Laser-Induced Transitions between Triply Excited Hollow States

L. B. Madsen,[1] P. Schlagheck,[1,2] and P. Lambropoulos[1,3]

[1]*Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Straße 1, D-85748 Garching, Germany*
[2]*Laboratoire de Physique Théorique et Modèles Statistiques, Bâtiment 100, F-91405 Orsay Cedex, France*
[3]*Foundation for Research and Technology Hellas, Institute of Electronic Structure and Laser, P.O. Box 1527, Heraklion 71110 Crete, Greece*

(Received 15 March 2000)

We present an *ab initio* calculation of the Li^+ photoion yield in the presence of laser coupling between the triply excited $2s^2 2p^2 P^o$ and $2s2p^2\,^2D^e$ resonances in lithium, the first of which is assumed excited by synchrotron radiation from the ground state. The laser coupling between the triply excited states is shown to lead to a significant and readily measurable modification of the line profile which provides a unique probe of the dipole strength between highly correlated triply excited states.

PACS numbers: 32.80.Hd, 32.80.Dz, 32.80.Fb, 32.80.Qk

A triply excited state in lithium, also referred to as a hollow state, represents a fundamental case of highly correlated three-electron dynamics in a purely Coloumbic four-body system, as attested by the continuing avalanche of related papers [1–20] over the last six years. Photoexcitation by synchrotron radiation has proven to be a very successful method to study energies and widths of such states. They have been studied by photoabsorption [1], photoion [2–4], and photoelectron measurements [5–10] and an impressive number of triply excited states has been reported. States with empty K and L shells have been observed [4,9] and also several Rydberg series have been identified [11]. The results have been compared with R-matrix [5–10,12,13] and Dirac-Fock calculations [3,4] and the agreement is generally good. There is also excellent agreement between experimental values and very accurate calculations using the saddle-point complex rotation method [9,14,15]. In addition, the hyperspherical coordinates approach has been used to analyze and visualize the electron correlations, in an effort to obtain a classification in terms of approximate quantum numbers [16–20].

The selectivity of the photoexcitation technique means that only states of $^2P^o$ symmetry can be reached from the ground state. It is, however, equally interesting to investigate states of different symmetry and parity, as in one experiment [7], where a laser excited the $1s^2 2p\,^2P^o$ state from which synchrotron radiation produced even-parity triply excited states. This is one way of reaching even parity states which still probes their connection with bound states of the neutral. Nothing is known, however, about the fundamental interaction of the triply excited states themselves with radiation. In particular, the induced coupling between such highly correlated states, which allows a much more detailed approach towards three-electron correlation than the excitation from the ground state, has not been examined yet. We have undertaken such an investigation and report here on the generic effect of photoabsorption from the Li ground state to the $2s^2 2p\,^2P^o$ triply excited state, when the system is embedded in a judiciously chosen laser field. Clearly, this allows the investigation of S and D symmetry states. Specifically, we consider the laser coupling between the $2s^2 2p\,^2P^o$ and $2s2p^2\,^2D^e$ triply excited states, which is at resonance at near-optical wavelength corresponding to a photon energy of $\simeq$2.5 eV. As we show, such a coherent coupling leads to a significant modification of the line profile of the Li^+ photoion spectrum. At sufficiently high, but still modest, laser intensity, the spectrum develops an ac Stark splitting which is directly related to and provides a measure of the dipole matrix element between the triply excited states.

To introduce the basic idea and scheme, let $|g\rangle$ be the $1s^2 2s\,^2S^e$ ground state and $|a\rangle$, $|E_{a,j}\rangle$ and $|b\rangle$, $|E_{b,k}\rangle$ the discrete and the continua parts belonging to the $2s^2 2p\,^2P^o$ and $2s2p^2\,^2D^e$ triply excited states, respectively. The indices j and k denote the multiple continua corresponding to different ionization thresholds. The $2s^2 2p\,^2P^o$ state is assumed excited by a synchrotron pulse of frequency $\omega_1 \simeq 142.3$ eV, in the presence of a laser of frequency ω_2 and of pulse duration preferably longer than that of the synchrotron (atomic units are used throughout). Both radiation sources are assumed linearly polarized along the same direction. The frequency ω_2 is chosen such as to be tunable around resonance with the transition $2s^2 2p\,^2P^o \rightarrow 2s2p^2\,^2D^e$, which means $\omega_2 \simeq 2.5$ eV. Note that the excited states $1s^2 2p\,^2P^o$ and $1s^2 3p\,^2P^o$ of Li are located about 1.85 and 3.8 eV, respectively, above $|g\rangle$, being thus far from resonance with ω_2. The transition induced by the relatively weak radiation at ω_1 can be described by a single rate, but the transition by the much stronger ω_2 cannot, requiring thus the strong (nonperturbative) coupling of the triply excited states. Given the short duration of both radiation sources involved and the fast autoionization of the resonances, spontaneous radiative decay may be safely ignored and the problem is conveniently formulated in terms of the time-dependent Schrödinger equation.

