Slow collisions of H⁻ and D⁻ with Cs

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Charge-transfer and electron-detachment cross sections for collisions of H⁻ and D⁻ with Cs atoms have been measured in the energy range from 3 to 300 eV.

I. INTRODUCTION

In a preceding paper[1] (hereafter referred to as I) we reported measurements of relative cross sections for charge transfer $\sigma_{CT}(E)$, and electron detachment $\sigma_e(E)$ in slow collisions of H⁻ and D⁻ with Na and K atoms. It was observed that both charge transfer and electron detachment were significant electron-loss mechanisms for these systems. Each process was found to exhibit a velocity-dependent isotope effect; $\sigma_{CT}(E)$ displayed a strong energy dependence and high energetic threshold (about 20 eV for H⁻ + Na and 40 eV for H⁻ + K), while $\sigma_e(E)$ displayed a weaker energy dependence and a near zero-energy threshold. In this paper we report the corresponding measurements for H⁻(D⁻) + Cs for collision energies ranging from 3 to 300 eV.

In addition to the intrinsic theoretical interest in the system H⁻ + Cs, it is also of practical concern. Cesium-metal vapor is often employed in H⁻ ion sources of the plasma-discharge type to enhance the efficiency of H⁻ production.[2] Although H⁻ ions appear to be primarily produced on cesium-metal-coated surfaces in such an ion source, the process H⁻ + Cs→H + ⋯ in the gas phase is one of the reactions leading to the destruction of H⁻ and thus determines the intensity of H⁻ that can be realized. Meyer[3] measured the total electron-loss cross sections (i.e., σ_{CT} and σ_e) for H⁻(D⁻) + Cs in the energy range from 150 eV to 2 keV, but there appear to be no previous measurements for lower energies, and none which separates the two channels. At collision energies above a few keV, there have been numerous studies (with somewhat disparate results) of electron-loss cross sections as well as equilibrium fractions; those investigations have been well summarized by Schlachter *et al.*[4]

II. EXPERIMENTAL METHOD

A detailed description of the cross-beam apparatus used in these measurements is given in I. Briefly, H⁻ and D⁻ ions are extracted from an arc-discharge source, focused electrostatically, and mass-selected with a Wien filter; the ion beam is then focused into the collision region. The Cs beam is produced in an alkali-metal oven with the typical operating temperature of 200 °C for Cs. A cesium ampule was cooled, broken, and loaded into the oven under liquid nitrogen to minimize contamination. The cesium target

beam emerging from the oven intersects the ion beam in the collision region which is within a one-sixth section of 127° cylindrical electrostatic energy analyzer. The voltage across the two curved plates of the analyzer allows the ion beam to pass through resonantly and is used, simultaneously, to extract the slow product anions and electrons. The extracted anions and electrons are then focused with an einzel lens, separated by a magnetic field, and detected with particle multipliers. The relative collection efficiencies for different collision energies for each product are determined by normalization to known cross sections[5] $\sigma_{CT}(E)$ and $\sigma_e(E)$ for H⁻ + O₂.

III. RESULTS AND DISCUSSION

The experimental results for σ_{CT} and σ_e for collisions of H⁻ and D⁻ with Cs are shown in Fig. 1 as functions of E/M. Since our measurements overlap the lower collision-energy range of the previous measurements of the total electron-loss cross sections by Meyer[3] (his results were obtained by monitoring the change of the attenua-
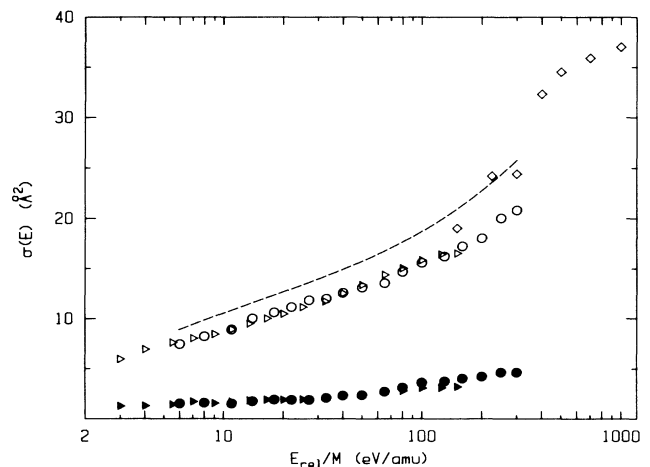

FIG. 1. Charge transfer (solid symbols) and electron detachment (open symbols) cross sections for H⁻ + Cs (circles) and D⁻ + Cs (triangles) vs E_{rel}/M, where E_{rel} is the relative collision energy and M the reduced mass of the projectiles. The dashed line is $\sigma_{CT} + \sigma_e$ for H⁻ + Cs. Open squares are $\sigma_{CT} + \sigma_e$ for H⁻ + Cs from Ref. 3.

tion of the H^- beam due to a change of target length of a Cs vapor cell with known Cs density), they have been normalized to Meyer's results as indicated in Fig. 1. Also shown in Fig. 2 are the ratios σ_{CT}/σ_e for H^- + Na, K, and Cs.

