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Authors

Gentry, W R

Lee, Yuan-tseh

Mahan, Bruce H

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April 1968

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CHARGE TRANSFER BETWEEN POSITIVE ALKALI IONS AND ATOMS

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April 1968

Charge Transfer Between Positive Alkali Ions and Atoms.

W. R. Gentry,^{*} Yuan-tseh Lee,[†] and Bruce H. Mahan

Department of Chemistry and Inorganic Materials Research
Division of the Lawrence Radiation Laboratory,
University of California, Berkeley, California.

The total cross sections for resonant charge exchange have been measured as a function of energy in the range from 10 to 500 eV for the Cs^+ -Cs, Rb^+ -Rb, and K^+ -K systems. The agreement with certain data obtained at higher energies for these systems, and with theoretical cross sections of Smirnov is satisfactory.

^{*}Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

[†]Present address: Department of Chemistry, Harvard University, Cambridge, Massachusetts.

Recently there has been considerable interest in the elementary reactions of charged species. Perhaps the simplest such process is the resonant transfer of charge from an atomic ion to its parent atom. While there have been several measurements of the total resonant charge transfer cross section between alkali metal ions and atoms, most of the results pertain to rather high relative kinetic energies. In this paper we present measurements of total charge transfer cross sections in the cesium, rubidium, and potassium systems for primary ion energies in the range of 10 to 500 eV.

EXPERIMENTAL

In this work, we used a crossed ion-molecular beam technique. The apparatus is shown schematically in Fig. 1. Ions were formed in the source S by surface ionization, accelerated, momentum selected by the magnet M, and allowed to pass through a beam of alkali atoms from an oven source O. The intensity profile of the atom beam was determined with a surface ionization detector which was mounted on a rotatable lid. Also mounted on the lid was a Faraday cup detector F which could be rotated through 90° so as to detect the primary ion beam, or the slower ions formed by charge transfer. A fixed Faraday cup G and a fixed surface ionizer W were provided to monitor the intensity of the primary ion beam and the atomic beam respectively. The vacuum tank was pumped by two 6" silicone-oil diffusion pumps equipped with liquid nitrogen cooled baffles, and the source was separately evacuated by a

similar pump. The main chamber was ringed by a liquid nitrogen cooled copper cold shield CS. The background pressure under operating conditions was $1-3 \times 10^{-7}$ Torr.

A. Ion Beam Source

Ions were formed by allowing the alkali metal vapor to diffuse through a porous tungsten button which was heated to approximately 1200°C . The alkali metal vapor pressure was controlled by regulating the temperature of its containing reservoir by a Hallikainen Thermotrol unit equipped with a platinum senser. The ions were extracted from the tungsten button with an accelerating potential of 500 V, and then focused with a series of cylindrical lenses onto the entrance slit of the magnetic mass spectrometer. The pole pieces of the magnet were designed to give high order focusing of an ion beam with an angular spread of the order of 10° . At the exit slit of the mass spectrometer there was an einzel lens to provide final collimation of the beam. The mass spectrometer and the collision chamber were maintained at ground potential, and the potential of the tungsten button determined the energy of the ions in the collision region. The final energy spread of the beam (full-width at half maximum) was 2.8% at energies above 50 eV, and increased to 4% at 10 eV, while the angular spread of the beam was approximately 2° .

B. Neutral Beam Source

The atomic beam source consisted of a reservoir and a rectangular Laval nozzle slit, all machined from nickel. The

reservoir was mounted on quartz insulators, heated by alumina insulated tantalum wire, and was equipped with an iron-constantan thermocouple for determination of the oven temperature which was recorded continuously during a run. The exit nozzle was machined from 5/8" thick nickel, had an entrance aperture of 1/4" x 1/2" and converged to an exit slit whose dimensions were 0.004" x 0.250". Following the oven sequentially there was a flag that could be used to block the beam, a wide liquid nitrogen cooled slit to condense unwanted parts of the beam, a heated slit to define the beam, parallel plate electrodes to deflect charged particles, and a final slit attached to the grounded cold shield to prevent penetration of the deflecting field to the scattering center. The approximate oven temperatures used and the corresponding vapor pressures were 665°K and 3.5 Torr for potassium, 610°K and 3 Torr for rubidium, and 585°K and 2.5 Torr for cesium.

