Entropy lowering in ion-atom collisions

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In ion-atom collisions, the charge transfer cross section is typically a strong function of the energy defect or Q value, typically with smaller energy defects giving rise to higher capture probabilities. In some theoretical treatments, for example those based on the Demkov model, the cross section is a strong function of the magnitude of the Q value, but is independent of its sign. In order to test this predicted sign independence, one must compare capture cross sections from energetically symmetric collision channels. In this work, relative capture cross sections, differential in scattering angle, are measured and compared for the energetically symmetric channels: $Rb^+ + Rb(5s) \rightarrow Rb(5p) + Rb^+$ and $Rb^+ + Rb(5p) \rightarrow Rb(5s) + Rb^+$. It is found that not only are the two cross sections not equal, but that in this case the endoergic channel was 3 times more likely. That is, the entropy reducing channel was preferred. An intuitive model, based on molecular potential curves, is suggested. The endoergic propensity is found to be consistent with this model.

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I. INTRODUCTION

In slow ion-atom collisions, charge transfer tends to be the dominant process. The past few decades has seen a great deal of work, both experimental and theoretical, devoted to the understanding of many aspects of this process, with the result that single charge transfer is fairly well understood. Coupled channel calculations seem to quite accurately predict experimentally measured cross sections, even when these cross sections are differential in capture channel (both initial and final states) and in scattering angle [1]. However, coupled channel calculations can be rather cumbersome and time consuming. Partially for this reason, the Demkov model [2] and its derivatives [3] are often used as estimators of channel selective charge transfer cross sections.

It is well known that the Q value, or energy defect, in a collision channel strongly affects the capture cross section for that channel. In the Demkov model, the *magnitude* of the Q value enters as the single strongest factor in determining a channel's cross section. From this, one might expect that the cross sections for energetically symmetric capture channels would be equal. Failing this, one might expect that the exoergic channel might be preferred over the endoergic since the former results in the greater entropy of the system. While a measurement of the relative cross sections for energetically symmetric channels has been made [4], to our knowledge, no measurements for energetically symmetric charge transfer channels exist in systems involving electronically excited species. In this work, relative cross sections were measured for the two channels: $Rb^+ + Rb(5s) \rightarrow Rb(5p) + Rb^+$ and $Rb^+ + Rb(5p) \rightarrow Rb(5s) + Rb^+$. One of the reasons that energetically symmetric channels such as this have not been studied in the past is that for accurate comparisons to be made, the excited state fraction in the latter channel must be accurately measured, a hithertofore technically difficult operation. Furthermore, in order to assist in the understanding of such a cross section measurement, the measurement should be made differential in scattering angle. These twin constraints on the measurement requirements point to the use of the MOTRIMS (magneto optical trap recoil ion momentum spectroscopy) methodology. The MOTRIMS technique has been demonstrated to have very good resolution in both Q value and scattering angle [5–7]. Furthermore, it has been demonstrated [6–8] that the technique can be used to simultaneously determine the excited state fraction when used on laser-excited targets. It was therefore decided to use the MOTRIMS methodology to compare the cross sections for the above-mentioned channels in 7 keV collisions between Rb^+ and Rb in the $5s$ and $5p$ states.

It will be shown that not only do the two channels have clearly different cross sections, but also the "counterintuitive" channel, i.e., the one leading to local reduction in the system's entropy, is preferred. The rest of the paper is organized as follows: In Sec. II, the essentials of the MOTRIMS experiment are briefly discussed. The results of the experiment as well as theoretical interpretation are given in Sec. III. A short summary is given in Sec. IV.

