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NOVEL DOUBLY EXCITED STATES PRODUCED IN NEGATIVE ION PHOTODETACHMENT

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Abstract

Eigenchannel R-matrix calculations (including effects of long-range multipole interactions beyond the reaction volume) for Li^- photodetachment partial cross sections from the vicinity of the Li 3s threshold to the Li 6s threshold (3.8 eV $\leq \hbar\omega \leq$ 5.65 eV) are presented. Excellent agreement with recent relative total cross section measurements of U. Berzinsh *et al.* [Phys. Rev. Lett. **74**, 4795 (1995)] in the vicinity of the Li 3s and Li 3p thresholds is found. The calculated resonance structures are analyzed in detail and compared with similar calculations for H^- photodetachment above the $H(n = 4)$ and $H(n = 5)$ excited state thresholds. The non-hydrogenic Li^+ core is shown to produce kinds of resonances in Li^- photodetachment that are not observed in H^- photodetachment.

1. Introduction

Experimental measurements of doubly-excited state atomic spectra have long served as stimuli for novel theoretical descriptions of correlated electronic states. Indeed, the first measurments of He doubly-excited state spectra below the $He^+(n = 2)$ threshold (Madden and Codling 1963) led theorists to abandon the independent-particle model in order to properly describe the observed experimental intensities (Cooper *et al.* 1963, Macek 1968). Recent experimental measurements of doubly-excited state spectra for H^- (Harris *et al.* 1990) and for He (Domke *et al.* 1991) in the vicinity of much higher detachment or ionization thresholds (i.e., below the $H(n)$ or $He^+(n)$ thresholds, where $n > 2$) have been interpreted by theorists as reflecting propensity rules for populating particular channels of '+'-type doubly-excited states (Sadeghpour and Greene 1990, Röst and Briggs 1990, Röst *et al.* 1991, Sadeghpour 1991, Sadeghpour *et al.* 1992, Sadeghpour and Cavagnero 1993). Even weak experimental features have been successfully described theoretically (Tang *et al.* 1992). These experimental and

theoretical advances have focused on the He and H^- two-electron systems, as these represent the prototypes for the study of correlated electronic states.

We report that such theoretical advances in the understanding of doubly-excited state spectra of two-electron systems have application to understanding doubly-excited state spectra of a four-electron system, Li^-. The eigenchannel R-matrix method (Fano and Lee 1973, O'Mahony and Greene 1985, Greene and Kim 1987, Greene 1988) has been used to calculate photodetachment cross sections for both H^- and Li^- up to the $n = 6$ thresholds (i.e., $H(n = 6)$ and $Li(n = 6)$). In order to successfully obtain converged results, the close-coupling equations without exchange were solved outside the R-matrix box, thereby treating long-range multipole effects. In what follows, we first compare our calculations for H^- photodetachment with experimental results (Harris *et al.* 1990) and with our theoretical results for Li^- photodetachment (Pan *et al.* 1994). We then compare our results for Li^- photodetachment (Pan *et al.* 1996) with recent experimental measurements in the vicinity of the Li 3s and 3p thresholds (U. Berzinsh *et al.* 1995). Finally we point out some other features of the Li^- photodetachment partial cross sections. This work has been carried out in collaboration with C. Pan and C.H. Greene (C. Pan *et al.* 1994, 1996).

2. H^- and Li^- Photodetachment Below the $H(n = 5, 6)$ and $Li(n = 5, 6)$ Thresholds

Our results for photodetachment of H^- with excitation of $H(n = 4)$ and $H(n = 5)$ are shown in figure $1(a)$ and (b) respectively together with the experimental results of Harris *et al.* (1990). The theoretical results have been convoluted with a Gaussian energy function to take into account the experimental energy resolution of 8.3 meV. Both the length and velocity form theoretical results are in excellent agreement with the experimental results up to the energy of the second window resonance in each case (i.e., up to ≈ 13.76 eV in (a) and ≈ 13.93 eV in (b)). The discrepancies beginning at these second window resonances, however, merely indicate that as one approaches the $H(n = 5)$ and $H(n = 6)$ thresholds one requires a larger R-matrix box to treat the increasingly broad extensions of the higher energy resonances. The results in Figs. $1(a)$ and $1(b)$ were obtained using R-matrix radii of 80 a.u. and 100 a.u. The inset figures shown the improvement obtained upon increasing the radii to 100 a.u. and 120 a.u. respectively.

Turning now to the comparison of H^- and Li^- photodetachment, Fig. 2 compares the partial cross sections for exciting the $n = 4$ state of the neutral atoms. To facilitate comparison, the spectra are plotted against energy relative to the double ionization threshold. One sees that on a coarse energy scale the two spectra are very similar, particularly as one approaches the double ionization threshold. The prominent series of window resonances (whose first members are labelled a) are strong features of both spectra. The weak features (whose first members are labelled b) are, however, different in the two spectra. These differences stem from the exact degeneracy of the H atom energy levels compared to the lack of degeneracy in the Li atom.