The full-width at half maximum of the atomic beams used in this research was 5°. The angular distribution of the neutrals was measured with a surface ionization detector consisting of a heated 0.003" dia tungsten wire suspended vertically with a 0.020" tantalum spring behind a slit 2 mm high. The wire was biased at 25 V with respect to the ion collector can so as to insure the collection of all ions, and to suppress all electron emission from the wire. The ion collector can had long entrance and exit channels to insure complete ion collection while allowing the atomic beam to pass through freely. Atoms that passed through the defining slit of the detector and did not hit the hot wire passed out of the detector without striking

the ion collector or its shield. A similar hot wire detector mounted in a fixed position opposite the atomic beam source was used to monitor the centerline intensity of the beam. Experiments were also performed to measure the vertical intensity distribution of the atomic beam, which was found to be uniform to within approximately 1% over the region traversed by the ion beam.

C. Detection System

For measurement of the primary beam attenuation and slow ion collection current, there was a Faraday cup detector surrounded by a shield which had a 1" diameter aperture located 1.072" from the scattering center. The resulting acceptance angle of the cup was $\pm 25^\circ$ measured from the scattering center.

The movable Faraday cup detector was connected to a Keithley Model 417 High-speed Picoammeter and a Moseley 2D-2A X-Y recorder. The electrometer-recorder combination was calibrated against a Keithley picoampere source with an overall accuracy of $\pm 0.4\%$. A Cary Model 31 vibrating reed electrometer was used to monitor the primary ion current at the fixed Faraday cup, and also to measure the intensity distribution of the neutral beam. The values of the input resistors of the electrometer were measured to 0.1%. The fixed neutral beam monitor was connected to a Keithley model 610B electrometer.

D. Experimental Procedure

The ion and molecular beams were turned on and allowed to reach stable operating conditions well before experimental data were collected. Most of the cross sections were determined by measuring the attenuation of the ion beam. In these experiments, the movable Faraday cup was located exactly opposite the ion beam source exit slit, the major part of the ion current reaching the cup was biased out, and the electrometer sensitivity increased so that the attenuation of the ion beam, which was usually 1%, would be a large fraction of the full scale current. The electrometer output was recorded as the neutral beam flag was opened and closed at intervals of several seconds. After a number of cycles had been recorded,, the electrometer bias current was turned off and the total primary ion current was determined. The small background current due to particles from the neutral beam was measured by shutting off the ion beam and recording the current to the Faraday cup as the beam flag was opened and closed. To minimize this background, adjustments were made to the potential of the deflecting plates at the neutral beam exit, and the neutral beam monitor was turned off during all ion current measurements. The background was always a small fraction of even the smallest signals measured.

To perform the slow ion collection experiments, the Faraday cup was rotated into the path of the neutral beam. Because of surface potentials, it was necessary to apply a negative

potential of up to 6 volts in order to collect the slow ions completely. This bias voltage was sufficient to deflect the primary beams of lowest energy, and consequently the charge collection experiments could not be performed at the lowest energies reached in the attenuation experiments.

The slow ion current was measured with the beam flag alternately open and closed, while the fixed Faraday cup was used to monitor the primary ion intensity. After each series of slow ion current measurements, the Faraday cup F was lifted out of the path of the neutral beam and the neutral monitor current recorded. The background current to the ion collector due to the neutral beam alone was also measured and found to be less than 10% of the lowest ion signal recorded.

To measure the distribution of the neutral beam, the output of the electrometer which measured the surface ionization current was connected to the Y-input of the recorder, and the X-input was taken from a helipot voltage divider driven by the sprocket used to rotate the lid of the main chamber on which the detector was mounted. This distribution was measured several times during the period in which data was collected to insure that the integral of the distribution normalized to the fixed monitor signal remained constant. The area under the distribution curve was calculated by using Simpson's rule.

