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Covering the Period June 1976 to December 1977

STUDY OF METASTABLE RARE GAS COLLISIONS WITH HALOGENS

By: K. T. Gillen and D. C. Lorents

Prepared for:

OFFICE OF NAVAL RESEARCH
Washington, D.C.

Attention: Dr. B. R. Junker

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An atomic beam scattering apparatus has been modified to allow detailed dynamic investigations of inelastic and reactive scattering between fast beams of metastable excited rare gases and halogen-containing target molecules. The first system investigated was $Ar^* + I_2$. Detailed double-differential (angle and energy) measurements of the ion-pair formation channel have been completed and compared with the analogous reactions of alkali atoms with I_2 . In additional preliminary measurements of the elastic scattering angular distribution and the total (over)		

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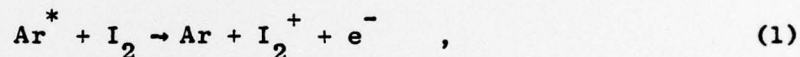
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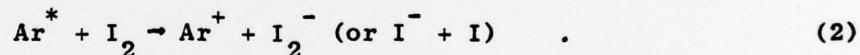
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INTRODUCTION

The development of the rare gas halogen laser over the past several years has stimulated a tremendous interest in the basic interaction mechanisms between rare gas metastable atoms Rg^* and halogen-containing molecules. We have chosen this same Rg^* -halogen system as a prototype reaction for probing interactions within a continuum. Although our work could make direct contributions to the understanding of the important laser processes, its potential impact on the understanding of the more general continuum coupling scattering problem is far greater. Few detailed experimental data (of the kind accessible using our sophisticated differential-scattering techniques) exist for interactions involving inelastic processes occurring in a continuum, and it is difficult to predict the competition between continuum interactions, e.g., Penning ionization,



and discrete state inelastic channels, e.g.,



Our experimental arrangement allows detailed investigations under single-collision conditions over an energy range from ~ 10 eV to ~ 2 keV. There are generally several accessible reaction channels whose relative importance may change with energy over this range. By studying several collision pairs, chosen to produce a systematic change in properties and a resulting systematic variation in the relative importance of the major reaction channels, we hope to observe and characterize the reaction dynamics in a manner that allows prediction by extrapolation for systems not as amenable to direct experimental investigation. We also hope to produce results that will both test existing theoretical treatments and stimulate

new theoretical investigations of interactions occurring within a continuum.

The reactions of Rg^* with RX (a halogen-containing molecule) are understood mainly by analogy with the well-studied reactions¹ of alkali ground state atoms, M, with RX. The $M + X_2$ reactions have been studied extensively in the thermal energy range,² and recently Los³ and co-workers and others have studied these collisions at energies up to several keV by monitoring the total cross-section energy dependence, the product ion branching ratios, and the angular and energy distributions of M^+ . These reactions are dominated by the surface crossing of the relatively flat $M + X_2$ diabatic surface with a coulombic $M^+ + X_2^-$ surface. The electron transfer generally occurs to a repulsive portion of X_2^- , permitting expansion and possible dissociation of the X_2^- in the course of the collision. At thermal energies, a stable M^+X^- is formed, but at higher energies dissociation to ionic products $M^+ + X^- + X$ or $M^+ + X_2^-$ can occur along the coulomb potential. The quite detailed scattering studies of Los and co-workers³ have shown that these reactions can be modeled quite simply as a two-body collision if proper account is taken of the effects due to stretching of the X_2^- bond during the collision: changes in the electron affinity, crossing distance, and H_{12} . These extensive studies are described in an excellent review article prepared by J. Los for ICPEAC X.³

Our recently initiated studies of $Rg^* + X_2$ reactions are beginning to provide similar detailed information on the ionic-covalent surface interaction in these systems. These collisions are potentially much more complicated than their alkali analogs because the high excitation energy implies the existence of other exit channels including covalent surfaces lying below the incoming channel or autoionization transfer to an underlying continuum level. However, our initial results on the $Ar^* + I_2$ collision indicate that the scattering patterns are qualitatively quite similar to those observed for the $M + I_2$ collisions.