II. EXPERIMENT

A complete description of the MOTRIMS methodology is available elsewhere [6,7]. A simplified schematic of the experimental setup is shown in Fig. 1. The setup consists of a magneto optical trap (MOT) and a recoil ion momentum

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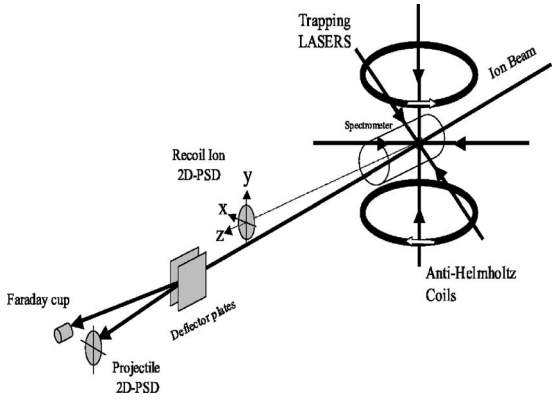

FIG. 1. Simplified schematic diagram of the experimental setup.

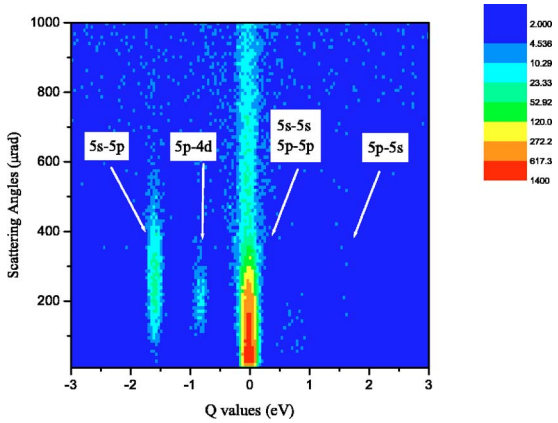

FIG. 2. (Color online) Doubly differential cross sections for 7 keV Rb^++Rb($5l$), where $l=s$ and p. Details of the quantitative data differential in scattering angle, which is beyond the scope of the current discussion, are reported in [7].

spectrometer (RIMS). The MOT consists of a system of diode lasers and accompanying optics, and a pair of anti-Helmholtz coils which are used to set up a magnetic field gradient of approximately 5 Gauss/cm. The spectrometer consists of a series of metal rings, appropriately biased to create two constant electric field regions, followed by a field-free drift region, followed by a two-dimensional position-sensitive detector (PSD). The dimensions of the three regions, and the values of the fields were carefully chosen so as to minimize the effects of the finite target dimensions. The low temperature of the target ensures that the initial momentum spread of the Rb atoms is small compared to the momentum "kick" given the recoils in the collision. Because of the combination of the MOT and RIMS techniques, this new approach has been dubbed MOTRIMS [5]. A key concept in RIMS is that one may relate the longitudinal component of the recoil ion momentum, $p_\parallel$ to the collision Q value and the transverse component of the recoil ion momentum, $p_\perp$, to the scattering angle by the following relationships [9–11]. For single electron capture,

$$Q = -p_\parallel v_p - \frac{m_e}{2} v_p^2, \tag{1}$$

where $p_\parallel$ is the component of recoil momentum parallel to the projectile axis, v_p is the projectile velocity, m_e is the mass of the electron, and Q, the collision Q value, is defined by

$$Q = E_{initial}^{binding} - E_{final}^{binding}. \tag{2}$$

Furthermore,

$$\theta_p = -\frac{p_\perp}{m_p v_p}, \tag{3}$$

where m_p is the projectile mass.

The longitudinal momentum component is determined through measurement of the difference in flight times of the projectile and the recoil ions. The perpendicular momentum component is determined through measurement of the position of the recoil ion on its PSD. Thus, in this apparatus, the Q value is determined by time of flight, and the scattering angle for each channel is determined by the recoil position on the target PSD. For the system presented here, the resolution in Q value is about 150 meV.

