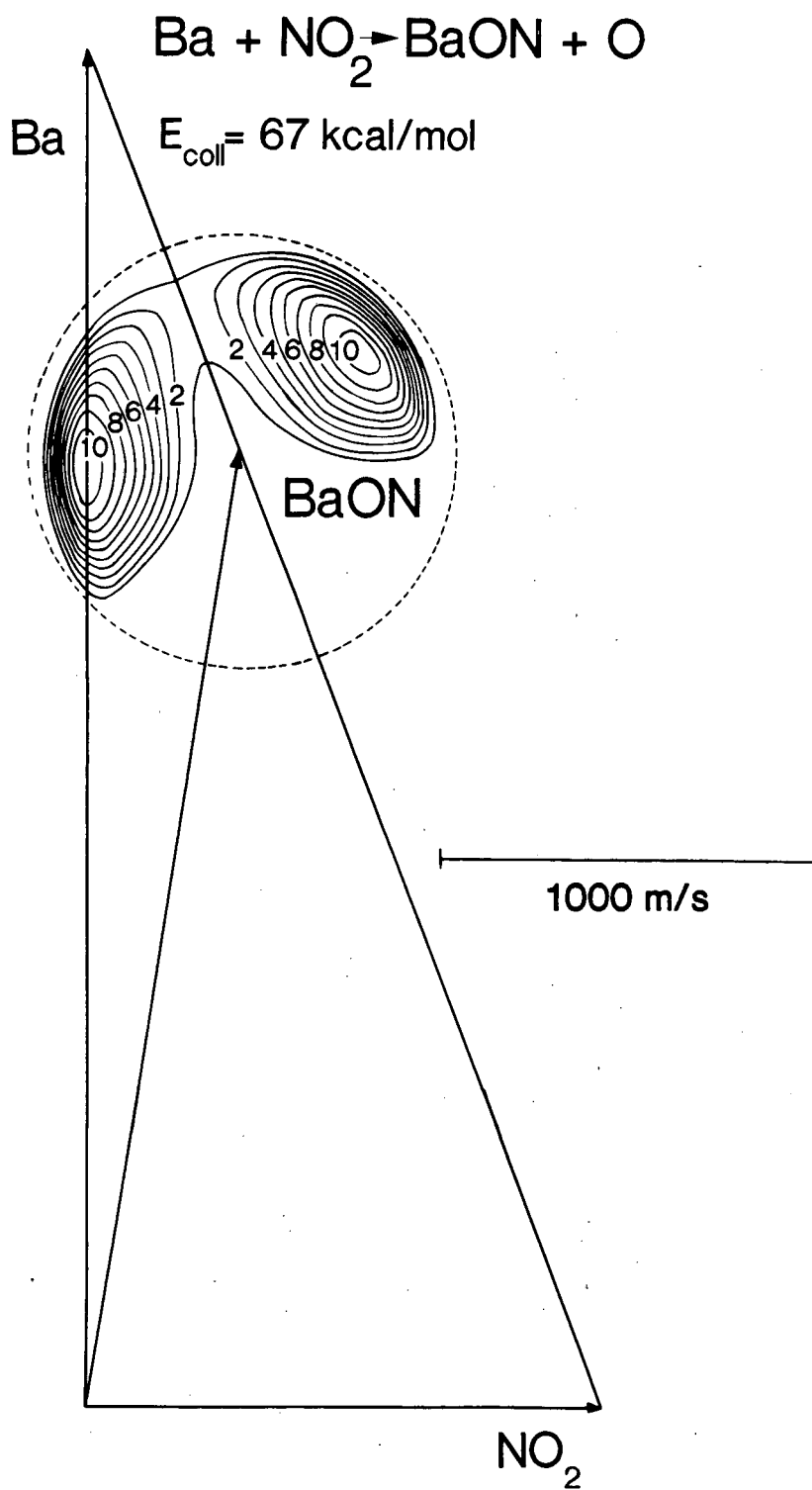


Fig. 7

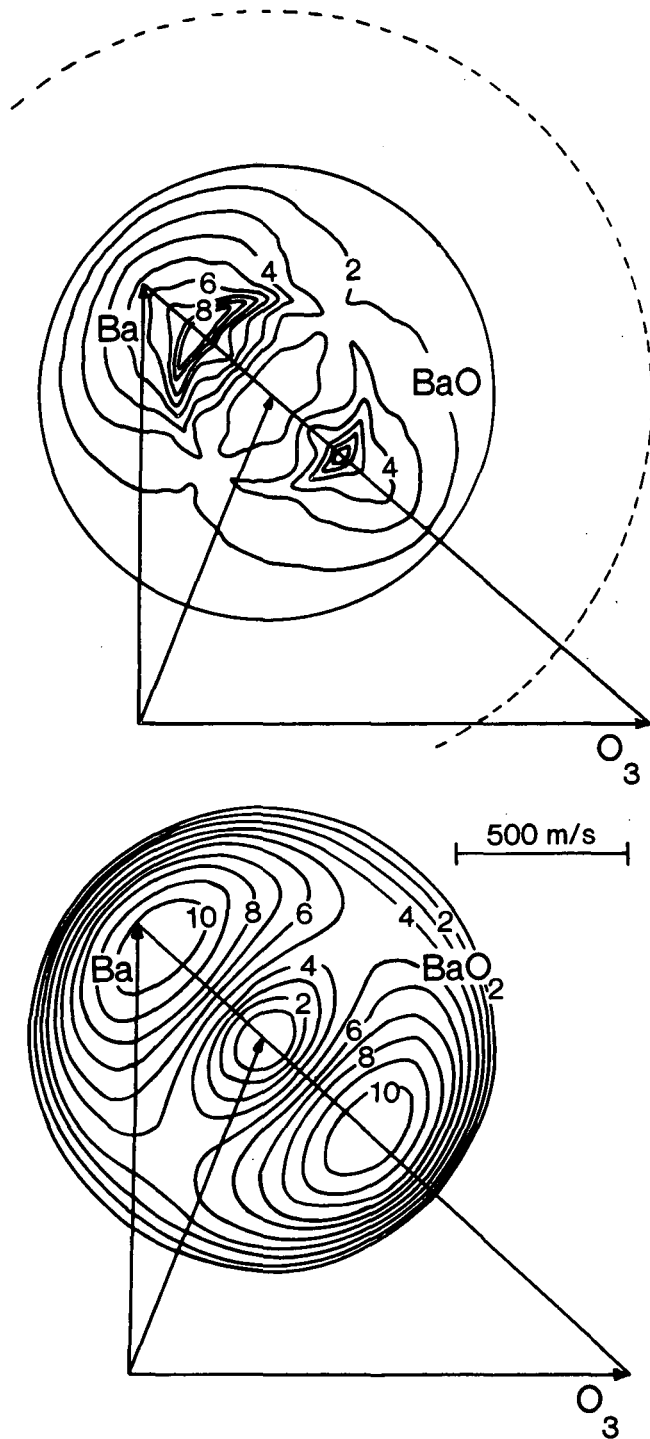


