Particle Interchange Reactions Involving
Plasma Impurity Ions and H$_2$, D$_2$ and HD

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Abstract

The kinetic energy dependence of the cross section of particle interchange reactions between a variety of plasma impurities (C\(^+\), O\(^+\), Si\(^+\), Ti\(^+\), V\(^+\), Cr\(^+\), Fe\(^+\), Ni\(^+\), Cu\(^+\), Al\(^+\), Mo\(^+\), Mn\(^+\), Mg\(^+\), B\(^+\), Si\(^+\), Ge\(^+\), Nb\(^+\), Ag\(^+\), Ne\(^+\), Ar\(^+\) and Kr\(^+\)) and the main plasma constituents, in molecular state (H\(_2\), D\(_2\) and HD), of a thermonuclear fusion device are reviewed. Most of the experimental results presented here were obtained with a guided ion beam mass spectrometer. Analytic fits to the data are presented for most cases.
1 Introduction

The edge plasma in a tokamac nuclear fusion reactor is characterized by low plasma temperatures and high plasma densities. In the divertor region, the plasma temperature may be as low as a few eV, and plasma densities may be as high as $10^{17}\text{cm}^{-3}$.(1) An important consequence of the low edge plasma temperature is that molecular species are present in this region, resulting either from plasma-wall interactions (e.g. hydrocarbons) or from recycling and plasma fueling (molecular hydrogen and its isotopes). In addition to the primary constituents of the plasma, e.g. D, T and He (in DT plasmas) and H, D, and He in the present tokamaks, a relatively large variety (with concentrations between 0.1 and 10%) of atomic impurities are present. The most common impurity generating processes are particle-surface interaction processes, mainly desorption, physical sputtering and evaporation. The main impurities in the plasma edge of most of the present generation tokamaks and fusion reactor designs are carbon ($\leq 10\%$), oxygen ($\leq 5\%$), various metallic (and related) impurities originating from structural materials (Ti, V, Cr, Fe, Ni, Cu, Al, Mo, Mn, Mg, B, Si, Ge, Nb, Ag; with a concentration of $\leq 2\%$) and various diagnostic species (Li, Ne, Ar). Under these plasma conditions, a wide range of atomic and molecular processes that are not important in the core plasma become relevant.

Heavy particle interchange reactions in ion-molecule collisions refer to processes in which heavy particle rearrangement occurs, such as

$$A^{q+} + BC \rightarrow AB^{q+} + C.$$  \hspace{1cm} (1)
In this report we will cover particle interchange reactions where the ion is a plasma impurity with a charge state \( q = 1 \) and the molecule is either \( H_2, D_2 \) or \( HD \). In general, there are two different types of these reactions. Endothermic reactions, which are characterized by a threshold below which the reaction does not take place (generally equivalent to the endothermicity of the reaction), and exothermic reactions, in which case the reaction often (but not always) occurs without an activation energy because of the attractive long-range interaction potential.\(^{(2),(3)}\) Of the reactions presented here, all but the \( O^+, Ar^+ \) and \( Kr^+ \) systems are endothermic. The kinetic energy dependence of the interchange cross section for these two types of reactions is, of course, quite different. For exothermic reactions, the cross section often follows a relatively simple \( E^{-1/2} \) decrease with increasing energy (in accord with the Langevin-Gioumousis-Stevenson prediction\(^{(4)}\)), but deviations from this behavior abound.\(^{(5)}\) For endothermic reactions, the cross section usually increases sharply starting at an energy close to the endothermicity of the reaction, peaks at an energy close to the molecular \( (H_2, D_2 \text{ or } HD) \) dissociation limit, and decreases drastically within a few eV. The reason for this sharp decrease at high energies is that the dissociation channel opens, i.e. the reaction

\[
A^+ + BC \rightarrow A^+ + B + C, \tag{2}
\]

with a higher cross section, takes place. This decline in the interchange cross section after the dissociation energy has been reached may be delayed in energy if the reaction dynamics tends to place much of the excess energy in product translation.
2 Experimental Description

2.1 General

The work described in this report has been performed on a guided ion beam tandem mass spectrometer, that has undergone several changes in its 10 year history.\(^{(6)-(8)}\) In this apparatus, ions exiting the ion source region are focused into a magnetic sector for mass analysis, decelerated to a desired kinetic energy, and injected into an octopole ion beam guide that passes through a collision cell filled with the neutral reactant. Pressures of this gas are generally kept sufficiently low that only single ion-molecule collisions are probable. (Deviations from single collision conditions are readily ascertained by examination of the pressure dependence of the product yield.) Product and reactant ions drift from the gas cell to the end of the octopole where they are extracted and focused into a quadrupole mass filter for mass analysis. The ions are then detected by using a secondary electron scintillation ion detector\(^{(9)}\) and counted by using standard pulse counting electronics. A computer sweeps the kinetic energy of the ion beam while monitoring the reactant ion and all product ions so that extensive signal averaging can be performed easily.

Ion intensities are converted to absolute reaction cross sections as described previously.\(^{(6)}\) Based on reproducibility, the relative uncertainty of cross sections at different energies is within about 5% for cross sections greater than \(10^{-17}\text{cm}^2\) and is limited by statistical counting uncertainties for smaller cross sections. The absolute accuracy of the cross sections is limited by systematic errors in the measurement of
the absolute neutral reactant pressure and our estimate of the effective path length for interaction, both estimated at about 10%. Although the use of an octopole minimizes losses of ions, the possibility of ion loss especially at very low and very high energies cannot be ruled out entirely. For the heavy on light mass systems discussed in this work, collection deficiencies are minimized by the forward scattering in the laboratory frame necessitated by linear momentum conservation. Under most circumstances, we estimate that the uncertainties in the absolute cross sections are within ±20%. Comparison of the absolute cross sections measured with this instrument with calculated capture rate constants\(^{(10)}\) and with thermal rate constant measurements\(^{(6),(11),(12)}\) suggest that our cross sections generally suffer from no serious systematic errors and that their accuracy is very good.

