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UPPER-LIMIT CHARGE EXCHANGE CROSS SECTIONS FOR MERCURY$^+$ ON MOLYBDENUM AND CESIUM$^+$ ON ALUMINUM

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UPPER-LIMIT CHARGE EXCHANGE CROSS SECTIONS FOR MERCURY$^+$ ON MOLYBDENUM AND CESIUM$^+$ ON ALUMINUM

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SUMMARY

Upper-limit charge exchange cross sections are calculated for Hg^+ on Mo and Cs^+ on Al. Both systems are of interest for spacecraft with electron bombardment thrusters. The cross-section values can be used for conservative sputtering estimates. The cross sections σ_{ex} are calculated from the polarization interaction at low ion energies (1 to 500 eV) and by assuming favorable curve crossings with a hard-core reaction radius at higher energies (500 eV to 10 keV). The approximations used are more reliable for Hg^+ + Mo because of the many curve crossings (high density in phase space), whereas the Cs^+ + Al estimate depends critically on the nature of just two or three curve crossings. The σ_{ex} for Hg^+ on Mo becomes greater than corresponding Hg-Hg^+ resonance values at ion energies below 2 eV. This process is exothermic by 3.3 eV so the value of σ_{ex} is large down to zero energy. The σ_{ex} values for Cs^+-Al remain considerably lower than the Cs^+-Cs resonance values at all ion energies. This process is 2.1 eV endothermic, so σ_{ex} falls to zero at 6 eV ion energy. It is also shown that change exchange of slow Hg^+ with Mo can compete with fast ion charge exchange for representative thruster conditions.

INTRODUCTION

Charge exchange of fast exhaust ions with sputtered metal vapors is of interest for spacecraft with electron bombardment thrusters (ref. 1). Two particularly interesting systems are mercury (Hg) ions on molybdenum (Mo) atoms (ref. 2) and cesium (Cs) ions on aluminum (Al) atoms (ref. 3). The charge exchange reactions are

$$Hg^+ + Mo \longrightarrow Hg + Mo^+ \tag{1}$$

and

$$Cs^+ + Al \longrightarrow Cs + Al^+ \qquad (2)$$

The charge exchange process converts fast ions to fast neutrals by means of collisions with exhaust neutrals. A small percentage of propellant neutrals is present in the beam since the ion thrusters operate at propellant utilization efficiencies of less than 100 percent. Neutrals of accelerator grid material are also present as a result of sputtering by the electrode impingement current. Charge exchange with sputtered neutrals can be a serious spacecraft problem because it can lead to condensation on various spacecraft surfaces. The resonance charge exchange cross sections for Hg^+ on Hg and Cs^+ on Cs are well known experimentally at these ion energies (ref. 4). However, experimental charge exchange cross sections for reactions (1) and (2) are not available. The purpose of this report is to calculate theoretical upper-limit values for Hg^+ + Mo and Cs^+ + Al charge exchange cross sections so that the relative importance of these processes under spacecraft conditions can be estimated.

To first order, the accelerator impingement current can be taken as 1 percent of the beam current for typical Hg and Cs thrusters (ref. 5). To first order also, the sputtering yield can be taken as 1 atom per impinging ion (ref. 6). Thus, the ion density n_I is $j_I/V_I e$, where j_I is the beam current density, V_I is the ion velocity, and e is the electronic charge. The sputtered neutral density n_n is $4\times10^{-2}\ j_I/V_n e$, where V_n is the average velocity of the randomly sputtered neutral. (All symbols are defined in appendix A.)

The rate of formation of slow ions by charge exchange R_1 is $n_I n_n \sigma_{ex} V_I$, where σ_{ex} is the microscopic charge exchange cross section. Thus, by rewriting,

$$R_1 = 4j_I \frac{10^{-2}}{e^2} \frac{j_I}{V_n} \sigma_{ex}$$

which says that, at a fixed current density, the rate of formation of slow ions is simply proportional to the charge exchange cross section.

THEORY

In this report we shall calculate plausible upper-limit cross sections for reactions (1) and (2) by using two different approaches which generally apply in separate regions of ion energy. The cross section for charge exchange is calculated by means of the general relation $\sigma_{ex} = \text{Probability} \times \text{Area} = P_z(\pi R_z^2)$, where P_z is the general probability for charge exchange and πR_z^2 is a reference cross section (ref. 7). At low energies (~0.1 to 10 eV), the reference cross section is calculated from the polarizability potential; the charge exchange probability is taken as 1/2. This cross-section value may actually exceed the resonance charge exchange value (i.e., σ_{ex} for Hg^+ on Hg) at lower energies. The cross section is large because the polarizability α of Mo was estimated by using a method outlined in reference 8 and as a result is considerably larger than α for Hg. The resonance charge exchange probability value of 1/2 may be an underestimate for a nonresonant exothermic process at low energies since it is energetically more stable for the electron to be on the atom of lower ionization potential. At high ion energies ($\sim 10^2$ to 10^4 eV), the net probability P_z is the product of two separate probabilities, $P_z = P_i P_c$. The P_i is the probability of the reacting system being on a favorable potential curve, and P_c is the probability of a crossing. The R_z is determined from estimation of the locations of the curve crossings between potential energy curves of molecular ion states. It should be noted that low-energy cross-section values predicted using the energy defects appropriate as $R \to \infty$ (i.e., the difference in ground-state ionization potentials) are much smaller than those given by the polarizability approach (ref. 7).