Fig. 8

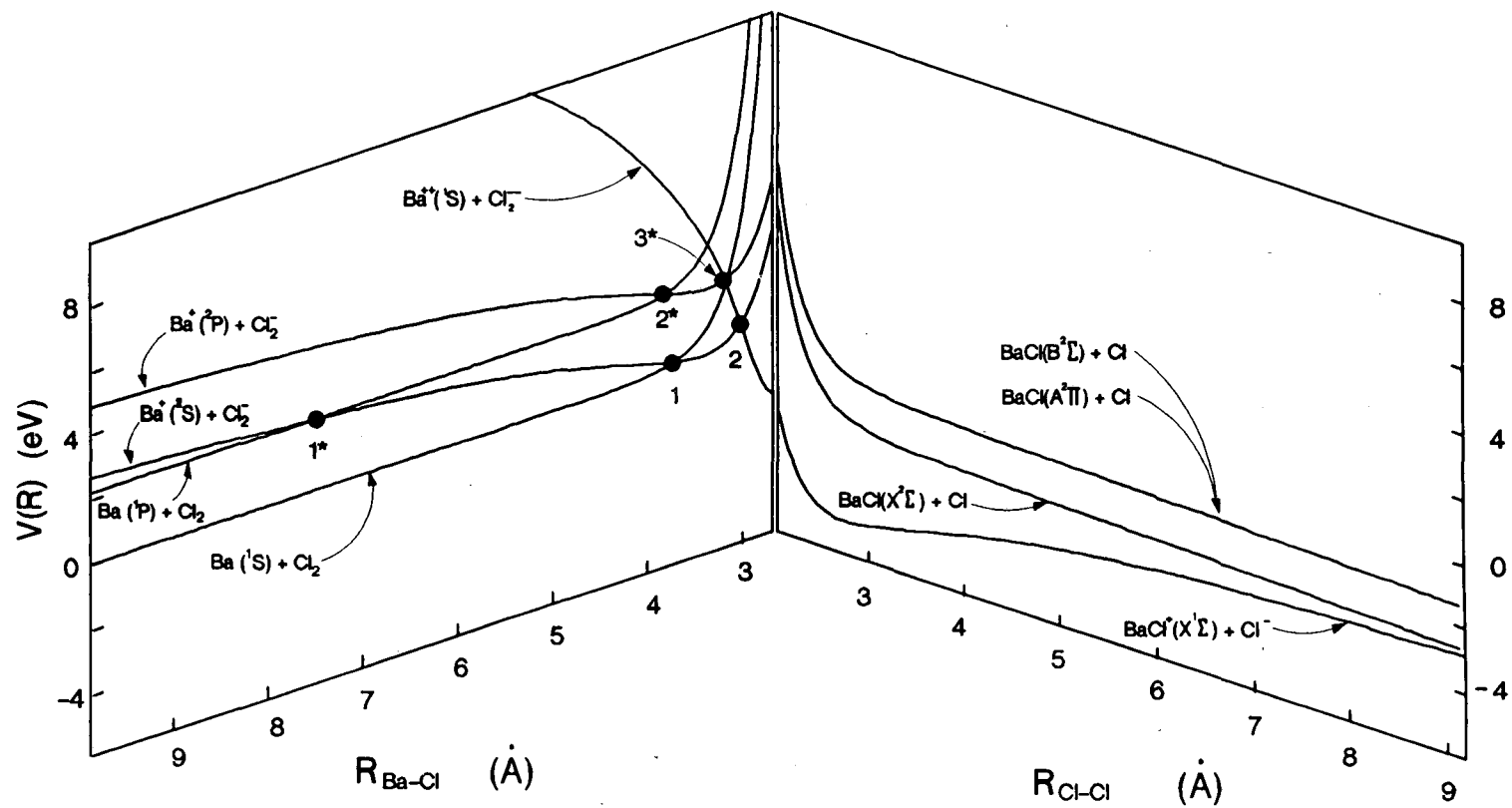


Fig. 9

