Title
Orbital Alignment Dependence and Angular Distributions of Ions form the Reaction of Ba\((^1S^1, ^1P)\) with Cl\((^2S^2)\)

Permalink
https://escholarship.org/uc/item/1sr1s6nx

Authors
Suits, Arthur G.
Hou, H.
Lee, Yuan T.

Publication Date
1990-05-01
Orbital Alignment Dependence and Angular Distributions of Ions from the Reaction of Ba\((^{1}S,^{1}P)\) with Cl\(_{2}\)

A.G. Suits, H. Hou, and Y.T. Lee

May 1990
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Orbital Alignment Dependence and Angular Distributions of Ions from the Reaction of Ba($^{1}$S,$^{1}$P) with Cl$_{2}$

Arthur G. Suits, Hongtao Hou and Yuan T. Lee

Department of Chemistry
University of California

and

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
ORBITAL ALIGNMENT DEPENDENCE AND ANGULAR DISTRIBUTIONS
OF IONS FROM THE REACTION OF Ba(1s,1P) WITH Cl₂

Arthur G. Suits, Hongtao Hou and Yuan T. Lee

Department of Chemistry
University of California, Berkeley, California 94720

and

Materials and Chemical Sciences Division
Lawrence Berkeley Laboratory
Berkeley, California 94720 USA

ABSTRACT

We report crossed molecular beams studies of positive ions produced in the reaction of ground state and electronically excited barium atoms with Cl₂ at collision energies of 0.75 and 3.0 eV. At 0.75 eV, angular distributions for BaCl⁺ from the exothermic chemi-ion channel were largely backscattered relative to the barium beam. For Ba(1P), the cross section for BaCl⁺ formation was much lower at both collision energies studied. At 3.0 eV the product Ba⁺ was observed and the yield increased 20-fold on electronic excitation. In addition, the Ba⁺ intensity was further enhanced two-fold when the barium p-orbital was aligned along the relative velocity vector over that seen with the p-orbital perpendicular to the relative velocity vector.
INTRODUCTION

The reaction of barium with chlorine is dominated by the production of ground electronic states of the radical pair BaCl and Cl, yet also features several electronically excited product channels and a chemi-ion channel, \( \text{BaCl}^+ + \text{Cl}^- \), which are exoergic from ground state reactants. These reactions are initiated by long-range electron transfer in the entrance channel like the analogous alkali metal - halogen reactions but owing to the divalent nature of barium, the subsequent dynamics reveals the participation of several excited electronic states of the collision complex. Menzinger's comprehensive review documents the richness of the alkaline earth - halogen systems as a source of insight into reaction dynamics. The chemi-ionization reaction forming \( \text{BaCl}^+ \) and \( \text{Cl}^- \) from ground state \( \text{Ba} + \text{Cl}_2 \) was investigated by Ross et. al. using the crossed molecular beam method. Their center of mass angular and velocity distributions suggest a strongly coupled collision complex which contrasts with the dynamics of the neutral channel \( \text{BaCl} + \text{Cl} \). We have studied the angular distributions and orbital alignment dependence of ion products in the reaction of Ba (\(^1\text{S},^1\text{P}\)) with \( \text{Cl}_2 \) using crossed molecular beams in an effort to trace the course of the reaction through intersections between different electronic potential energy surfaces.
EXPERIMENTAL

A seeded supersonic barium atomic beam was formed by expanding mixtures of Ba and rare gas from the nozzle at the end of a resistively heated molybdenum tube connected to a Ba reservoir which was surrounded by a graphite radiation heater. The barium beam passed through a heated molybdenum skimmer, an initial differential pumping region then a collimating slit on its way to a liquid nitrogen cooled chamber maintained at $10^{-7}$ torr. The barium beam was crossed at 90° by a Cl$_2$ beam (15% in helium) under single collision conditions. Different collision energies were obtained by varying the average mass number of the barium beam through the choice of carrier gas.

The interaction region of the two beams was surrounded by a molybdenum and stainless steel electrode which was floated field-free at 20 volts above ground. Ions produced in the reaction were allowed to pass through an aperture in the field free region then accelerated to ground potential at the entrance to a quadrupole mass spectrometer through a series of focusing elements and a retarding electrode. Ions were counted by means of a Daly detector and associated electronics. The entire detector assembly could be rotated in the plane of the two beams. Angular distributions were obtained by monitoring ion signal at a given mass as a function of laboratory angle.