To convert the measured surface ionization current to an atom flux we used the surface ionization coefficients of 0.977 for Cs, 0.859 for Rb, and 0.690 for K, as calculated from the Saha-Langmuir equation using 4.58 eV for the work function of

tungsten, and a temperature of 1860°K. The temperature of the tungsten wire as a function of heating current was taken from the Jones-Langmuir tables.¹

To calculate the cross section the quantity needed is the integral of the neutral particle density along the primary ion path. The hot wire neutral detector measures the flux at a position somewhat removed from the scattering center. The atom flux at the scattering center along the ion path was calculated from straightforward geometric considerations.² The atom density in the neutral beam was calculated by dividing the flux by the average atomic velocity. The latter was determined in separate experiments by using a velocity analyser. The number density velocity distribution in these Mach 3 beams was found to be very nearly symmetric about the most probable velocity, and the number average velocity was $31 \pm 2\%$ higher than the average velocity of atoms in the oven. This shift toward higher velocities is somewhat greater than that found by Hundhausen and Pauly³ for a potassium atom beam operating under conditions similar to ours.

A source of error in the density determination is the possible presence of diatomic molecules of the alkali metals in the beam. These would most probably be recorded as one equivalent charge by the surface ionization detector, but would have a charge transfer cross section much smaller than the atoms since the process would be several tenths of an electron volt exothermic. Calculations based on the thermodynamic data of Wagman et al.⁴ suggest the fractional concentration of diatomic molecules at the oven temperature and

pressures we used is approximately 1.5%. One might expect the concentration of the diatomic molecules in the beam to be at least as great, due to the observed tendency of heavier molecules to concentrate near the center of nozzle beams. On the other hand, measured fractional concentrations of K_2 in potassium beams from ovens apparently similar to ours and operated in the same temperature range have been quoted⁵ to be only $1-2 \times 10^{-3}$, which is negligible for our purposes. It is unlikely that molecules in the beam constitute an important source of error.

A possible source of error in the attenuation measurements is the elastic scattering of ions without charge transfer, which would cause the apparent charge transfer cross section to be too large. This error was largely eliminated by using an ion collector that intercepted an angle of $\pm 50^\circ$ in the center of mass system. According to an estimation based on classical differential scattering cross sections calculated by Mason and Vanderslice,⁶ the elastic scattering at angles greater than $\pm 50^\circ$ is only approximately 2% of the measured total cross section. In the attenuation measurements the elastic contribution makes the observed cross section too large, whereas it makes the cross sections derived from charge collection too small. The two methods gave results which were almost identical, and the same within experimental scatter.

RESULTS AND DISCUSSION

The numerical values of the total charge transfer cross sections are given as a function of energy in Table I. Figures 2-4 show a comparison between our results and those of Marino, Smith, and Caplinger⁷ (MSC), Perel, Vernon, and Daley⁸ (PVD), Kushner and Buchma⁹ (KB), and Chkuaseli, Nikoleishvilli, and Guldashvilli¹⁰ (CNG). Also shown are the theoretical predictions of Smirnov,¹¹ and Rapp and Francis.¹² The form of the graphs was suggested by the well-known^{11,12} expectation that the square root of the charge transfer cross section decreases linearly with the logarithm of the velocity over limited ranges.

For the Cs⁺-Cs system, the agreement between our values of σ at our high velocity limit with those of Perel et al.⁸ at their low velocity limit is quite good. Both sets of results give cross sections 20% smaller than those reported by Marino et al.,⁷ and approximately the same amount larger than those determined by Kushnir and Buchma.⁹ Smirnov's theoretical cross section¹¹ is only 20% smaller than our results at low velocities, and is in nearly exact agreement with the measurements of Chkuaseli et al.¹⁰ at high velocities. The cross sections reported by CNG have been reduced by 15% to compensate for their miscalculation of the neutral atom density. The theoretical prediction of Rapp and Francis¹² is smaller by nearly a factor of two than our cross sections in the low velocity range.

For the Rb^+ -Rb system, the agreement between the present experiments and those of Perel and coworkers⁸ is very good in the overlapping range of velocity. The theoretical cross-section of Smirnov¹¹ is too small by no more than 25% in the low velocity range, and intersects the high energy data of Perel et al.⁸ and Chkuaseli and coworkers¹⁰ at velocities of approximately 10^7 cm/sec. The slope of the $\sigma^{1/2} - \ln v$ curve predicted by Smirnov is rather close to that found in the present work.

