Series of Doubly Excited Quartet States of He$^-$

I. Yu. Kiyan,* U. Berzinsh,† and D. Hanstorp
Department of Physics, Chalmers University of Technology and Göteborg University, SE-412 96 Göteborg, Sweden

D. J. Pegg
Department of Physics, University of Tennessee, Knoxville, Tennessee 37996

(Received 1 June 1998)

Twelve previously unobserved Feshbach resonances associated with the autodetaching decay of doubly excited states of He$^-$ have been observed in the process of photodetachment. Seven resonant states of ^4P symmetry and one of ^4S symmetry have been identified in the energy range which encompasses the He($n = 4, 5$) thresholds. Their measured energies and widths agree with recent calculations. A functional form representing the energies of members of the ^4P series has been derived. This form is fundamentally different from the Rydberg-dipole formula that describes doubly excited states of H$^-$. [S0031-9007(98)07265-2]

PACS numbers: 31.50.+w, 32.80.Fb, 32.80.Gc

Investigations of the dynamics of a pair of excited electrons can provide valuable insights into the general problem of correlated motion in many-particle systems. Negative ions exhibit an enhanced sensitivity to correlation effects due to the suppression of the normally dominant long range Coulomb force associated with the core. The autodetaching decay of a doubly excited state is manifested as a resonance in the photodetachment cross section in the vicinity of an excited state threshold. Measurements of the energies and widths of such resonances provide sensitive tests of the ability of theory to go beyond the independent electron model.

In the simplest two-electron ion H$^-$, double excitation involves an outer electron moving in the short range permanent dipole field arising from the nucleus and the inner electron. A series of resonances associated with the decay of these states have been predicted [1] and observed [2].

In the present paper we describe an experimental investigation of doubly excited quartet states in the three-electron He$^-$ ion. Complementary information on the corresponding doublets has been previously obtained in electron scattering experiments [3]. The lowest energy state of the He$^-$ ion is the metastable state $(1s2s2p)\,^4P$, which is bound by 77.516(6) meV relative to the $(1s2s)\,^3S$ state of He [4]. This ion can be considered an effective two-electron system since the small but inert He$^+(1s)$ core appears to only slightly perturb the motion of the two active electrons [5]. Its presence does, however, lift the degeneracy characteristic of the H atom excited state thresholds. Consequently, the outer electron is bound in an even shorter range field of an induced dipole. From an experimental viewpoint high lying states of He$^-$ are more accessible than those of H$^-$ to high resolution measurements since excitation energies in the case of He$^-$ fall in the range of commercially available dye lasers. In this experiment we have investigated the He$(3\,^3P) + e^-(\epsilon p)$ partial photodetachment cross section in the ranges 3.7–4.0 eV and 4.1–4.3 eV. These ranges encompass the He($n = 4$) and He($n = 5$) thresholds, respectively. We have identified three resonances of ^4P symmetry below the He$(4\,^3P)$ threshold and four resonances of the same symmetry below the He$(5\,^3P)$ threshold. In addition, a resonance of ^4S symmetry below the He$(4\,^3S)$ threshold has been identified. We have also observed four other resonances that we are unable to positively identify at the present time.

A collinear laser-negative ion beam apparatus [6] has been used in the measurement. The experimental method is based on a selective excitation-detection scheme that involves resonance ionization spectroscopy. In the first step, a laser of frequency ω_1 populates a doubly excited state of ^4S, ^4P, or ^4D symmetry in a transition from the ^4P ground state of the He$^-$ ion. This is followed by the autodetachment of this state via the He$(3\,^3P) + e^-(\epsilon p)$ channel. In the second step, the He atoms produced in the $3\,^3P$ state by autodetachment are resonantly excited into a Rydberg state by use of a laser of frequency ω_2. The Rydberg atoms thus produced are subsequently ionized in a static electric field. The signal of He$^+$ ions was recorded as a function of frequency ω_1, while the frequency ω_2 was held constant on the transition to the Rydberg state. Since the intensity of laser ω_2 and the ion beam current are held constant during a scan, the He$^+$ signal, normalized to the intensity of laser ω_1, is proportional to the partial photodetachment cross section.