Low-Energy Range

The ion-atom interaction at separations of several Å (10^{-10} m) or greater is described by the ion-induced dipole potential

$$V(R) = \frac{-\alpha e^2}{2R^4} \tag{3}$$

where α is the electronic polarizability and e is the magnitude of the electronic charge (ref. 7). The critical Langevin impact parameter which defines capture in the ion-atom collision is

$$b_L = \left(\frac{2\alpha e^2}{\epsilon}\right)^{1/4} \tag{4}$$

where ϵ is relative translational energy ($\epsilon = mv^2/2$, where m is the reduced mass and v is the ion-atom relative velocity which is effectively the ion velocity V_I). The low-energy theory of resonance charge exchange is based on the approximation that the mean probability of charge transfer is 1/2 for impact parameters less than b_L. Thus we can write the charge exchange cross section as

$$\sigma_{ex} = \frac{\pi}{2} b_L^2 = \frac{\pi}{2}\left(\frac{2\alpha e^2}{\epsilon}\right)^{1/2} \tag{4a}$$

One way of setting an upper limit to σ_{ex} is to estimate an upper-limit polarizability for the target atom (i.e., Mo and Al) and assume that σ_{ex} is given by equation (4a). The critical assumption in this theory is that nonresonant charge exchange (energy defect not equal to zero between initial and final states) proceeds just like resonance charge exchange at small separations (e.g., 10^{-10} to 5×10^{-10} m (1 to 5 Å)). In resonance charge exchange the probability of charge transfer oscillates between 1 and 0 (with a mean value of 1/2 for separations less than a critical value R_c (ref. 9)).

High-Energy Range

In the high-energy range (10^2 to 10^4 eV), it is useful to discuss asymmetric charge exchange between nonresonant systems in terms of potential energy curves, that is, plots of interaction potential against ion-atom separation. For example, a hypothetical variation for the system $A^+ + B \rightarrow A + B^+$ is shown in figure 1. There is no interaction at large separations R. As R decreases, the polarization potential, $-\alpha e^2/2R^4$, becomes significant at roughly the same separation (several Å (10^{-10} m)), where exchange forces take over. We would expect curve crossings at some separation R_x in this region. A sample attractive-repulsive crossing is illustrated in figure 1 (crossing (1)) from a bonding state (having a minimum) of $(AB^+)^*$ with the initial state $A^+ + B$ to a repulsive curve for the same system with the lower state asymptote $A + B^+$. A radiationless transition can occur at the crossing, leading to formation of $(AB^+)^*$, which finally crosses to the antibonding $A + B^+$ (ref. 10). The solid curves are the "fast" curves, where no such transition occurs. The charge transfer corresponds to switching fast curves or staying on a "slow" curve (ref. 11). In any consideration of curve crossings, it is presumed that the ion-molecule pair can reach the separation of interest for certain values of impact parameter. Obviously, crossings between two repulsive curves must occur at relatively small separations and only if the lower curve is much more sharply repulsive (see crossing (2) of fig. 1) for the $A^+ + B \rightarrow A + B^+$ system.

Actually, in quantum mechanics curves of the same multiplicity do not cross, but there is nevertheless a finite probability for the transition at the "avoided" crossing (refs. 7 and 11). Most of the curves of interest here do cross (different multiplicity), but for simplicity we must assume "avoided" crossings since it is beyond the scope of this report to calculate transition matrix elements between all the states of interest. We shall assume that the asymptotes of all curves correspond to ground states for all ions and atoms.

Since the ionization potential of Hg is 10.4 eV and that of Mo is 7.1 eV, the initial state in the Hg^+ + Mo collision is 10.4 eV minus 7.1 eV, or 3.3 eV above the final Hg + Mo^+ state (fig. 2). The ionization potential of Cs is only 3.9 eV and the value for Al is 6 eV, so the initial state in the Cs^+ + Al collision is 6 eV minus 3.9 eV, or 2.1 eV below the final Cs + Al^+ state (fig. 3). The relative locations of these asymptotic states suggest the type of likely curve corssings shown in figures 2 and 3 for the two colliding systems. The depths of the bonding curves and the strength of the repulsive interactions which determine the crossing point are discussed in the following section.

