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Quenching of Li low-*n* Rydberg atoms by ground-state He atoms: A low-energy molecular-state calculation

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Total cross sections for quenching of low-n Rydberg states of Li ($n<10$, $l=0$) in collision with the ground state He have been calculated in the low-energy region ($v \leqslant 0.1$ a.u.) by employing the molecular orbital approximation. Results for the total depopulation of the parent states, along with those for excitation and de-excitation mechanisms have been presented. Present cross sections exhibit the low-energy Stueckelberg oscillations. Using a model two-state calculation we present a detailed comparative study between the quantum-mechanical and semiclassical findings. Except at very low energies, the semiclassical cross sections agree nicely with their quantum counterparts. The reaction rates at thermal energies are also reported.

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I. INTRODUCTION

Rydberg atoms are highly excited atoms whose energy spectrum can be determined by a Rydberg series characterized by an effective quantum number $n^* = n - \delta_l$, where δ_l is referred to as the quantum defect. These atoms are easily perturbed by external influences, fields, or collisions [1], and hence can be used as an effective probe for very weak fields [2], or chaotic behavior of quantum environments [3].

When such an atom is in highly excited state its collision with any neutral projectile (often referred to as perturber) can be viewed as a binary encounter between the incoming projectile and the loosely bound electron. Such a simplifying picture can be transformed through a ''Free-electron model'' [4] to investigate many reactions involving these atoms [5–9]. In this model the electron perturber or the core-perturber interactions are treated quite independently [10]. However, for low-lying excited states such a simplifying assumption not only breaks down but also fails to provide a correct description of the involved collision dynamics [11]. Similarly, in case where the long-range interactions are important, e.g., collisions of Rydberg atoms with ions or polar molecules [12–14], one cannot ignore the influence of the core of the excited target on the binary encounter between the electron and the perturber. A complete three-body interaction, therefore, must be taken into account while exploring such collisions.

A possible way to investigate the collisions involving low-lying Rydberg atoms is through a semiclassical approach, where the use of a classical trajectory to account for the relative nuclear motion seems justified in light of the fact that it involves two heavy particles; the electron's motion is treated quantum mechanically. Employing this method Kumar, Lane, and Kimura [11] have studied the total depopulation of the spherically symmetric Na(6*s*,9*s*) states by the ground state He at thermal energies (see also Ref. [15]). Since the important collision dynamics in these studies is associated with the He atom being located in the outer parts of the Rydberg electron's wave function, close encounters of the perturber (He atom) with the Na^+ core (i.e., small impact parameters) are not that important [16]. Recently, we revisited those reactions by extending the integration region out to larger internuclear separation (*R*) in order to assess the influence of the long-range interactions on quenching [17]. Encouraged by these findings we, in this paper, have undertaken a similar study on the depopulation of low-*n* Rydberg Li, from spherically symmetric initial 6*s* and 7*s* states, colliding with the same perturber He for $3\times10^{-4} \leqslant v_{rel} \leqslant 1\times10^{-1}$ a.u.:

$$\mathrm{Li}(6s/7s) + \mathrm{He} \rightarrow \mathrm{Li}(nl) + \mathrm{He}, \tag{1}$$

where the final state of the target Li is completely different from its initial state. We use the multistate semiclassical molecular orbital (MO) approximation [17,18]. To examine the suitability of these MO results at these low energies we recently performed a two-channel quantum-mechanical calculation [19] for a representative collision. This enabled us not only to reflect on the reliability of our semiclassical results but also to look for the signature of the quantal effect, if any, in such energy regime.

The outline of the paper is as follows: a brief description of the theoretical method is provided in the next section. In the subsequent section we present our calculated cross sections along with the estimated reaction rates. The semiclassical MO result is compared with the model two-channel quantum-mechanical cross sections; the details of our 11-state semiclassical MO calculations follow. We conclude our article with a short conclusion. Atomic units are used throughout except where stated explicitly.

II. THEORETICAL METHODS

The semiclassical and quantum-mechanical descriptions of the atomic collisions have been presented in detail in some of our recent articles [11, 17, 19; see also Ref. [18] for details]; we, therefore, provide only the basics in this paper. In the molecular approach the Rydberg electron of the Li

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atom is considered moving in a combined nuclear field of the core Li^+ and the perturber He, forming a transient quasimolecule $[(\mathrm{LiHe})^+\text{-}e^-]$. It is the adiabatic potential surfaces of this transient quasimolecule that encompasses the entrance and final channels of the reaction (1). The method of pseudopotential [20] has been employed to account for the effective interaction of the loosely bound electron in this quasimolecule. A Linear Combination of Atomic Orbital (LCAO) method is used to generate the electronic wave function. The essentials of the electronic wave function, and the details of the semiclassical MO method have been shown in our recent article [17]. In the following the quantum-mechanical description is presented in short; for details we, however, refer to our recent article [19].

