Alignment and Orientation in $\text{Li}(2p_m)\text{--H}^+$ Charge-transfer Collisions

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Initial orbital alignment and orientation effects, have been studied in slow (0.2–10 keV) quasi-resonant charge-transfer collisions of laser-excited $\text{Li}^*(2p)$ atoms with H^+ ions. The standard semi-classical impact parameter method with a common translation factor has been employed using an adiabatic molecular basis. Pronounced alignment effects for the transition to $\text{H}^*(n=2)$ were found to be a function of collision energy but orientation preferences from $\text{Li}^*(2p_{-1})$ were obtained over the entire energy range.

Lithium beam activated charge-exchange spectroscopy (Li-CXS) has been proposed by Winter¹ as a novel method for fusion-plasma diagnostics. In particular $\text{Li}^*(2p)$ could cause an attenuation of a Li beam when entering the plasma owing to charge-exchange reactions with plasma protons:

These reactions are analogous to the prototype quasi-one-electron system $\text{H}^+\text{--Na}(3s, 3p_m)$. During the last few years this non-resonant charge-transfer system has been extensively studied. In experimental studies sodium atoms have been prepared by polarized tunable dye lasers in specific excited states with controlled alignment and orientation. Capture into different $\text{H}(n)$ levels² and alignment effects in total cross-sections³ were measured. Good agreement with both molecular⁴ and atomic⁵ calculations was found for the 0.3–5 keV energy range. Furthermore the enhanced $\text{L}\alpha$ emission by $\text{H}^*(2p)$ after charge transfer⁷ was predicted theoretically.^{4–6} Moreover, the orientation effect on the state-to-state amplitude probabilities was calculated with the molecular basis⁸ and, recently, the influence of orientation and alignment asymmetries on the differential cross-section has been measured⁹ and calculated.¹⁰

However, to our knowledge no experimental study has so far been carried out for collisions involving protons and oriented or aligned $\text{Li}^*(2p)$ atoms. In an earlier paper¹¹ we found a strong $\text{L}\alpha$ enhancement for capture to $\text{H}^*(2p)$ from the quasi-resonant excited $\text{Li}^*(2p)$ at low energies. The present paper reports a complete state-to-state amplitude probability calculation for the charge-transfer reaction (I) in the 0.2–10 keV energy range where the $\text{Li}^*(2p_m)$ atom is aligned or oriented.

Theoretical Description: Molecular States and Dynamical Model

To evaluate potential energies, dynamic couplings and translation factor terms of the LiH^+ complex, we use a particular form of a model potential, already used previously:¹²

$$V(r) = -\frac{1}{r} - \frac{2 + 3.31r}{r} \exp(-3.33r) \quad (1)$$

which guarantees the correct long- and short-range limits. Molecular potential has been calculated from eigenvalues of the model molecular Hamiltonian using Slater type orbitals basis set centred on each atom. The adiabatic molecular states used in this calculation are the following eight asymptotically lower-energy states:

totically lower-energy states:

$$2^2\Sigma(2s\sigma\text{Li}), 3^2\Sigma(2p\sigma\text{Li}), 1^2\Pi(2p\pi^\pm\text{Li}), 2^2\Pi(2p\pi^\pm\text{H}), \\ 4^2\Sigma(\phi^+\text{H}), 5^2\Sigma(\phi^-\text{H})$$

where ϕ^+ and ϕ^- correspond to the two sigma states split by the Stark effect in $\text{H}^*(n=2)$, and the ‘ $\pm$ ’ label refers to the symmetry of the π molecular states with respect to reflection in the collision plane defined perpendicular to the laser beam. The ‘ $-$ ’ symmetry states are only coupled to other states with this symmetry. In this first calculation we consider only these eight molecular states because they are well separated in energy from others except at small values of the internuclear distance.