Given the relative positions of initial- and final-stage asymptotes, we shall adopt the crude approximation that attractive bonding curves for the initial Hg^+ + Mo system make transitions to the antibonding (completely repulsive) curve and the repulsive segments of bonding curves for the final Hg + Mo^+ state. We shall, because of similar considerations, assume that the opposite occurs for Cs + Al. Actually, of course, crossings can occur between two attractive curves (with somewhat different bonding energies) at separations of several angstroms.

Based on comparison with neutral molecule curves, the attractive bonding curves for molecular ions have minimums at 0.75×10^{-10} to 4.0×10^{-10} meter (0.75 to 4.0 Å), with depths from 1 to 4 or 5 eV (ref. 10). The classical polarization force goes over into chemical exchange forces, which dominate the interaction at small separations. The ion-atom interaction on the antibonding curve should be sufficiently strong (roughly 1 eV) at R of approximately 10^{-10} to 3×10^{-10} meter (1 to 3 Å) for a crossing to occur, since the curves have asymptotes which differ by 2 to 3 eV.

The molecular ion states of figures 2 and 3 are assumed to be divided between bonding and antibonding states (ref. 10) in the following manner: There are seven possible states for the Hg^+ + Mo system, and it is assumed that four of the seven are bonding states. There are only three curves for Hg + Mo^+, and it is reasonable to assume that two of them have minimums. We shall assume that all three of these curves cross with the attractive Hg^+ + Mo curves. For Cs^+ + Al there are only three states, and we have assumed two of them to be bonding states. There is just one Cs + Al^+ state, which undoubtedly has a minimum.

Aside from the polarization contribution, the most significant interaction is due to the outer-shell unpaired electrons. We shall assume that this repulsive interaction becomes significant (i.e., $\approx$1 eV) only at distances less than 2.5×10^{-10} meter (2.5 Å). This assumption is based on the interaction of Cl with Cl (very electronegative) and Li with Li (very electropositive) as representative limits of repulsive exchange forces.

Approximate polarizability values have been computed for Al and Mo from mean radii of outer electrons (ref. 8, pp. 951 to 954). These radii are estimated by using Slater's rules for screening and by assuming spherical symmetry of the atoms. The ion-atom bonding interaction probably occurs at about 2×10^{-10} meter (2 Å) for Cs^+ + Al since AlH^+ has an equilibrium bond distance of 1.6×10^{-10} meter (1.6 Å) (ref. 10). The

Cs^+ ion has a significant electronic core and will not penetrate the Al cloud as much as a proton. The polarizability of Al is estimated to be 7×10^{-30} cubic meter (7 $Å^3$) so that the maximum bond energy is about 1.5 eV. The repulsive interaction $Cs^+ + Al$ could be, at most, 1 eV at 2×10^{-10} meter (2 Å). The $Cs + Al^+$ curve must have a minimum at a relatively large separation, but it is unlikely this value will be as great as the equilibrium separation of 3.40×10^{-10} meter (3.40 Å) for CsI (ref. 10).

We conclude that the upper-limit curve crossings occur at an R_x of approximately 2×10^{-10} meter (2.0 Å) for $Cs^+ + Al$. Estimates of the polarizability of Mo using the hydrogenic formula of reference 8 (pp. 951 to 955) suggest it is alkali-like (i.e., $\alpha \cong 50\times10^{-30}$ m (50 $Å^3$)) thus the attractive $Hg^+ + Mo$ curve could be several eV deep at an R of 3×10^{-10} meter (3 Å). It is reasonable to assume that $Hg + Mo^+$ has somewhat larger equilibrium bond distance (~3.50×10^{-10} m (3.50 Å)). On the basis of these estimates the critical curve-crossing separation R_x chosen for $Hg^+ + Mo$ was 3.00×10^{-10} meter (3.00 Å).

The assumptions made concerning angular momentum coupling of the atomic states and details of the resulting molecular states are included in appendix B.

Curve-Crossing Probability

For low energies the probability of charge exchange is 1/2, as discussed; for high energies the probability is estimated from curve crossings as follows: The probability of the transition from curve segment Ia to segment IIb in figure 1 is given by the Landau-Zener formula (ref. 11).

$$P = \exp\left(\frac{-4\pi^2 E_{12}^2}{hv|S_1 - S_2|}\right) \tag{5}$$

where E_{12} (the "interaction" energy) is one-half the energy difference between the curves, v is the relative velocity of the ion and atom (cm/sec), $|S_1 - S_2|$ is the absolute value of the difference in slopes at the crossing, and h is Planck's constant. We shall maximize the net curve-crossing probability, $P_c = 2P(1 - P)$. The system traverses the crossing twice, thus the factor 2; and the sum of the quantum mechanical transition probabilities for the forward and reverse crossings is unity. The derivative dP_c/dP is equal to $2 - 4P$; thus the maximum occurs at a P of 1/2, corresponding to a P_c value of 1/2. Since we are interested in assuming a large transition probability (P = 1/2), it is useful to estimate the (unknown) resonance energy if an approximate slope difference $|S_1 - S_2|$ is chosen on the basis of the long-range polarizability interaction. Approximate slopes from $\partial V/\partial R = \partial/\partial R(-\alpha e^2/2R^4)$ are 1 to 5 eV per angstrom, and values of $|S_1 - S_2|$ of 0.1 to 0.01 of $\partial V/\partial R$ are reasonable for strongly interacting curves. This $|S_1 - S_2|$ inserted in equation (3) gives an interaction energy E_{12} of 0.05 eV, which is plausible for such a crossing.