Quantum-Mechanical Collision Theory

In the quantum mechanical approach, both the nuclear and electronic motions are treated quantum mechanically, and the resulting Schroedinger equation is solved numerically. For this, the wave function of the total colliding system is expanded in terms of products of molecular electronic wave functions, nuclear wave functions and the phase factors that encompasses the electron translation factor (ETF) [18,21]. Substituting this wave function into the time-independent Schroedinger equation, one obtains, after some simplifications, a set of coupled equation [19]. We, however, eliminate the first-order derivatives by resorting to a diabatic representation [22], which also provides a convenient way to solve these equations numerically. In our present model calculation, we retain only two states of the same molecular symmetry. By proceeding in this manner we finally obtain the following coupled equations

$$[\{d^2/dR^2-J(J+1)/R^2\}I-2\mu V^d+2\mu E]\phi(R)=0 \quad (2)$$

where different terms are given in Ref. [19]. The coupled radial part of the above equation is solved by the usual partial wave decomposition. The log derivative method [23] has been used to obtain the S matrix; the cross sections are then obtained by employing the following relation [24]:

$$\sigma_{if}=(\pi/k_i^2)\sum J(J+1)|S_{ij}^J|^2, \quad (3)$$

where $k_i^2=2\mu E$, and E is the collision energy.

III. RESULTS AND DISCUSSION

We have used a large STO basis set; $1s$ through $3d$ is taken from Kimura, Olson, and Pascale [25]; the excited STO's (up to $nl=10s$) are, however, obtained by suitably adjusting the nodal positions of the valence electron wave function expanded in these orbitals employing the experimental quantum defects. Altogether 20 and 17 configurations, respectively, are used for obtaining the Σ and Π molecular states that are important in this study. The total depopulation cross sections in the velocity range $4\times10^{-4}\leqslant\nu\leqslant0.1$ a.u. for reaction (1) have then been calculated through a close-coupled scheme in which 11 molecular states (six Σ and five Π) are retained. For the $\mathrm{Li}(7s)+\mathrm{He}$ pair, the model two-channel quantum-mechanical results are compared with its semiclassical counterparts. In both calculations we have used the identical potentials and the corresponding coupling matrix elements.

A. Quantum-mechanical and semiclassical results for Li(7s): A comparative study $[\mathrm{Li}(7s\,\Sigma)+\mathrm{He}\rightarrow\mathrm{Li}(6p\,\Sigma)+\mathrm{He}]$

For the above colliding pair we have coupled the initial channel $7s\,\Sigma$ with its immediate neighboring state $6p\Sigma$ in a two-channel close-coupled approach; the preliminary findings of this calculation were reported recently in a comparative study [19]. Even though it does not provide the details of the collision dynamics, this approach is sufficient to reflect on the accuracy and suitability of our semiclassical results, especially at low velocities, where only transitions among nearest states are expected to dominate the process of state changing.

We have retained sufficient number of partial waves in the quantum-mechanical calculations. For example, 100 partial waves are required to obtain a convergence up to 0.01% at $\nu=0.0045$ a.u., whereas we have to include 850 partial waves at $v_{\mathrm{rel}}=0.1$ a.u. These cross sections are compared with their semiclassical counterparts in Fig. 1; the discussion is presented in the next subsection.

The agreement between the quantal and semiclassical two-channel calculations are excellent at velocities $\nu\geqslant0.002$ a.u.; they yield not only nearly identical magnitudes but also show similar pattern in the oscillatory structures. Even in the velocity region $0.0006\leqslant\nu\leqslant0.002$ a.u., the two sets of results show very good qualitative agreement; the magnitudes of the semiclassical cross sections are smaller than their quantal counterparts. The semiclassical calculation has not been extended beyond $v=0.0006$ a.u. as they were found to show larger deviation from the quantal results. The increased disagreement at lower energies suggests that the semiclassical approximation fails to account for the inherent quantal effects.