Figure 1 shows the He$(3\,^3P) + e^-(\epsilon p)$ partial cross section below the He($n = 4$) and He($n = 5$) thresholds. In the upper figure a cusp at the $1s4s\,^3S$ threshold is apparent. Fits of the experimental data to Shore profiles [7] with linear backgrounds have been performed in order to determine energies and widths of the resonances labeled (a–f) and (g–l). Closely spaced resonances, such as (a–b), (c–e), and (h–k), have been fitted together to a sum of Shore profiles. Solid lines in Fig. 1 represent the best fits. The extent of each line corresponds to

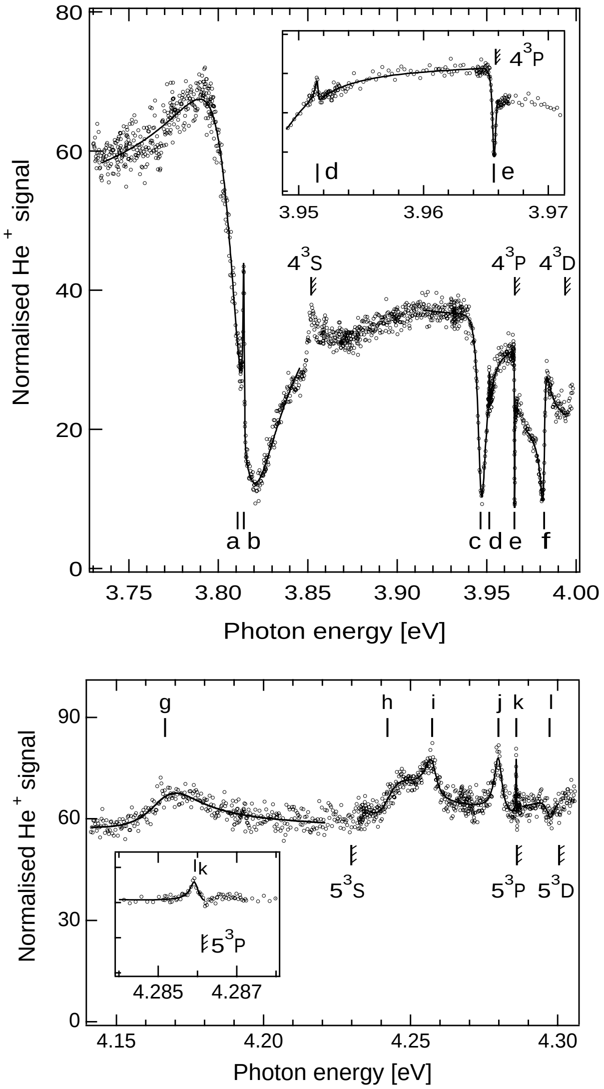

FIG. 1. Partial cross sections for photodetachment of He$^-$ via the He($3\,^3P$) + $e^-(\epsilon p)$ channel. The upper and lower spectra show the region below the He($n = 4$) and He($n = 5$) thresholds, respectively. Circles represent the experimental data. The fits of the data to sums of Shore profiles with linear backgrounds are shown by solid lines. The energies of the resonances (a–l) obtained from the fits are represented by short vertical lines. The Doppler shift has been taken into account in the final determination of the energy scale. The insets show the regions near the $4\,^3P$ and $5\,^3P$ thresholds in greater detail.

the range of the individual fits. Resonance energies and widths obtained from the fits are presented in Table I, together with the results of recent calculations. The quoted uncertainties arise primarily from the statistical scatter of the fitted resonance parameters. It can be seen that, in general, there is a good agreement between the experimental and theoretical results. The most significant disagreement concerns the widths of two resonances labeled e and k. In this case, our measured widths are an order of magnitude narrower than the theoretical values of Bylicki [8]. Presumably this is due to the fact that it is difficult to calculate the parameters of these resonances since they are so close to the $4\,^3P$ and $5\,^3P$ thresholds, respectively. By comparison of resonance energies and widths with complex rotation calculations [8,9], resonances a, c, e, g, i, j, and k have been identified as being associated with doubly excited states of ^4P symmetry and the resonance b with a state of ^4S symmetry. Angular correlations in He$^-$ lead to a breakdown of the independent electron model. We continue, however, to label states according to the major configuration $nlml$, where n and m correspond to the principal quantum numbers of the inner and outer electrons, respectively.