Since there are many crossings possible for the $Hg^+ + Mo$ system, we shall assume that P_c is constant at 1/2 even though the various probabilities P are changing with velocity as described by the Landau-Zener formula. In the case of the $Cs^+ + Al$ interaction, we shall also explicitly account for the relative energy dependence of the cross section by means of the P factor.

The probability P_i that $Hg^+ + Mo$ is on an attractive curve in order for a favorable crossing to occur can be taken as 1/2. This value is chosen by assuming that roughly one-half the states are attractive and have favorable crossings with repulsive $Mo^+ + Hg$ curves.

RESULTS AND DISCUSSION

Cross Sections

We shall calculate an upper-limit cross section based on orbiting and curve-crossing calculations. The calculation of upper-limit cross section based on the assumption that asymmetric resonance charge transfer is an oscillating function of ion-atom separation transfer inside the Langevin impact parameter is not inconsistent with the assumption of curve crossings. All Langevin trajectories with $b > b_L$ have a distance of closest approach R_L of $b_L/\sqrt{2}$ (ref. 12). If curve crossings occur at separations larger than this distance of closest approach, the curve-crossing cross section for $Hg^+ + Mo$, $\sigma_{ex} \cong P_i P_c \pi R_x^2 \cong \frac{\pi}{4} R_x^2$, will be larger than the orbiting prediction, $\sigma_{ex} \cong \frac{\pi}{2} b_L^2 = \frac{\pi}{4} R_L^2$. The variation of cross section with energy is computed and plotted in figure 4 for Hg^+ on Mo. The results are compared with the $Hg^+ + Hg$ resonance cross section (ref. 13). It is assumed that the net curve-crossing probability P_c is independent of ion energy, that is, $P_c = 2P(1 - P) = 1/2$; so the cross section is constant over the entire energy range for the $Hg^+ + Mo$ system. The cross section is finite at zero ion energy because the process is exothermic by 3 eV, and we further assume that it has no activation energy. It has been suggested that the σ_{ex} curve for $Hg^+ + Mo$ is nearly flat (approximately 1×10^{-20} to 3×10^{-20} m^2 (~1 to 3 $Å^2$)) until 50 to 100 keV, with a broad maximum in that region (private communication from Prof. J. B. Hasted, Dept. of Physics, Birkbeck College, Univ. of London).

The σ_{ex} curve for $Cs^+ + Al$ may have quite a different shape. The process is endothermic (by 2.1 eV), so σ_{ex} must be zero at an ion energy of 6 eV[1] (2.1 eV in center-of-mass system) and thereafter will be quite sensitive to the possible curve crossings

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[1] The polarization potential can accelerate the particles to a relative energy of several eV, but then the particles would have to remain bound.

between the Σ bonding state of $Cs + Al^+$ and the π^+ and π^- states of $Cs^+ + Al$. It is thus advisable to at least consider the explicit velocity dependence of P_c and to calculate an additional σ_{ex} curve for $Cs^+ + Al$. This velocity dependence of the net curve-crossing probability is

$$P_c = 2P(1 - P) = 2e^{-a/v}(1 - e^{-a/v}) \tag{6}$$

where a is a constant. Fixing P_c at 1/2 somewhat arbitrarily at 3 keV to maximize the probability at an energy of interest, we calculate $P_c(v)$ and the related $\sigma_{ex}(v)$ values shown in figure 5. We ignore the fact that the resonance energy may vary depending on which curve crossing is most important. The estimated behavior of the $Cs^+ + Al$ system energy dependence is plotted in figure 5 and compared with the $Cs^+ + Cs$ resonance charge exchange curve (taken from ref. 14). Since cesium has a very low ionization potential, the resonance values are very large, of the order of several hundred square angstroms (10^{-20} m^2) at several keV. The charge exchange cross section could exceed the corresponding resonance value at a fixed ion energy even though symmetrical exchange forces operate in resonant electron transfer. The resonance charge exchange at low energies goes very much like $\frac{\pi}{2} b_L^2$ (ref. 9), that is, Langevin capture with a charge exchange probability of one-half. For the cesium case, the condition $\sigma_{ex} < (\sigma_{ex})_{res}$ is fulfilled. For the $Hg^+ + Hg$ case, it is satisfied from 500 to 3000 eV, although the Hg + Mo cross section should cross over the resonance value at very low energies. This is a consequence of the rapidly rising polarization curve since $\alpha(Mo) > \alpha(Hg)$.

