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Larger scale eigenchannel R-matrix calculations than those of Pan *et al.* [Phys. Rev. A **53**, 840 (1996)] confirm the prediction of a 2-meV-wide resonance feature at a photon energy of 5.421 eV in the Li ($3s$) partial cross section resulting from photodetachment of Li^-. This resonance was neither clearly observed nor identified in measurements of Ljungblad *et al.* [Phys. Rev. Lett. **77**, 3751 (1996)]. We identify this resonance as a ${}_N\{v\}_n^A = {}_5\{1\}_6^-$ state [having angular symmetry $(K,T)^A = (2,0)^-$ or $(n_\lambda, n_\mu, m) = (1,7,0)$]. This state, which is forbidden by propensity rules in H^- photodetachment, is predicted to be prominent also in the Li($4l$) partial cross sections, for $l \geq 1$. Besides the ${}_5\{1\}_6^-$ state, the Li($3s$) partial cross section in the energy region 20–60 meV below the Li($5p$) threshold is dominated by two other doubly excited states, which have been observed in H^- photodetachment. Our calculations are in excellent agreement with the measurements of Ljungblad *et al.* in the energy region from the Li($5p$) threshold to 20 meV below. [S1050-2947(98)04612-5]

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Photodetachment plus excitation of atomic negative ions is a fruitful means of observing and studying highly correlated, three-body Coulomb states. The lack of Rydberg series in the spectra of negative ions means that besides shape-resonance or threshold effects, the major and most numerous features in the spectra are doubly excited state resonances. For photodetachment of negative ions heavier than the most fundamental one (e.g., H^-), it has been shown theoretically [1,2] that certain doubly excited states not seen in H^- photodetachment do occur in the spectra of the heavier negative ions. Their non-Coulomb core thus allows some states that are quasiforbidden in H^- photodetachment [3,4] to become visible.

Li^- has recently been a focus of both theoretical [1,2,5] and experimental work [6–8] because of the similarities of its doubly excited state structure to that of the fundamental H^- system. Generally the relative experimental measurements have been in excellent agreement with the theoretical predictions. Recently, however, discrepancies were reported in the Li($3s$) partial cross sections below the Li($5p$) threshold [7]. Specifically, in the energy region from the Li($5p$) threshold to about 20 meV below, theoretical [2] and experimental [7] resonance positions differ by 0–2 meV and the relative depths of resonance windows disagree even qualitatively. More significantly, in the energy region 20–60 meV below the Li($5p$) threshold, theory [2] predicts resonance structure which is unresolved by the experimental data [7] despite the stated 25 μeV energy resolution. These discrepancies are a concern for theory since they may indicate limitations on theory's ability to describe highly excited, doubly excited states. They are also a concern for experiment since the reported energy resolution should certainly be adequate to observe the theoretically predicted resonance features.

We report here new eigenchannel R-matrix calculations for Li^- photodetachment using a much larger R-matrix radius than in previous calculations by Pan *et al.* [1,2] in order to encompass better the highly excited double excitations just below the Li($5p$) threshold. Our results for the Li($3s$) partial cross sections now agree completely with the recent experimental results from the Li($5p$) threshold to 20 meV below. In the region 20–60 meV below the Li($5p$) threshold, however, while our results change quantitatively as compared to the results of Pan *et al.* [2], they confirm qualitatively the resonance features predicted earlier [2]. Moreover, while our results give better agreement with experiment, they still indicate a sharp resonance feature that is only barely discernible in the experimental data. Consequently we present an analysis of the resonances in this region in which there remain discrepancies with experiment [7].

We show that the structure in the Li($3s$) partial cross section in this region is due to three doubly excited states, the middle one of which produces a sharp peak in the predicted cross section; the other two resonances are very broad. In contrast, experiment [7] labeled two resonances in this region without giving positions. Because the main discrepancy between theory and experiment concerns the middle resonance, we present a more detailed analysis for it. We find it is of the ''$-$'' type that is not observed in experiments for H^- photodetachment and is forbidden theoretically by propensity rules [3,4]. It is thus a resonance in the Li^- photodetachment spectrum that is made visible by the non-Coulomb Li^+ core. We analyze here also the effect of this resonance on all energetically allowed $n = 3,4$, and 5 partial cross sections and show that its effects are most prominent in the Li($4p$), Li($4d$), and Li($4f$) partial cross sections. Experimental measurements of these other partial cross sections would provide additional opportunities to test theoretical predictions of the existence of this highly correlated, doubly excited state which has not been observed in H^- and whose experimental observation in the Li^- photodetachment partial cross section for the Li($3s$) state is not yet definite.