2.2 The Octopole Ion Beam Guide

The octopole ion beam guide, first developed by Teloy and Gerlich\(^{(13)}\) is the primary key to the unique capabilities of this apparatus when compared with more conventional tandem mass spectrometers. A comprehensive analysis and description of such inhomogeneous rf devices has been made recently by Gerlich\(^{(14)}\). In our instrument, the octopole comprises eight rods (3.2 mm diameter) held in a cylindrical array (17.2 mm bolt circle). Alternate phases of an rf potential are applied to alternate rods such that an effective potential well in the radial direction is established. Energies along the axis of the octopole are perturbed little because the potential well, which depends on the inverse sixth power of the distance from the
center, is flat at the bottom and has steep sides.$^{6,14}$ One of the virtues of the octopole is that it enables the use of retarding field analysis to measure the absolute energy of the ion beam and its distribution. The octopole avoids problems associated with contact potentials, space charge effects and focusing aberrations because the analysis and interaction regions are physically the same. Further, the octopole trapping field prevents anomalous losses of ions even at very low kinetic energies. We have verified the ability of the octopole to accurately measure kinetic energies by comparison with time-of-flight experiments$^{6}$ and with calculated cross sections.$^{10}$ We estimate that the uncertainty associated with measuring the zero of energy is about 0.05 eV in the laboratory frame.

2.3 Kinetic Energy Scale and Doppler Broadening

Laboratory energies are converted to center-of-mass (CM) energies by using the stationary target assumption. Thus,

$$E_{CM} = E_{lab} \times m/(M + m),$$

(3)

where m and M are the masses of the neutral and ionic reactants, respectively. At the very lowest energies, this approximation is not adequate because the ion energy distribution is being truncated. In such circumstances, the mean energy that is reported properly reflects the truncated distribution of ions as described in detail previously.$^{6}$ This kinetic energy scale in the center-of-mass frame does not include the thermal motion of the reactant neutral, which adds another $(3/2)\gamma kT$ to the average energy where $\gamma = M/(M + m)$. These molecules have a Maxwell-
Boltzmann distribution of velocities at the temperature of the gas cell, usually \( T = 305 \, K \) in our work. The effects of this motion are to obscure sharp features in the true cross sections, a result that is especially obvious at a reaction threshold. In addition, the velocities of the neutral reactant molecules can be comparable to or larger than the ion velocities at very low kinetic energies. At these energies, the full distribution of neutral and ion velocities must be considered in order to fully describe the average interaction energy. The means necessary to describe this so-called Doppler broadening were first developed in detail by Chantry\textsuperscript{(16)} for the cases of a monoenergetic ion beam and extended to include consideration of ion energy distributions by Lifshitz et al.\textsuperscript{(17)} The width of the energy distribution (fwhm) contributed by the neutral molecules at a center-of-mass energy, \( E \), is given by Chantry as approximately \((11.1\gamma kT E)^{1/2}\).

### 2.4 Ion Sources

The guided ion beam apparatus shown in Figure 1 is capable of using several types of ion sources: commonly, surface ionization (SI), electron impact (EI) ionization, and two high pressure sources - a drift cell and a flow tube source. In some studies, several of these sources are used in order to systematically vary the degree of internal excitation of the ion. The SI source\textsuperscript{(18)} can be used to ionize species with low ionization energies (IEs) such as metal atoms and is believed\textsuperscript{(19)} to produce ions with a Maxwell-Boltzmann distribution of internal states at the temperature of the ionizing filament, 1900-2300 \( K \). EI\textsuperscript{(18)} can ionize and fragment any volatile gas,
but can produce internally excited species depending on the electron energy. The flow tube source, developed as a more versatile version of an earlier drift cell (DC) source,\textsuperscript{(20)} is modeled after those of Lineberger\textsuperscript{(21)} and Squires,\textsuperscript{(22)} and is detailed in the literature.\textsuperscript{(8)} This high pressure source ($\approx 0.5$ Torr) is designed to produce atomic ions with a minimum of internal energy, that is, species thermalized to near room temperature.

3 Theoretical Considerations

The theoretical study of the particle-interchange reactions considered here is still an undeveloped field. It started about twenty years ago with the trajectory surface-hopping model first suggested by Bjerre and Nikitin\textsuperscript{(23)} and the multivibronic curve crossing model introduced by Bauer, Fischer and Gilmore.\textsuperscript{(24)} These two methods are based on the Landau-Zener model for the transition probability of a transition from one adiabatic curve to another. Quantum mechanical calculations are scarce, and mostly devoted to collinear systems or to three dimensions employing the infinite order sudden approximation.\textsuperscript{(25)} Alternative simpler theories include statistical theories, such as phase space theory (PST) or transition state theory (TST), and empirical or semi-empirical approximations. Theoretical results for the reactions presented here are very scarce. In a few cases, PST results can be found in the literature.\textsuperscript{(26)} Simons and coworkers have examined the $B^+$ and $Al^+$ targets by ab initio methods.\textsuperscript{(27)}

The phase space theory for ion-molecule reactions\textsuperscript{(26),(28)-(30)} uses the long range
ion-induced dipole potential (Langevin model) to determine the complex-formation cross section. These complex can then be decomposed into products or back to reactants via "loose" transition states.\(^{(26)}\) Total energy and angular momentum are explicitly conserved. The presumption of loose transition states means that only the molecular parameters of isolated reactants and products are required to determine the number of states available in each channel. No explicit information regarding the complex or transition states is needed for PST calculations. In its simplest form, PST does not differentiate among any of the states in the reactant or product channels. All states which are accessible while conserving both energy and momentum are included in the statistical sum of states. Sums for electronic states which are degenerate are multiplied by the appropriate degeneracy factor.

