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Theoretical Research on Charge Exchange of Uranium
Ions at Thermal Energies

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ABSTRACT

The cross section for resonant charge transfer in U^+-U collisions is calculated as a function of the energy in the center-of-mass coordinate frame. The computed value decreases monotonically from approximately $300\text{\AA}^2$ at 0.025 eV to $100\text{\AA}^2$ at 50 eV. The latter value would be appropriate for ions of energy 100 eV moving through a gas of neutral atoms at thermal velocities.

I. Introduction

We have been involved in the study of resonant charge transfer for several ions including U^+ . In this report we describe our calculations for U^+-U collisions, but also will summarize our results for other ions for which comparison with experimental data is possible.

The mathematical formulation of the theory of charge transfer can be described in terms of the formation and dissociation of molecular ions. The states of these ions, e.g. U_2^+ , can be characterized as gerade or ungerade according to the parity of the states. In our model of charge transfer we assume that only two molecular states are involved in each collision. One of these states is gerade (g) and the other is ungerade (u). The charge transfer cross section is then determined largely by the difference in energy, $\Delta E(R)$, between the potential curves corresponding to these states. For large values of R , this energy difference can be related to the density of electrons on the median plane, which bisects at right angles the line between the two nuclei.

A more direct physical model for the charge transfer process can be obtained by considering the net flux of electrons across this median plane. Clearly this flux is also dependent upon the electron density on the plane so that the two pictures are closely related.

The first step in the calculation of the cross section is the computation of the molecular energy splittings, $\Delta E(R)$. In a recent paper¹, which is attached to this report, we have shown that at large values of R the value of this splitting can be expressed in terms of the asymptotic form of the electron density in the undistorted neutral atom. In that work we did not consider the effects of spin-orbit forces, which are significant for heavy atoms such as Xe and U. These effects will be discussed in a

second paper that will be submitted to the Physical Review. In secs. II & III we will summarize the results of this investigation.

Following the impact parameter method the motion of the nuclei is treated classically using trajectories that are determined by the ion-atom interaction. At energies above 10 eV the curvature of the trajectories is negligible. However at low energies the attractive polarization force increases the cross section significantly. Thus we need to know the polarizability of the uranium atom. To the best of our knowledge, there have been no measurements of this quantity. Thus we estimated the polarizability from the oscillator strength rule using the oscillator strengths compiled by Corliss; obtaining a value of 162 a.u. However there is considerable uncertainty in the values of the oscillator strengths and the intensity of many lines is unknown. Thus we performed calculations using values of the polarizability of 120, 162 and 200 a.u.

Having defined the nuclear trajectories for each value of the impact parameter, b , one must compute the probability that charge transfer occurs, which we denote by $P(b)$. We find that at small values of b this probability oscillates rapidly between 0 and 1. In this region one can assume that the average value of $P(b)$ is 0.5. Indeed it has often been suggested that the cross section is predicted well by means of the very simple assumption

$$\begin{aligned} P(b) &= \frac{1}{2} & b \leq b_F \\ P(b) &= 0 & b > b_F \end{aligned} \quad (1)$$

This model was first suggested by Firsov² and the critical parameter b_F is often called the Firsov parameter. The charge transfer cross section is then $\frac{1}{2}\pi b_F^2$.

Our own procedure is to evaluate $P(b)$ at decreasing values of b until the region of rapid oscillations is reached. We then obtain the cross section using

$$\sigma_{CT} = \frac{1}{2}\pi b_o^2 + \int_{b_o}^{\infty} P(b) b db \quad , \quad (2)$$

where b_o is a value in the oscillatory region at which $P(b_o)$ is either zero or one. The integral is evaluated numerically.

II. Calculation

The ground state configuration of the uranium atom is $(5f_{5/2})^3(7s_{1/2})^2(6d_{3/2})$. In the ground state of the ion, U^+ , the configuration is $(5f_{5/2})^3(7s_{1/2})^2$. Thus if both ion and atom are in the ground state, the charge transfer process involves the exchange of the $6d_{3/2}$ electron. Since this orbital is much more diffuse than the $5f_{5/2}$ orbital we will assume that the coupling of the 6d and 5f electrons has little effect on the electron density in the asymptotic region.

In the molecular ion U_2^+ the orbitals which correlate with the $6d_{3/2}$ atomic orbital have the component of angular momentum along the inter-nuclear axis, m_j , equal to either $3/2$ or $1/2$. As usual we can form even and odd combinations of the atomic orbitals. We write the difference in energy between the corresponding g and u states as $\Delta E_{3/2, m_j}^J(R)$. These differences can be related to the splittings that would be obtained in L-S coupling using

$$\Delta E_{3/2, m_j}^J = \sum_{m_\ell m_s} (C_{m_\ell - m_\ell \quad m_j}^{2 \quad 1/2 \quad 3/2})^2 \Delta E_{2, m_\ell}^{LS} \quad (3)$$

in which we have set the orbital angular momentum equal to 2, since the active electron is in a d-orbital.