The wave function of the atom under the fields can then be expressed as $|\Psi(t)\rangle = C_g(t)|g\rangle + C_a(t)|a\rangle + C_b(t)|b\rangle + \sum_j \int dE_{a,j}\, C_{E_{a,j}}(t)|E_{a,j}\rangle + \sum_k \int dE_{b,k}\, C_{E_{b,k}}(t) \times |E_{b,k}\rangle$. This expression is substituted into the time-dependent Schrödinger equation $i\partial_t|\Psi(t)\rangle = H|\Psi(t)\rangle$,

 0031-9007/00/85(1)/42(4)$15.00

where H is written as $H = H_0 + V + D$, with $H_0|s\rangle = E_s|s\rangle$ ($s = g, a, b, E_{a,j}, E_{b,k}$), V being the configuration interaction coupling the discrete parts of the triply excited states to the continua and D the dipole interaction. Projection on the individual states in the expansion of $|\Psi(t)\rangle$ leads to a set of coupled differential equations containing amplitudes for the discrete parts as well as for the continua, including also laser-induced continuum-continuum couplings. Ignoring the latter is usually a well justified approximation at the intensities we need consider. We introduce the slowly varying amplitudes $c_g(t) = C_g(t)e^{iE_g t}$, $c_a(t) = C_a(t)e^{i(E_g+\omega_1)t}$, $c_b(t) = C_b(t)e^{i(E_g+\omega_1+\omega_2)t}$, $c_{E_{a,j}}(t) = C_{E_{a,j}}(t)e^{i(E_g+\omega_1)t}$, and $c_{E_{b,k}}(t) = C_{E_{b,k}}(t)e^{i(E_g+\omega_1+\omega_2)t}$ and keep only the time-dependent exponentials which are resonant with the photon frequencies (the rotating wave approximation). As the final step, we eliminate the continua adiabatically, which basically means that they are treated as sinks. We finally arrive at the following set of equations for the discrete-state amplitudes:

$$
\begin{aligned}
i\dot{c}_g &= \left[S_g - \frac{i}{2}\gamma_g\right]c_g + \tilde{\Omega}_{ga}\left(1 - \frac{i}{q_a}\right)c_a + \left[S_{gb} - \frac{i}{2}\gamma_{gb}\right]c_b\,,\\
i\dot{c}_a &= \tilde{\Omega}_{ag}\left(1 - \frac{i}{q_a}\right)c_g - \left[\delta_1 + \frac{i}{2}(\Gamma_a + \gamma_a)\right]c_a + \tilde{\Omega}_{ab}\left(1 - \frac{i}{q_{ab}}\right)c_b\,,\\
i\dot{c}_b &= \left[S_{bg} - \frac{i}{2}\gamma_{bg}\right]c_g + \tilde{\Omega}_{ba}\left(1 - \frac{i}{q_{ab}}\right)c_a - \left[\delta_1 + \delta_2 + \frac{i}{2}(\Gamma_b + \gamma_b)\right]c_b\,,
\end{aligned}
\tag{1}
$$