As Fig. 4 shows, our resonant charge exchange cross section for the K^+ -K system is in excellent agreement with the predictions of Smirnov. The Rapp-Francis calculation, apparently made with a low, incorrect ionization energy for potassium, still gives results 30% smaller than our experimental values. It should be remarked that if the surface ionization coefficient of potassium on tungsten were higher than the value of 0.690 we used to analyse our data, the true cross sections for charge exchange would be higher than the ones we report here. The range of velocities in the experiments of Chkuaseli et al. does not overlap with ours, so a comparison of the two sets of results is difficult. Other reported cross sections for the potassium system^{13,14} are so badly scattered and show such peculiar velocity dependence that their reliability is questionable.

Several theoretical approaches^{11,12} to the resonant charge transfer problem show that the total cross section is largely determined by the variation with internuclear distance of the

energy separation of the lowest symmetric and antisymmetric states of the molecule-ion. The approximate charge transfer cross section is expressed as $\sigma = 1/2 \pi b_c^2$, where b_c is a critical impact parameter, in this case equal to the distance of closest approach for which the charge transfer probability first reaches a value of one half. The charge transfer cross section is most sensitive to the difference in energy between the symmetric and antisymmetric states at an internuclear separation equal to b_c . In our work the cross sections reflect the potential curves in the internuclear region of 14.5 to 17 Å for the cesium system, for the rubidium system 13.5 to 15.5 Å, and 10.5 to 12.5 Å for the potassium system. In the high energy work of Chkuaseli et al,¹⁰ the smallest cross sections correspond to minimum internuclear separations of 9.5, 8.5, and 7.5 Å for cesium, rubidium, and potassium, respectively.

The splitting of the symmetric and antisymmetric states at large internuclear distances is small, and calculations of it should be relatively reliable. Rapp and Francis use the LCAO method to calculate this splitting, and employ very simple nodeless atomic wavefunctions which are scaled by the exact experimental atomic ionization energies. Their calculation thus involves a major simplification, but no adjustable parameters. This procedure leads to cross sections considerably smaller than those measured experimentally.

In his analysis of the problem, Smirnov notes that the splitting between the symmetric and antisymmetric states cannot be calculated in a perturbation power series in reciprocal

internuclear separation, and proposes a method which relates the splitting to the radial atomic wave function. His calculation is still basically a two state analysis, and he uses simple nodeless atomic wavefunctions which are larger, for a given experimental ionization energy, than those of Rapp and Francis. Consequently, Smirnov's cross sections lie noticeably closer to the experimental values. In the alkali atoms there are low lying excited states which make the two state approximation used by Rapp and Francis and Smirnov somewhat dubious at the higher collision energies. Nevertheless, the agreement between the theoretical cross sections of Smirnov and the experimental values is encouraging, and suggests the two-state analysis of the charge transfer process may be a useful approximation for the prediction of total cross sections.

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Table I. Resonant Charge Transfer Cross Sections.^a

Cs ⁺ -Cs			Rb ⁺ -Rb			K ⁺ -K		
E _{lab} (eV)	$\sigma \times 10^{14}$ (cm ²)	$v \times 10^5$ (cm/sec)	E _{lab} (eV)	$\sigma \times 10^{14}$ (cm ²)	$v \times 10^5$ (cm/sec)	E _{lab} (eV)	$\sigma \times 10^{14}$ (cm ²)	$v \times 10^5$ (cm/sec)
10	4.09	5.05	12	3.23	6.81	20	2.08	1.27
10	4.01		17	3.16	8.12	35	1.97	1.69
10	4.35		20	3.21	8.80	50	1.95	2.01
12	4.02	5.53	22	3.11	9.24	60	1.93	2.21
12	4.07		25	3.11	9.85	60	1.91	2.21
15	3.94	6.18	30	3.03	10.8	80	1.87	2.54
17	4.01	6.58	35	3.08	11.6	100	1.85	2.85
20	3.89	7.14	40	3.00	12.4	125	1.79	3.19
20	3.84		45	3.02	13.2	150	1.76	3.49
25	3.71	7.98	50	2.95	13.9	200	1.72	4.02
30	3.67	8.75	60	2.88	15.2	200	1.72	4.02
35	3.57	9.44	70	2.79	16.5	250	1.66	4.50
40	3.53	10.1	100	2.69	19.7	320	1.62	5.09
45	3.44	10.7	140	2.55	23.2	400	1.58	5.70
60	3.28	12.4	200	2.49	27.8	500	1.54	6.38
70	3.30	13.3	35	2.93	11.6			
80	3.16	14.3	50	2.81	13.9			
100	3.14	16.0	60	2.81	15.2			
140	3.18	18.9	70	2.77	16.5			
60	3.32	12.4	100	2.59	19.7			
70	3.25	13.3	140	2.50	23.2			
80	3.23	14.3	200	2.45	27.8			
100	3.13	15.9						
140	3.03	18.9						
200	2.94	20.1						