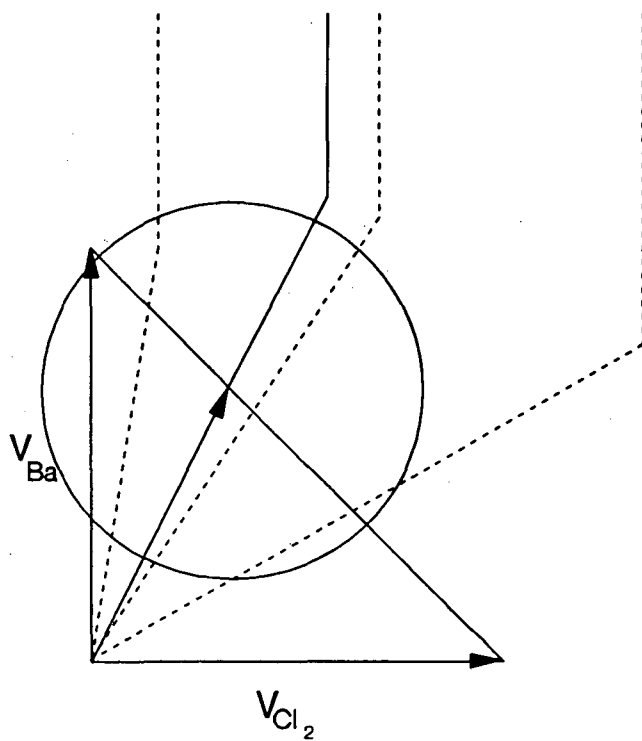
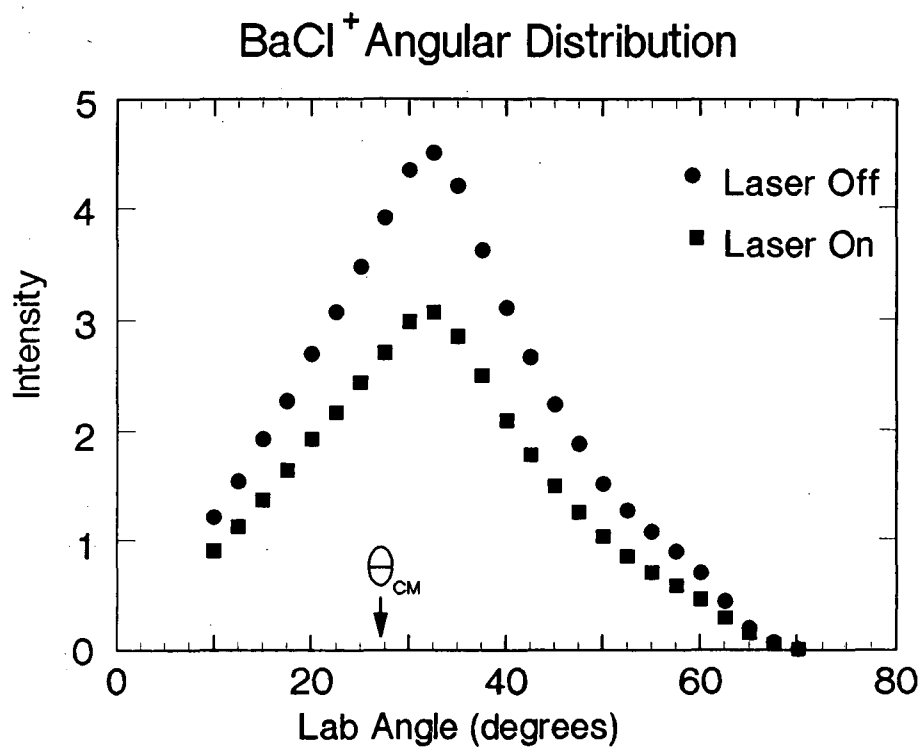