with $\delta_1 = \omega_1 - (E_a^r + S_a - E_g)$, $\delta_2 = \omega_2 - (E_b^r + S_b - E_a^r - S_a)$ the detunings, E_i^r and Γ_i ($i = a, b$) the resonance energy and width of the triply excited states, S_g, S_a, S_b, S_{gb} and $\gamma_g, \gamma_a, \gamma_b, \gamma_{gb}$ the laser-induced shifts and widths, $\tilde{\Omega}_{ga}$, $\tilde{\Omega}_{ab}$ the Rabi frequencies $\frac{1}{2}F(t)D_z$ with $F(t)$ the electric field amplitude, D_z the dipole along the polarization direction $\hat{z}$, and q_a and q_{ab} the Fano line shape parameter for the $|g\rangle \rightarrow |a\rangle$ and its generalization for the $|a\rangle \rightarrow |b\rangle$ transition. The laser-induced couplings between the discrete state $|a\rangle$ ($|b\rangle$) and the nonresonant parts of the continua $|E_{b,k}\rangle$, $k = 1, 2, 3, \ldots$ ($|E_{a,j}\rangle$, $j = 1, 2, 3, \ldots$) are expected to be very small since the dominant configurations do not share common orbitals. Thus, to an excellent approximation, we can neglect the ionization rates γ_a and γ_b to these nonresonant background parts. We can also neglect γ_{gb} and S_{gb} which describe a width and a shift due to the laser-induced coupling from $|g\rangle$ to $|b\rangle$ via the nonresonant part of the continua, $|E_{a,j}\rangle$. Equations (1) are readily solved once the atomic parameters are known. The ionization probability is then calculated as $P_{\text{ion}} = 1 - |c_g(T)|^2$, where T is the pulse duration of the synchrotron radiation. A detailed account of the derivation of Eq. (1) and the parameters entering it will be presented elsewhere. The spirit and steps of the derivation has much in common with the approach in Ref. [21], even though the latter was cast in terms of the resolvent operator.

The atomic parameters entering the model represent a major task and have been obtained through *ab initio* calculations based on the complex-scaling method, in combination with a fully correlated discretized basis constructed in terms of B splines. The calculations provide energies and widths, as well as the wave functions needed for the calculation of the dipole matrix elements. For given total angular momentum, spin, and parity, the three-electron eigenstates and energies are obtained by diagonalizing the complex rotated atomic Hamiltonian (see, e.g., the review [22] and references therein) in a basis spanned by three-electron basis functions, constructed by coupling of the angular momenta and spins of the three electrons and expressed in terms of antisymmetrized linear combinations of products of one-electron orbitals. The complex-rotation method allows us to represent the continuum of the outgoing (autoionized or laser-ionized) electrons in the limited box and simultaneously reveals the triply excited states through the complex energy, $E = E^r - i\Gamma/2$, where E^r is the position and Γ is the width of the resonance. The one-electron orbitals are expanded in terms of spherical harmonics and the radial parts $P_{n,l}(r) = rR_{n,l}(r)$ are subsequently expanded in terms of a number N (200) of B splines, of order $k = 5$ within a spherical box $[0; R]$: $P_{n,l}(r) = \sum_i^N c_i^{nl} B_i^k(r)$ defined on a sinusoidal grid. The boundary condition is $P_{n,l}(0) = P_{n,l}(R) = 0$ and the c_i^{nl}'s are determined by matrix diagonalization. The radius of the box has to be chosen judiciously for the physical problem at hand. Obviously, we need to be able to describe the high degree of correlation between three intrashell electrons. The demand on correlation and the fact that each electron in the triply excited state on the average sees a larger nuclear charge than if the K shell were not empty, favor a rather small box and we have indeed obtained good results with $R = (15\text{–}20)a_0$. Although, in principle, other ways of implementation with B splines can be contemplated, in practice, it is essential to have the one-electron orbitals available, as this allows a detailed choice of configurations for the final diagonalization, which makes the problem tractable with respect to computer memory and CPU time. We note in passing that a similar complex-scaling and B splines approach has recently been used to determine resonances in He^- [23].