B. Semiclassical results for $\mathrm{Li}(6s,7s)+\mathrm{He}$

Encouraged by the noticeable agreement between the quantal and semiclassical results we employ the latter approach to calculate the total depopulation cross sections of low-lying Rydberg states of Li, namely $6s$ and $7s$, in collision with ground state He (reaction 1). Through a number of test studies we find that an 11-state calculation (see Table I) is essential to obtain the sufficient convergence of the estimated cross sections; further increase in the number of coupled states does not introduce any significant change in their magnitudes. We have also taken considerable care to ensure the numerical convergence to 1% within our 11-state calculations. To explore the peaks and valleys of the structure, if any, we have made calculations at sufficiently small energy grids.

Figure 2 shows the adiabatic potential curves for the Σ states (Π states have been left out for clarity); we retain 11 states in our coupled scheme for investigating the quenching of $\mathrm{Li}(6s)$ colliding with the low-energy He (see also Table

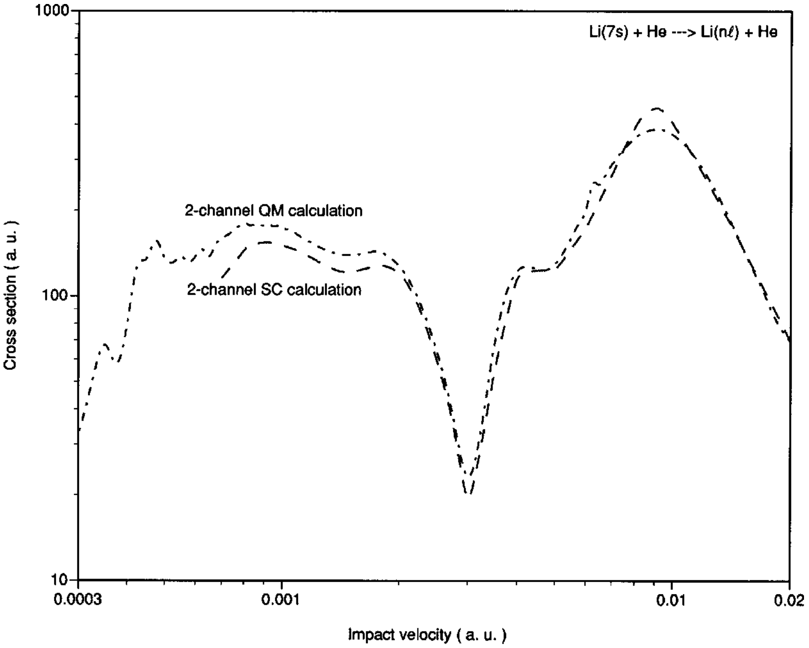

FIG. 1. Comparison of integrated cross sections —semiclassical vs quantum-mechanical — for $7s\Sigma \rightarrow 6p\Sigma$ transition for the reaction (1): Different curves are marked as such.

I). The initial channel $6s\,\Sigma$ has two strong avoided crossings with the immediate lower state $5f\,\Sigma$ around $R=4.5a_0$ and $10a_0$. They are reflected through strong radial couplings in the same region of R (not shown here). The $5f\Sigma$ state then couples with the $5d\,\Sigma$ channel at larger R values, and there also exists coupling of significant strength between $5d\Sigma$ and $5p\Sigma$ channels. The rotational coupling $6s\Sigma\langle\text{---}\rangle 6p\Pi$ strongly couples the initial state with the immediate exoergic state corresponding to Na$(6p)$. In comparison to this the rotational couplings involving the $6s\Sigma$ channel and $5f\,\Pi$ or $5d\,\Pi$ states are relatively weak.

The above collision dynamics depopulates the initial $6s$ state of Li atom through both excitation and de-excitation processes. In Fig. 3, we present our cross sections for both excitations (to $6p$ and $6d$ states of Li) and de-excitation (to $5f$, $5d$ and $5p$ states of Li) along with the total quenching cross sections. In the thermal energy region the process of de-excitation dominates; the quenching of the initial $6s$ state of Li proceeds mainly through the population of Li$(5f)$. The multistep transition $[(n-2),l\geqslant 2]$ does take place similar to the earlier findings on the He-Na pair [11,18]; the role of radial couplings that can transfer flux via $5f\Sigma\rightarrow 5d\Sigma \rightarrow 5p\Sigma$ become important only at comparatively higher velocities. It is basically the strong radial coupling between $6s\Sigma$ and $5f\Sigma$ states around $R=10a_0$, which is responsible for most of the transfer of probability at lower velocities. The nature of this coupling gives rise to Stueckelberg oscillations, which is also visible as structures in the total depopulation cross sections. It may here be noted that Saha and Lane [26] have also reported such oscillations in their calculations on Na$(8s)$-He pair. At low velocities, the process of excitation is very small. It is only at $\nu\geqslant 0.005$ a.u. ($E \geqslant 0.0454$ a.u.) that the excitation to exoergic states of Li starts making significant contribution towards depopulating the parent Li$(6s)$, although the asymptotic energy defect for the Li$(6s)\rightarrow$Li$(6p)$ transition is only 0.002 a.u.