Once the molecular basis functions are known, we can use the semi-classical impact parameter method for nuclear motion and to develop the electronic wavefunction on this molecular basis. In order to take into account the electron-transfer momentum in the collision, a modified basis set has been proposed including electron-translation factors.¹³

$$\psi_n = a_n \chi_n \exp(i\mathcal{U}) \quad (2)$$

where the dynamical factor $\mathcal{U}$ is chosen to have the simple form:

$$\mathcal{U}(r, R) = \frac{z}{R} \mathbf{v} \cdot \mathbf{r} - \frac{1}{2} \frac{z^2}{R^2} v^2 t \quad (3)$$

where r and R are, respectively, the electronic and nuclear coordinates, and $z = \mathbf{R} \cdot \mathbf{r}$. The coupled equations deduced from the time-dependent Schrödinger equation in the body-fixed coordinate system are:¹⁴

$$i \frac{da_m}{dt} = \left[\langle \chi_m | E_m - i \frac{dR}{dt} \frac{\partial}{\partial R} + i \frac{d\gamma}{dt} i\hat{L}_y | \chi_n \rangle \right. \\ \left. - \frac{i}{R} \langle \chi_m | z \frac{\partial}{\partial z} | \chi_n \rangle - i \langle \chi_m | x \frac{\partial}{\partial x} \right. \\ \left. + z \frac{\partial}{\partial x} | \chi_n \rangle \frac{d\gamma}{dt} + 1.5 \langle \chi_m | x^2 | \chi_n \rangle \left(\frac{d\gamma}{dt} \right)^2 \right] a_n \quad \forall m \quad (4)$$

where $R^2 = b^2 + v^2 t^2$, γ the angle between the incident velocity v and the internuclear distance R , and b is the impact parameter.

As we consider collisions involving electron capture by an incident proton into $\text{H}^*(n=2)$, we treat in an exact way the problem of the long-range mixing degenerate states of the same symmetry due to the proximity of the alkali-metal atoms. The linear Stark effect induces a large coupling between $\text{H}^*(2s)$ and $\text{H}^*(2p)$ that is first order in the electric field strength and must be included in the evolution matrix $\mathcal{U}$ in order to find the correct final-state distribution population in $\text{H}^*(n=2)$.¹⁵

Moreover, to take the residual internuclear axis rotation

[†] 1 eV $\approx 1.60218 \times 10^{-19}$ J.

into account, the rotational coupling term $ivb\langle i\hat{L}y\rangle/R^2$ between any $\Sigma(2p\sigma)$ and $\Pi(2p\pi)$ quasi-degenerate states must also be included in the evolution matrix $\mathbb{U}$. The coupled eqn. (4) that give transition amplitudes are integrated up to $z_0 = 30 a_0^\dagger$ for each impact parameter and the final amplitudes $a_m(+\infty)$ are obtained by:

$$a_m(+\infty) = \mathbb{U}(z_0, +\infty)a_m(z_0) \quad (5)$$

for the kinetic energy range $0.2 < E_{\text{cm}}/\text{keV} < 10$.

A similar transformation of the rotation axis is also required for the initial states in the general case. The projection into the fixed frame of observation is achieved using eqn. (4) of ref. 16 in the case of P states, to obtain the circularly polarized states in the collision plane, $|np_{-1}\rangle$ or $|np_{+1}\rangle$.

We shall consider, from the coupled eqn. (4) the following modified matrix elements:

$$\begin{aligned} \langle \chi_m | \frac{\partial}{\partial R} + \frac{z}{R} \frac{\partial}{\partial z} | \chi_n \rangle & \quad \text{radial coupling} \\ \langle \chi_m | i\hat{L}y + x \frac{\partial}{\partial z} + z \frac{\partial}{\partial x} | \chi_n \rangle & \quad \text{rotational coupling} \end{aligned} \quad (6)$$

between $\text{Li}^*(2p)$ and $\text{H}^*(2s, 2p)$. Potential-energy curves and the most important couplings are shown in Fig. 1 and 2.

It may at first be remarked that charge-exchange transition from $\text{Li}^*(2p_m)$ is expected to take place at large internuclear distances. A near resonant Demkov-type transition region is expected to lie around $R = 15 a_0$ between $\Pi(2p\pi\text{Li}) - \Pi(2p\pi\text{H})$, close to the maximum of the radial coupling associated with these two states. In addition to the above transition, strong rotational couplings between $\Pi(2p\pi\text{Li})$ and pseudo-crossed $\Sigma(\phi^+ \text{H})$ and $\Sigma(\phi^- \text{H})$ states at around 20 and 10 a_0 respectively, may populate $\text{H}^*(2s, 2p\sigma)$ states that are split by the Stark effect.