Other resonances observed in this experiment (d, f, h, l) cannot be positively identified at this time due to a lack of theoretical input. We can, however, make speculations based on their resonance positions and widths. Some of the unidentified resonances are, presumably, of ^4S or ^4D symmetry, since they did not appear in the calculations of ^4P resonances [8]. Resonance d is narrow, which indicates it is an intershell resonance. Resonances f and l lie between the ^3P and ^3D thresholds. They are relatively broad and could be intrashell resonances with the major configuration of the type $4d^2$ and $5d^2$, respectively.

A modified Rydberg formula has been previously used to parametrize the energies of highly correlated two-electron states of nl^2 configuration, the intrashell resonances ($m = n$) [3]:

$$E(n,n) = -\frac{(1 - \mu)^2}{(n - \delta)^2}\,, \tag{1}$$

where $E(n,n)$, in a.u., is the energy relative to the double detachment limit, μ is a screening parameter, and δ is a quantum defect. Fitting Eq. (1) to the energies of the $4p^2$ and $5p^2$ intrashell resonances of ^4P symmetry measured in this experiment yields the values $\mu = 0.1699$ and $\delta = -0.2572$. These values are quite similar to those obtained for the intrashell resonances of H$^-$ ($\mu = 0.1659$, $\delta = -0.333$) [2]. This result confirms the assumption that the inner electron of He$^+$ is inert and that there is, in general, some similarity between the spectra of doubly excited states of H$^-$ and He$^-$.

The observed intershell resonances ($m \neq n$) of ^4P symmetry consist of a series of states of configuration $npmp$ converging to a $n\,^3P$ excited state threshold of the parent atom. Here one finds a qualitative difference in the spectra of H$^-$ and a nonhydrogenic negative ion such as He$^-$. The degeneracy of excited states of the H atom makes the H$^-$ ion a special case because here the outer electron moves in a field of a permanent dipole. The potential has an asymptotic form $\sim -1/r^2$ and it can, in principle, support an infinite number of states that exponentially converge on the parent threshold [12]. The energies of the intershell states in H$^-$ follow a Rydberg-dipole formula [1].

In a nonhydrogenic negative ion such as He$^-$, the outer electron moves in a field of a dipole induced in the

TABLE I. Energies E_r (eV) and widths Γ (meV) of resonances below the He($n = 4$) thresholds (a)–(f) and He($n = 5$) thresholds (g)–(l). Energies are relative to the $1s2s2p\,^4P$ state of He$^-$. Labels refer to the resonances shown in Fig. 1.

		This work		Theory	
Label	State	E_r	Γ	E_r	Γ
a	$1s4p^2\,^4P$	3.8109(6)	30(2)	3.8113[a] 3.81138[b] 3.81895[c]	26.7[a] 28.18[b] 23.48[c]
b	$1s4s5s\,^4S$	3.81429(9)	0.8(2)	3.8146[d]	1.0[d]
c	$1s4p5p\,^4P$	3.9466(3)	5.4(6)	3.9468[a] 3.94754[b]	6.5[a] 5.97[b]
d	⋯	3.9515(1)	0.3(2)	⋯	⋯
e	$1s4p6p\,^4P$	3.96564(3)	0.33(5)	3.967[a]	3.8[a]
f	⋯	3.9822(2)	2.4(4)	⋯	⋯
g	$1s5p^2\,^4P$	4.167(5)	22(8)	4.1687[a] 4.1376[b] 4.17383[c]	21.8[a] ⋯ 17.4[c]
h	⋯	4.242(6)	11(8)	⋯	⋯
i	$1s5p6p\,^4P$	4.257(1)	5(3)	4.2597[a]	7.1[a]
j	$1s5p7p\,^4P$	4.2799(6)	3.2(6)	4.283[a]	3.8[a]
k	$1s5p8p\,^4P$	4.28594(8)	0.25(8)	4.288[a]	2.2[a]
l	⋯	4.297(2)	4(4)	⋯	⋯

[a]Ref. [8], [b]Ref. [10], [c]Ref. [11], [d]Ref. [9].

core. It is represented by an asymptotic potential $-\alpha/2r^4$, where α is dipole polarizability of the core. Such a potential is able to support a finite number of bound states. The functional dependence of their energies $E(n,m)$ is, therefore, expected to be different from the Rydberg-dipole formula which characterizes the energies of analogous states in the H$^-$ ion.