Electronically excited barium atoms were prepared by optical
pumping at (Ba(\(^1\)P)), or upstream (Ba(\(^1\)D)), of the interaction region by means of a single frequency ring dye laser tuned to the Ba (\(^1\)P-\(^1\)S) transition at 553.7 nanometers. The laser polarization was rotated using a double Fresnel-rhomb driven by a stepper motor. The laser polarization was either collinear with the Cl\(_2\) beam (when rotating the polarization out of the plane of the beams) or perpendicular to the plane of the beams (for in-plane polarization rotation). Alignment of the Ba (\(^1\)P) orbital was monitored by viewing the fluorescence perpendicular to the plane of the two beams in the former configuration. The nozzle of the Cl\(_2\) beam source was heated to 190°C to inhibit cluster formation.

RESULTS AND DISCUSSION

Figure 1 shows several important diabatic potential curves for collinear Ba\(^+\)Cl\(_2\) obtained by empirical correlations. The covalent curves are based on alkali metal - rare gas scattering results obtained by Beck and Loesch,\(^7\) while the ionic curves were obtained using a Rittner potential\(^8\) 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\(_2\).\(^9\) As can be seen from this figure, laser excitation of Ba to its (\(^1\)P) state adds 2.2 eV of available energy and moves the first crossing between the ionic and covalent curves to a much
greater internuclear distance. Furthermore, electronic excitation changes the symmetry of the reactants' electronic configuration, resulting in a conical intersection\(^{10}\) of the two potential energy surfaces 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. The chemi-ion products, \(\text{BaCl}^+\) and \(\text{Cl}^-\), correlate to the doubly ionic surface: both barium valence electrons must be transferred to chlorine. This represents the adiabatic reaction path, and the \(\text{BaCl}^+\) is a direct measure of the flux on this doubly ionic surface.

Shown in Figure 2 is a laboratory angular distribution for \(\text{BaCl}^+\) obtained from the reaction of \(\text{Ba}\) with \(\text{Cl}_2\) at a collision energy of 0.75 eV. The \(\text{BaCl}^+\) was largely backscattered relative to the barium beam indicating that direct reactions resulting from collinear, low impact parameter collisions dominate in the formation of this product. This is consistent with the results obtained by Ross et al., although they saw sufficient forward scattered product that they were unable to exclude the possibility of a forward-backward symmetric angular distribution implying long-lived intermediates. This backscattering is in marked contrast to the neutral \(\text{BaCl}\) product, for which the strongly forward scattered\(^{11}\) angular distribution implies a stripping mechanism similar to that
seen for the alkali metal-halogen reactions. As noted above, the BaCl\textsuperscript{+} chemi-ion product requires that the second electron be transferred from the barium atom, on which it will be localized even in the (Ba\textsuperscript{+}Cl\textsubscript{2}\textsuperscript{−}) intermediate, to the departing chlorine atom. This second electron transfer thus occurs only at short BaCl-Cl distances. But it is only for low impact parameter collisions and collinear geometries that this will occur, since otherwise prompt dissociation to neutrals follows the first electron transfer. These observations also explain the relatively small yield of chemi-ion product\textsuperscript{2} (cross section 1.4 Å\textsuperscript{2}) compared to total reactive yield\textsuperscript{1} (cross section 60 Å\textsuperscript{2}).

Figure 2 also shows an angular distribution for BaCl\textsuperscript{+} obtained under the same conditions but with a laser saturating the Ba(\textsuperscript{1}P)-Ba(\textsuperscript{1}S) transition at the interaction region. We observed a 35\% depletion of intensity independent of laboratory angle. We estimate that under these conditions the beam contained about 25\% Ba(\textsuperscript{1}P), 25\% Ba(\textsuperscript{1}D) and the remainder Ba(\textsuperscript{1}S); most of the signal thus represents the residual ground state reaction. Reaction of the D states alone appeared to be less effective at inhibiting the BaCl\textsuperscript{+} channel, so we conclude that excitation to the (\textsuperscript{1}P) state resulted in depletion of 50-100\% of the BaCl\textsuperscript{+} product. 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 yield the BaCl$^+$ channel. Laser excitation to the $^1P$ state moves the crossing point to a greater Ba-Cl$_2$ distance and reduces the coupling matrix element. These factors compete in their effect on the cross section for neutral products, so little overall change may result. But for BaCl$^+$ formation, which requires an intimate Ba-Cl-Cl interaction, the consequences of laser excitation are much more dramatic. The longer range electron transfer results in stretching of the Cl-Cl bond before the Ba atom can approach close enough for the second electron transfer to occur, precluding intimate Ba-Cl-Cl interaction unless the barium approach happens to be in phase with the Cl$_2^-$ vibration. The distance between the first and second crossing points, which changes dramatically on laser excitation, is critically important for determining the branching onto the doubly ionic surface.