Relative Importance of Charge Exchange with Slow Hg^+

It is of interest to estimate the relative importance of the charge exchange process involving low-energy (10 to 50 eV), secondary Hg^+ which are formed in the primary resonance charge exchange process (ref. 2). These ions are formed with thermal energy (at 500° C) but may pick up about 50 volts drifting under the influence of electric fields in the exhaust beam. An upper-limit estimate of this effect can be obtained by using the upper-limit σ_{ex} for $Hg^+ + Mo$ at 50 eV, which is equal to 1/2 the resonance value $(\sigma_{ex})_{res}$ (see fig. 4). The rate of production of slow Mo^+ from fast Hg^+ is, from the INTRODUCTION,

$$R_1 \cong n_I n_n \sigma_{ex} V_I = 4\times10^{-2} \frac{j_I^2 \sigma_{ex}}{V_n e^2} \tag{7}$$

Since σ_{ex} in the low-keV region is approximately equal to $10^{-1}(\sigma_{ex})_{res}$, we can rewrite equation (7) as

$$R_1 = 4\times10^{-3}\, j_I^2 \left[\frac{\left(\sigma_{ex}\right)_{res}}{V_n e^2}\right] \tag{7a}$$

The rate of production of slow Mo^+ from slow Hg^+ is similarly

$$R_2 = n_s n_n (\sigma_{ex})_s V_s \equiv \frac{16\times10^{-2} j_I j_s}{V_n e^2} (\sigma_{ex})_s V_s \tag{8}$$

where

$$j_s = \frac{n_s V_s e}{4}$$

where n_s is the number density of slow Hg^+, $(\sigma_{ex})_s$ is the σ_{ex} value at an energy of 50 eV, and V_s is the ion velocity at this energy. We can rewrite equation (8) by using $(\sigma_{ex})_s = (\sigma_{ex})_{res}/2$ from figure 4, so equation (8) becomes

$$R_2 \cong 8\times10^{-2} \frac{j_I j_s \left(\sigma_{ex}\right)_{res}}{V_n e^2} \tag{8a}$$

For the slow (secondary) Hg process to be as important as the fast (primary) Hg^+ charge exchange with Mo,

$$\left.\begin{aligned} R_1 &= R_2 \\ j_s &\cong \frac{j_I}{20} \end{aligned}\right\} \tag{9}$$

where j_s is a representative value of slow ion current density. This says that the slow ion current density of Hg^+ must be 0.05 of the fast ion current density within a meaningful distance D of the thruster, say 2 thruster diameters (~1 m). Let us take j_s to be $1/4\ j_R$, where j_R is the current density of slow ions with random velocity vectors.

This random current density of slow ions is simply given by

$$j_R = j_I\left\{1 - \exp\left[-n_o\left(\sigma_{ex}\right)_{res} D\right]\right\} = j_I\left[1 - \exp\left(\frac{-D}{\lambda}\right)\right] \tag{10}$$

where n_o is the neutral Hg density in the exhaust and λ is the mean free path for charge exchange at 3 keV.

For a representative n_o value of 7×10^{11} per cubic centimeter, D/λ is approximately 0.4, so $j_R \approx j_I/5$ and equation (9) can be satisfied. Thus the secondary process for formation of Mo^+ can be a significant process because of the relatively high value of σ_{ex} at low energy.

CONCLUDING REMARKS

Upper-limit values of the charge exchange cross section have been estimated for the $Hg^+ + Mo$ and $Cs^+ + Al$ systems. These values can be used to obtain estimates of maximum possible deposition rates of slow Mo^+ and Al^+ species on the spacecraft. At energies near thermal for 500° C, the $Hg^+ + Mo$ cross section varies by several orders of magnitude from the upper-limit polarization value to a lower-limit adiabatic estimate.

The $Cs^+ + Al$ cross section depends critically on the nature of two or three curve crossings for that system. Consequently, it is more likely that this cross section is a strong function of velocity through the curve-crossing probability $P_c(v)$, although a realistic estimate of the actual interaction energy E_{12} is critical.

Reliable experimental values for σ_{ex} should be easily obtainable in the region from low keV values to several hundred eV. However, the cross section for slow ions (~0.1 eV) is not readily gotten and must be obtained by extrapolation. Such a procedure is valid as long as the mechanism of charge exchange does not change in the low-energy region. Fabrication of a Mo vapor source and reliable pressure measurements are probably the most severe problems that will be encountered in experimentally studying the $Hg^+ + Mo$ system.