PROGRESS

The initial phase of the experimental program included a series of modifications of the metastable differential scattering apparatus.⁴ These changes were specifically designed to enhance its experimental capabilities in handling the extra complications expected with halogen target species. First, a completely new gas handling system was designed and constructed. This system allows I_2 to be introduced reproducibly as a vapor from a reservoir outside the main apparatus, thereby avoiding the many problems associated with relying on a heated I_2 container within the vacuum system. The resolution of time-of-flight (tof) experiments⁵ has been improved by approximately a factor of three by modifications in the pulsing method, the total flight path, and the detector geometry. The entire scattering cell region has been redesigned to allow interchangeable scattering cells, measurements of scattered particles at large angles (up to $\sim 95^\circ$ from the original beam direction), and extraction of slow product ions. We have built a new detector, which can be used to measure total destruction cross sections as a function of collision energy. Finally, we have interfaced the apparatus to our PDP 11/40 computer; this will produce faster and more efficient data reduction and soon will allow computer control of the experimental parameters.

The first collision pair being investigated is $Ar^* + I_2$. In analogy to the alkali-halogen results, an expected major reaction path involves a transfer (at $r \sim 5.6 \text{ \AA}$) from the incoming covalent $Ar^* + I_2$ potential surface to an attractive ionic $Ar^+ + I_2^-$ surface. Although at thermal energies the reactants pass adiabatically from the covalent to the ionic configuration, at higher energies there is a significant probability of diabatic behavior at the crossing. Collisions at energies from several eV up to several hundred eV can exit on the ionic surface and yield products $Ar^+ + I_2^-$ or $Ar^+ + I^- + I$ after exploring either a covalent $Ar^* + I_2$ or

an ionic $\text{Ar}^+ + \text{I}_2^-$ surface inside $r \sim 5.6 \text{ \AA}$. The two pathways yield different deflection patterns, and the product Ar^+ angular distribution should reflect these two distinct contributions.

Figure 1 shows several product Ar^+ angular distributions measured over a large range of collision energy. At the higher energies, two major peaks are observed. The low angle peak is due to scattering on the covalent surface, and the maximum at larger angles is due to scattering along the ionic surface. At lower energies the ionic peak develops additional structure and increases in intensity relative to the covalent peak. These results are all strikingly similar to recent results observed in the reactions of alkali atoms with I_2 at comparable energies.⁶

A simple Landau-Zener picture would predict that the two major peaks have comparable total intensities. The reason that the ionic path yields more product ions can be understood by examining the nature of trajectories that explore the ionic surface inside the initial crossing $r = 5.6 \text{ \AA}$. As indicated in the simplified picture in Figure 2, the electron jump occurs to an I_2 molecule near its equilibrium internuclear distance, forming an I_2^- molecule on its repulsive inner wall. As the Ar^+ continues to approach, reaches the turning point, and then recedes from the I_2^- , the I_2^- bond is stretching. At the second crossing of the ionic and covalent surfaces, the I_2^- bond is larger, implying a larger effective electron affinity, a larger crossing distance, and a more diabatic crossing. At high collision velocities, the bond length changes little between the two crossings; at lower velocities, as the first crossing becomes more and more adiabatic, bond stretching can yield enhanced diabatic probabilities (and hence enhanced ion-pair formation) on the return passage. Such effects have been observed in alkali-halogen collisions³ at energies comparable to ours. Thus the alkali analogy is indeed useful for describing the ion pair formation channel, just as it was⁷ for predicting laser properties in thermal energy collisions.

