Electron capture collisions between $^7Li^+$ and H_2 over the energy range 0.2–3.0 keV

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Absolute charge-transfer cross sections for the production of 10 excited levels of the lithium atom produced in the $Li^+ + H_2 \rightarrow Li^* + H_2^+$ reaction have been determined as a function of the lithium ion energy over the 0.2–3.0-keV energy range. These cross sections are observed to follow the functional form $\sigma(v, \Delta E) = K\exp(-\Delta Ea/\hbar v)$, where v is the ion velocity and $\Delta E(n, l)$ is the "energy defect" for the charge transfer into the n, l excited level of lithium. This functional dependence can be rationalized in terms of a semiclassical coupled-harmonic-oscillator model. We find that at constant v the relative magnitudes of the capture cross section are governed by the energy defect and the angular momentum quantum number of the final state. Specifically, we observe that $\sigma_{CT}(nd) > \sigma_{CT}(np) > \sigma_{CT}(ns)$, where σ_{CT} is the charge-transfer cross section.

I. INTRODUCTION

The charge-transfer reaction is the simplest molecular three-body rearrangement collision and is an effective mechanism for transferring large amounts of internal energy between the interacting particles. This process is of fundamental importance to a diverse number of systems, ranging from biological to astrophysical. Because of this importance, the charge-transfer reaction has been intensively investigated both theoretically and experimentally for the past three decades.[1-9]

In a previous paper[10] (hereafter referred to as I), we reported absolute charge-transfer cross sections for the $Na^+, XY \rightarrow Na^*, XY^+$ ($XY = CO, N_2, O_2$) reacting systems.[11] We report here our results for the absolute charge-transfer cross sections in the $Li^+, H_2 \xrightarrow{\sigma} Li^*, H_2^+$ system. The cross sections are evaluated from an analysis of the observed lithium emission lines. We have observed the formation of ten excited lithium levels and have investigated the energy dependence of each of these cross sections over the energy range 0.2–3.0 keV. The dependence of the cross section on the n, l quantum numbers and on the energy defect or endoergicity of the reaction is discussed. We also compare the present results with the cross sections obtained in our investigation of the Na^+, XY systems.

It is our hope that these experimental results will stimulate a complementary theoretical development of the charge-transfer process in ion–diatomic-molecule collisions.

II. EXPERIMENTAL

The apparatus used to perform these experiments has been described in detail in I. The apparatus consists essentially of a lithium-ion source, light-detection system, and ion-current collector housed in a vacuum chamber. The basic experimental arrangement is the following: a beam of lithium ions of known energy passes below the first lens of a light detection system. Light emitted from the collision/reaction of the Li^+ ions with the H_2 target gas is focused on the entrance slit of a monochromator–photomultiplier-tube (PMT) system. After passage below the light-detection system, the lithium-ion beam is collected on a Faraday cup. The photon count rate as a function of the ion beam energy and intensity, wavelength of the emitted light, and H_2 gas density form the raw experimental data from which the absolute electron capture cross sections are evaluated. Figure 1 shows a simplified schematic diagram of the apparatus.

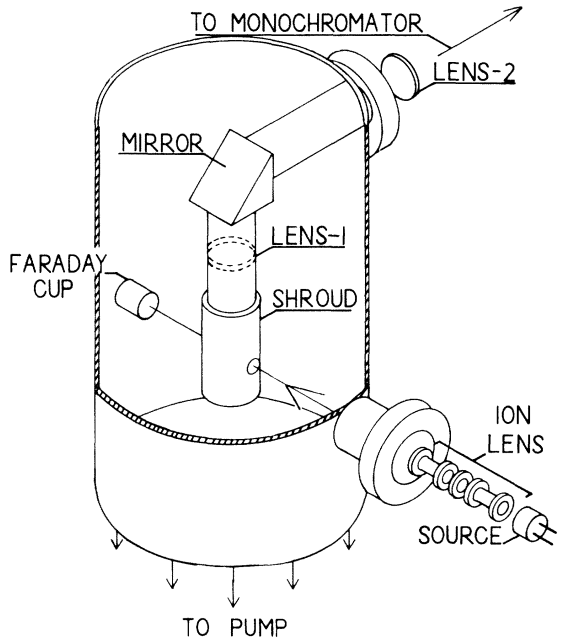

FIG. 1. Simplified schematic diagram of the apparatus.