Fig. 10

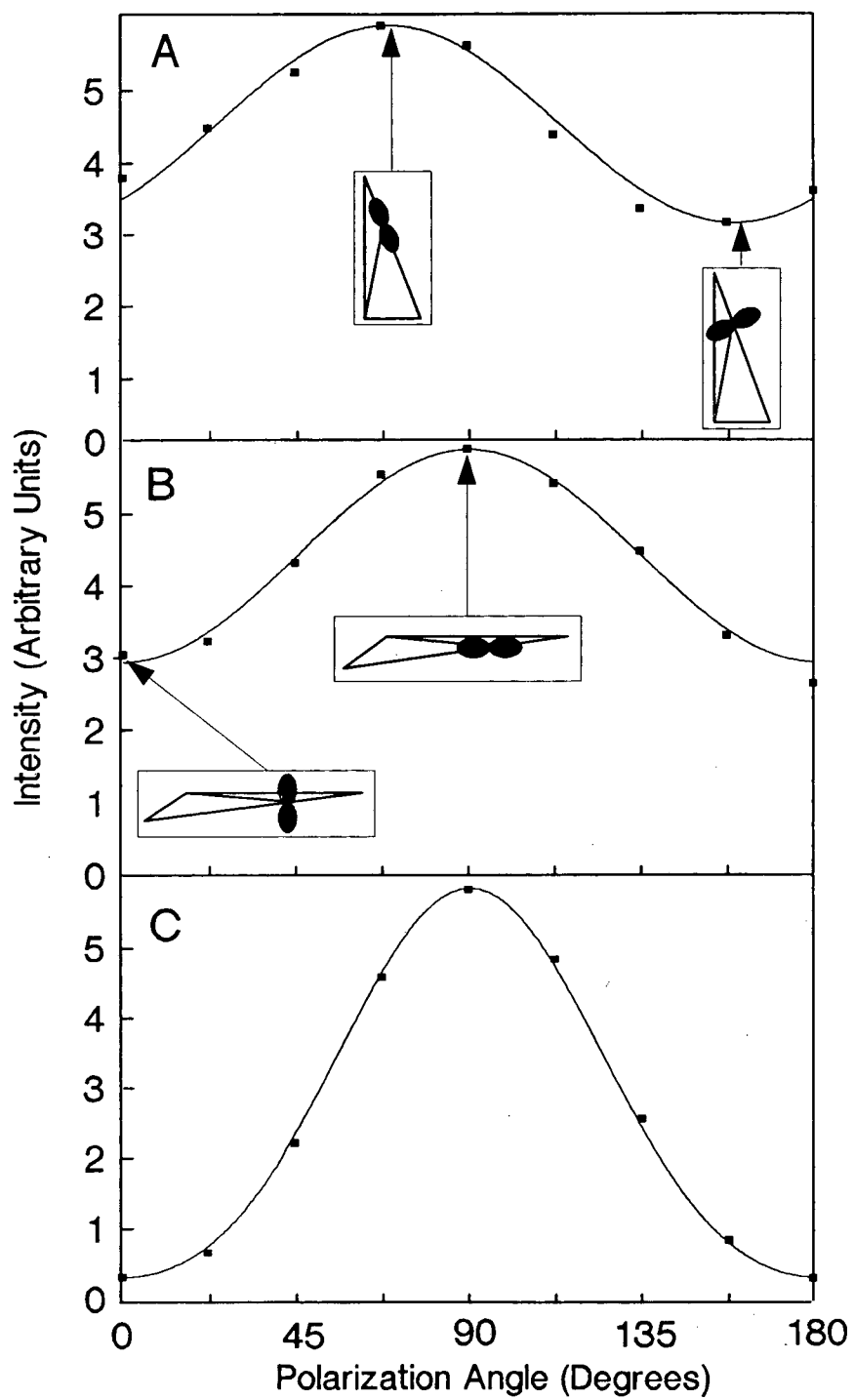


Fig. 11

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