On the other hand the $\Sigma(2p\sigma\text{Li}) - \Pi(2p\pi\text{H})$ energy splitting and the corresponding rotational coupling are such that the transition region is expected to lie in the range $5 < R/a_0 < 25$. Moreover two important radial couplings are expected to be responsible for the capture to $\text{H}^*(2s, 2p\sigma)$ from $\text{Li}^*(2p\sigma)$ at several critical regions.

Transition Probabilities and Orientation

Charge Exchange from Linearly Polarized $\text{Li}^*(2p)$

For charge-exchange channels $\text{H}^*(2s\sigma, 2p\sigma, 2p\pi^+)$ the capture cross-sections from $\text{Li}^*(2p\sigma)$ and $\text{Li}^*(2p\pi)$ are calculated as in

Fig. 1 Adiabatic potentials of LiH^+ molecule obtained by a model potential method in order of increasing asymptotic energy: (—) $3^2\Sigma(2p\sigma\text{Li})$, $4^2\Sigma(\phi^+ \text{H})$, $5^2\Sigma(\phi^- \text{H})$; (---) $1^2\Pi(2p\pi\text{Li})$, $2^2\Pi(2p\pi\text{H})$. [$1 E_h$ (hartree) $\approx 4.359 75 \times 10^{-18}$ J.

$\dagger 1 a_0$ (bohr) $\approx 5.291 77 \times 10^{-11}$ m.

Fig. 2 Radial and rotational coupling matrix elements [eqn. (6)] between: (a) $1^2\Pi$ and $2^2\Pi$ (---); $1^2\Pi$ and $4^2\Sigma$ (-*-); $1^2\Pi$ and $5^2\Sigma$ (—) and (b) $3^2\Sigma$ and $4^2\Sigma$ (—); $3^2\Sigma$ and $5^2\Sigma$ (-*-); $3^2\Sigma$ and $2^2\Pi$ (---)

the similar NaH^+ case,⁴ by solving the impact parameter equations. The $\sigma_\sigma(n=2)$, $\sigma_{\pi^+}(n=2)$ and $\sigma_{\pi^-}(n=2)$ cross-sections are obtained by the following symmetry selection rules:

$$\begin{aligned} \sigma_\sigma(n=2) &= \sigma_\sigma(2s\sigma) + \sigma_\sigma(2p\sigma) + \sigma_\sigma(2p\pi^+) \\ \sigma_{\pi^+}(n=2) &= \sigma_{\pi^+}(2s\sigma) + \sigma_{\pi^+}(2p\sigma) + \sigma_{\pi^+}(2p\pi^+) \\ \sigma_{\pi^-}(n=2) &= \sigma_{\pi^-}(2p\pi^-) \end{aligned}$$

and

$$\sigma_\pi(n=2) = \frac{1}{2}[\sigma_{\pi^+}(n=2) + \sigma_{\pi^-}(n=2)] \quad (7)$$

if a linearly perpendicularly polarized light excites the Li atom.

Fig. 3(a) shows the $\sigma_\sigma(n=2)$ and $\sigma_\pi(n=2)$ total cross-sections as a function of incident centre-of-mass energies. Up to $E_{\text{cm}} = 2$ keV, the capture from $\text{Li}^*(2p\pi)$ is preferred. At $E_{\text{cm}} > 2$ keV, the alignment of the $\text{Li}^*(2p)$ state changes drastically. This effect could be seen in Fig. 3(b) by means of the anisotropy parameter defined as:

$$A = \frac{\sigma_\sigma - \sigma_\pi}{\sigma_\sigma + \sigma_\pi} \quad (8)$$

Unfortunately, as far as we know, neither experimental nor theoretical results are available for charge transfer from an Li excited state, with which comparison might be made.

The capture probabilities are drawn as a function of the impact parameter at the energy $E_{\text{cm}} = 0.5$ keV [Fig. 4(a) and (b)].

Fig. 3 One-electron capture cross-sections by H^+ in Li(2p) collisions: (a) from Li(2p π) to H($n=2$) (—□—); Li(2p σ) to H($n=2$) (---); Li(2p) to H($n=2$) (—). (b) The Σ - Π anisotropy parameter defined in eqn. (8) as function of incident proton energy.

From the Li*(2p σ) state, the main features for the charge-exchange channels are three peaks at $b = 9, 15$ and $20 a_0$, mainly due to population of H*(2p π^+). This can be explained by the aforementioned important $\Sigma(2p\sigma Li) - \Pi(2p\pi H)$ rotational coupling. The population of H*(2s σ) and H*(2p σ) can be explained as a direct transition induced by the dynamical radical couplings in these regions where the energy differences are small [Fig. 2(b)].