III. DATA ACQUISITION AND CROSS-SECTION EVALUATION

A. Data acquisition

For each of the observed excited lithium transitions, the photon count rate as a function of the lithium-ion energy was recorded. The signal count rate is the difference between 10-sec averages of the observed count rate with and without target gas in the chamber. For the strong transitions, e.g., $2p \rightarrow 2s$, we observed maximum signal count rates on the order of 1000 counts per second (cps), and for the weaker transitions, e.g., $5s \rightarrow 2p$, signal count rates on the order of 5 cps were typical, with a "dark-count" rate of 2–3 cps. We also measured the dependence of the signal count rate on the hydrogen gas pressure, and these studies showed that for each transition observed, the signal count rates extrapolated to zero at zero pressure and were linear over the sampled pressure range $[(0.1-5)\times10^{-4}$ Torr$]$. These results affirm that single-collision conditions prevailed at the target gas pressure used ($\sim 3\times10^{-4}$ Torr) in this work.

B. Cross-section evaluation

As in I, we evaluate the absolute charge-transfer cross sections from the observed emission rates by using the expression

$$\sigma_{CT}(j) = \frac{q\tau_{j\rightarrow i}}{iN_B\mathcal{T}_j f(z_0, v, \mathcal{T}_j)}\left(\frac{N_j(z_0)}{\tau_{j\rightarrow i}} - \frac{iN_B\mathcal{T}_j}{q\tau_{j\rightarrow i}}\sum_{k>j}\frac{\sigma_{CT}(k)\mathcal{T}_k}{(\mathcal{T}_k-\mathcal{T}_j)\tau_{k\rightarrow j}}[\mathcal{T}_k f(z_0, v, \mathcal{T}_k) - \mathcal{T}_j f(z_0, v, \mathcal{T}_j)]\right) \quad (1)$$

where

$$f(z_0, v, \mathcal{T}_j) = z_0\{1-(v\mathcal{T}_j/z_0)[1-\exp(-z_0/v\mathcal{T}_j)]\}.$$

This equation relates the charge-transfer cross section of the jth level, $\sigma_{CT}(j)$, to the observed emission rate and to the various upper levels which can cascade into the jth. The observed emission rate is given by $N_j(z_0)/\tau_{j\rightarrow i}$, where $N_j(z_0)$ is the population of level j at a position z_0 from the ion source and $\tau_{j\rightarrow i}$ is the mean lifetime for the observed transition. In our apparatus, z_0 is the distance between the ion source and the end of the viewing region of the primary-focus lens. The charge-transfer cross sections into the highest observable cascading levels are given by $\sigma_{CT}(k)$. We have assumed initially that these levels ($5d$, $5p$) are populated only by direct charge transfer. Later we discuss the consequences of relaxing this restriction (see next paragraph and Sec. IV). The mean lifetime of the $k \rightarrow j$ transition is given by $\tau_{k\rightarrow j}$; $\mathcal{T}_j$ and $\mathcal{T}_k$ are the net lifetimes against all possible decay channels for the jth and kth levels, respectively. Finally, v and i/q are the velocity and particle flux of the ion beam and N_B is the H_2 gas density. We assume that the particle flux is constant over z_0. This approximation is justified by the fact that we observe a beam attenuation of only $\sim 5\%$.

The important populating and depopulating channels for the ten observed excited levels of the lithium atom are listed in Table I. This table also gives the observed transitions and transition wavelengths. The ns states can be formed either by direct charge transfer or by a cascading transition from their respective np level. We have ignored the higher $p \rightarrow ns$ transitions, because their oscillator strengths are several orders of magnitude less than those within the same principal quantum number. The depopulating channels for the ns states are of course the $ns \rightarrow$ (lower p)

TABLE I. Populating and depopulating channels for the observed lithium states.