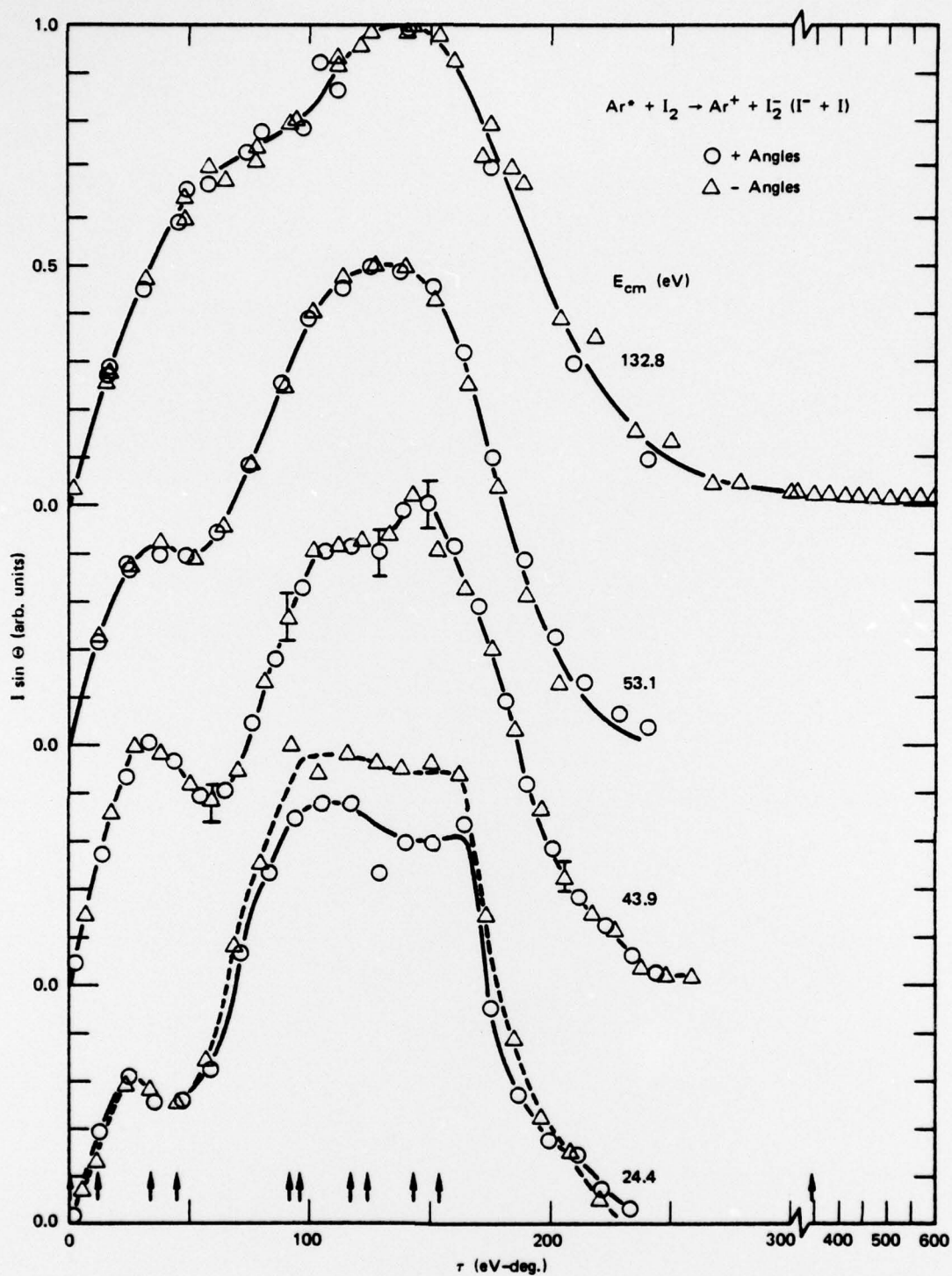


Figure 1. Angular distributions of product Ar^+ ions from collision of Ar^* with I_2 at the four center-of-mass energies E_{cm} indicated. The measured differential cross section has been weighted by $\sin \theta_{c.m.}$ and plotted against the reduced angle $\tau = E_{cm} \times \theta_{c.m.}$. The vertical arrows indicate τ values where an energy distribution of product Ar^+ ions has been measured.