It has been shown that classical phase space theory\(^{(31),(32)}\) can be used instead of the full quantum mechanical version for the system for which PST calculations are presented here \((C^+ + H_2)\). Details of the calculation can be found elsewhere.\(^{(26)}\)

The reaction cross section is given by:

\[
\sigma(E) = \frac{1}{Q_{tot}} \sum_J (2J + 1) g_i e^{-BJ(J+1)/kT} \sigma(E, J),
\]

(4)

where \(Q_{tot}\) is the rotational partition function, \(B\) is the rotational constant, \(g_i\) is the nuclear spin degeneracy factor, \(T\) is the temperature of the target gas and \(\sigma(E, J)\) is the cross section for a particular rotational state \(J\) of reactant hydrogen as a function of relative energy \(E\) given by\(^{(31)}\)

\[
\sigma(E, J) = \frac{\pi \hbar^2}{2\mu E} \frac{s}{2JG} \int_{K_-}^{K_+} dK 2KN_{\text{reag}}^{\text{rots}}(E, J, K) \times N_{\text{prod}}^{\text{rots}}(E_0, K)/N_{tot}^{\text{rots}}(E_0, K),
\]

(5)
where $G$ and $\mu$ are the total number of degenerate electronic surfaces, and the reduced mass; $s$ is the symmetry number; $E$ and $K$ are the relative translational energy of the reactants and the total angular momentum; $E_0$ is the total system energy defined as

$$E_0 = E + E_{\text{rot}} + E_{\text{vib}};$$

(6)

$N_{\text{reag}}^{\text{ots}}(E, J, K)$ is the sum of orbital states of the reactants for given values of $E$, $J$ and $K$; $N_{\text{prod}}^{\text{ots}}(E_0, K)$ is the total sum of states of the products for given values of $E$ and $K$ and $N_{\text{tot}}^{\text{ots}}(E_0, K)$ is the sum of the $N_{\text{reag}}^{\text{ots}}(E_0, K)$ (total summ of states in channel $i$) over all available channels. Note that in all sums $N$ all accessible electronic surfaces and reaction path degeneracy have been explicitly taken into account. Finally, $K^{-}$ and $K^{+}$ are the maximum and minimum values of the total angular momentum $K$ for which the reactive flux is greater than zero.

An important aspect of the reactions studied here are the isotopic effects, e.g. comparisons between the interchange cross sections for $H_2$, $D_2$ and $HD$. In particular, the branching ratio between reactions

$$A^+ + HD \rightarrow AH^+ + D$$

(7)

$$\rightarrow AD^+ + H$$

(8)

appears to be quite sensitive to reaction dynamics and is still not fully understood. For endothermic reactions, there seems to be three different types of behavior:

1) the branching ratio is nearly unity; 2) the process in which $AH^+$ is formed is favored by a factor of about 3; and 3) the process in which $AD^+$ is formed is favored.
by a large factor. In the first two types of reactivity, the reaction thresholds are observed to correspond to the thermodynamic thresholds, while in the third type, the experimental thresholds are higher than the thermodynamic thresholds and those for reactions 4 and 5 differ from each other and from those for reaction with \( H_2 \) and \( D_2 \).

The first type of isotopic behavior reflects approximately a statistically behaved system. This can be illustrated by examining the density of states for the products of the reactions given in Eq. 7 and 8. If we assume that the mass of \( A \) greatly exceeds the mass of \( H \) and \( D \), a reasonable approximation for all cases studied here, the density of internal states favors the formation of \( AD^+ \). In the classical limit, the density of vibrational states is given by \( 1/\hbar\omega \), \( \omega \) being the vibrational frequency. Because \( \omega = (k/\mu)^{1/2} \) and the reduced mass \( \mu(AH^+) \approx 1 \) while \( \mu(AD^+) \approx 2 \), this favors the formation of \( AD^+ \) by a factor of \( 2^{1/2} \). The classical density of rotational states is \( 1/hcB \), where \( B \approx 1/\mu \), hence the formation of \( AD^+ \) is favored by a factor of 2. The density of translational states is proportional to \( m^{3/2} \), where \( m \) is the reduced mass of the reactant or product channel, \( m(AD^+ + H) \approx 1 \), while \( m(AH^+ + D) \approx 2 \). This gives an extra factor of \( 2^{3/2} \) in favor of \( AH^+ \). Overall, these factors approximately cancel such that the classical statistical isotope effect is about 1:1 formation of \( AH^+ \) and \( AD^+ \). This simple treatment ignores all quantum effects but does capture the essence of a statistically behaved system. More detailed calculations using PST give a branching ratio close to 1:1 for this cases.\(^{(26)}\)

In the second type of systems, the formation of \( AH^+ \) is favored by a factor
which could be interpreted as a simple mass factor. In the analysis above, the internal density of states is the one favoring the formation of $AD^+$. If only the translational degrees of freedom are taken into account, the formation of $AH^+$ is favored by a factor of $2^{3/2} = 2.8$. This would reflect a direct reaction in which the internal degrees of freedom are unimportant.