a. Data above dotted line were taken by the beam attenuation method, those below by the charge collection method.

Footnotes

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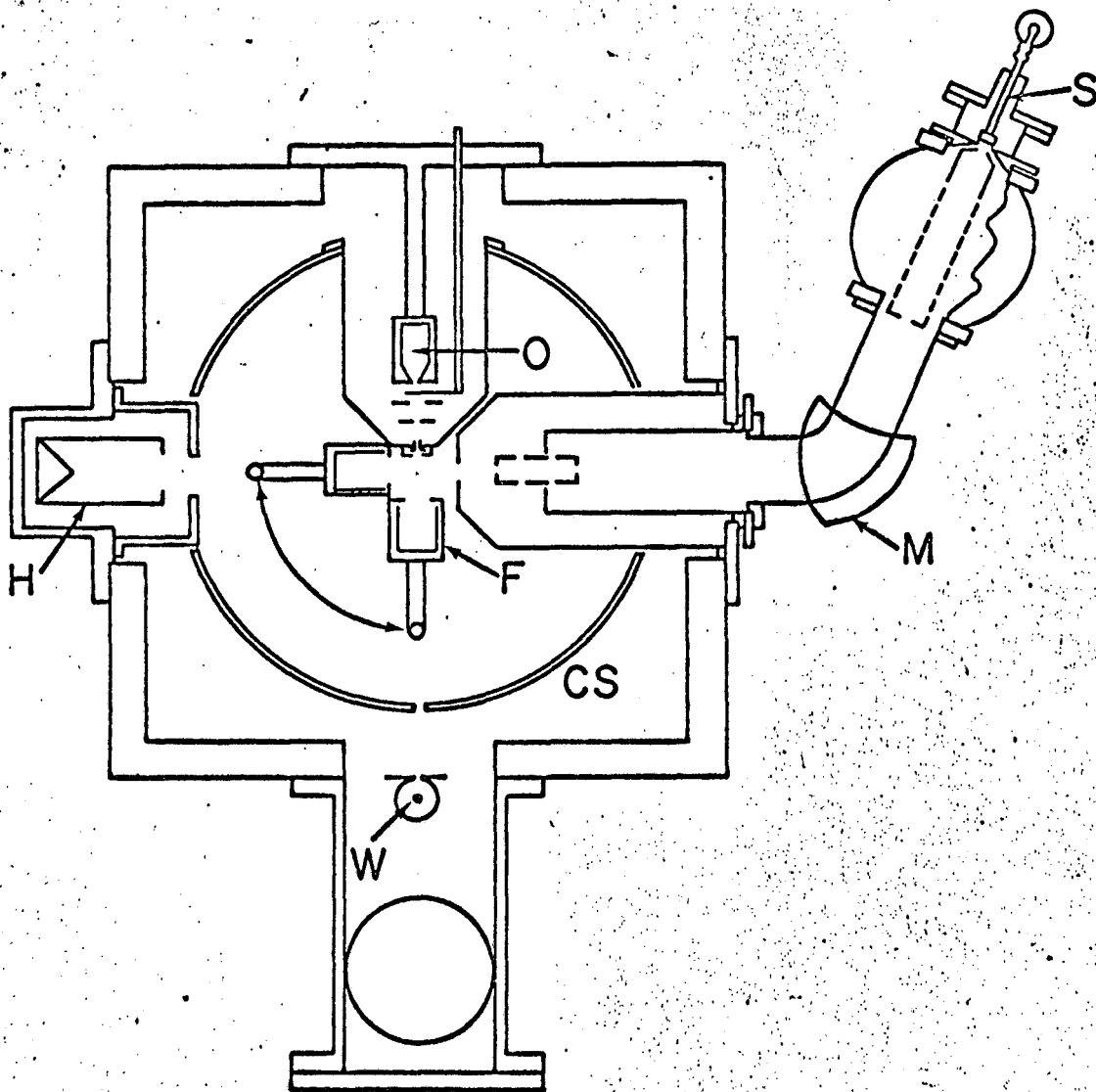


Figure 1. Ion-atom crossed beam apparatus. See text for identification of symbols.