TABLE I. Molecular states of the quasimolecule $[(\mathrm{LiHe})^+ - e^-]$ correlated to the atomic states of Li.

Atomic states	Molecular Σ states	Molecular Π states
Li$(5/6p)+$He	$5/6p\ \Sigma$	$5/6p\ \Pi$
Li$(5/6d)+$He	$5/6d\ \Sigma$	$5/6d\ \Pi$
Li$(5/6f)+$He	$5/6f\ \Sigma$	$5/6f\ \Pi$
Li$(6/7s)+$He	$6/7s\ \Sigma$	
Li$(6/7p)+$He	$6/7p\ \Sigma$	$6/7p\ \Pi$
Li$(6/7d)+$He	$6/7d\ \Sigma$	$6/7d\ \Pi$

The adiabatic potential energy surfaces for the colliding system $[\mathrm{Li}(7s)+\mathrm{He}]$ have more or less similar features (see Fig. 4) seen earlier for the $[\mathrm{Li}(6s)+\mathrm{He}]$ pair; the only difference is in the magnitude of the involved energy defects. Changing from the initial state $6s$ to $7s$ of Li we move up in the energy level diagram, consequently the various couplings responsible for the quenching of Li$(7s)$ turn stronger as the involved energy defects become smaller. For example, the entrance channel $7s\Sigma$ and the immediate neighboring state $6f\Sigma$ still have avoided crossings around $R=4a_0$ and $10a_0$, but the energy defect has been reduced significantly $[\Delta E(R\approx 10a_0)=1.8\times 10^{-4}$ a.u.]. This produces larger radial couplings between the two states; other radial couplings also gain in strength. The initial channel $7s\Sigma$, however, has weaker rotational couplings with the neighboring endoergic Π states.

The total cross sections for depopulating the parent Li$(7s)$ state by He, along with the contributions from the excitation and de-excitation processes are depicted in Fig. 5. Although the characteristic features of the total as well as the partial cross sections are similar to those of the Li$(6s)$ case, the details in terms of the velocity dependence and magnitude of the cross sections deserve some comments. The pro-

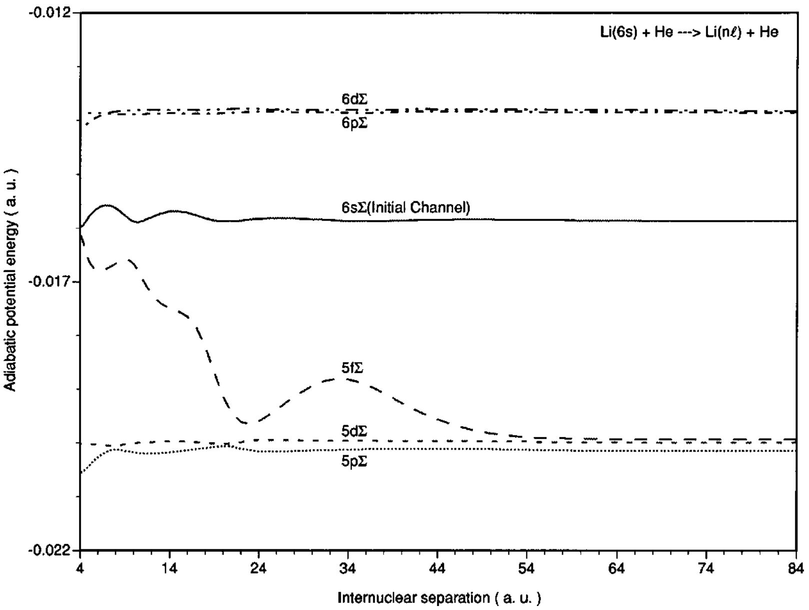

FIG. 2. Adiabatic potential surfaces of Li$(6s)+$He: Different Σ states are shown.

cess of excitation takes over that of de-excitation at much lower energies ($\nu \geqslant 0.002$ a.u.). In the higher domain of our investigated velocity region the process of excitation always remains a much more effective way of quenching the parent Li$(7s)$ state.