The third type of behavior may be explained in a case where the energy relevant to a particle-interchange reaction is not the center-of-mass (CM) energy, but a "pairwise" interaction energy. In the CM frame, the energy available for chemical change is the relative kinetic energy between the incoming atom of mass $M_A$ and the reactant molecule with mass $(M_B + M_C)$. The center of mass energy is given by Eq. (3) with $m = M_B + M_C$ and $M = M_A$. In a pairwise interaction, A is sensitive only to the potential between A and the interchanged atom B. Therefore, the pairwise energy for transfer of B from molecule BC is:

$$E_{B,BC} = E_{\text{lab}} \frac{M_B}{M_A + M_B}.$$  

(9)

In cases where $M_A \gg M_B$ or $M_C$, substitution of Eq. (3) into Eq. (9) leads to the approximate relation:

$$E_{B,BC} = E_{CM} \frac{M_B}{M_B + M_C},$$  

(10)

such that the energy available for chemical change in a pairwise reaction is always less than $E_{CM}$. For reactions with $BC=H_2$ or $D_2$, this pairwise mass factor $\delta = M_B/(M_B + M_C)$ is 1/2. If $BC=HD$, then $\delta = 1/3$ if the transferred atom is H, while if the transferred atom is D then $\delta = 2/3$. This means that if the thermodynamic
threshold occurs at $E_0$, the pairwise threshold will occur at $E_0/\delta$. Therefore, the enhanced production of $AD^+$ may be due to the lower apparent threshold for this reaction, $1.5E_0$, as compared to the one in which $AH^+$ is formed, $3E_0$. This pairwise scheme also explains the shift in the thresholds observed for the $H_2 (2E_0)$, $D_2 (2E_0)$, and $HD$ systems.

### 4 Results

#### 4.1 Carbon, Oxygen and Silicon

In many presently operating fusion devices carbon is one of the main impurities in a fusion plasma, reaching concentrations of up to 10%. Its presence in the plasma comes from the preferred use of graphite as plasma facing material, from first wall carbonization and from carbon contained in first wall alloys. The reaction

$$C^+(^2P) + H_2[D_2, HD] \rightarrow CH^+[CD^+] + H[D]$$

is probably the best studied endothermic reaction. The endothermicity of $0.398 \pm 0.003$ eV is known extremely well from spectroscopic data.\(^{20}\)

The cross sections for reactions (11) are shown in Figure 2.\(^{20}\) The reactions are clearly endothermic, with an extended plateau followed by a decline beginning at the dissociation energy of $H_2[D_2, HD]$. The apparent threshold is lower than the endothermicity, as shown more clearly in Figure 3. This is a consequence of the thermal motion of the $H_2[D_2, HD]$ reactant gas, as has been demonstrated elsewhere\(^{34}\) and is illustrated by comparison with experimental results of Gerlich.
where a crossed beam of $H_2$ was used to drastically reduce this thermal motion. This broadening is a feature that is common to all the endothermic reactions discussed here. The reaction with $D_2$ has a cross section about two-thirds of that with $H_2$. In reaction with HD, formation of $CD^+$ is favored over that of $CH^+$ by a factor of about 1.4 from threshold until the onset of product dissociation, indicating type 1, statistical behavior. In part, $CD^+$ is favored slightly because this channel has a lower zero point energy and therefore a lower threshold by 45 meV.

Phase space theory calculations for this reaction agree well (within 15%) with experimental results. The input parameters to the PST calculation include the molecular parameters from reactants and products, all of which are well established, and the electronic degeneracies of the reactants and products. The agreement between PST and the experimental results shown in Figure 3 is obtained only when 1/3 of the reactant $C^+ + H_2$ surfaces are presumed to lead to products. This factor may be easily explained by molecular orbital analysis. PST or any other theory is not able to fully explain the branching ratio observed in the HD reaction, indicating that dynamics play an important role in this reaction.

Oxygen is a common impurity in the plasma, reaching concentrations of up to 5%, basically because of its chemical activity and omnipresence, initially in the form of adsorbed $H_2O$ films and after activation in the form of other oxygen containing compounds. One of the difficulties of examining the reactions of atomic oxygen ions is that excited electronic states are easily produced. The experimental results presented in Figure 4 were obtained with $O^+$ generated in an EI/DC source. Ions
are first generated by electron impact ionization and fragmentation of \(CO_2\), and then are passed through a drift cell filled with molecular nitrogen. Excited states of \(O^+\) rapidly react with \(N_2\) by charge transfer, while the ground state \(O^+{(4S)}\) ions react very slowly. The \(O^+\) emerging from the cell is found to have less than 0.1% of excited states. The reaction

\[
O^+{(4S)} + H_2[D_2, HD] \rightarrow OH^+ [OD^+] + H[D]
\]

(12)
is exothermic by 0.6 eV.\(^{36}\)

The cross sections for reactions (9) are shown in Figure 4.\(^{10}\) They show three distinct energy regimes. At the lower energies, \(\approx 0.25\) eV, the cross section decreases as \(E^{-1/2}\) as predicted by the Langevin-Gioumousis-Stevenson (LGS) collision model.\(^4\) At energies above about 0.3 eV, the cross sections deviate from the LGS prediction such that the reaction efficiency drops. In the region between 0.3 and 5 eV, the cross sections fall approximately as \(E^{-1}\). This behavior has been explained\(^{10,33}\) in terms of angular momentum conservation, because the reactants are higher in energy than the products but have a larger reduced mass than the products. This shifts the limiting transition state for reaction from the entrance channel at low energies to the exit channel at higher energies. Another effect may involve the lifetime of the ion-induced dipole bound \(O^+ - H_2\) complex formed during the reaction. At low kinetic energies, the \(O^+{(4S)} + H_2\) system has time to orient into the collinear configuration favored by electronic considerations, while at higher kinetic energies, the time available to orient decreases (or equivalently the lifetime of the \(O^+ - H_2\) complex decreases) such that the reaction efficiency falls off. At still
higher energies (above 5 eV), the cross sections drop more rapidly. This is due to the dissociation of the product ion in reaction 12, although dissociation to $O + H^+$ can also occur. The thermodynamic threshold for both dissociations is 4.5 eV. The observed onset of the decline in the $OH^+$ cross section is somewhat higher, about 6 eV, suggesting that some of the energy available to the products is preferentially placed in translation. Flesch and Ng$^{37}$ find that the $H^+$ product appears at its thermodynamic threshold, but this could occur by a dissociative charge transfer process. The $HD$ and $D_2$ system cross sections show the same energy behavior and comparable magnitudes as those of the $H_2$ system.