In order to make connection with predicted propensity rules and to identify the features in the calculated cross sections, special R-matrix calculations were carried out with an interaction volume of radius $r_0 = 120$ a.u. All basis functions were set to zero on the boundary of V. Thus only the discrete structures were calculated, in order to see which ones appeared at the energies corresponding to the features seen in the cross sections shown in Fig. 2. In particular, resonances were found at the energies indicated by a and b in Fig. 2 in each system. When the probability distributions for these discrete two-electron resonances are plotted (cf. Pan *et al.* 1994), one finds that the a resonances have a strong antinode along the so-called Wannier ridge (at $r_1 = r_2$) whereas the b resonances have a node on this ridge. Actually, in H^- this node for the b resonance is nearly exact, whereas in Li^- it is more approximate (because of the non-hydrogenic Li atom core). For this reason the b resonance is predicted to produce a distinct window resonance feature in the Li^- photodetachment spectrum, whereas this resonance is predicted to be only evident as an extremely sharp, narrow feature in the H^- photodetachment

Fig. 1. Photodetachment cross sections for the processes $H^- + \gamma \rightarrow H(n) + e^-$ plotted against the photon energy, where (*a*) $n = 4$ and (*b*) $n = 5$. Theoretical curves: Present results using the velocity form (full curve) and length form (dotted curve) of the dipole operator. The theoretical results have been convoluted with the experimental resolution of 8.3 meV. Inset figures show the effect of increasing the size of the R-matrix sphere (see text). Experimental points: Harris *et al.* (1990). (From Pan *et al.* (1994).)

Fig. 2. (*a*) Photodetachment cross sections for the process $H^- + \gamma \rightarrow H(n = 4) + e^-$. (*b*) Photodetachment cross sections for the process $Li^- + \gamma \rightarrow Li(n = 4) + e^-$. The abscissae show the final state energy relative to the double ionization threshold. Full curves, present dipole velocity results; broken curves, present dipole length results. Labels *a* and *b* denote the locations of doubly-excited resonances (see text). The cusp-like structure in (*b*) at the energy -0.02364 is located at the Li(5s) threshold. (From Pan *et al.* (1994).)

Fig. 3. Comparison of our calculated Li^- total photodetachment cross sections in dipole velocity (solid curve) and dipole length (dotted curve) approximation with results of Berzinsh *et al.* (1995). The relative experimental results of Berzinsh *et al.* (1995) are normalized to our theoretical velocity curve at $\hbar\omega = 4.45$ eV. (*a*) Comparison with experimental results (+) over the energy range $4.1 \leq \hbar\omega \leq 4.55$ eV. (*b*) Comparison with experimental results (+) in the vicinity of the Li(3p) threshold. (*c*) Comparison with theoretical results (dashed curve) of Lindroth (Berzinsh *et al.* 1995, Lindroth 1995). (From Pan *et al.* (1996).)

spectrum. Results for the $H(n = 5)$ and $Li(n = 5)$ partial cross sections are similar to those in Fig. 2 (Pan *et al.* 1994). Part of the reason for the similarity of Li^- and H^- partial photodetachment cross sections is undoubtedly the fact that only *s*-wave quantum defects are large for Li.

3. Li^- Photodetachment Near the Li(3s) and Li(3p) Thresholds

Our total cross section results for Li^- are in excellent agreement with recent relative measurements near the Li 3p threshold (Berzinsh *et al.* 1995), as shown in Fig. 3. Both on the broad energy scale shown in Fig. 3(*a*) and on the fine energy scale shown in Fig. 3(*b*) (near the 3p threshold), our calculated total detachment cross section shows a very accurate prediction of experimentally observed features. Furthermore, Fig. 3(*c*) compares our total cross section results with those of Lindroth (Berzinsh *et al.* 1995, Lindroth 1995); there is excellent qualitative agreement, although our results lie $\approx 5\% - 10\%$ higher in this energy region.

Doubly excited states in the vicinity of the Li(3s) and Li(3p) thresholds hold the key to interpreting the features observed in Fig. 3 in the Li^- photodetachment cross section (such as the broad minimum and subsequent maximum near 4.2 eV and 4.35 eV respectively as well as the sharper minimum and subsequent maximum just below the 3p threshold). Prior theoretical studies of Li^- doubly-excited state resonances below the 3p threshold predict only a single $^1P^o$ resonance located at a photon energy of about 4.39 eV (Fung and Matese 1972; Steward *et al.* 1974). Recently Lindroth (Berzinsh *et al.* 1995; Lindroth 1995) has performed a discrete basis set, complex rotation calculation that finds a resonance at 4.32 eV, somewhat below the previously predicted energies. Lin (1983) carried out a diabatic hyperspherical calculation for the $^1P^o$ potential converging to the Li 3p threshold. He found that this potential supports a bound state (which he labelled "3s3p") at an energy of 4.18 eV, which is quite a bit below the other predictions.