Level	Transition observed	λ (nm)	Populating channels	Depopulating channels
$5s$	$5s \rightarrow 2p$	427.3	CT, [a] $5p \rightarrow 5s$	$5s \rightarrow 2, 3, 4p$
$4s$	$4s \rightarrow 2p$	497.1	CT, $4p \rightarrow 4s$	$4s \rightarrow 2, 3p$
$3s$	$3s \rightarrow 2p$	812.6	CT, $3p \rightarrow 3s$	$3s \rightarrow 2p$
$5p$	$5p \rightarrow 2s$	256.2	CT	$5p \rightarrow 2, 5s; 3, 4d$
$4p$	$4p \rightarrow 2s$	274.1	CT, $5s, 5d \rightarrow 4p$	$4p \rightarrow 2, 4s; 3d$
$3p$	$3p \rightarrow 2s$	323.3	CT, $4, 5s; 4, 5d \rightarrow 3p$	$3p \rightarrow 2, 3s$
$2p$	$2p \rightarrow 2s$	670.8	CT, $3, 4, 5s; 3, 4, 5d \rightarrow 2p$	$2p \rightarrow 2s$
$5d$	$5d \rightarrow 2p$	413.3	CT	$5d \rightarrow 2, 3, 4p$
$4d$	$4d \rightarrow 2p$	460.3	CT, $5p \rightarrow 4d$	$4d \rightarrow 2, 3p$
$3d$	$3d \rightarrow 2p$	610.3	CT, $4, 5p \rightarrow 3d$	$3d \rightarrow 2p$

[a] Charge transfer.

transitions. Sufficient signal count rates for the $ns \rightarrow 2p$ transitions were obtained only in the 2–3-keV energy range. The populating channels for the np levels include both $s \rightarrow np$ and $d \rightarrow np$ transitions. As an initial approximation, we have ignored the cascade contributions from the $6s, 6d \rightarrow np$ transitions. We present in Sec. IV a method for estimating the effects of these transitions upon the capture cross section.

The $5p$ level is formed only by direct charge transfer if we use the initial approximation; the input channels into the $4p$ and $3p$ levels are the $5s, d \rightarrow 4p$ and $4, 5s$; $4, 5d \rightarrow 3p$ transitions, respectively. For the $2p$ level, there exist cascading contributions from the $3, 4, 5s$ and $3, 4, 5d \rightarrow 2p$ transitions. No approximations are needed in treating the np output channels, but the $5p \rightarrow 4s$ and $4p \rightarrow 3s$ transitions were ignored because of their small oscillator strengths.[12] Finally, for the nd levels, we initially treat the $5d$ level as being formed only by charge transfer, thus ignoring the $6p, 6f \rightarrow 5d$ transitions. We have also ignored the $5, 6f$, and $6p \rightarrow 4d$ and $4–6f \rightarrow 3d$ input channels. Output channels for the nd levels include the $5d \rightarrow 2–4p$, and $4d \rightarrow 2, 3p$, and $3d \rightarrow 2p$ transitions. The oscillator strengths for the $5d \rightarrow 5p, 4f$, $4d \rightarrow 4p$, and $3d \rightarrow 3p$ transitions are all orders of magnitude less than the above-mentioned depopulating transitions; because of this, these weaker transitions have not been considered.

The error analysis presented in I was applied to this experimental work. We obtain an overall random error in the absolute cross-section measurement ranging between 15% and 27%, and estimate the error in the relative cross sections to be within 10% of the values reported below.

IV. DISCUSSION

The electron capture cross sections are observed to *increase* exponentially with increasing collision velocity and *decrease* exponentially with increasing energy defect. We have observed similar dependences in the formation of excited sodium atoms in the Na^+, XY charge-transfer systems.[10] The present results are summarized in Figs. 2–5. Figures 2–4 are semilogarithmic plots of the absolute charge-transfer cross sections versus $1/v$; Fig. 5 plots cross section versus energy defect ΔE. These energy defects are internal energy differences at infinite nuclear separation between the initial (Li^+, H_2) and final (Li^*, H_2^+) states of the collision system. The cross sections reported in Fig. 5 are the observed cross sections normalized by the angular momentum degeneracy of the particular level.