Since the σ_{ex} for $Hg^+ + Mo$ is large ($\sim10^2$ Å^2) at low energies (~50 eV), it appears that formation of slow Mo^+ from slow secondary Hg^+ can be a relatively important rate process.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 19, 1972,
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APPENDIX A

SYMBOLS

b	impact parameter, m (Å)
b_L	critical impact parameter for polarizability potential, m (Å)
D	characteristic beam distance, m
E	energy of ion-atom system referenced to incident ion and target atom at infinity, eV
E_1	ion kinetic energy, eV
E_{12}	interaction energy between molecular ion potential curves at crossing, eV
e	magnitude of electronic charge, 1.6×10^{-19} C
h	Planck's constant, 6.625×10^{-34} joule-sec
J_1, J_2	total angular momentum quantum number for molecular ion electronic state
j_I	current density of thruster beam (fast Hg ions), A/m^2
j_n	current density (flux) of Mo atom, particles/(m^2)(sec)
j_R	random current density of slow ions found in Hg resonance charge exchange, A/m^2
j_s	current density of slow Hg ions, A/m^2
L	orbital angular momentum quantum number for molecular ion state
M_J	projection of total angular momentum of atom or ion along internuclear axis
m	reduced mass of ion-atom pair, kg
n_I	number density of Hg ions in exhaust beam, m^{-3}
n_n	sputtered neutral density, m^{-3}
n_o	number density of Hg neutrals in exhaust beam, m^{-3}
n_s	number density of slow Hg^+, m^{-3}
P	probability that curve crossing occurs (i.e., system remains on fast curve)
P_c	net probability that curve crossing occurs from initial to final state, $2P(1 - P)$
P_i	probability that ion-atom system is on favorable curve for charge exchange to occur

P_z	general probability for charge exchange (1/2 for low-energy process for all $b < b_L$)
R	ion-atom separation, m (Å)
R_c	radius inside which charge exchange probability oscillates for low-ion-energy polarizability cross section, m (Å)
R_L	distance of closest approach for polarizability potential, m (Å)
R_x	critical ion-atom separation for curve-crossing calculation which defines hard-core cross section, m (Å)
R_z	ion-atom separation which defines general reference cross section (πR_z^2), m (Å)
R_1	rate of charge exchange for fast Hg ions with Mo neutrals, events/(m^3)(sec)
R_2	rate of charge exchange for slow Hg ions with Mo neutrals, events/(m^3)(sec)
S	spin angular momentum quantum number
S_1, S_2	slopes of ion-atom electronic states, eV/Å
$V(R)$	polarizability interaction potential, joule
V_I	fast Hg ion velocity, m/sec
V_n	velocity of sputtered Mo neutrals, m/sec
V_s	slow Hg ion velocity, m/sec
v	relative velocity of ion and atom, cm/sec
α	electronic polarizability of atom, m^3 ($Å^3$)
ϵ	relative translational energy, $mV_I^2/2$, joule
Λ	projection of vector sum of J-values on internuclear (ion-atom) axis
λ	mean free path for resonance charge exchange, m
$^{2S+1}\pi_{g,u}$	symbol for $L = 1$ molecular ion state
$^{2S+1}\Sigma_{g,u}$	symbol for $L = 0$ molecular ion state
σ_{ex}	charge exchange cross section for fast ion with sputtered neutral, m^2
$(\sigma_{ex})_{res}$	resonance charge exchange cross section, m^2
$(\sigma_{ex})_s$	charge exchange cross section for slow ion with sputtered neutral, m^2

APPENDIX B

MULTIPLICITIES OF MOLECULAR ION STATES

Molecular states are assumed to have angular momentum values which are the sums of the two (atomic) total angular momentum quantum numbers J_1 and J_2. This limit of J-J coupling is chosen because coupling between the individual orbital L_i and spin S_i quantum numbers generally breaks down for heavy atoms (ref. 11). The molecular states of interest are either Σ or π (total angular momentum, 0 or 1) states where the superscripts + and - and the subscripts g and u describe them further as to behavior under symmetry operations. We shall not concern ourselves about the individual molecular ion states, but instead we shall assume that their density is sufficient to allow for curve crossings. There is an important qualification to be made in this respect for the Al-Cs^+ system. The resulting total angular momentum about the line joining the nuclei Ω is $\left|M_{J_1} + M_{J_2}\right|$, where the possible M_{J_1} values are $-J$, $-J + 1$, . . ., $+J$. For each combination of two M_J values, there is a different molecular state. The term multiplet $\left\{{}^{2S+1}L_J\right\}$ specifies $2S + 1$ including the spin quantum number S, the angular momentum state L, and their sum J for an atom in a fixed electronic state. For example Cs^+ has a completely filled outer electron shell, no unpaired electrons, and its term symbol is ${}^1S_0$ since $S = 0$, $L = 0$ (an S state), and $J = L \pm S = 0$. The term multiplets for all the atomic species of interest are given in table I. The designation for the molecular electronic states arising from given states of separated unlike atoms is given by the Wigner-Witmer rules (ref. 10, p. 318). These molecular electronic states and their symmetries are listed in table I also. The probability that the Hg^+ + Mo or Cs^+ + Al systems are on attractive bonding or repulsive antibonding ground-state curves is simply the ratio of the ground-state multiplicity to the total multiplicity of all the states formed from the separated atom ground-state configurations. In the case of J-J coupling, each M_{J_1}-M_{J_2} combination is a singly degenerate state. It should be noted that the probability of being on a particular curve of the molecular ion is not very sensitive to the assumption of angular momentum coupling in the isolated atoms. If we assume Russel-Sanders coupling of the L vectors for one atom (probably accurate for Al), then $\Lambda' = \left|M_{J_1} + M_{L_2}\right|$ is the quantum number which specifies each molecular state which has a degeneracy of $2S_2 + 1$, where S_2 is the spin of Al. The general features of the hypothetical molecular curves for Hg^+ + Mo are illustrated in figure 2.