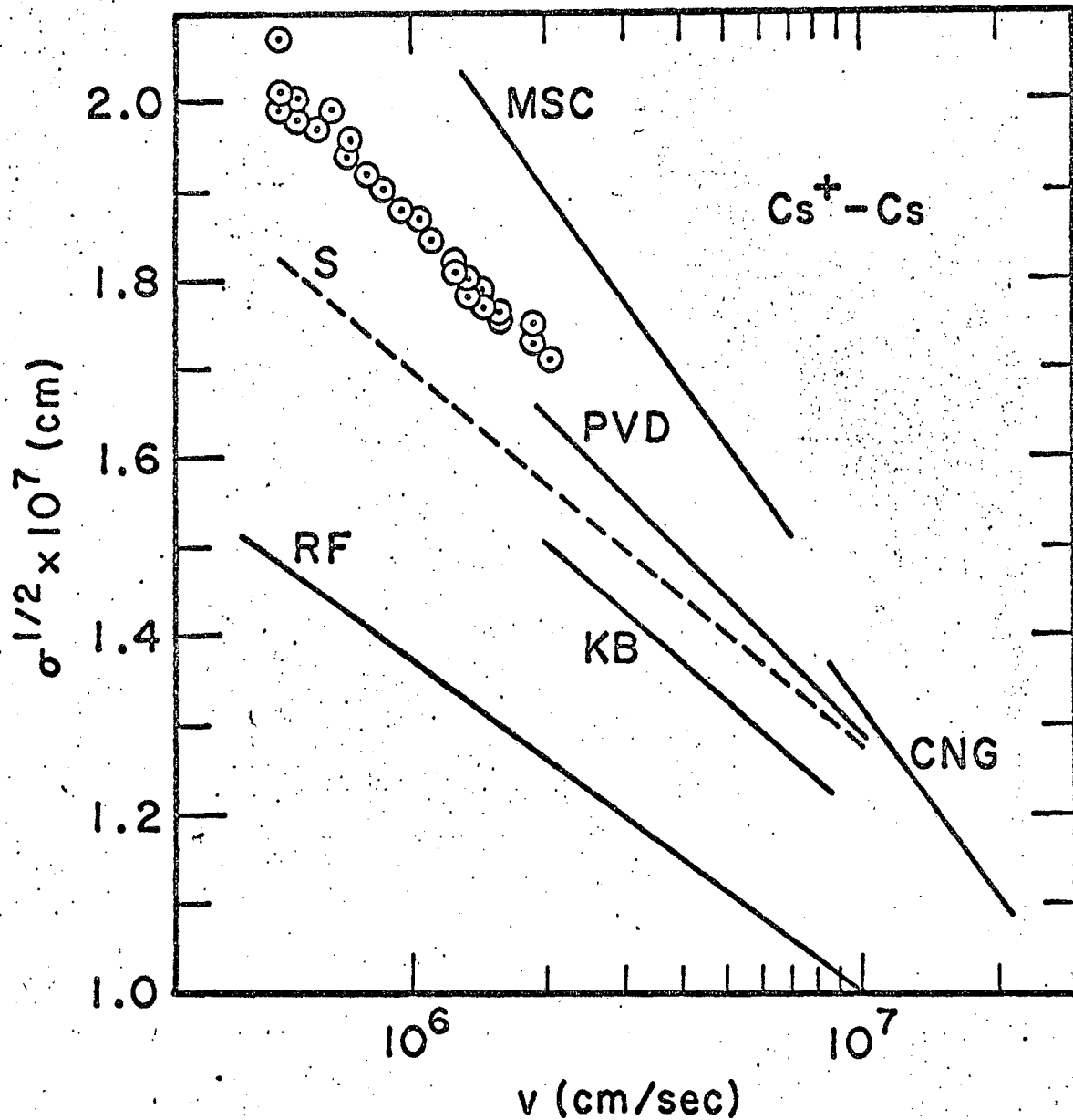


Figure 2. The square root of the charge transfer cross section plotted as a function of the logarithm of the laboratory velocity for the $Cs^+ - Cs$ system. Circles represent this research, other authors are identified in the text.