From a Li*(2p π^+) initial state, a very large capture cross-section at large impact parameter ($b > 10 a_0$) is also found, due to population of H*(2s σ) and H*(2p π^+). This is well explained by a direct Demkov-type radial coupling for the H*(2p π^+) state at around $R = 15 a_0$ and by the long-range rotational coupling $\Sigma(2p\sigma H) - \Pi(2p\pi H)$ transition.

The largest population is the H*(2s σ); this state has a maximum at $b = 15 a_0$ in the region of a large $\Pi(2p\pi Li) - \Sigma(\phi^- H)$ rotational coupling [Fig. 2(a)]. However at smaller impact parameters ($b < 10 a_0$) the H*(2p σ) is populated. This transition peaks at $b = 8 a_0$, and can be explained through the rotational $\Pi(2p\pi Li) - \Sigma(\phi^- H)$ coupling in this region.

Comparison of the probabilities at $E_{cm} = 2$ keV (Fig. 5) shows that at higher collision energy the probabilities when the initial state is $\Sigma(2p\sigma Li)$, are shifted to larger impact parameters (corresponding to smaller scattering angles), and when the initial state is $\Pi(2p\pi^+ Li)$ they remain quite similar. That is a consequence of the quasi-resonance of this reaction especially between Li*(2p) and H*(2s) states.

Fig. 4 Charge-exchange probabilities as a function of impact parameter at $E_{cm} = 0.5$ keV: (a) initial state 3 $\Sigma(2p\sigma Li)$, the final state: (---) $\Sigma(2s\sigma H)$; (-*-*) $\Sigma(2p\sigma H)$; (-□-□-) 2 $\Pi(2p\pi^+ H)$; (—) sum over the states H($n=2$). (b) Initial state 1 $\Pi(2p\pi^+ Li)$ and the same notation as in (a).

Fig. 5 Charge-exchange probabilities as a function of impact parameter at $E_{cm} = 2$ keV from: (---) 1 $\Pi(2p\pi^+ Li)$ to H($n=2$); (—) 3 $\Sigma(2p\sigma Li)$ to H($n=2$)).

This behaviour of the probabilities in the Li^*H^+ system, differs in detail from that in Na^*H^+ ,⁴ because of the different positions of $\text{Na}^*(3p)$ and $\text{Li}^*(2p)$ levels relative to $\text{H}^*(2s,2p)$.

Orientation

A laser beam with right or left circularly polarized light excites the atoms in a coherent mixture of $\Sigma(2p\sigma)$, $\Pi(2p\pi^+)$ and $\Pi(2p\pi^-)$ Li states, in such a way that the collision plane is chosen to be perpendicular to the direction of the photon beam. The angular momentum quantisation axis is perpendicular to the collision plane (supposing no experimental out-of-plane orientation) and the wavefunction must be expressed in the laboratory-fixed frame. Projection from molecular frame to the fixed frame for the P states gives:

$$|2p_{\pm 1}\rangle = [\pm |2p_{\sigma}\rangle - i|2p_{\pi^+}\rangle]/\sqrt{2} \quad (9)$$

Probabilities of charge exchange as a function of impact parameter and collision velocity from 0.14 to 0.75 $a_0 E_h/h$, with different initial polarization directions are shown in Fig. 6(a) and (b). The figures are quite different especially in the long-range scattering region where the probabilities at any collision velocity are dominant in the surface starting from a left circularly polarized target $|2p_{-1}\rangle$. Fig. 7 shows the results for both initial conditions, with three peaks at similar

Fig. 6 Probabilities for electron capture from initial Li(2p) states circularly polarized in collision plane to $\text{H}(n=2)$ states plotted as a function of collision velocity from 0.14 to 0.75 $a_0 E_h/h$; (a) $\text{Li}(2p_{-1})$ initial state, (b) $\text{Li}(2p_{+1})$ initial state

Fig. 7 Probabilities for electron capture from initial Li(2p) circularly polarized in collision plane to $\text{H}(n=2)$ states at $v = 0.15 a_0 E_h/h$ ($E_{cm} = 0.5$ keV): (—) $\text{Li}(2p_{-1})$ initial state; (---) $\text{Li}(2p_{+1})$ initial state

positions in b , but with different intensities. This strong orientation effect may be understood in terms of the couplings between the molecular states.