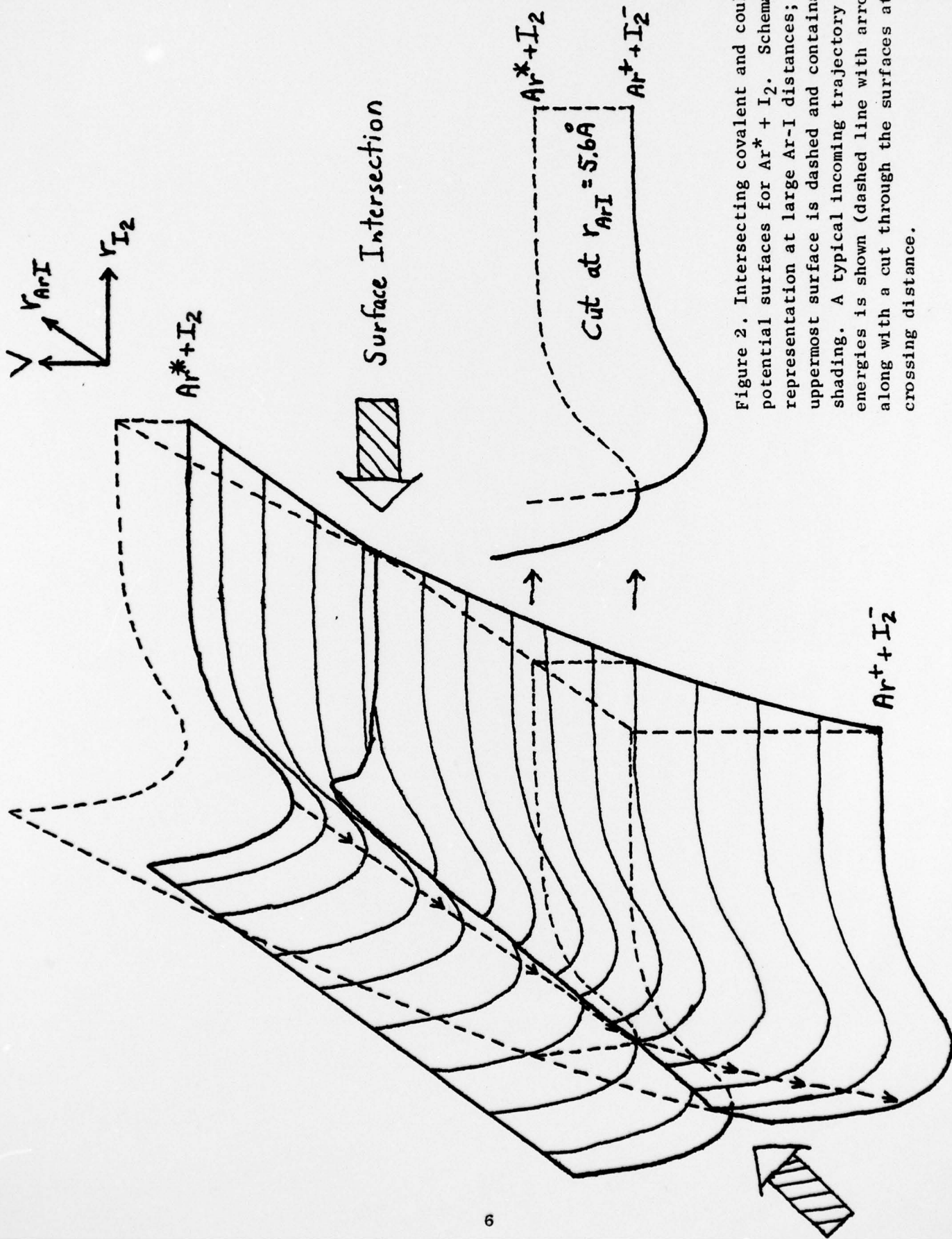


Figure 2. Intersecting covalent and coulombic potential surfaces for $\text{Ar}^* + \text{I}_2$. Schematic representation at large Ar-I distances; the uppermost surface is dashed and contains no shading. A typical incoming trajectory at low energies is shown (dashed line with arrows) along with a cut through the surfaces at its crossing distance.

We have also determined the energy distribution of product Ar^+ ions at several values of collision energy and scattering angle (the τ values for the various energy distribution measurements are indicated in Figure 1). In all cases, the product ions fall in a narrow energy loss range with an average energy loss of 2.7 ± 0.5 eV and a typical width of ~ 0.8 eV FWHM. An energy loss of 2.7 eV is just sufficient to allow I_2^- dissociation

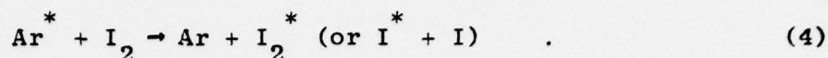


We have concluded from the energy loss values and their small range that the electron transfer involves a near-vertical transition in I_2 to the lowest I_2^- potential curve and that the I_2^- products can be either highly excited or dissociated to $\text{I}^- + \text{I}$. We will soon measure the ratio of I^- to I_2^- by collecting and analyzing the slow negative ions. Since the alkali analogy seems to work so well for the ion-pair channel, we might expect an I^-/I_2^- ratio of $\sim 1/4$ in agreement with the results of Hubers et al.⁸

We have also measured the angular distribution of elastically scattered Ar^* . This elastic channel also has two contributions corresponding to encounters that explored either the covalent or coulombic surfaces at distances inside their crossing point. The interesting component comes from collisions that transfer to the coulombic surface on the approach trajectory and transfer back on the outgoing trajectory. A rainbow peak is predicted from the coulomb potential well, but the I_2^- bond stretching that enhances the ion-pair channel at low energies (Figure 1) should also severely attenuate the elastic rainbow scattering. Our preliminary results show a peak at $\tau \sim 50$ eV-deg followed by a very sharp dropoff at larger angles. This is qualitatively consistent with our expectations and is worthy of more detailed examination.