As may be seen, both σ_{CT} and σ_e for $H^-(D^-)$ + Cs, as for Na and K, show a velocity-dependent isotope effect. (This isotope effect was also observed in Meyer's earlier measurements.) Electron detachment is the dominant electron-loss channel; as for the Na and K targets, $\sigma_e(E)$ for H^- + Cs shows a stronger energy dependence at the higher energies than do the H^- + rare-gas systems where electron detachment is explained purely by the coupling between the ionic state and the continuum.[6] This stronger energy dependence suggests that additional dynamic mechanisms are also involved in electron detachment for these H^- + alkali-metal systems. The ratios σ_{CT}/σ_e in Fig. 2 illustrate that the relative importance of charge transfer as an electron-loss mechanism decreases as the mass of the alkali-metal increases. Unlike the results for Na and K, $\sigma_{CT}(E)$ for H^- + Cs shows no obvious threshold. These features can be understood with the help of a schematic diagram (Fig. 3) of the potential curves for CsH^- and CsH which are based on the calculations of the ground molecular states of CsH^- and CsH by Karo et al.[7] and the calculations of the low-lying molecular states of NaH^- and NaH by Olson and Liu.[8]

Cs has a larger polarizability than Na, thus the $X^2\Sigma$ state of CsH^- has a stronger long-range attraction potential. This, combined with the smaller electron affinity of Cs, leads to a larger gap between the $X^2\Sigma$ and $A^2\Sigma$ states which consequently reduces their charge exchange coupling. Additionally, the $A^2\Sigma$ state crosses into the $X^1\Sigma$ continuum at an internuclear separation R_2 which is larger than the corresponding crossing for the Na target because of the smaller electron affinity of Cs.

As discussed in I, the key to understanding the collisional dynamics is to identify various effects associated with the $X^2\Sigma - A^2\Sigma$ coupling. To clarify the situation it is
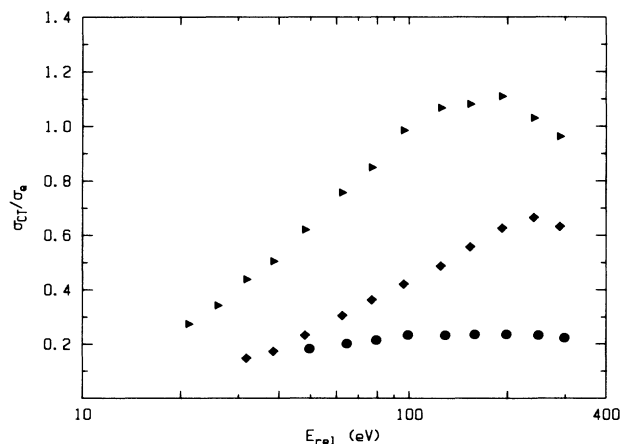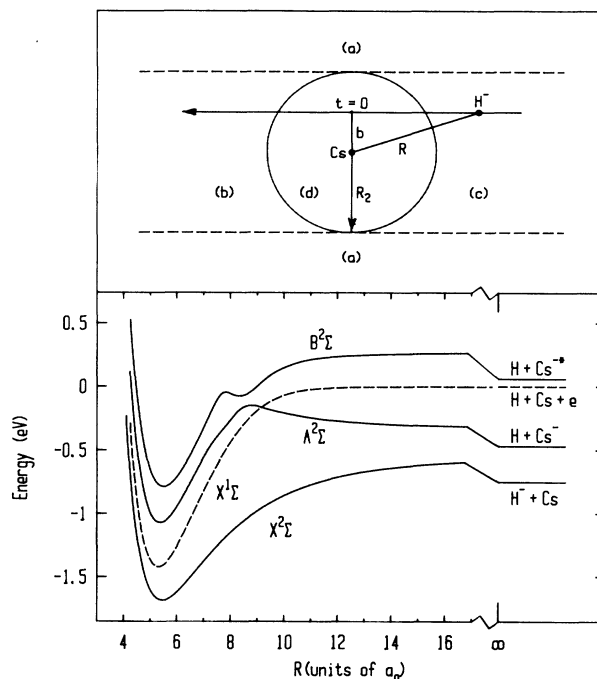

FIG. 3. Low-lying molecular states of CsH^- (solid lines) and ground state of CsH based on Refs. 7 and 8. The upper portion of the figure indicates the various regions [(a)–(d)] which are used to discuss the collisional dynamics for this system.

helpful to divide the collisional space into regions as follows:

$$X^2\Sigma - A^2\Sigma \begin{cases} R > R_2 \begin{cases} b > R_2 & \text{1(a)} \\ b < R_2 \begin{cases} t > 0 & \text{1(b)} \\ t < 0 & \text{1(c)} \end{cases} \end{cases} \\ R < R_2 , & \text{1(d)} \end{cases}$$

where $t < 0$ corresponds to the incoming trajectory (taken to be a straight line). These regions are illustrated in the upper portion of Fig. 3.