Let us consider the modified matrix elements of eqn. (6) between $\text{Li}^*(2p_{\pm 1})$ and $\text{H}^*(2s,2p)$: $\langle \text{Li}(2p_{\pm 1}) | \hat{\mathcal{O}} | \text{H}(2s,2p) \rangle$. Taking into account the relation (9), it is easy to see, that only the following molecular coupling terms:

$$\langle \Sigma(2p\sigma\text{Li}) | \partial/\partial R | \Sigma(\phi^+, \phi^- \text{H}) \rangle \quad \text{and}$$

$$\langle \Sigma(2p\sigma\text{Li}) | i\hat{L}_y | \Pi(2p\pi^+ \text{H}) \rangle$$

contribute with different signs to the transition probabilities for the two initial conditions: $\text{Li}^*(2p_{\pm 1})$. Inspection of Fig. 2(b), shows that the rotational coupling is the most important over the range $5 < R/a_0 < 25$.

Probabilities of transitions with different initial and final polarization directions are shown in Fig. 8(a)–(d). As in the previous case the four figures are completely different, transition probabilities from oriented $\text{Li}^*(2p_{-1})$ state being preferred, and capture to $\text{H}^*(2p_{-1})$ state enhanced [Fig. 8(a)].

As in the NaH^+ system,⁸ the classical effect of ‘velocity matching’ is also found here. When the initial and final states are $|2p_{-1}\rangle$ a maximum of probability at large impact parameter is observed when the collision velocity is 0.45 $a_0 E_h/h$, i.e. very close to the classical value for the electron velocity in the $\text{Li}^*(2p)$.

Conclusions

We have presented a detailed theoretical investigation of the electron-transition mechanism, for the charge-exchange reactions of protons incident on lithium atoms that have been prepared in an excited state by polarized laser light. The inspection of the various molecular interactions and the analysis of the evolution of the transition probabilities as a function of the impact parameter, reveal three important regions of internuclear distance, $5 < R/a_0 < 10$, $10 < R/a_0 < 18$ and $18 < R/a_0 < 25$, corresponding to the maxima of the transition probability from linear $\text{Li}^*(2p)$ or circularly polarized $\text{Li}^*(2p_{\pm 1})$ excited states. An interpretation of the state-to-state transition mechanisms for each region has been successfully attempted. From the calculated sum of the probabilities over all the states $\text{H}^*(n=2)$ from the three components of the linearly polarized $\text{Li}^*(2p)$ atom [eqn. (7)], we have derived the anisotropy parameter. A strong alignment of the $\text{Li}(2p\sigma)$ state is shown for $E_{cm} > 2$ keV. Concerning orien-

Fig. 8 Probabilities for electron capture from initial circularly polarized $\text{Li}(2p_{\pm 1})$ to final circularly polarized $\text{H}(2p_{\pm 1})$. (a) $|p_{-1}\rangle$ to $|p_{-1}\rangle$, $|p_{-1}\rangle$ corresponding to the same rotation direction as the internuclear axis. (b) $|p_{-1}\rangle$ to $|p_{+1}\rangle$. (c) $|p_{+1}\rangle$ to $|p_{+1}\rangle$. (d) $|p_{+1}\rangle$ to $|p_{-1}\rangle$.

tation effects, these theoretical results show that the electron-capture process is indeed dominated by the $|2p_{-1}\rangle$ to $|2p_{-1}\rangle$ transition, in which the long-range peak is most pronounced at $v = 0.45 a_0 E_n/h$.

To illustrate the effect of the initial condition on the electron capture we have summed over all $\text{H}^*(n=2)$ states. Results show that the initial state $|2p_{-1}\rangle$ leads always to a much bigger capture probability.

We plan further theoretical investigations (including $n=3$ states) in order to see the influence of these states on capture through rotational couplings at short distances. An open question, recently manifested in the $\text{H}^+ + \text{Na}^*(3p)$ system,^{9,10} is the influence of orientation on the differential cross-section. We also wish to study the differential cross-section for the $\text{H}^+ + \text{Li}^*(2p)$ collision. It is hoped that our findings will stimulate new experimental work.

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