TABLE I. Couplings all expressed in atomic units. The atomic unit of intensity is 3.51×10^{16} W/cm^2.

q_a	q_{ab}	Γ_a	Γ_b	$\tilde{\Omega}_{ga}$	$\tilde{\Omega}_{ab}$	γ_g
-2.9	48	4.83×10^{-3}	3.06×10^{-3}	$0.0091F_1(t)/2$	$2.1F_2(t)/2$	$0.06I_1(t)/4$

The complex scaling angle $\theta = 0.2$ and the basis were chosen so as to represent sufficiently accurately the triply excited states as well as the dominant decay channels with $1s2s$ and $1s2p$ cores. For the $2s^2 2p\,^2P^o$ resonance, with 501 three-electron basis states, we obtain $E_a^r = -2.24$ a.u. and $\Gamma_a = 131$ meV and for the $2s2p^2\,^2D^e$, with 520 basis states, $E_b^r = -2.14$ eV and $\Gamma_b = 83$ meV which compare well with benchmark [14] and other theoretical values [6]. For the ground state we find an energy of ~ -7.43 a.u. (to be compared with the table value of ~ 7.47 a.u.) with bases ranging from $\sim 300-900$ in size. The value for the dipole matrix element $D_{ga} = 0.0091$ a.u. is nevertheless in good agreement with the value 0.0117 a.u. extracted from the oscillator strength [24]. Also our value of $q_a = -2.9$ is in reasonable agreement with published results (-2.2) [1–3]. Table I summarizes our results for the couplings entering Eq. (1). Note that couplings between the triply excited states are here obtained for the first time. The field strength is the square root of the intensity in atomic units, $F_i(t) = \sqrt{I_i(t)}$, and $F_i(t) = F_i \sin(\frac{\pi t}{\frac{8}{3}\tau_i})$, with τ_i approximately the full widths at half maximum of the intensity $(i = 1, 2)$. If the laser pulse is much longer than the synchrotron one, $F_2(t)$ can be assumed constant. Note that the intensity of the synchrotron radiation is sufficiently weak to place the transition in the perturbative regime, which implies that the results presented later on can be scaled with respect to intensity and pulse duration. The ionization rate from the ground state to the nonresonant background, γ_g, is calculated via the spectral decomposition of the Green's function as is standard in complex scaling calculations of the photoaborption cross section [25], the difference here being that the lower triply excited state is excluded from the intermediate summation.

Figures 1 and 2 show the Li^+ photoion yield as a function of the detunings of the light sources for a series of intensities and detunings as detailed in the captions. In all cases studied, we see how the line shapes change drastically with the intensity of the laser coupling the $2s^2 2p\,^2P^o$ and $2s2p^2\,^2D^e$ triply excited states. At the lowest intensity, we have the line shape corresponding to the absence of a coupling between the two triply excited states. As the intensity is increased, a double peak structure builds up in Fig. 1, while we observe a window resonance in Fig. 2. The double peaked structure in Fig. 1 is due to the ac Stark splitting as a result of the laser-induced oscillation between $|a\rangle$ and $|b\rangle$. At the highest intensity in Fig. 1a, the separation between the two peaks is $\sim 2.8\Gamma_a$ and also equal to twice the Rabi frequency, $2\tilde{\Omega}_{ab}$. Hence the photoion spectrum carries direct information about the dipole matrix element between the triply excited states. In Fig. 1b, the splitting at the largest intensity is approximately equal to twice the generalized Rabi frequency, $2\sqrt{\tilde{\Omega}_{ab}^2 + \delta_2^2/4}$. In Fig. 1a we have chosen $\delta_2 = 0$ while in Fig. 1b $\delta_2 = \Gamma_a$ and we see how, e.g., the line shape at $I_1 = 1.4 \times 10^{11}$ W/cm^2 is significantly different in the two cases. The difference in height of the peaks in the structures of Fig. 1a is due to the slight asymmetry in the line shape of the triply excited $2s^2 2p\,^2P^o$ resonance (in absence of the laser). In Fig. 1b this difference is enhanced by asymmetric off-resonant excitation.

In Fig. 2 the frequency ω_1 is on resonance $(\delta_1 = 0)$ while the laser frequency ω_2 is varied. At the lowest intensity, no coupling to the $2s2p^2\,^2D^e$ triply excited state occurs, as demonstrated by the straight line in the figure. With increasing intensity, the triply excited states become coupled and a window resonance appears. We note that the minimum in the window moves to the left as the laser intensity is increased due to Stark splitting. We know of no other way that such coupling between triply excited states, or equivalent transitions exploring the highly correlated manifold of the four-body Coulomb problem, can be studied.