At higher collision energies we observed the same magnitude laser induced depletion of the BaCl$^+$ signal, but a new ion channel appeared. As can be seen from Figure 1, at 3 eV collision energy the threshold for Ba$^+$ and Cl$_2^-$ formation from ground state reactants is just exceeded. At 3 eV collision energy we indeed saw this channel from ground state reactants, near the center of mass angle. But excitation to the ($^1P$) state resulted in greater than 20-
fold enhancement in Ba\textsuperscript{+} intensity. This Ba\textsuperscript{+} signal, monitored in the backward direction, showed a very strong dependence on the initial alignment of the barium p-orbital. Figure 3 shows the Ba intensity at a laboratory angle of 15 degrees measured as a function of laser polarization for in-plane (3a) and out-of-plane (3b) rotation of the barium p-orbital. The fluorescence monitored simultaneously (3c) confirmed that the p-orbitals were well aligned. The Ba\textsuperscript{+} intensity was enhanced two-fold when the laser polarization was along the relative velocity vector (3a) or in-plane (3b) over that seen when the polarization was perpendicular to the relative velocity vector. The Ba\textsuperscript{+} signal obtained is well reproduced by the function

$$K(\theta_v) = \frac{J_{\text{max}}^{\text{max}} - J_{\text{min}}^{\text{min}}}{2} - \frac{J_{\text{max}}^{\text{max}} - J_{\text{min}}^{\text{min}}}{2} \cos(\theta_E - \gamma)$$

where $\gamma$, the alignment angle, is zero, and $\theta_E$, is the angle between the electric vector of the laser and the relative velocity vector (3a) or the collision plane (3b).\textsuperscript{12} For the collinear case, the polarization dependence was precisely that expected from the nature of the conical intersection at the outer crossing (1' in Figure 1): collision geometries for which the p-orbital is aligned along the relative velocity vector result in a covalent surface of $\Sigma$ symmetry which can then interact with the $\Sigma$ ionic surface. This geometry favors electron transfer, leading then to the
singly ionic surface which correlates to both Ba\(^+\) product and neutral BaCl. When the p-orbital is perpendicular, however, the diabatic curves are of different symmetry and cross without interaction.

If this dramatic polarization dependence were the result of control over the branching onto the ionic surface at 1\(^*\) then one might expect a similar polarization dependence to appear in the neutral BaCl as well. Yet no laser dependent signal was seen for the neutral products. Consideration of the consequences of a non-adiabatic transition at 1\(^*\) may help resolve this apparent contradiction. The reactants remain on the covalent surface as they approach the inner crossing point, where another opportunity for escape to an exoergic product channel is presented (2\(^*\)). Here the curves are of the same symmetry so this crossing is fully avoided rather than conical. For most of the reactive flux through here, the temptation is too great to resist: the s-electron is transferred resulting in electronically excited, neutral BaCl products. For large impact parameter collisions there may be no access to the inner crossing point, 2\(^*\). Instead, the flux remaining on the covalent surface will have another opportunity to cross to the ionic surface at 1\(^*\) on exit; for large impact parameters, the transition probability on exit may be similar to that on approach.
These results are complementary to those obtained by Rettner and Zare in studies of the alignment dependence of chemiluminescence in the reaction of Ca(1P) with Cl₂.¹³ They observed a peak in chemiluminescence intensity for perpendicular p-orbital alignment, though the polarization dependence they reported was considerably weaker than that seen in our experiments. The Ba⁺ signal we observed derives largely from flux on the adiabatic path at 1⁺, while the electronically excited CaCl described by Rettner and Zare represents the remaining flux which has not undergone electron transfer at the outer crossing point. By looking in the backward direction, we have preferentially selected products resulting from collinear, low impact parameter collisions. The magnitude of the polarization dependence we observed may be attributable to the fact that we are weighting more heavily those geometries which will show the strongest effect. This may also explain why γ, a measure of the extent to which the polarization dependence reflects deviation from the space-fixed geometry of the reactants at long distance, is zero in our experiment. Because these are mainly low impact parameter collisions, and the crossing point is at a large internuclear distance, the space fixed coordinates remain accurate in describing the interaction.
ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
REFERENCES


Figure Captions

Figure 1. Sections of the relevant diabatic potential curves for collinear Ba + Cl₂. The energy is scaled relative to ground state reactants.

Figure 2. Experimental angular distribution for BaCl⁺ at a collision energy of 0.75 eV shown with the nominal Newton diagram.

Figure 3. 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.
Ba + Cl₂ Collinear

Fig. 1  XBL 905-1781
BaCl\(^+\) Angular Distribution

![Graph showing angular distribution with markers for Laser Off and Laser On.]

Intensity

Lab Angle (degrees)

\(\theta_{CM}\)

\(V_{Ba}\)

\(V_{Cl_2}\)

XBL 905-1776

Fig. 2
Fig. 3