Both of the parent states, thus, favor the de-excitation as the primary mode of depopulating the parent state except at higher velocities where the process of excitation starts making significant contributions. They also agree in another feature: *the dominance of radial couplings at low energies*. It is only at higher energies that the angular couplings become important and various Π states playing important role. These general features were also observed earlier for the Na-He system [17]. We would like to point out that we do not include the excited STOs of Li for $l \geqslant 3$ in our structure calculations, because the involved energy defects for these substrates are very small; even at thermal energies they can be reached diabatically. It is our belief that the transition to $l=3$ substate should actually represent the population of the near-degenerate manifold $[n, l \geqslant 3]$ of the exit level [11,17]. It is important to note here that Li+He and Na+He pairs although differ significantly in their collision dynamics, there is a remarkable similarity in populating the endoergic substates of $l \geqslant 2$. The only difference is that in the present case this is achieved through a direct transition from the parent level, whereas in Na+He a multi-step process is responsible for this outcome. Moreover, the manifolds populated in this way are different in terms of the principal quantum number; $n-1$ for the Li+He pair but $n-2$ for the Na+He system.

To the best of our knowledge there is no experimental measurement on the quenching rate of low-Rydberg Li atom colliding with the ground state of He atom. Since most of the

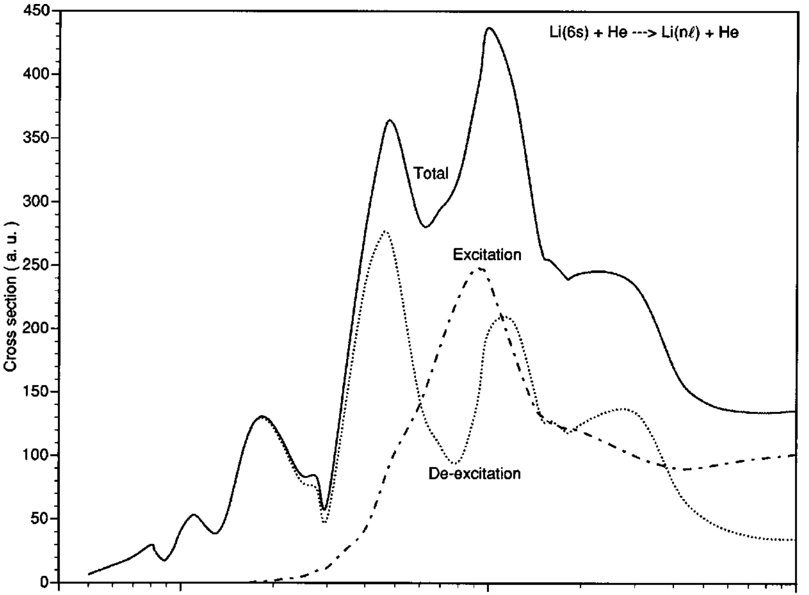

FIG. 3. Eleven-state calculation of total depopulation cross sections for Li$(6s)+$He interaction: Partial contributions of excitation and de-excitation are shown separately.

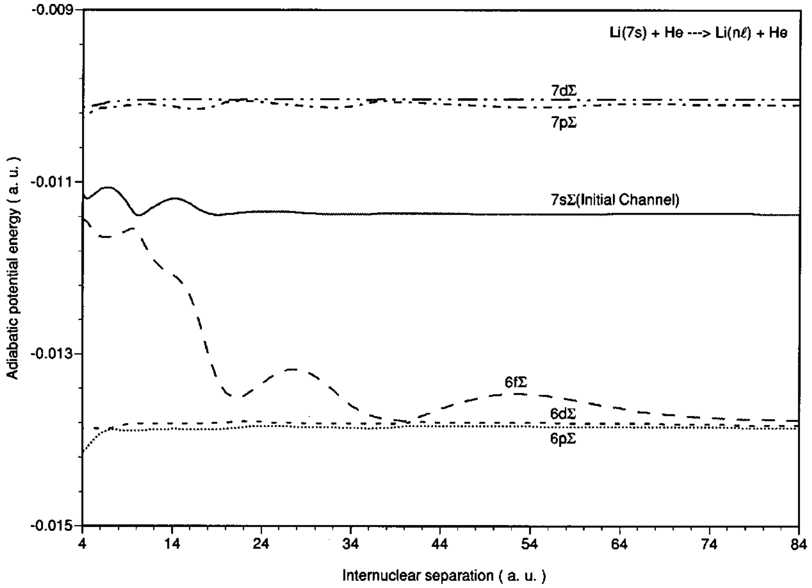

FIG. 4. Adiabatic potential surfaces of Li$(7s)+$He: Different Σ states are shown.