Our theoretical calculations employ the same eigenchannel R-matrix method [9,10] as in Refs. [1,2]. In brief, the Li^- negative ion is treated as a two-electron system in which the outer two electrons move in a semiempirical potential. Within a reaction volume enclosed by the surface defined by $\max(r_1, r_2) = r_0$, where r_1 and r_2 are the electron distances from the nucleus, many-electron interactions are treated by discrete-state, configuration interaction techniques using independent electron functions and LS coupling. Outside r_0 it is assumed there is only a single electron. All long-range multipole interactions in the outer region are treated numeri-

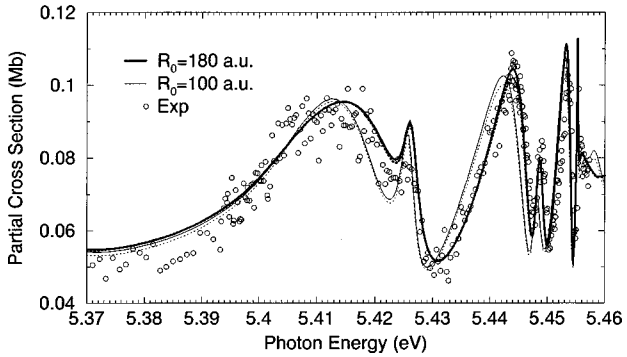

FIG. 1. Partial cross section for the process $Li^- + \gamma \rightarrow Li(3s) + e^-$ below the Li($5p$) threshold at $\hbar\omega = 5.4553$ eV. Thick curves: present results in dipole velocity (solid) and dipole length (dotted) gauges. Thin curves: results of Pan *et al.* [2]. Open circles: experimental measurements of Ljungblad *et al.* [7].

cally by close-coupling techniques. Our calculations employ an R-matrix radius r_0 of 180 a.u. and include 2294 two-electron configurations. This contrasts with $r_0 = 80$–120 a.u. and inclusion of 794 two-electron configurations in Ref. [2].[1]

Our results for the Li($3s$) partial cross section are shown in Fig. 1 together with the experimental measurements of Ljungblad *et al.* [7] and the theoretical results of Pan *et al.* [2]. For photon energies in the range 5.43 eV$\leqslant\hbar\omega\leqslant$5.45 eV, the agreement of the present results with experiment is excellent. This improved agreement stems from the present use of a much larger R-matrix box size and a corresponding increase in the number of configurations employed. For energies below 5.41 eV agreement with the results of Ref. [2] is excellent.

In contrast to this generally good agreement of the present results and experiment [7] just below the Li($5p$) threshold, in the neighborhood of $\hbar\omega = 5.426$ eV the present theory confirms the predictions of Ref. [2] that there is a distinct peak about 2 meV wide which is not resolved experimentally. Owing to this discrepancy, we have carried out a separate configuration interaction calculation in which all basis functions were set to zero at $r_0 = 180$ a.u. in order to find the discrete states corresponding to the features in the region 5.40 eV$\leqslant\hbar\omega\leqslant$5.44 eV. We found three doubly excited states in this energy region, at $\hbar\omega = 5.403$ eV, 5.421 eV, and 5.434 eV.

Figure 2 demonstrates the effect that these three states have on the Li($3s$) partial cross section. The thick lines are our predictions for the Li($3s$) partial cross section, while the thin lines show the results obtained by removing the effect of one or more of the doubly excited states (by orthogonalizing our exact final state wave function to the doubly excited state or states). Figure 2(a) shows that the state at 5.403 eV produces a broad resonance just above 5.41 eV; Fig. 2(b) shows

