Observation of the $(2p,nd)\,{}^1P^o$ Double-Excitation Rydberg Series of Helium

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Double-excitation Rydberg resonances of He below the $N=2$ threshold of He^+ were studied with an energy resolution of $\cong 4$ meV by photoionization using synchrotron radiation. All three Rydberg series of ${}^1P^o$ resonances accessible by photoabsorption, including the hitherto "missing" $(2p,nd)\,{}^1P^o$ series, were resolved. This settles a long-standing discrepancy between experiment and theoretical predictions and establishes a firm basis for testing the accuracy of atomic multiconfiguration calculations.

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Doubly excited He is the archetypical example for autoionization phenomena, since it represents the most fundamental autoionizing atomic system, which is—due to its relative simplicity—also readily accessible to theoretical treatment. After the initial pioneering experimental [1] and theoretical [2] work, progress in this field was relatively slow due to severe spectroscopic limitations, in particular of available photon sources in the 60- to 80-eV range. In recent years, however, considerable attention has been paid to these states, as well as to related states in H^-, from both the theoretical [3–7] and the experimental [8] point of view.

Upon excitation of both electrons to states below the $N=2$ ionization threshold of the He^+, IP_2, final states with six different symmetries $({}^1S^e, {}^3S^e, {}^1P^o, {}^3P^o, {}^1D^e, {}^3D^e)$ can be populated, each containing up to three Rydberg series [3,9,10]. In photoexcitation, the dipole-selection rule allows only ${}^1P^o$ final states, which reduces the number of observable Rydberg series to three [10]: Only two of them, the $(sp,2n+)\,{}^1P^o$ and the $(sp,2n-)\,{}^1P^o$ series could be observed until now [3,8], while the third $(2p,nd)\,{}^1P^o$ series was missing [11]. This situation has led to considerable confusion, since the various theoretical calculations are characterized by substantial discrepancies with respect to the energies and widths of the $(2p,nd)\,{}^1P^o$ states [5–7,11–15].

In the present Letter we report on the first observation of the four lowest states of the $(2p,nd)\,{}^1P^o$ series by high-resolution photoabsorption spectroscopy using synchrotron radiation. With a resolving power of $E/\Delta E \cong 16000$ combined with high photon flux, the $(sp, 2n+)\,{}^1P^o$ and $(sp,2n-)\,{}^1P^o$ series were in addition resolved up to the $n=20$ and the $n=11$ state, respectively. These results complete the identification of the simplest double-excitation states of He, i.e., the three Rydberg series of states accessible by photoexcitation below IP_2. They also clarify a long-standing theoretical controversy concerning the correct energies of these states and provide a means to check the quality of existing as well as of future atomic multiconfiguration calculations for He.

The measurements were performed with the high-resolution SX700/II monochromator operated by the Freie Universität Berlin at BESSY. With this beam line, a resolving power of $E/\Delta E \geq 10000$ at $h\nu=60$ eV had previously been achieved [8,16]. In the present work, the resolution at high photon flux could be further improved by making use of a newly installed 2442-line/mm grating as well as of an improved small-source-high-current beam optics of BESSY. Photon energies were calibrated by measuring the C $1s^{-1}\pi^*$ resonance of gas-phase CO, with its ground-vibrational state at $h\nu=287.40$ eV [16]. Photoabsorption spectra were recorded by monitoring the total ionization current as a function of photon energy with an ionization chamber of 10-cm active length filled with 0.1 to 1 mbar of He. A 1500-Å-thick Al(1% Si) window served to separate the gas-filled volume from the ultrahigh-vacuum monochromator.

Figure 1 displays the photoionization spectrum of He below IP_2: Part (a) gives an overview of the spectrum, while (b) and (c) show the upper part of the spectrum with increasing magnification of the energy scale from the 4+ and 10+ states, respectively, up to IP_2. Note that the total width of spectrum (c) is only 150 meV. The $(sp,2n+)$ states, which dominate the spectrum, could be resolved up to $n=20$ in (c). As discussed previously, the bare number of resolved $(sp,2n+)$ states provides already a good quantitative estimate for the monochromator resolution based on simulation spectra [8]: $n=20$ corresponds to $\Delta E \cong 4$ meV, by far the best value achieved so far in this energy region.