Although the results have been obtained by numerical integration of Eq. (1), it is interesting to note that an

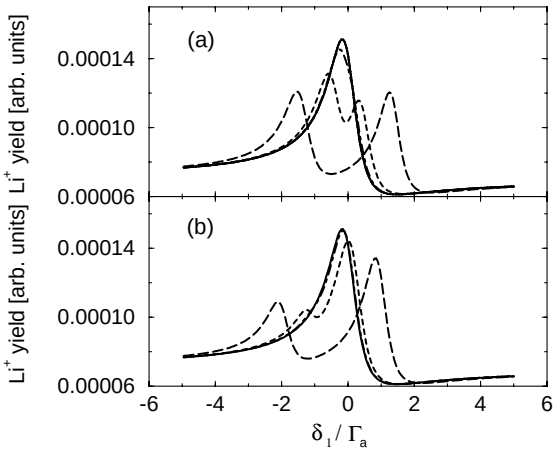

FIG. 1. Li^+ photoion yield as a function of the detuning δ_1, associated with the transition between the ground state and the $2s^2 2p\,^2P^o$ triply excited state. The laser coupling the $2s^2 2p\,^2P^o$ and $2s2p^2\,^2D^e$ states is (a) on resonance with the transition $(\delta_2 = 0)$ and (b) detuned off resonance by the width of $2s^2 2p\,^2P^o$ $(\delta_2 = \Gamma_a)$. The full, dot-dashed, dashed, and long-dashed curves correspond to $I_2 = 1.4 \times 10^7, 1.4 \times 10^{10}, 1.4 \times 10^{11}$, and 1.4×10^{12} W/cm^2, respectively. The intensity of the $\tau_1 = 10$ ps synchrotron pulse is $I_1 = 4 \times 10^8$ W/cm^2. We clearly see that the laser coupling induces an ac splitting of the line, the peak separation of which equals twice the Rabi frequency.

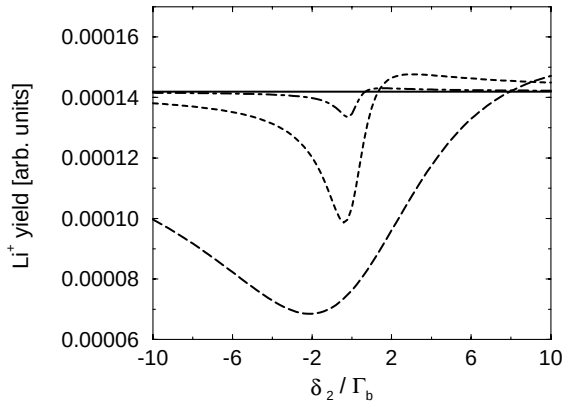

FIG. 2. Li^+ photoion yield as a function of the detuning δ_2, associated with the $2s^2 2p\,^2P^o \rightarrow 2s2p^2\,^2D^e$ transition. The synchrotron coupling the ground state with the $2s^2 2p\,^2P^o$ triply excited state is on resonance ($\delta_1 = 0$). The full, dot-dashed, dashed, and long-dashed curves correspond to $I_2 = 1.4 \times 10^6, 1.4 \times 10^{10}, 1.4 \times 10^{11}$, and 1.4×10^{12} W/cm^2, respectively. The intensity of the $\tau_1 = 10$ ps synchrotron pulse is $I_1 = 4 \times 10^8$ W/cm^2. With increasing laser intensity, the triply excited states become coupled and a window resonance appears.

analytical formula for the photoion rate R can be derived in the weak-probe limit ($\tilde{\Omega}_{ga} \ll 1$)

$$R \simeq \gamma_g + \frac{2\tilde{\Omega}_{ga}^2}{|f(\delta_1, \delta_2)|^2} \times \mathrm{Re}\left[i\left(1 - \frac{i}{q_a}\right)^2 \left(\delta_1 + \delta_2 + \frac{i}{2}\Gamma_b\right) f^*(\delta_1, \delta_2) \right], \quad (2)$$

with $f(\delta_1, \delta_2) = (\delta_1 + \delta_2 + \frac{i}{2}\Gamma_b)(\delta_1 + \frac{i}{2}\Gamma_a) - \tilde{\Omega}_{ab}^2(1 - \frac{i}{q_{ab}})^2$, which accounts qualitatively for the variations in Figs. 1 and 2.