Silicon is a relatively important impurity in the plasma, frequently with a concentration of the order of a few percent. The main source of Si impurity atoms is from erosion of silicon additives. The reaction

$$ \text{Si}^+(^2P) + H_2[D_2, HD] \rightarrow \text{SiH}^+[\text{SiD}^+] + H[D] $$  

has an endothermicity of 1.26 ± 0.03 eV. Figure 5 shows the cross sections corresponding to reaction 10.$^{33,38}$ In contrast with $C^+$ and $O^+$, the reaction with $D_2$ has a greater cross section than with $H_2$ (although they are within experimental error of one another), but with similar energy behavior. The plateau present in $C^+$ becomes a sharper peak because the reaction threshold is higher for $Si^+$. The position of the peak correlates with the dissociation threshold of $H_2[D_2]$. The reaction with $HD$ is of type 1, based on the branching ratio in the threshold region. At higher energies, the formation of $SiH^+$ is favored over $SiD^+$ formation, an observation that was also true for the $C^+$ and $O^+$ systems and almost all cases presented here. This
simply is an indication that the $D$ atom product carries away more energy than the $H$ atom product, a result of it being more massive.

4.2 Metals

The presence of metallic impurities in the plasma edge is due mainly to erosion of structural materials. The expected relative abundance of these impurities in a fusion reactor is of the order of 1-2% for Al, Ti, Cr, Fe, Ni, Cu, B and V and less than 0.1% for the others. The reactions of $H_2 \,[D_2, HD]$ with the cations of these elements are all endothermic, with endothermicities of the order of a few eV. A common feature of metal ions that makes measurements of these reactions difficult is the large number of electronic states. For instance, $V^+$ has eight electronic states below 2 eV (28 spin-orbit levels) which form 186 separate potential energy surfaces in the interaction with $H_2$. Clearly, explicit account of all these surfaces is quite difficult.

Because of the multitude of electronic states, the way the metal ions are produced has a very important influence on the results reported here. As noted in Section 2.4, there are three main ion sources used in these studies, surface ionization, electron impact and high pressure sources. In many cases, there exist cross section data for metal ions produced with different ion sources. Here, we present mainly those obtained by surface ionization, based on the fact that SI normally produce a high population of ions in the ground state, as compared to EI, for example.

Figure 6 shows the cross sections for the reaction

$$M^+ + H_2[D_2, HD] \rightarrow MH^+[MD^+] + H[D]$$  \hspace{1cm} (14)
for $M = Al$. Notice that all reactions are very inefficient, with cross sections not exceeding $10^{-18} cm^2$. The reaction with $H_2$ is more efficient than the one with $D_2$. The reactions have a large threshold that varies for all four reactions and that is higher than the thermodynamic threshold of 3.8 eV in all four cases. This energetic behavior and the branching ratios for the $HD$ reaction indicate that this system has isotopic behavior that is largely type 3. In the $HD$ system, $AlH^+$ formation is favored by a very large factor except at the lower energies, because $AlD^+$ formation has a lower energy threshold and maximum. An interesting dynamical explanation for this behavior has been forwarded by Simons and coworkers.\(^{(26)}\)

Figures 7 and 8 show the cross sections for reaction (11) with $M = Ti$ and $M = V$, respectively. The cross sections for the reactions with $H_2$ are bigger than with $D_2$, but still within experimental error. In the $HD$ systems, formation of $MH^+$ and $MD^+$ have about the same cross section magnitudes in the threshold regions. All four reactions for both metals have similar thresholds. This indicates that these systems behave statistically (isotopic behavior type 1). At high energies in the $HD$ reactions, the cross sections for $MD^+$ drop much faster than for $MH^+$, for reasons described above.

Figure 9 shows the cross sections for reaction (11) with $M = B$. Results for $B^+$ are rather atypical and resemble those for $Al^+$. The cross section for $H_2$ is almost a factor of two larger than that for $D_2$, and the $HD$ reaction has a mixed isotopic behavior, with formation of $BH^+$ favored at most energies but $BD^+$ favored at low energies. In both this and the analogous $Al^+ + HD$ system, the thresholds
are displaced from each other and from the thresholds of the $H_2$ and $D_2$ systems. Also the peaks in the various product cross sections are displaced from one another by several eV, and do not correspond to the dissociation energy for $H_2$, $D_2$, or $HD$. Also shown in Figure 9 are results of Ruatta, et al.$^{(43)}$ (open squares) divided by 2.75. The reason for this factor is not understood.

Figure 10 shows the cross sections for reaction (10) with $M = Cr$. For this system, the reaction with $H_2$ is almost identical to the reaction with $D_2$, while the $HD$ reaction has a mixed isotopic behavior most characteristic of type 3 because formation of $CrD^+$ is favored over formation of $CrH^+$. This mixed dynamic behavior accounts for the unusual double-peak structure in the latter cross section. Data appropriate for excited state $Cr^+$ generated by EI are also available in the literature.$^{(44)}$

Figure 11 shows the cross sections for reaction (11) with $M^+ = Fe^+(6D)^{(45)}$ and $Fe^+(4F)^{(45)}$ for $D_2$ and $HD$. Notice that in this case the reactivity of the ground state ($Fe^+(6D)$) is much lower than the reactivity of an excited state ($Fe^+(4F)$). The $HD$ reaction in both cases is of type 2, formation of $FeH^+$ being favored by a factor of about 2.5.