Since, to our knowledge, there exists no adequate

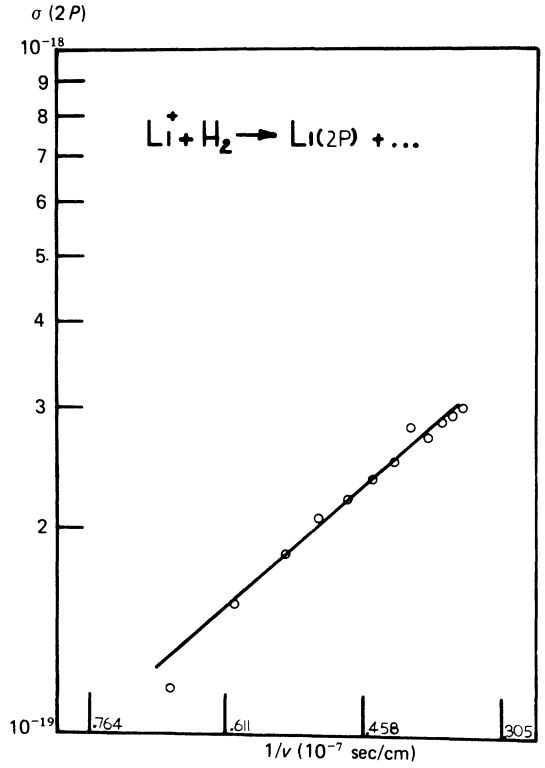

FIG. 2. Semilogarithmic plot of the charge-transfer cross section into the $2p$ level vs the reciprocal of the ion velocity, $1/v$.

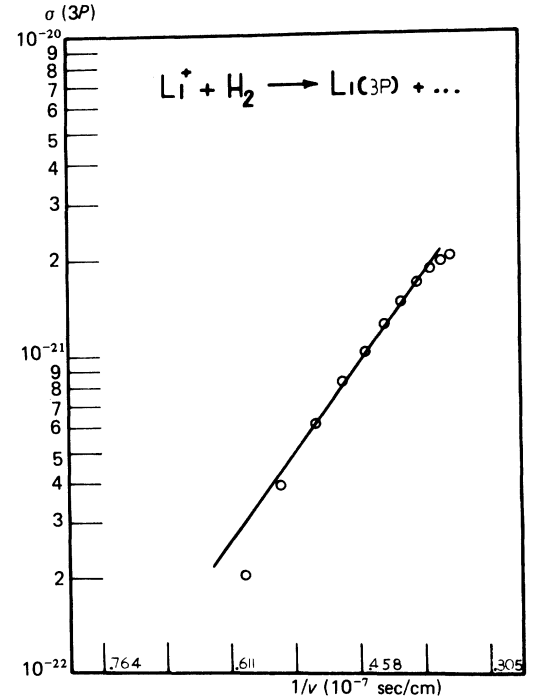

FIG. 3. Semilogarithmic plot of the charge-transfer cross section into the $3p$ level vs $1/v$.