In our calculations (Pan *et al.* 1996), we carried out two different searches for doubly excited resonances below the Li(3p) threshold. In the first kind, we did not include any one-electron orbitals lower in energy than 3p in our calculations. Our results agree best with the results of

Fig. 4. Total (σ_T) and partial (σ (ns)) photodetachment cross sections for Li^- for photon energies 4.8 eV $\leq \hbar\omega \leq$ 5.2 eV. Dipole velocity (length) results are indicated by the solid (dotted) lines. (*a*) σ_T and σ(2s). (*b*) σ(3s). (*c*) σ(4s). (From Pan *et al.* (1996).)

Fung and Matese (1972) and Stewart *et al.* (1974); namely, we find a single resonance below the Li(3p) threshold at a photon energy of 4.39 eV. However, a density plot of this resonance (Pan *et al.* 1996) shows that it is not well-localized. Furthermore, using the isolated resonance theory (Fano 1961; Starace 1977) to remove the effect of this resonance on the calculated cross section leaves a "background" cross section which still has much structure (Pan *et al.* 1996).

However, in our second calculation (Pan *et al.* 1996), we included the 3s one-electron orbital. We then found two resonances below the Li(3p) threshold, at 4.22 eV and 4.44 eV. The lowest resonance is very well-localized, whereas the higher one, lying just below the Li(3p) threshold, is not. Furthermore, removing the effects of these two resonances on our calculated cross sections by means of the isolated resonance theory (Fano 1961, Starace 1977) gives "background" cross sections that are smooth and structureless. We conclude that the lowest resonance is the "3s3p" resonance first calculated by Lin (1983). It has a distinct antinode along the $r_1 = r_2$ Wannier ridge and dominates the behavior of the Li^- photodetachment cross selection below the Li(3p) threshold. Because the second resonance we obtained is so diffuse and close in energy to the Li(3p) threshold, it is not certain that it is truly bound (because inclusion of the 3s orbital in our non-standard calculation introduces coupling with continuum channels). Nevertheless, the resonance we obtain is the major influence on the detachment cross section near the Li(3p) threshold.

4. Li^- Photodetachment at Higher Energies

We have calculated all partial cross sections for the process $Li^- + \gamma \rightarrow Li(n\ell) + e^-$ up to the 6s level. In Fig. 4 we show the $n\ell$ =2s, 3s, and 4s partial cross sections over the energy range 4.8 eV $\leq \hbar\omega \leq$ 5.2 eV, which is the region of the 4s and 4p threshold. Clearly the Li(2s) partial cross section gives the largest contribution to the total cross section. However, the Li(3s) and Li(4s) partial cross sections have far stronger interactions with the doubly-excited states below the Li(4p) threshold. Indeed, the Li(3s) and Li(4s) partial cross sections are completely dominated by interactions with these doubly-excited states; they exhibit very deep window resonances that in many instances plunge the partial cross sections by nearly 100%, to values close to zero. Note further that the minima in the Li(3s) and Li(4s) partial cross sections occur at different energies within the resonance. Indeed, one sees that these partial cross sections are nearly mirror images of one another. The kind of behavior has been predicted (cf. Fig. 3 of Starace 1977).

Finally, note that the Li(4s) partial cross section shown in Fig. 4 has a very sharp onset at threshold. According to the well-known Wigner threshold law, the cross section should increase as the $\ell + 1/2$ power of the detached electron's kinetic energy, where $\ell = 1$ (cf. Fano and Rau 1986). Calculations on a very fine energy mesh (Pan *et al.* 1996) confirm the validity of this threshold law, but find that it applies only over the first 0.2 meV above threshold in the case of the Li(4s) partial cross section. This small range of validity is consistent with experimental results for Cs^- (Slater *et al.* 1978). As noted by Pan *et al.* (1996), Li(nℓ) states have large dipole polarizabilities that limit the usefulness of the threshold law.

5. Conclusions

We conclude that when long-range interactions are treated properly, the eigenchannel *R*-matrix method does very well in describing doubly-excited resonance structures in negative ion photodetachment, even for fairly high levels of excitation. Furthermore, knowledge of doubly-excited state propensity rules and structures in the prototype He and H^- systems carries over to Li^- and may also apply to heavier systems. Finally, the non-hydrogenic Li^+ core gives prominence to types of doubly excited resonances that are not significant in the prototype He and H^- three-body Coulomb systems. Such resonances, occurring primarily above the Li(4s) threshold, have yet to be experimentally observed in Li^- photodetachment.

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7. References

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