In conclusion, we have presented what we believe to be the first results on stimulated transitions between highly correlated triply excited states in a fundamental system. In view of ongoing developments in synchrotron and other bright short-wavelength sources combined with laser technology, our findings point to a unique tool for the exploration of manifolds of triply excited states and the unusual correlation properties they entail. Not only can couplings between such states be thus probed, but also selective study of decays into single- or double-electron breakup can be pursued for states lying in energy above the first doubly excited state of Li^+. For example, in view of the presented results, we can realistically contemplate the control, in a channel specific way, of the decays of triply excited states above 151.7 eV where the phenomenon of two-step double autoionization from triply excited Li via doubly excited Li^+ to Li^{2+} becomes possible [11]. Specifically, the excitation of a state like $2s2p(^1P)3s\,^2P^o$ from the ground state in the presence of a laser coupling it to an even parity state (like, e.g., $2s2p^2\,^2D^e$) which decays predominately to Li^+ would single out that route of decay of the initially excited resonance, instead of the multiple cascade that it would otherwise follow.

L. B. M. thanks A. Saenz for discussions on complex scaling and acknowledges support from the Danish Natural Science Research Council (Grant No. 9800755). P. S. acknowledges support by the Feodor Lynen-Stipendium (V-3FLF-106691) from the Alexander von Humboldt-Stiftung. LPTMS is a Unité de recherche de l'Université Paris XI associée au CNRS.

[1] L. M. Kiernan *et al.,* Phys. Rev. Lett. **72,** 2359 (1994).
[2] L. M. Kiernan *et al.,* J. Phys. B **28,** L161 (1995).
[3] Y. Azuma *et al.,* Phys. Rev. Lett. **74,** 3768 (1995).
[4] Y. Azuma *et al.,* Phys. Rev. Lett. **79,** 2419 (1997).
[5] L. Journel *et al.,* Phys. Rev. Lett. **76,** 30 (1996).
[6] S. Diehl *et al.,* Phys. Rev. Lett. **76,** 3915 (1996).
[7] D. Cubaynes *et al.,* Phys. Rev. Lett. **77,** 2194 (1996).
[8] S. Diehl *et al.,* Phys. Rev. Lett. **79,** 1241 (1997).
[9] S. Diehl *et al.,* Phys. Rev. A **56,** R1071 (1997).
[10] S. Diehl *et al.,* Phys. Rev. Lett. **84,** 1677 (2000).
[11] S. Diehl *et al.,* J. Phys. B **30,** L595 (1997).
[12] K. Berrington and S. Nakazaki, J. Phys. B **31,** 313 (1998).
[13] L. VoKy *et al.,* Phys. Rev. A **58,** 3688 (1998).
[14] K. T. Chung and B. C. Gou, Phys. Rev. A **52,** 3669 (1995).
[15] K. T. Chung and B. C. Gou, Phys. Rev. A **53,** 2189 (1996).
[16] T. Morishita and C. D. Lin, Phys. Rev. A **59,** 1835 (1999).
[17] T. Morishita, Y. Li, and C. D. Lin, Phys. Rev. A **58,** 4214 (1998).
[18] T. Morishita and C. D. Lin, Phys. Rev. A **57,** 4268 (1998).
[19] T. Morishita, O. I. Tolstikhin, S. Watanabe, and M. Matsuzawa, Phys. Rev. A **56,** 3559 (1997).
[20] X. Yang, C. G. Bao, and C. D. Lin, Phys. Rev. Lett. **76,** 3096 (1996); Phys. Rev. A **53,** 3934 (1996).
[21] P. Lambropoulos and P. Zoller, Phys. Rev. A **24,** 379 (1981).
[22] A. Junker, Adv. At. Mol. Phys. **18,** 207 (1982).
[23] N. Brandefelt and E. Lindroth, Phys. Rev. A **59,** 2691 (1999).
[24] K. T. Chung, Phys. Rev. A **25,** 1596 (1982).
[25] J. M. Rost, K. Schulz, M. Domke, and G. Kaindl, J. Phys. B **30,** 4663 (1997).