Figures 12 and 13 show the cross sections for reaction (11) with $M = Ni$ and $M = Cu$. In both cases, the $H_2$ and $D_2$ reactions are similar to one another, within experimental error, and the $HD$ reaction is of type 2, formation of $MH^+$ favored by a relatively large factor (5 in the case of $Ni^+$ and almost 7 in the case of $Cu^+$ in the threshold region). All reactions rise from their thermodynamic thresholds.
and reach maxima corresponding to the $H_2$, $D_2$, or $HD$ bond energy (although the peaks in the $MD^+$ cross sections in the $HD$ systems are somewhat lower because of competition with the $MH^+$ cross sections). Figure 14 corresponds to $M = Mo$.\(^{(47)}\)

In this case, the $H_2$ and $D_2$ are very similar and the $HD$ reaction almost behaves statistically, type 1 behavior.

Figure 15 and 16 show data for reaction of $D_2$ and $HD$ with $Mn^+$ generated by SI and EI.\(^{(49)}\) The SI source produces 99.83\% of the ions in their $^7S$ ground state and 0.15\% in the $^5S$ first excited state. The behavior of the $D_2$ cross section is very unusual. The cross section actually rises at an energy below the thermodynamic threshold for reaction of the $^7S$ state of \(\approx 2.5\) eV, indicating an observable contribution from the excited state. The reactivity of the ground state does not become appreciable until 5 eV, and the peak of the cross section is at an energy much higher than the thermodynamic onset of the dissociation channel, reaction 2.

In fact, both the apparent threshold and the peak of the product ions are at energies approximately twice the thermodynamic values, in agreement with the predictions for type 3 behavior given in Section III. This is confirmed by the behavior of the $HD$ data which shows a large preference for formation of $MnD^+$ and a shift in the threshold and peak of the cross section from the $D_2$ system. Figure 16 also shows results for reaction of $D_2$ and $HD$ with $Mn^+$ in excited states,\(^{(49)}\) obtained by EI ionization of $Mn_2(CO)_{10}$ at 50 eV electron energy. It is believed that the $Mn^+$ produced under these conditions has a population of about 50\% state, and the remainder in other uncharacterized states. The excited states are much more reactive than the
ground state of Mn$^+$, as is obvious from comparison of the $D_2$ results for the two source conditions. In contrast to the behavior of Mn$^+$(7S), the excited Mn$^+$ behaves more like most of the transition metal ions presented here. The HD reaction is of type 2, with formation of MnH$^+$ being favored by a factor of about 3. Notice the double peak structure of the MnD$^+$ channel. This clearly shows the presence of both ground and excited state Mn$^+$ ions.

Figures 17-20 show data for reaction of $H_2$, $D_2$ and HD with Ag$^+$, Ge$^+$, Mg$^+$ and Zn$^+$. The concentration of these metallic ions in a fusion plasma is less than 0.1%.

### 4.3 Rare Gases

Rare gases are present in the plasma mainly due to their use for plasma diagnostics. Their concentration may reach up to a few percent. Rare gas ions (Rg$^+$) have the valence electron configuration $(ns)^2(np)^5$. Therefore the ground state are $2P$, like C$^+$ and Si$^+$. However, the reactivity of the $2P$ states of Rg$^+$ are quite different from that of carbon and silicon ions. In the reactions of $O^+$, C$^+$, and Si$^+$ with $H_2$, the reactants in the particle interchange process readily reach the products on a single adiabatic potential energy surface in the entrance channel.\(^{(59)}\) For the Rg$^+$, there is a second important surface in the entrance channel, namely the charge transfer channel Rg + $H_2^+$. Mahan\(^{(58)}\) has pointed out that the RgH$^+ + H$ products correlate with Rg + $H_2^+$ and not with Rg$^+ + H_2$. This is demonstrated by the observation that the endothermic reaction $He + H_2^+ \rightarrow HeH^+ + H$ is efficient and easily driven by
traslational and vibrational energy. \( ^{60} \) The coupling between these two entrance channel surfaces depends strongly on their relative energies as determined by the relative ionization potentials of \( H_2 \) and the rare gases. Therefore, the effects of this coupling vary substantially among different rare gases.

The reaction

\[ Rg^+ + H_2[D_2,HD] \rightarrow RgH^+ + H \] \( ^{15} \)

for \( Rg = Ne \) is exothermic by 5.6 eV. Yet this reaction show no reactivity until the relatively high energy of 9.8 eV, \( ^{26} \) as shown in Fig. 21. The basic reason for this non-reactivity is the fact that the reaction \( Ne^+ \) with \( H_2 \) occurs on a surface which lies well above that corresponding to \( Ne + H_2^+ \), and this surface correlates with the desired products, \( NeH^+ + H \). \( ^{58},(61),(62) \) Further insight into this reaction may be obtained from the work of Jones \textit{et al.} \( ^{62} \) who studied the \( He^+(2S) \) reaction and examined the luminiscence from this reaction. Since reaction 15 with \( Rg = He \) shows a similar behaviour as the one with \( Rg = Ne \), their conclusion may be extended to \( Ne \). \( ^{26} \) Extensive Balmer and Lyman emission was observed with an onset for Lyman \( \alpha \) emission coincident with the onset for \( HeH^+ \) formation. Thus the process being observed is

\[ Rg^+(2X) + H_2(1^1\Sigma_g^+) \rightarrow RgH^+(1^1\Sigma) + H^+(2p). \] \( ^{16} \)

Since \( H(2p) \) is 10.2 eV above the \( H(1s) \) ground state, reaction 16 is endothermic by 1.9 eV for \( He^+(2S) \) and by 4.6 eV for \( Ne^+(2P) \). While this can explain the endothermicity of reaction 15, the observed threshold of \( \approx 10 \) eV is well above
the calculated endothermicity. Furthermore, the peak in the cross section is also displaced to \( \approx 18 \) eV. Examination of this reaction with \( D_2 \) and \( HD \) helps explain this behaviour. The cross section for reaction 15 with \( D_2 \) is identical in shape but vary somewhat in magnitude compared to the \( H_2 \) reaction cross section. The threshold for this reaction is twice the thermodynamical threshold of 4.6 eV (9.2 eV in the CM frame). For reaction with \( HD \) to form \( NeH^+ \), the pairwise threshold is 13.8 eV (3 \times 4.6) and to form \( NeD^+ \) it is 6.9 eV (1.5 \times 4.6). While the agreement with the data is not quantitative, these energies are in rough agreement with the observed thresholds.