III. RESULTS AND DISCUSSION

The trapping and cooling process leaves some fraction of the rubidium in the Rb($5p_{3/2}$) state; it is critical to determine what this fraction is. One might use target fluorescence to measure target excited state fraction [12], however this method inherently yields large uncertainty in the excited state fraction measurement [13]. Fortunately, a careful measurement of the relative count rate in the Rb($5s$)-Rb($5p$) channel as the trapping lasers are switched on and off can be used to accurately determine the fraction of atoms in the $5p$ state [6–8]. It was found in the measurements reported here that typically 23% of the atoms were in the $5p$ state while the trapping lasers were on. Because the trapped atoms are made to "cycle" between the $5s_{1/2}$ $F=2$ and $5p_{3/2}$ $F=3$ levels, in this work it should be understood that "$5s$" means the former state, while "$5p$" means the latter state. Furthermore, because the six circularly polarized trapping lasers are pairwise incident from three orthogonal directions, one would expect that the magnetic sublevels of the target are *approximately* statistically populated.

Figure 2 shows experimental results differential in both Q value and scattering angle. The distinct groups of capture channels are clearly visible. Note that this spectrum has not been corrected for the measured ~5 times greater number of atoms in the Rb($5s$) state. Nevertheless, from the near absence of any counts in the outgoing Rb($5p$) channel (at about 1.6 eV) one can easily anticipate that this exoergic channel has a much smaller cross section than the corresponding endoergic one at −1.6 eV. Projections of this spectrum along the vertical axis yields the total Q-value spectrum. Applying the appropriate gates in time corresponding to the laser chopping cycle yields Q-value spectra for when the lasers are on and off. Figure 3(a) is the Q-value spectrum taken while the lasers were blocked. Figure 3(b) is the Q-value spectrum

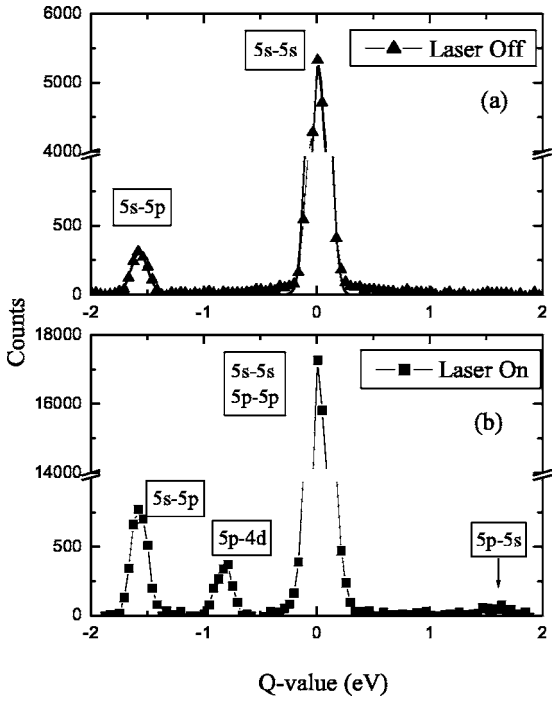

FIG. 3. Counts vs Q value for 7 keV Rb^++Rb(5l), where $l=s$ and p. In (a) the trapping lasers are blocked, while in (b) they are unblocked.

taken while the lasers were unblocked. Thus, the former represents capture from the ground state only, while the latter represents capture from both the ground, Rb(5s), and the excited state, Rb(5p). In comparing these two plots, the additional channels opened up through capture from Rb(5p), particularly capture to Rb(4d) are readily visible. When weighted by the measured excited state fraction, and by the duty cycle of the trapping lasers (here, 75%) these two curves directly yield relative cross sections for capture from a pure ground state and a pure excited state into all of the various final states. In particular, the ratio of the cross sections (integrated over scattering angles) for the two channels of interest is

$$\frac{\sigma_{5s\text{-}5p}}{\sigma_{5p\text{-}5s}} = 2.96 \pm 0.24. \tag{4}$$

(The relative capture cross sections for the energy degenerate channels, as well as for the nearly energy degenerate channels of other collision systems are presented elsewhere [14].) This surprising result is qualitatively explained in the following section.