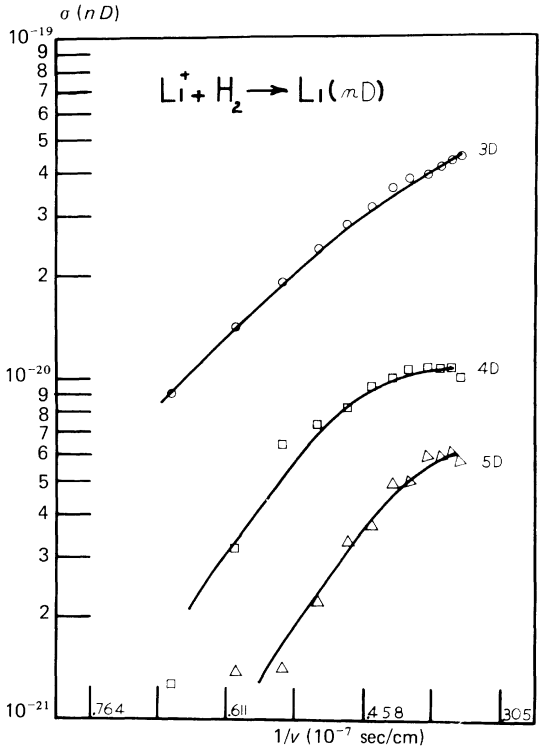

FIG. 4. Semilogarithmic plot of the charge-transfer cross sections into the nD levels vs $1/v$.

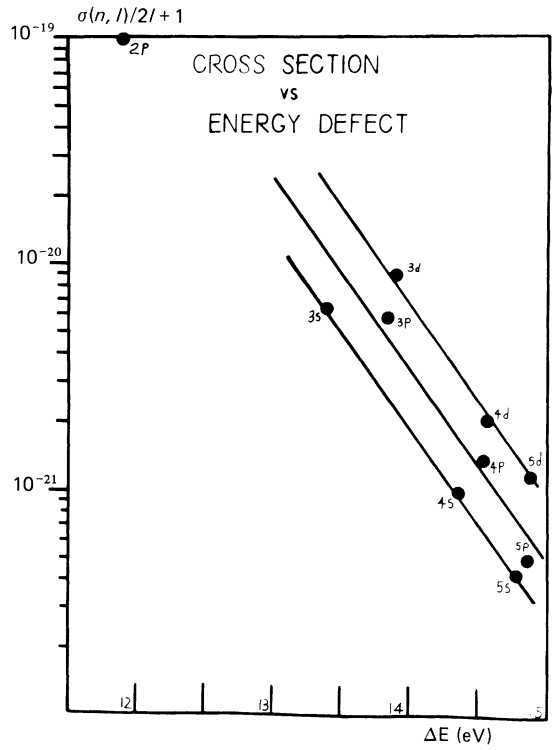

FIG. 5. Semilogarithmic plot of the normalized capture cross section $\sigma_{CT}(n,l)/(2l+1)$ vs the energy defect ΔE at a fixed ion beam energy of 3.0 keV.

theory of charge transfer applicable to the present conditions, viz., small relative velocities ($\sim 10^7$ cm/sec) and large energy defects (>12 eV), we have proposed a semiclassical coupled-harmonic-oscillator model to explain the observed dependence of the cross section on these two quantities.[10] The cross section obtained from this model has the following functional form:

$$\sigma_{b\rightarrow a}(v, \Delta E) = K(v, \Delta E) \exp(-\Delta E \alpha/\hbar v), \qquad (2)$$

where the preexponential term $K(v, \Delta E)$ contains a $1/v^3$ dependence and $\alpha = 2B$, where B is the impact parameter. This expression gives the correct exponential dependence of the cross section and also indicates a weak preexponential velocity dependence. A more extensive discussion of Eq. (2) is given in I.

The model predicts that a semilogarithmic plot of the capture cross section versus $1/v$ will yield a straight line with a slope equal to $-2\Delta EB/\hbar$ and an intercept equal to $\ln[K(v, \Delta E)]$, the preexponential term. We note that over the energy range of 0.2–3.0 keV the preexponential term varies about 15% if we assume a constant value for B. We have evaluated the slopes of the lines presented in Figs. 2–4 and list the resulting ΔEB values in Table II. This table also gives the ΔE values for infinite nuclear separation. If we assume reasonable values for the interaction length, e.g., $1 \leq B \leq 10$ Å, the ΔE values calculated from the ΔEB product are between a factor of 4 and 40 less than values of infinite internuclear separation. The obvious conclusion from these results is that the charge transfer takes place on the steeply rising portion of the potential energy surface, where the energy differences between surfaces are significantly less than at infinite separation.