The coupling in regions 1(a) and 1(b) can only lead to charge transfer. In 1(c), on the other hand, charge exchange to the $A^2\Sigma$ state will result in a subsequent crossing into the $X^1\Sigma$ continuum at $R = R_2$, leading to electron detachment. To discuss the coupling in region 1(d), it should be pointed out that the adiabatic $A^2\Sigma$ curve is a mixture of two very different states in a diabatic representation for CsH^-. In this region ($R < R_2$) the $A^2\Sigma$ state is mainly the diabatic H^- + Cs(6p) state; although it lies within the $X^1\Sigma$ continuum, its p-wave centrifugal barrier may trap the extra electron temporarily. As discussed in I, the $X^2\Sigma - A^2\Sigma$ coupling in this region might be large because of the localized electron wave of the $A^2\Sigma$ state and the large polarizability of Cs. If the system makes a

FIG. 2. Measured ratios σ_{CT}/σ_e for H^- + Na (triangles), K (squares) and Cs (circles).

transition to the $A^2\Sigma$ state, it may end up in the $B^2\Sigma$ state (H + Cs$^-$*, Ref. 9) due to a transition near the avoided crossing between $A^2\Sigma$ and $B^2\Sigma$. Cs$^-$* would then autodetach and contribute to the electron-detachment measurement. The importance or role of these diabatic states in such collisions could be investigated by studying photon production in "cleaner" systems such as Cl$^-$ + Na where the final state Cl$^-$ + Na($3p$) lies below the Cl + Na$^-$* state.[9,10]

For the H$^-$ + Na system, the charge-transfer contribution from region 1(a) is larger than that from 1(b). This may no longer be the case for H$^-$ + Cs because of the effectively shorter range of the $X^2\Sigma$-$A^2\Sigma$ coupling and the larger value of the $A^2\Sigma$-$X^1\Sigma$ crossing. As pointed out in I, the $X^2\Sigma$-$A^2\Sigma$ coupling in 1(b) is responsible for a larger fraction of the total charge-transfer cross section at low energy because the "effective radius" of the coupling decreases when the impact velocity decreases. This relative importance of the coupling in 1(b) perhaps is the principal reason why $\sigma_{CT}(E)$ for Cs has a threshold behavior different from those for Na and K.

Another mechanism leading to electron detachment (in addition to the contribution from the $X^2\Sigma$-$A^2\Sigma$ coupling discussed above) is the possible curve crossing between $X^2\Sigma$ and $X^1\Sigma$. The molecular potential curves of CsH$^-$ and CsH presented by Karo et al.[7] suggest that a crossing

between $X^2\Sigma$ and $X^1\Sigma$ is likely at an internuclear separation, $R < 4a_0$. This curve-crossing mechanism is expected to be weakly energy dependent at high energy,[6] while the $X^2\Sigma$-$A^2\Sigma$ coupling in the region 1(d) is strongly energy dependent because of the near-resonant nature of these two states.[11]

It should be mentioned that the calculation in Ref. 8, which overestimates the relative importance of charge transfer over the energy range of these experiments, fails to agree with the present measurements.

IV. CONCLUSION

In summary, electron detachment is the dominant electron-loss channel in slow collisions of H$^-$ and D$^-$ with Cs; charge transfer is less important for Cs than for Na and K. Both processes exhibit velocity-dependent isotope effects for H$^-$ and D$^-$; i.e., the cross sections are equal at comparable values of E/M. The observed isotope effects are consistent with the two-state PSS model for such collisions.

ACKNOWLEDGMENTS

[1]Yicheng Wang, R. L. Champion, and L. D. Doverspike, Phys. Rev. A **35**, 1503 (1987).

[2]J. R. Hiskes, A. M. Karo, and M. A. Gardner, J. Appl. Phys. **47**, 3888 (1976).

[3]F. W. Meyer, J. Phys. B **13**, 3823 (1980).

[4]A. S. Schlachter, K. R. Stalder, and J. W. Stearns, Phys. Rev. A **22**, 2494 (1980).

[5]M. S. Huq, L. D. Doverspike, and R. L. Champion, Phys. Rev.

A **27**, 785 (1982).

[6]R. L. Champion, Adv. Electron. Electron Phys. **58**, 143 (1982).

[7]A. M. Karo, M. A. Gardner, and J. R. Hiskes, J. Chem. Phys. **68**, 1942 (1978).

[8]R. E. Olson and B. Liu, J. Chem. Phys. **73**, 2817 (1980).

[9]A. R. Johnston and P. D. Burrow, J. Phys. B **15**, L745 (1982).

[10]V. N. Tuan and V. A. Esaulov, Phys. Rev. A **32**, 883 (1985).

[11]J. P. Gauyacq, J. Phys. B **12**, L387 (1979).