Let us consider the semiclassical motion of the outer electron in a potential arising from an induced dipole and apply the Bohr-Sommerfeld quantization rule to determine the spectrum of bound energies. In our model we assume that the radius r_0, which separates the asymptotic and inner regions, is much smaller than the classical turning point r_b: $r_0 \ll r_b$. Then, in the inner region the electron momentum is primarily determined by the depth of the potential, and the contribution of this region to the semiclassical phase can be assumed constant. Under this condition, the phase over half a period of the motion can be written as (a.u. are used below)

$$\Phi(E) = \Phi_0 + \int_{r_0}^{r_b} \sqrt{\frac{\alpha}{r^4} - \frac{l(l+1)}{r^2} + 2E}\, dr\,, \quad (2)$$

where Φ_0 is a contribution from the $r \ll r_0$ region, E is the electron energy, and l is the angular momentum. The integral in Eq. (2) can be expressed in terms of elliptic integrals. By expanding the subsequent equation into a series in $(r_0/r_b)^k$ and omitting terms with $k \geq 1$, we obtain

$$\Phi(E) = \Phi_{\max} - \frac{\pi}{2}[l(l+1)]^{1/2} \times \left[\frac{f(y)}{f(0)}(1+\lambda)^{1/4} - 1\right], \quad (3)$$

where

$$\lambda = -8E\alpha/[l(l+1)]^2, \qquad y = (1 - 1/\sqrt{1+\lambda})/2\,,$$

$$\Phi_{\max} = \Phi_0 + \frac{\sqrt{\alpha}}{r_0} - \frac{\pi}{2}[l(l+1)]^{1/2} \quad (4)$$

is the value of the phase at $E = 0$,

$$f(y) = 2F(y) - K(y) + (2y-1)F'(y) + (1-y)K'(y)\,.$$

Here $K(y)$, $F(y)$ are complete elliptic integrals of the first and second kinds, respectively, and $f(y)$ is a monotonic function of y which varies from $f = 3\pi/4$ at $y = 0$ to $f \simeq 1.275$ at $y = 1/2$.

When $\Phi/\pi - 1/2 = m$, where m is an integer number, the corresponding value of $E = E(n,m)$ is the energy of a bound state, and m is its principal quantum number. The inequality $\lambda \gg 1$ is satisfied for the resonance energies of all members of the $4pmp$ and $5pmp$ series listed in Table I (the exception is the $4p6p$ state for which a less rigorous inequality $\lambda > 1$ is valid). In this limit, using Eqs. (3) and (4), we obtain

$$E(n,m) = -\frac{2C^4}{\alpha}(m_{\max} - m)^4, \quad (5)$$

where the left-hand side is the energy of a series member $E(n,m)$ relative to the threshold energy $E(n)$, $C = f(0)/f(1/2) \simeq 1.848$ is a constant, and $m_{\max} = \Phi_{\max}/\pi - 1/2$ is a noninteger parameter. Its integer part is the maximum quantum number of the outer electron in the $nlml$ series. In the present case the orbital angular momenta of the inner and outer electrons

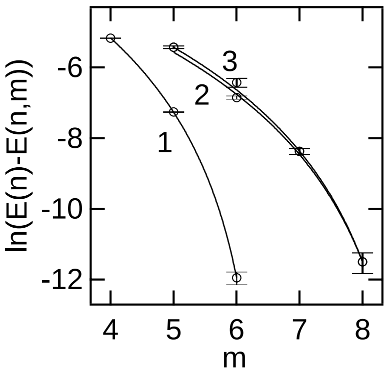

FIG. 2. Energies of resonances of the $1s4pmp\,{}^4P$ and $1s5pmp\,{}^4P$ series listed in Table I vs the principal quantum number m of the outer electron. Solid lines represent the fits of the measured energies to Eq. (5): Curve 1—$4pmp$ series; curve 2—$5pmp$ series; curve 3—$5pmp$ series under the assumption that the $5p6p$ configuration corresponds to the resonance labeled h instead of i.

are the same but this is not a necessary condition for the application of Eq. (5). It should be noted that in the case $l = 0$ the inequality $\lambda \gg 1$ doesn't need to be met for Eq. (5) to be valid.