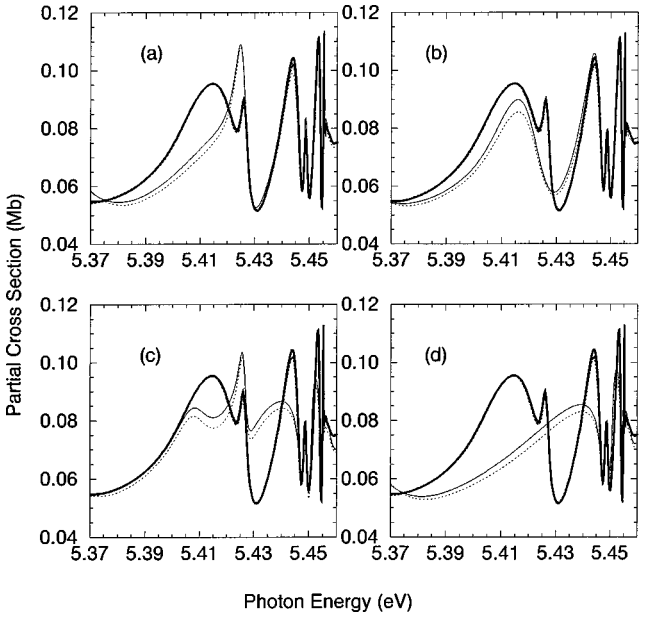

FIG. 2. Partial cross section for the process $Li^- + \gamma \rightarrow Li(3s) + e^-$. Thick curves: present results in dipole velocity (solid) and dipole length (dotted) gauges. Thin curves: results obtained by removing one or more doubly excited resonances from the calculation. (a) ${}_5\{0\}_6^+$ state at 5.403 eV removed; (b) ${}_5\{1\}_6^-$ state at 5.421 eV removed; (c) ${}_5\{0\}_7^+$ state at 5.434 eV removed; (d) all three states removed simultaneously.

that the state at 5.421 eV produces a sharp, narrow resonance at 5.426 eV; Fig. 2(c) shows that the state at 5.434 eV produces a window resonance at 5.43 eV and affects the cross section magnitude at lower energies; finally, Fig. 2(d) shows that removing all three states results in a smoothly varying cross section in this region in contrast to the sharply varying resonance structures predicted by our calculations that include the states. Clearly, interference effects among these three states are significant.

The identification of these three states is made by a comparison with the corresponding ones in the pure three-body Coulomb system, H^-. Specifically, on an energy scale in which the $5p$ thresholds in H^- and Li^- are lined up, corresponding highly excited, two-electron states are expected to lie close in energy in the two spectra. Furthermore, by plotting their probability densities we can label their symmetries.[2] The states located at $\hbar\omega = 5.403$ eV and 5.434 eV in Li^- have been observed in H^- photodetachment [15]

[1]The convergence of the present calculations was tested by comparing them with results obtained below the Li($5p$) threshold for $r_0 = 180$ a.u. and either 1500 or 3000 configurations and for $r_0 = 220$ a.u. and 3000 configurations. At the energy of the 5.421 eV resonance, all dipole velocity (length) results agree to within 0.5% (2.0%).

[2]We employ the notation ${}_N\{v\}_n^A$ introduced in Refs. [4(b), 4(c)]. Here v is the vibrational quantum number, indicating the number of nodes in θ_{12} (in the hyperspherical coordinate representation) or in λ (in the prolate spheroidal coordinate representation); A indicates the possible symmetry of the wave function with respect to $r_1 = r_2$, with $A = +$ indicating an antinode at $r_1 = r_2$ and $A = -$ indicating a node at $r_1 = r_2$; finally $N(n)$ is the principal quantum number of the lower- (higher-) energy member of the doubly excited electron pair. Alternate notations for the angular symmetry of the two-electron resonances include the group-theoretical notation [11,12] $(K,T)^A$ and the molecular-orbital notation [13,14] (n_λ, n_μ, m). A review of the relations between these latter two notations is given in Ref. [3(b)].