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TABLE I. - TERM MULTIPLETS FOR ATOMS AND IONS WITH MOLECULAR ION STATES FORMED FROM GROUND ELECTRONIC STATES OF FOUR ION-ATOM PAIRS

[Molecular states are based on J-J coupling.]

Atom or ion	Unpaired electrons	Term designation	Number of molecular ion states	Symmetry of molecular ion states
Hg^+	1	$^2S_{1/2}$	7	Σ^+ (doubly degenerate)
Mo	6	$^7S_3^a$		
Hg	0	$^1S_0$	3	Σ^+, Π, Δ
Mo^+	5	$^6D_{1/2}$		
Cs^+	0	$^1S_0$	3	Σ^+, Π^+, Π^- (J-J)
Al	1	$^2P_{1/2}$		Σ^+, Π (quadruply degenerate J-L)
Cs	1	$^2S_{1/2}$	1	Σ^- (doubly degenerate, J-J or J-L)
Al^+	0	$^1S_0$		

[a] Half-filled subshell plus one s electron.

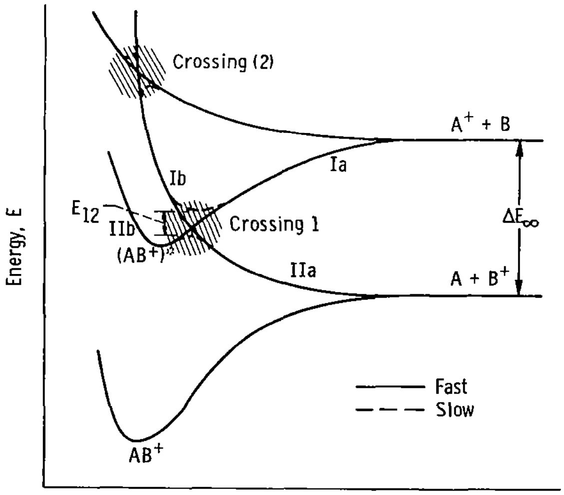

Figure 1. - Hypothetical potential energy curves for molecular ion states formed from ground electronic states of $A + B^+$ and $A^+ + B$ with "avoided" curve crossings (1) between attractive and repulsive curves and (2) between a pair of repulsive curves.

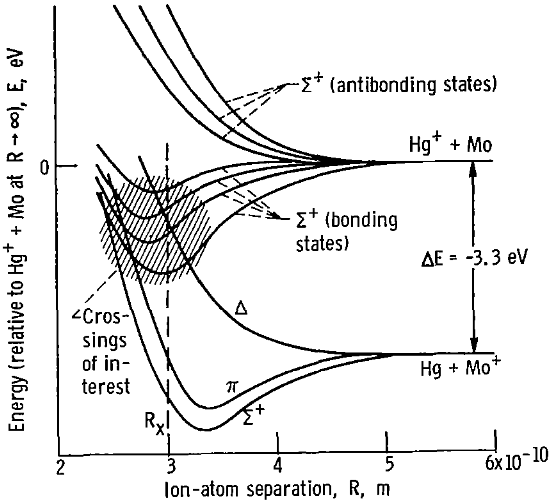

Figure 2. - General features of molecular ion states for Hg$^+$ + Mo, Hg + Mo$^+$ system accounting for symmetry (Wigner-Wittmer rules) assuming four of seven initial states are attractive (bonding) at separations of 2×10^{-10} to 3×10^{-10} m (2 to 3 Å).

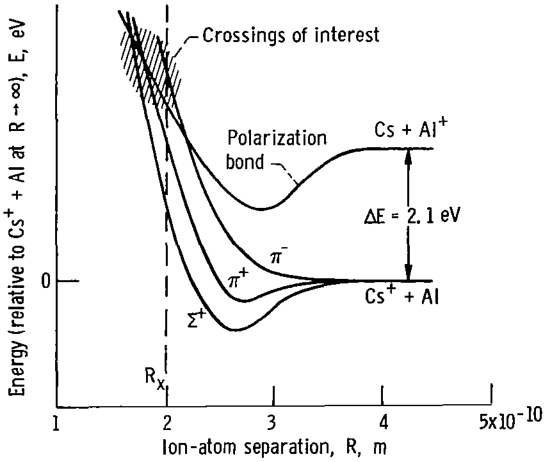

Figure 3. - General features of molecular ion states for Cs$^+$ + Al, Cs + Al$^+$ system accounting for symmetry considerations (Wigner-Wittmer rules) assuming J-J coupling and that two of the three Cs$^+$ + Al curves are attractive.