The energies of the $4pmp$ and $5pmp$ series members obtained in the present experiment have been fitted to Eq. (5) using two fit parameters, $m_{\max}$ and α. The values $m_{\max} = 6.45$, $\alpha = 147\,392$ a.u. and $m_{\max} = 8.88$, $\alpha = 1\,389\,170$ a.u. were obtained in a fit of the $4pmp$ and $5pmp$ series, respectively. Figure 2 shows the measured energies of members of the $4pmp$ and $5pmp$ series vs the quantum number m, together with the curves calculated according to Eq. (5). The energies are in a.u. and are relative to the corresponding parent threshold. It can be seen that the experimental data follow the predicted theoretical dependence. Equation (5) describes the $5pmp$ series better, however, if we assign the $5p6p$ configuration to the resonance labeled h, instead of i (see curve 3). Resonances h and i are close lying and overlapping and only one state of ${}^4P$ symmetry is predicted in this region [8]. The resonance i is closer to the calculated value. We believe that the $5p6p$ state is perturbed by the presence of another state and is shifted from its expected position. It should be noted that a Rydberg-dipole formula, derived for corresponding states in the H$^-$ [1], would exhibit a linear dependence on the logarithmic scale of Fig. 2.

We estimated lower limits of the dipole polarizabilities of the He($4\,{}^3P$) and He($5\,{}^3P$) states using available oscillator strength data. Despite the simplicity of the theoretical model described above, the values of polarizabilities obtained from the fits were found to agree with the estimates of the lower limits to within approximately 15% in the case of He($4\,{}^3P$) and 30% in the case of He($5\,{}^3P$)).

In conclusion, we have determined the energies and widths of twelve previously unobserved doubly excited quartet states of He$^-$. The parameters were obtained from an analysis of resonance structure in the He($3\,{}^3P$) + $e^-(\epsilon p)$ partial photodetachment cross section below the He($n = 4$) and He($n = 5$) thresholds. Energies of the ${}^4P$ states of the $4pmp$ and $5pmp$ series are found to obey a semiempirical form [Eq. (5)] derived in the semiclassical approximation. Similarities and differences in the spectra of doubly excited states of He$^-$ and H$^-$ have been found. In both cases, the energies of intrashell resonances are well described by a modified Rydberg formula, Eq. (1). Similar values for the screening parameter and quantum defect were obtained for He$^-$ and H$^-$. However, the energies of a series of intershell resonances $nlml$, converging to the nl threshold, has been found to have a fundamentally different functional dependence on the quantum number m in He$^-$ than in H$^-$. This is clearly due to the different nature of the interaction of the outer electron with the atomic core in the asymptotic limit.

Financial support for this research has been provided by the Swedish National Science Council (NFR). Personal support has been received for I. K. from the Wenner-Gren Center Foundation and the Royal Swedish Academy of Sciences, and for U. B. from the Swedish Institute. D. J. P. acknowledges support from the Royal Swedish Academy of Sciences through its Nobel Institute of Physics and the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

---

*Permanent address: Russian Academy of Sciences, General Physics Institute, Vavilova St. 38, 117 942 Moscow, Russia.

†Permanent address: Institute of Atomic Physics and Spectroscopy, University of Latvia, LV 1586 Riga, Latvia.

[1] For example, H. R. Sadeghpour and C. H. Greene, Phys. Rev. Lett. **65**, 313 (1990).
[2] For example, P. G. Harris *et al.*, Phys. Rev. Lett. **65**, 309 (1990).
[3] J. N. H. Brunt, G. C. King, and F. H. Read, J. Phys. B **10**, 433 (1977); S. J. Buckman and D. S. Newman, J. Phys. B **20**, L711 (1987).
[4] P. Kristensen *et al.*, Phys. Rev. A **55**, 978 (1997).
[5] M. Le Dourneuf and S. Watanabe, J. Phys. B **23**, 3205 (1990).
[6] G. Haeffler *et al.*, Phys. Rev. A **53**, 4127 (1996).
[7] B. W. Shore, Phys. Rev. **171**, 43 (1968).
[8] M. Bylicki, J. Phys. B **30**, 189 (1997).
[9] N. Brandefelt and E. Lindroth (private communication).
[10] J. Xi and C. Froese Fischer, Phys. Rev. A **53**, 3169 (1996).
[11] S. I. Themelis and C. A. Nicolaides, J. Phys. B **28**, L379 (1995).
[12] M. Gailitis and R. Damburg, Zh. Eksp. Teor. Fiz. **44**, 1644 (1963) [Sov. Phys. JETP **17**, 1107 (1963)].