Using Eq. (34) of the attached paper we can write

$$\Delta E_{2, m_\ell}^{LS}(R) = (-)^m \frac{5}{4 m!} \frac{(2+m)!}{(2-m)!} \left(\frac{\nu}{2R}\right)^m \left(\frac{4}{e}\right)^\nu \bar{R} u_0^2\left(\frac{R}{2}\right) (1 + O(1/k)) \quad (4)$$

with $\nu = 1.50$. The function $\bar{u}_0(r)$ is the radial part of the orbital of the active 6d electron. Asymptotically this takes the form

$$\bar{u}_0(r) \approx q r^{\nu-1} \left[1 + \frac{3.94}{r}\right] e^{-r/\nu} \quad (5)$$

The normalization constant, q , was obtained by comparing the expectation values of r^4 and r^6 predicted using eq. (5) with the relativistic Hartree-Fock results of Mann (private communication). Mann's value of $\langle r^4 \rangle$ is reproduced with $q = 0.382$, whereas his value for $\langle r^6 \rangle$ is given by $q = 0.404$. In our calculations we set $q = 0.40$.

The computed cross sections are given in table 1, as a function of the relative velocity and the energy in the center of mass coordinates. The lowest energy, 0.025, is approximately equal to kT at room temperature. In thermal collisions between two particles each with kinetic energy equal to kT the amount of energy in center-of-mass coordinates is, on average, also equal to kT . However if the energy of the ion is much greater than that of the neutral atom, the center-of-mass energy is approximately half of the ion's energy.

In columns 3 and 4 of table 1 we give the cross sections appropriate to collisions of atoms in which the valence electron has the quantum number m_j equal to $1/2$ and $3/2$. In practice we expect to obtain an equal mixture of these two probabilities. The average cross sections are given in columns 5 through 7, corresponding to the three different values of the polarizability.

For values of the center-of-mass energy, E , between 0.025 eV and 100 eV our results with $\alpha = 162$ a.u. are well fitted by the following formula

$$\sigma = (12.6 - 1.55 \log_{10} E)^2 + 1.153 E^{-1.12} \quad (6)$$

if E is expressed in eV and σ in $\text{\AA}^2$.

III. Comparison of theory and experiment for other ions

We have computed the cross sections for resonant charge transfer involving Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Ca^+ , Kr^+ and Xe^+ , each interacting with a neutral atom of the same species. A description of these results, together with a comparison with experimental data, is being prepared for submission to Physical Review. For the ions Li^+ , Rb^+ and Cs^+ our results at energies between 10 eV and 100 eV are in very good agreement, i.e. better than 10%, with the experimental results of Lorents et al.³ and Gentry et al.⁴ At energies around 1 keV our calculated cross sections are 15-20% above the experimental results. We would not be surprised if part of this difference is due to deficiencies in our theory, since the molecular model is less appropriate at higher energies. In K^+ we do not get agreement at any energies but suspect that there was an error in the experimental results of Gentry et al.⁴ They express uncertainty concerning their measurements on this ion.

For Ca^+ - Ca collisions our results are consistent with the experimental results of Panev et al.⁵, but are only 40% of the values measured by Rutherford et al.⁶ This comparison is of particular interest, since Ca and U have similar ionization potentials so that the charge transfer cross sections might be expected to be of similar magnitude. We can find no reasonable explanation for the cross section of over $400\text{\AA}^2$ at 50 eV measured by Rutherford et al.

The only other system we have examined in which spin-orbit forces are significant is Xe^+ -Xe. We have compared the cross sections for ions in the lowest $^2\text{P}_{3/2}$ and $^2\text{P}_{1/2}$ states, and find a 6% difference at thermal energies. This should lead to a similar difference in the mobilities of the ion. An experimental measurement of this difference is in progress.

IV. Conclusions

Our recommended values of the cross section were given in eq. (6). We believe that the error in our result should be less than 20%, but should warn that uranium is the most complex case that has been treated using our theory. Also the typical error in experiments on resonant charge transfer is of the order of 15 to 20%, so that we cannot claim that our calculations on other systems have been checked conclusively. On the other hand the measurement of the U^+-U charge transfer cross section is so difficult that we believe that at least equal weight should be given to the theoretical values if they should differ from the experimental values that are reported to you.

From the evidence that is available on resonant charge transfer it appears that the cross section is determined mainly by the size of the valence orbitals in the neutral atom and depends only weakly on the quantum structure of the atom or ion. Thus we would not expect the cross section to change drastically if the ions were produced in excited states.

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Table 1

$U^+ + U$ Cross Sections

Velocity a.u.	C.M. Energy ev.	$Q(m_j=1/2)A^{\circ 2}$		Q average: $A^{\circ 2}$		
		$\alpha = 162$	$\alpha = 162$	$\alpha = 120$	$\alpha = 162$	$\alpha = 200$
0.92 - 4	0.025	323.6	274.9	278.2	299.3	318.2
0.2 - 3	0.117	241.8	178.4	205.5	210.1	215.4
0.4 - 3	0.469	205.2	142.9	172.5	174.6	175.5
0.8 - 3	1.88	177.5	118.9	148.0	148.2	149.1
0.1 - 2	2.93	170.2	112.9	140.9	141.6	141.8
0.2 - 2	11.73	146.3	97.2	120.3	120.4	120.5
0.4 - 2	46.91	121.9	72.4	99.9	100.0	100.0
0.8 - 2	187.6	105.6	62.3	86.40	86.5	86.5