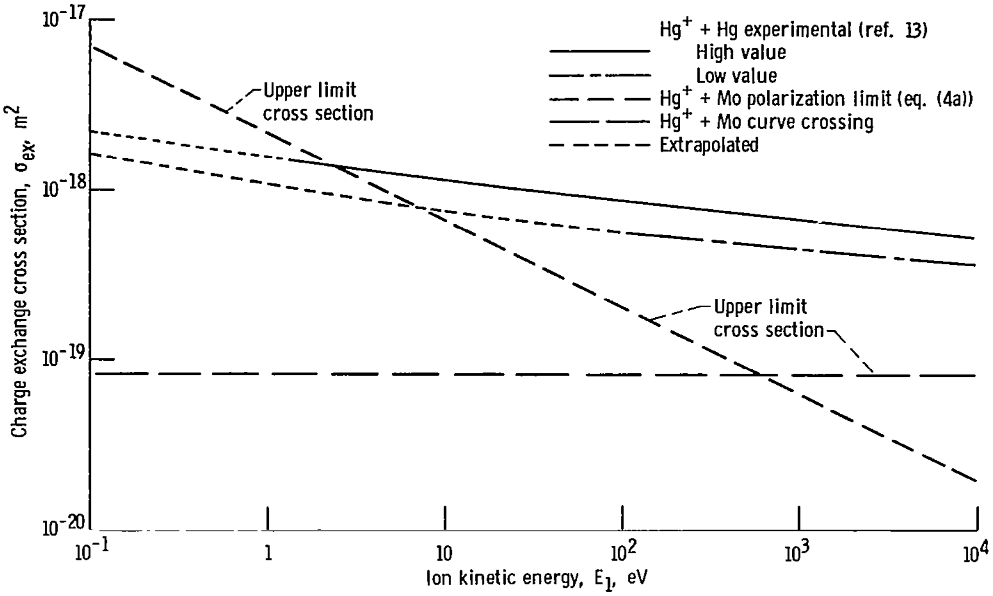

Figure 4. - Comparison of Hg$^+$ + Mo charge exchange cross sections with corresponding Hg$^+$ + Hg resonance values as function of ion kinetic energy.

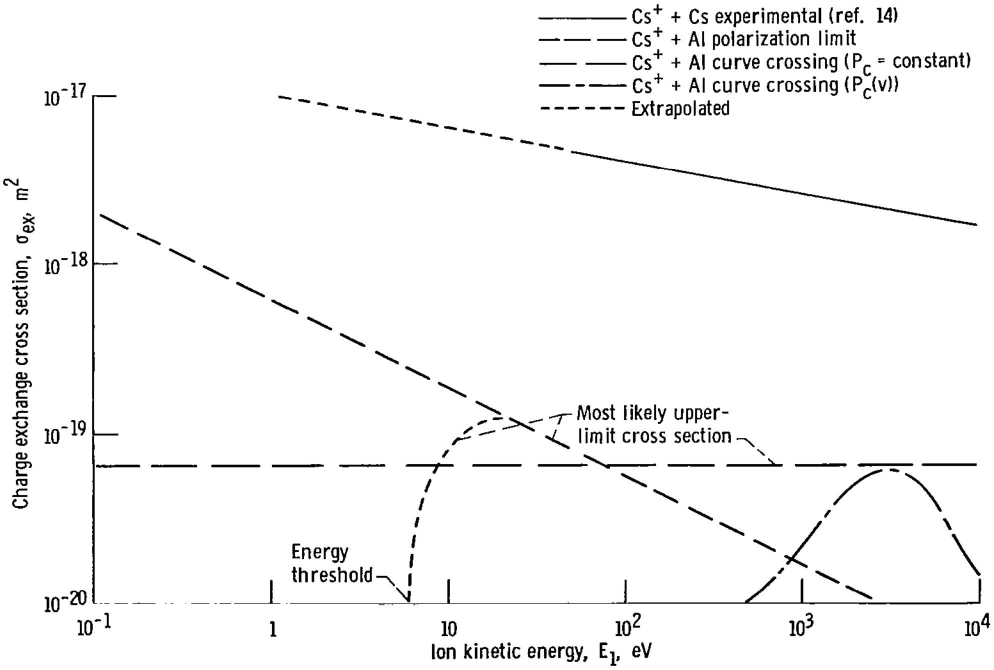

Figure 5. - Comparison of Cs$^+$ + Al charge exchange cross sections with corresponding Cs$^+$ + Cs resonance values as function of ion kinetic energy.

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