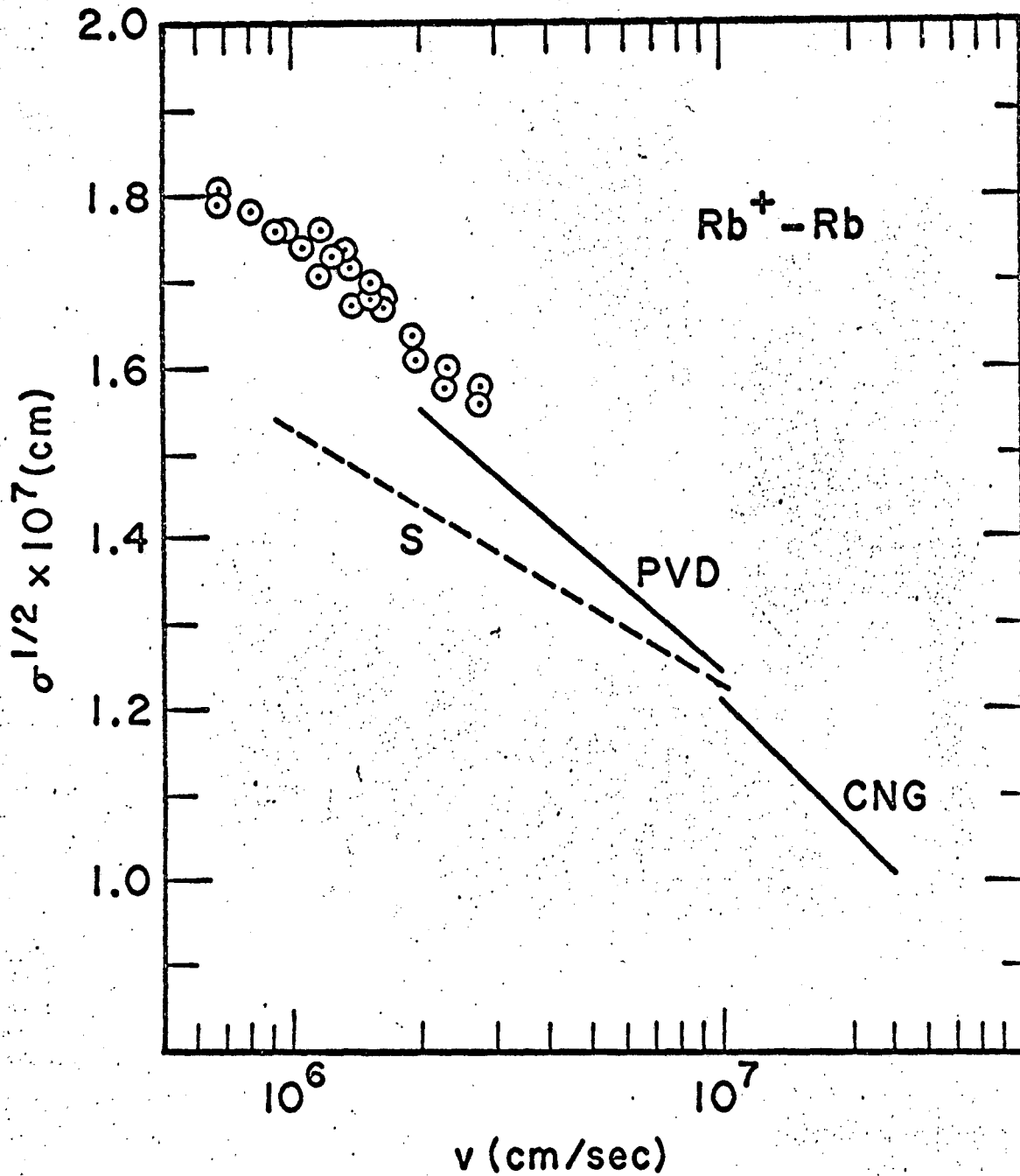


Figure 3. The square root of the charge transfer cross section plotted as a function of the laboratory velocity for the $\text{Rb}^+ - \text{Rb}$ system.