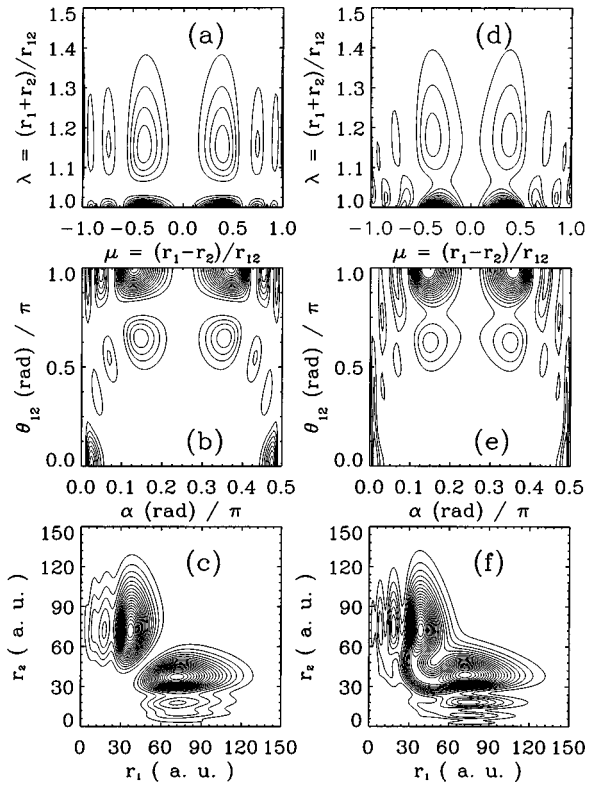

FIG. 3. Doubly excited state $_5\{1\}_6^-$ wave function density plots in H^- [(a), (b), and (c)] and Li^- [(d), (e), and (f)]. (a) and (d): Plotted in prolate spheroidal coordinates λ and μ at the maximum wave function amplitude at $R=\sqrt{r_1^2+r_2^2}=83$ a.u. (b) and (e): Plotted in hyperspherical coordinates θ_{12} and α at $R=83$ a.u. (c) and (f): Plotted in (r_1,r_2) with angular variables averaged.

and have been predicted theoretically for H^- [4(a),16–18]. We calculated the corresponding states in H^- and compared the radial and angular density plots to those for Li^- (not shown here). From this comparison we designate[2] the doubly excited state in Li^- at 5.403 eV as a $_5\{0\}_6^+$ state and the one at 5.434 eV as a $_5\{0\}_7^+$ state. The angular symmetries of these two resonances are the same and may be designated in alternative notations[2] as $(3,1)^+$ and (0,6,1).

More interesting, however, is the doubly excited state located at $\hbar\omega=5.421$ eV. The corresponding state has not been observed in H^- photodetachment [15], although bound state calculations for H^- have predicted such a state [16,17]. We have also carried out bound state calculations for H^- and show in Fig. 3 comparisons using three different density plots: a plot in (r_1,r_2); a plot in the hyperspherical coordinate angles θ_{12} and α $[\equiv\tan^{-1}(r_2/r_1)]$; and a plot in the prolate spheroidal coordinates μ and λ. Both the radial and angular structures of these corresponding doubly excited states are very similar. We identify[2] from this comparison that this is a $_5\{1\}_6^-$ state [alternatively, $(2,0)^-$ or (1,7,0)]. Because of the nodal lines in θ_{12} (equivalently, in λ) and along $r_1=r_2$ (equivalently, in μ or along $\alpha=\pi/4$), propensity rules [3,4] forbid population of this state in H^- photodetachment. In fact it is not observed [15]. The nodal lines in H^-, however, are sharp whereas in Li^- they are not. It is precisely because the state in Li^- does not have sharp nodal lines (i.e., it is not a pure $_5\{1\}_6^-$ state) that it is more prominent in Li^- photodetachment.

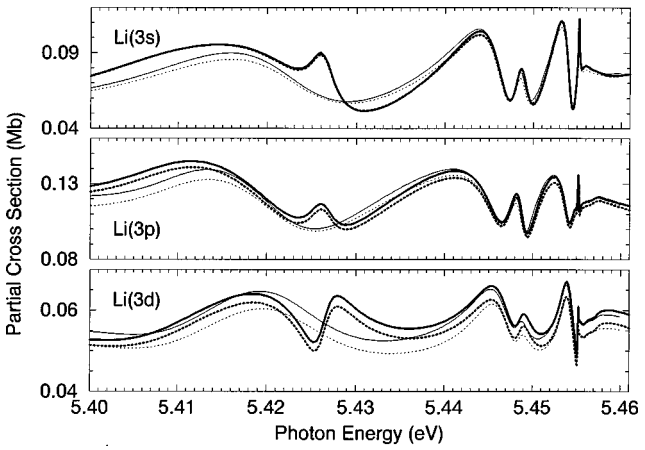

FIG. 4. Partial cross sections for the process $Li^-+\gamma\rightarrow Li(nl)+e^-$, for $nl=3s,3p$, and $3d$. Thick curves: present results in dipole velocity (solid) and dipole length (dotted) gauges. Thin curves: results obtained by removing the $_5\{1\}_6^-$ doubly excited state.