So far there is no clear evidence of any significant perturbations of the important ion-pair channel by the energetically accessible competing channels, Penning ionization (reaction 1) and excitation transfer to

excited I_2 states,



This may be understood by comparing the expected size of the various channels. Ion-pair formation rates in alkali- I_2 systems in this energy range are quite large⁹ ($\sim 100 \text{ \AA}^2$), whereas representative¹⁰ total destruction cross sections are typically $\sim 20 \text{ \AA}^2$ for rare gas metastables interacting with species that can be Penning ionized. We had made preliminary measurements of the total destruction cross section for $Ar^* + I_2$ using an attenuation technique. Our values ($200\text{-}250 \text{ \AA}^2$) were determined without an accurate pressure measuring tool. We have now installed a Baratron capacitance manometer and are repeating the measurements. The total cross sections are somewhat smaller ($100\text{-}150 \text{ \AA}^2$), but are still large enough to suggest that the ion-pair formation channel might dominate other channels.

Although a wealth of additional detailed information should be available for $Ar^* + I_2$ in the next few months, along with comparable data for other collision partners, we have decided that the current results on the ion-pair channel are interesting enough that they warrant immediate publication. A short note is being written.

PERSONNEL

D. C. Lorents is Project Supervisor and K. T. Gillen is Project Leader for this work. Other important contributors to this work included T. D. Gaily, R. Leon, R. E. Olson, and J. R. Peterson.

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