The cross sections for reaction (15) with \( Rg = Ar \) are shown in Fig. 22. This reaction has been considered as a classic example of an exothermic reaction which proceeded at the LGS collision limit. It has been shown\(^6\) that the cross section, as shown in Fig. 22, deviates from the LGS for both \( D_2 \) and \( H_2 \). The total cross section for \( HD \) is also comparable, except in the region where dissociation of the product becomes important, > 4 eV. At the lowest energies, reaction (15) occurs with a reaction efficiency of two-thirds, in agreement with several rate constant measurements\(^{64}(65)(66)\). This disagrees with the conclusion of a simple MO treatment that only one-third of the surfaces should be reactive. This disagreement may be explained by the fact that spin-orbit effects play an important role (see for example Refs.\(^{67}(68)\)), since a reaction efficiency of two-thirds is expected in beam with a statistical mixture of \( ^2P_{3/2} \) and \( ^2P_{1/2} \) states. Fig. 23 shows spin-orbit-state dependence of the cross section for the reaction \( Ar^+ + H_2 \rightarrow ArH^+ + H \). As the
kinetic energy increases, the reaction efficiency increases to about 90% near 1 eV. Above this energy, the cross section drops as $E^{-1}$ until about 4 eV, where it falls off rapidly. The branching ratio between ArH$^+$ and ArD$^+$ is nearly unity until dissociation.

The cross sections for reaction (15) with $R_g = Kr^{(2P_{3/2})}$ are shown in Fig. 24.$^{69}$ This reaction is exothermic by 0.29±0.06 eV, while the $^{2}P_{1/2}$ state reaction also shown in Fig. 25 is exothermic by 0.96 eV. Notice that the spin orbit dependence of the reaction is very strong. The cross section for the $^{2}P_{3/2}$ state shows a feature at high energies which is not found for the $^{2}P_{1/2}$ state. The total cross sections of Fig. 24 show an unusual intermolecular isotoppe effect such that the relative magnitudes are $\sigma(HD) > \sigma(H_2) > \sigma(D_2)$. Some of these features may be explained by examination of the diabatic and adiabatic surface correlations (see Ref.$^{59}$)

5 Analytic representation

In many applications, plasma modeling for example, cross sections or rate coefficients of different processes are required over a wide energy region. Analytic fits to the data serve this purpose, because with few parameters and a given function, the cross sections can be generated easily. Compared to polynomial fits, non-linear analytic fits do not have spurious oscillations and can represent the low and high energy limits properly.

In this work, we have made analytic fits to all data presented. The functions used are ($E$ refers to center of mass energy in eV):

23
Expression 1:

\[
\sigma = a_1 \exp \left[ \frac{-(E - a)^2}{a_3} \right] E^{a_4} + a_5 \exp (-a_6 E) E^{a_7}
\]  \hspace{1cm} (17)

Expression 2:

\[
\sigma = a_1 \frac{\exp(-a_2/E^a)}{1 + a_4 E^{a_5}} + a_6 \exp \left( \frac{-a_7}{E^2} \right) E^{a_8}
\]  \hspace{1cm} (18)

Expression 3:

\[
\sigma = a_1 \frac{\exp(-a_2/E^a)}{1 + a_4 E^{a_5}} + a_6 \exp \left( \frac{-a_7}{E^{1.3}} \right) E^{a_8}
\]  \hspace{1cm} (19)

Expression 4:

\[
\sigma = a_1 \exp \left[ \frac{-(E - a^2)^2}{a_3} \right] (1 + a_4 E^{a_5})
\]  \hspace{1cm} (20)

Expression 5:

\[
\sigma = a_1 \exp (-a_2 E)(E^{a_3} + a_4 E^{a_5}) + a_6 \exp (-a_7 E)
\]  \hspace{1cm} (21)

Expression 6:

\[
\sigma = a_1 \exp (-a_2 E) E^{a_3} + a_4 E^{a_5} \exp (-a_6 / E)
\]  \hspace{1cm} (22)

Expression 7:

\[
\sigma = \frac{a_1 \ln(a_2 E^{-a_3} + a_4)}{1 + a_5 E^{a_6}} + a_7 \exp -a_8 E^{a_9}
\]  \hspace{1cm} (23)

Table 1 gives the expression used to represent the cross sections for each reaction and the corresponding parameters in equations 15 - 20.
In using these analytic fits to model systems, it should be remembered that the experimental conditions for the system being modeled may differ from the experimental conditions used to generate these data. The kinetic energy distributions of the ions and neutrals and the electronic states of the ions influence the shapes of these cross sections. Reactions taking place at higher neutral reactant densities may also lead to different reaction channels than those shown here, which correspond to single collision conditions in all cases.