Blaney and Berry[13] have recently reported relative electron capture cross sections for the formation of eight excited levels of lithium in the Li^+, H_2 system. The lithium-ion energy used in this work

TABLE II. ΔEB values obtained from $\ln\sigma(v, \Delta E)$ vs $1/v$ plots.

Level	ΔEB (eV Å)	$\Delta E(\infty)$ (eV) [a]
$2p$	3.23	11.88
$3p$	5.18	13.86
$4p$	6.87	14.55
$3d$	4.10	13.91
$4d$	3.54	14.57
$5d$	5.43	14.88

[a] Evaluated from the expression $\Delta E = I(H_2) - I(Li) + E^*(Li)$; ionization potential ($I$) data taken from Ref. 14, E^* data from Ref. 12.

TABLE III. Comparison of relative cross sections at 2.0 keV. The notation A $(-x)$ denotes $A\times10^{-x}$.

	$\sigma(n,l)/\sigma(2p)$		
Transition	Present results	Previous results	Absolute $\sigma(n,l)$ (cm^2)
$3s\rightarrow2p$	0	1.9± 0.9 (−2)	~0
$4s\rightarrow2p$	3.0± 0.7 (−3)	1.9± 0.7 (−3)	7.2 (−22)
$5s\rightarrow2p$	0	<4 (−4)	0
$2p\rightarrow2s$	1.0	1.0	2.42 (−19)
$3p\rightarrow2s$	3.8± 0.7 (−2)	2.3± 0.9 (−2)	9.1 (−21)
$3d\rightarrow2p$	1.5± 0.2 (−1)	1.4± 0.4 (−1)	3.55 (−20)
$4d\rightarrow2p$	4.0± 0.8 (−2)	2.5± 0.6 (−2)	9.6 (−21)
$5d\rightarrow2p$	1.8± 0.4 (−2)	<1 (−3)	4.5 (−21)

was 2.0 keV, and the cross sections were reported relative to $\sigma(2p)$. In Table III we present a comparison of the two sets of results and also list our values for the absolute cross section for each level. We note that our error limits and those quoted by Blaney and Berry overlap, with the exception of the $3s$ and $5d$ states. In view of the fact that the two experimental techniques are significantly different, we consider the observed agreement satisfactory.

We mentioned in Sec. III that it is possible to estimate from our experimental data the capture cross sections for the $4-6f$ levels. This is done in the following manner: From the plot of $\ln[\sigma(n,l)/(2l+1)]$ vs ΔE (Fig. 5), we draw a line parallel with the nd line which is vertically offset with a spacing equal to the distance between the np and nd lines. We are able to locate the positions of the nf cross sections along this line by using the known energy defects. From this line, we obtained the following *estimated* cross sections: $\sigma(4f)=2.94(-20)$, $\sigma(5f)=1.61(-20)$, and $\sigma(6f)=1.12(-20)$. If we include these cross sections in the cascading scheme, we find that the $nf\rightarrow nd$ process lowers the $3d$ cross section by 23%, the $4d$ by 55%, and the $5d$ by 18%. Thus the $\sigma(4d)$ cross section is the most strongly influenced by cascading from the nf levels.

It is of interest to compare the $\ln\sigma(n,l)$ vs ΔE plots for the Li^+,H_2 and Na^+,XY systems. In the latter case, we observe that the cross sections show no dependence on the angular momentum quantum number, i.e., one line could be drawn through all of the data points irrespective of the s, p, or d character of the orbital. For the Li^+,H_2 system, however, we note a definite dependence of the cross section on l, and in particular observe that for a constant ΔE, $\sigma(nd)>\sigma(np)>\sigma(ns)$. Thus the active electron appears to exhibit a definite sensitivity to the final-state orbital angular momentum.

In summary, we observe charge-transfer cross sections which depend exponentially on the energy defect and relative collision velocity. We have proposed a semiclassical model to rationalize the observed exponential dependence of the cross section. However, the model cannot accurately predict the magnitude of the cross section without a more detailed knowledge of the potential energy surfaces. In contrast to the Na^+ data, we observe a definite dependence of the capture cross section on the angular momentum quantum number for the Li^+,H_2 system.

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