A. Theoretical interpretations

The Demkov model, which depends only on the magnitude of the Q value, predicts the cross sections for two energetically symmetric channels to be equal. Failing this, one might expect the exoergic channel to be preferred, since it is this one which results in a greater increase in the entropy of the system. The counterintuitive result observed for 7 keV Rb^++Rb(5l) in which the entropy lowering channel is 3

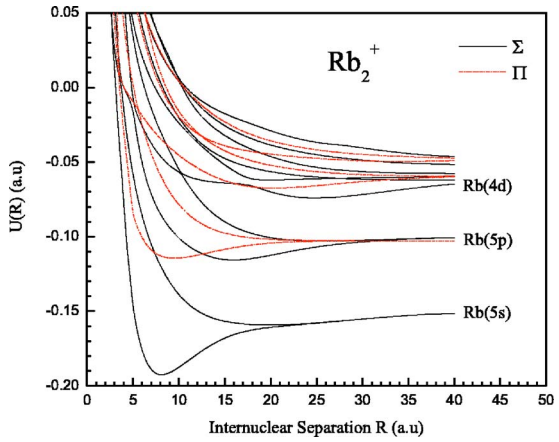

FIG. 4. (Color online) Rb_2^+ molecular potential curves.

times more likely than the entropy raising channel can be understood through inspection of the potential curves in Fig. 4. For the exoergic channel Rb(5p)-Rb(5s), the principal charge transfer mechanism is the coupling between the Σ and Π symmetry states at an internuclear separation of about 7 a.u. However, this mechanism must compete with the coupling of the endoergic charge exchange channel Rb(5p)-Rb(4d) whose internuclear separation is at about 10 a.u. In contrast, for the endoergic channel with the same magnitude in energy defect, Rb(5s)-Rb(5p), the coupling between the Σ and Π symmetry states is the overwhelmingly dominant process for capture into Rb(5p). Thus, one can qualitatively explain the difference in cross sections by noting that the incoming Rb(5s) state almost exclusively feeds the Rb(5p) state, while the incoming Rb(5p) state feeds *both* the Rb(5s) *and* the Rb(4d) exit channels.

The experimental differential cross section results support this model. In Fig. 2 the scattering angles of all the major charge transfer channels are contrasted. Comparing, for example, the 5s-5p and 5p-4d channels, one can see that the latter peaks at smaller angles, suggesting the electronic transition occurs in curve-crossing region at larger internuclear separation. Unfortunately, the count rate into the 5p-5s channel is too small to allow anything to be said about its peak scattering angle, and therefore its curve crossing distance. Nevertheless, the scattering angle data for all the significant channels, e.g., the energy degenerate channels 5s-5s and 5p-5p are entirely consistent with the curve crossing model [14].

Finally, the failure of the Demkov model to predict the observed asymmetric results in this energetically symmetric system is discussed. The Demkov model is essentially a two-channel model. On the other hand, as indicated in the curve crossing discussion above, the reason for the difference in cross sections is due to competition from other channels. Thus, there is no reason to expect that the Demkov model should give the correct result.

IV. SUMMARY

In summary, relative charge transfer cross sections, differential in scattering angle, were made for the energetically

symmetric channels $Rb^+ + Rb(5s) \rightarrow Rb(5p) + Rb^+$ and $Rb^+ + Rb(5p) \rightarrow Rb(5s) + Rb^+$, at a collision energy of 7 keV. It was observed that even though the magnitude of the energy defect, or Q value for these two channels are equal, the cross section for the former channel was 3 times greater than that for the latter. Not only does this result contradict predictions of the Demkov model, but also seems to violate the intuitive result in which one might expect the entropy of the system to maximally increase. The results are qualitatively explained using a simple model based on molecular curve crossing arguments. These arguments are also in qualitative agreement with the scattering angle measurements. Finally, the reason for the failure of the Demkov model is discussed.

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