Given that experiment [7] has not confirmed the theoretical predictions for the existence of the $_5\{1\}_6^-$ state in the Li($3s$) partial cross section, we present in Figs. 4 and 5 the effects of this state on all other allowed Li(nl) partial cross sections for $n=3,4$, and 5. As in Fig. 2, the thick curves give the results of our full calculation; the thin curves give the results obtained by orthogonalizing our final state wave function to the $_5\{1\}_6^-$ doubly excited state. Comparison of the thick and thin curves shows the effect of this resonance on each partial cross section. One observes the most dramatic effects in the Li($4l$) partial cross sections for $l\geqslant 1$. The partial cross sections having the largest magnitudes that still exhibit significant effects are those for Li($3l$) $(0\leqslant l\leqslant 2)$ and for Li($4p$).

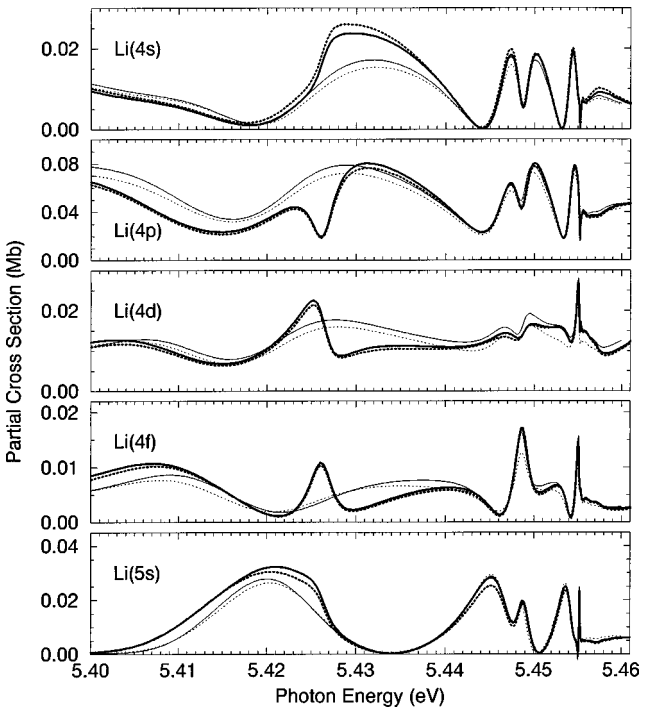

FIG. 5. Same as in Fig. 4 for $nl=4s,4p,4d,4f$, and $5s$.

It is also of interest to note the mirror effects of the resonances on different partial cross sections. Thus, for example, the ${}_5\{1\}_6^-$ resonance appears as a window in the Li($4p$) partial cross section but as a peak in the Li($3s$), Li($3p$), and Li($4f$) partial cross sections. In addition, it exhibits both peak and window features in each of the Li($3d$) and Li($4d$) partial cross sections, but with opposite phases. Such mirroring effects have been noted in partial cross section branching ratios [19].

In summary, we have carried out eigenchannel *R*-matrix calculations for Li^- photodetachment similar to those of Pan *et al.* [2] but employing a much larger *R*-matrix radius and a much larger number of configurations. Our results account for nearly all of the prior discrepancies between theory [2] and experiment [7] except for the energy region around $\hbar\omega = 5.421$ eV where theory predicts a resonance structure not clearly observed nor identified experimentally. We identify this resonance as a ${}_5\{1\}_6^-$ doubly excited state that is quasiforbidden in H^- photodetachment by propensity rules [3,4], but which has significant effects on all Li^- photodetachment partial cross sections owing to the non-Coulomb Li^+ core.

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