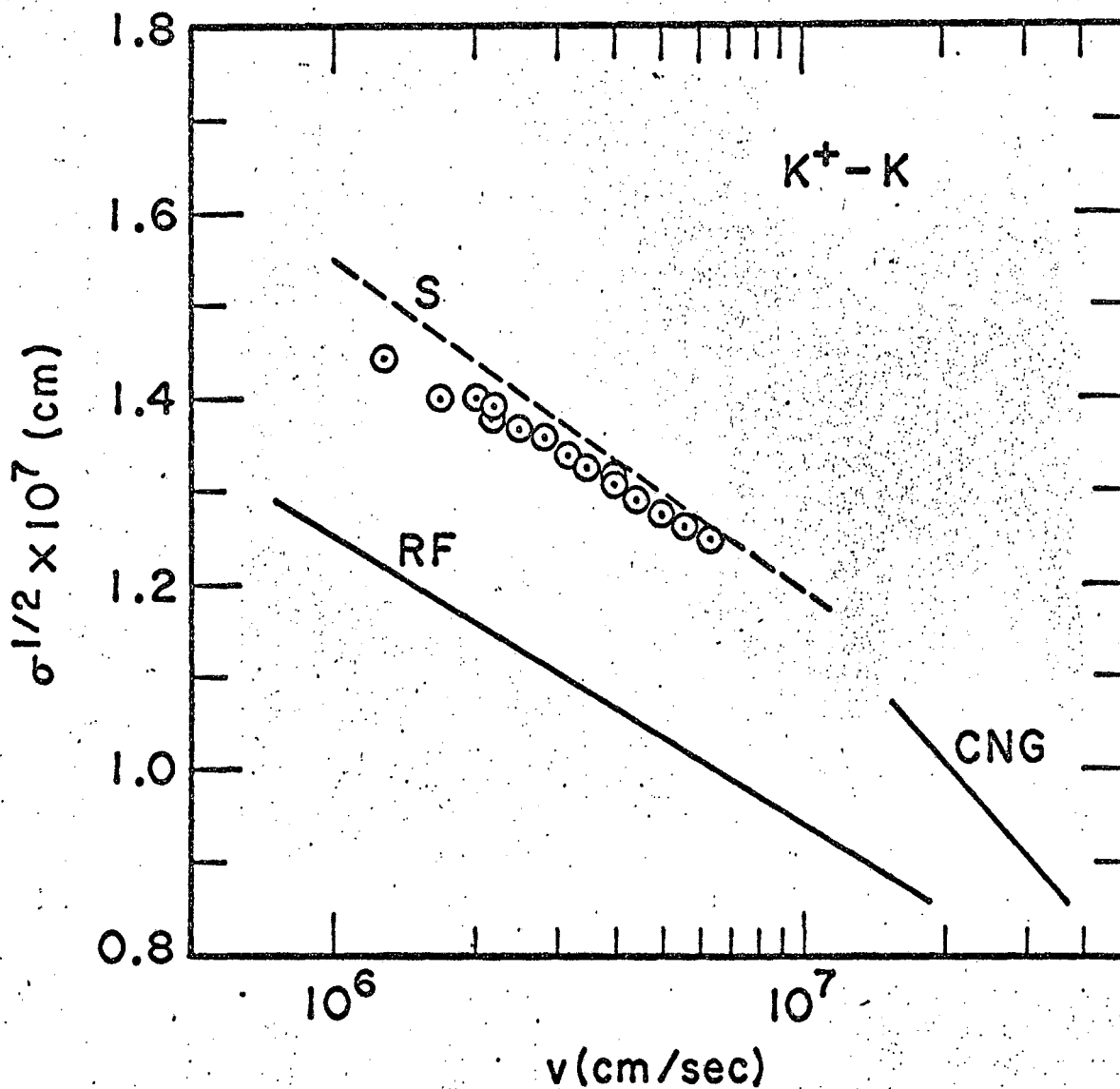


Figure 4. The square root of the charge transfer cross section plotted as a function of the laboratory velocity for the $K^+ - K$ system.

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