6 Discussion

We have seen that many endothermic particle interchange reactions between metallic ions and \( H_2 \) (or \( D_2 \)) follow a pattern: the cross section rises from an apparent threshold, peaks at an energy close to the dissociation energy of the neutral reactant, and then decreases relatively rapidly. This regularity can be seen clearly in Figure 26, where we show the cross sections \( \sigma/\sigma_0 \) as a function of scaled energy \( E/E_0 \), where \( \sigma_0 \) and \( E_0 \) are the values of the cross section and the energy at the peak. For most of these reactions, \( E_0 \) is close to the bond energy of \( D_2 \), while for \( M = Al, B, Mg, Mn, \) and \( Zn \) the value is displaced to higher energies.

The similarities between these various curves reflect the similarity in the overall physical processes. In the case of transition metal ions, a more detailed comparison can be found elsewhere.\(^{(70)}\) The apparent symmetry above and below the peak for each particular system is largely serendipitous because the molecular characteristics that control the onset of reaction (formation of \( MD^+ + D \)) are not the same as
those that control the decline (dissociation to $M^+ + 2D$). This is evident from the data for $M = C$, shown in Figure 2, that does not exhibit this type of symmetry. Some correlation between how rapidly the cross section rises from threshold and how fast it declines above its maximum is observed because the threshold for reaction is lowest when the $MD^+$ bond is strongest, and this also means that the $MD^+$ product is less likely to dissociate at higher energies.

Although not presented here in detailed form, the interested reader can also find kinetic energy dependent cross sections in the literature for reaction of $H_2$, $D_2$, and $HD$ with other rare gas ions ($He^+$, $Xe^+$), other atomic metal ions ($Ag^+$, $Mg^+$, $Zn^+$, $Ca^+$, $Sr^+$, $Sc^+$, $Y^+$, $La^+$, and $Lu^+$), other atomic ions ($H^+$, $D^+$, $N^+$, $S^+$), and several molecular ions ($O_2^+$, $N_2^+$, $N_4^+$, $H_2^+$, $H_3^+$, and $D_3^+$).

**Acknowledgments**

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Tabla 1: Parameters for the analytic fits.

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* Refers to the expressions given in Equations (17)-(23).

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</tbody>
</table>

* Refers to the expressions given in Equations (17)-(23).

1. $M^+ + HD \rightarrow MH^+ + D$
2. $M^+ + HD \rightarrow MD^+ + H$
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fit</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_5$</th>
<th>$a_6$</th>
<th>$a_7$</th>
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</tbody>
</table>

* Refers to the expressions given in Equations (17)-(23).

1 $M^+ + HD \rightarrow MH^+ + D$

2 $M^+ + HD \rightarrow MD^+ + H$
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Fit *</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_5$</th>
<th>$a_6$</th>
<th>$a_7$</th>
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* Refers to the expressions given in Equations (17)-(23).

1 $M^+ + HD \rightarrow MH^+ + D$
2 $M^+ + HD \rightarrow MD^+ + H$
Figure 1: Schematic overview of the guided ion beam tandem mass spectrometer. (Reprinted with permission of VCH Publishers).
Figure 2: Cross sections for reaction of $C^+$ with $H_2, D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 3: Cross sections for reaction of $C^+$ with $H_2$ at low relative kinetic energy. The dashed and dotted lines show phase space calculations for this process\textsuperscript{26,35} The full lines gives the calculation convoluted with the experimental energy broadening.
Figure 4: Cross sections for reaction of $O^+$ with $H_2, D_2$ and $HD$ as a function of relative kinetic energy. For clarity of presentation the $H_2$ data and fit are multiplied by 16, the $D_2$ by 8, and the $HD$ channels by 4 and 1/2 respectively. The lines show the analytic fits with the coefficients given in Table 1.
Figure 5: Cross sections for reaction of Si\(^+\) with \(H_2\), \(D_2\) and \(HD\) as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 6: Cross sections for reaction of \( \text{Al}^+ \) with \( H_2, D_2 \) and \( HD \) as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 7: Cross sections for reaction of $Ti^+$ with $H_2, D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 8: Cross sections for reaction of $V^+$ with $H_2, D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 9: Cross sections for reaction of $B^+$ with $H_2$, $D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 10: Cross sections for reaction of $Cr^+$ with $H_2$, $D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 11: Cross sections for reaction of $Fe^+(^4F$ and $^6D)$ with $H_2$ ($^6D$ only), $D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 12: Cross sections for reaction of $Ni^+$ with $H_2$, $D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 13: Cross sections for reaction of Cu\(^+\) with \(H_2\), \(D_2\) and \(HD\) as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 14: Cross sections for reaction of $Mo^+$ with $H_2, D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 15: Cross sections for reaction of Mn\(^+\) produced by surface ionization (S.I.) and electron impact (E.I.) with \(D_2\), as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 16: Cross sections for reaction of $Mn^+$ produced by surface ionization (S.I.) and electron impact (E.I.) with $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 17: Cross sections for reaction of $Ag^+$ with $H_2$, $D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 18 Cross sections for reaction of Ge$^+$ with $H_2$, $D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 19: Cross sections for reaction of \( Mg^+ \) with \( H_2, D_2 \) and \( HD \) as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 20: Cross sections for reaction of $Zn^+$ with $H_2$, $D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 21: Cross sections for reaction of \( Ne^+ \) with \( H_2, D_2 \) and \( HD \) as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 22: Cross sections for reaction of $Ar^+$ with $H_2, D_2$ and $HD$ as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 23: Spin-orbit-state dependence of the cross section for reaction of $\text{Ar}^+$ with $\text{H}_2$. 

$\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}$
Figure 24: Cross sections for reaction of Kr\textsuperscript{+} with H\textsubscript{2}, D\textsubscript{2} and HD as a function of relative kinetic energy. The lines show the analytic fits with the coefficients given in Table 1.
Figure 25: Spin-orbit-state dependence of the cross section for reaction of Kr\(^+\) with H\(_2\).
Figure 26: Scaled cross sections for reaction of metals with $D_2$ as a function of scaled relative kinetic energy (see text).