measurements with Rydberg atoms are carried out at thermal velocities, we also take the cell temperature $T=425\,\mathrm{K}$ (see also Refs. [11], [17] and [27]). In order to estimate the quenching rate we make a polynomial fit of our calculated cross sections for total depopulation, and then integrate it over the Maxwellian velocity distribution corresponding to 425 K. These reaction rates are compared with the rates for the Na$(ns)+$He system in Table II.

IV. CONCLUSION

We have carried out a close coupled molecular-orbital calculation, in the impact parameter formalism, for obtaining the cross sections for the total quenching of low-lying Rydberg states of Li atom colliding with the ground state of He atom over a range of impact velocities $(0.003\leqslant v_{rel}\leqslant 0.1\,\text{a.u.})$. The process of de-excitation dominates in the low-velocity region, and excitation to upper states makes significant contributions only at higher velocities. The validity of our semiclassical approach for investigating such collisions was presented through a model two-channel quantum-mechanical calculation. Except at very low velocities both cross sections show excellent agreement that establishes without doubt that our semiclassical approach is quite capable of revealing the true collision dynamics of the low-n Rydberg processes. This also suggests that treating the internuclear movement classically or quantum mechanically hardly makes any difference in the final outcome of the state-changing cross sections. Therefore, till a large quantum-mechanical calculation, with sufficient number of coupled states, is available, our MO approach would furnish a convenient way to explore the low-Rydberg atom problems involving collisions with neutral atomic or molecular perturbers [11,15–17] at low velocities. It is also important to note

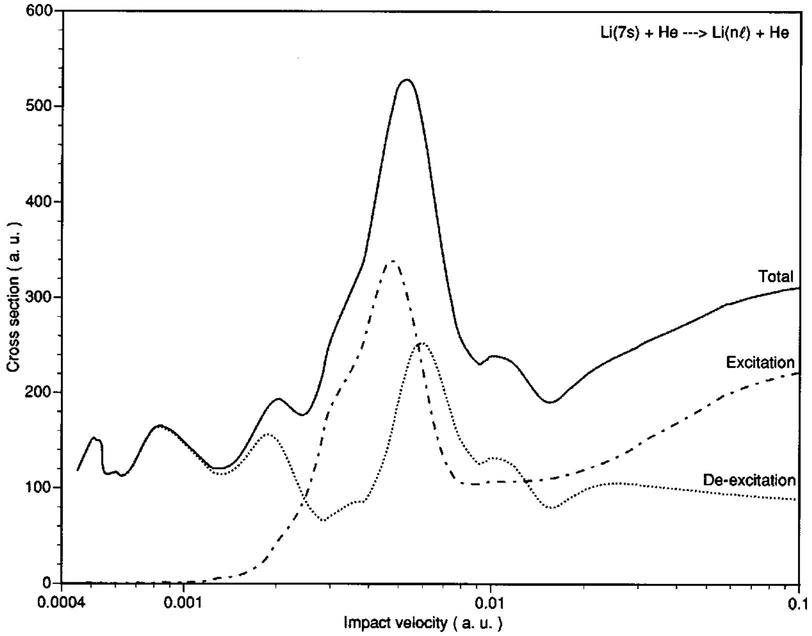

FIG. 5. Eleven-state calculation of total depopulation cross sections for Li$(7s)+$He interaction: Partial contributions of excitation and de-excitation are shown separately.

TABLE II. Reaction rates (a.u.) for quenching of Li (ns) colliding with ground state He ($T = 425$ K)

Initial target state	Rate for Li (ns)	Rate[a] for Na (ns)
6s	0.0223	0.00046
7s	0.0952	
8s		0.0447
9s		0.1386

[a] These results are taken from Ref. [17].

that the reported partial cross sections are sensitive to small changes in the potential energy surfaces and the resulting coupling matrix elements. But we believe that the present prescription provides a fairly reliable picture of the involved collision dynamics, and hence the subsequent transfer of the flux in the systems studied here.

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