The spectrum in Fig. 1 contains also weak lines from the autoionization decay of the $(sp,2n-)$ states, which were previously observed up to $n=7$ only [8], but are now identified up to $n=11$. The $(sp,2n-)$ states are at lower energies than the respective $(sp,2n+)$ states and are observed with $\cong 75$ times smaller spectral intensities due to their much narrower lifetime widths [1,8,12]. The lowest six of the $(sp,2n-)$ resonances are shown in more detail in Fig. 2, recorded with a density of two points per meV. Except for $n=3-$, all of the $(sp,2n-)$ signals exhibit an additional peak in the leading-edge region, marked by solid vertical bars. For $n=4-$, this additional peak is well separated by $\cong 16$ meV from the main resonance, while it gradually approaches the $(sp,2n-)$ state with increasing n: For $n=7-$, the separation has shrunk to a mere $\cong 4$ meV.

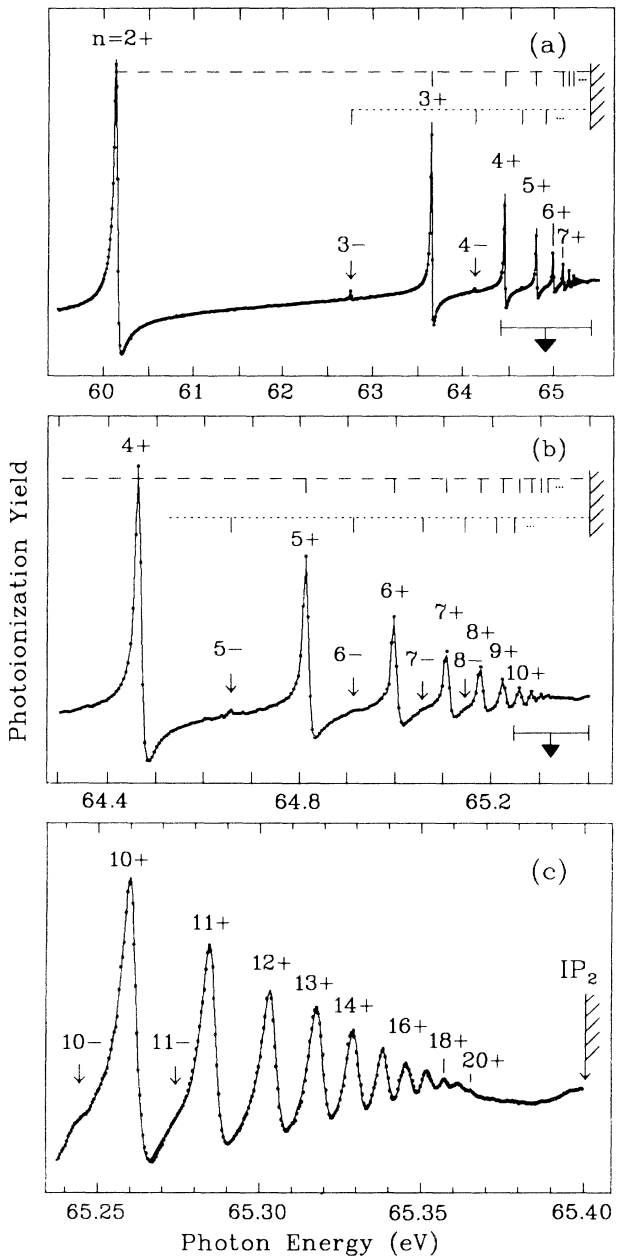

FIG. 1. Autoionizing resonances of doubly excited He below the $N=2$ threshold (IP_2) of He^+

These additional peaks are obviously not caused by a splitting of the $(sp,2n-)$ series, but represent members of a third series converging towards IP_2, as do the $(sp,2n+)$ and the $(sp,2n-)$ series: We identify this third Rydberg series with the hitherto "missing" $(2p,nd)^1P^o$ states. It is clear now that these states could not be observed before, since both high energy resolution and high photon flux are required to separate them from the $(sp,2n-)$ states as well as from noise.

Before discussing the new results in more detail, a few comments on the various classification schemes for the double-excitation states of He appear appropriate. Besides the early classification by Madden and Codling used here [1], a scheme based on the correlation quantum numbers $(K,T)^A$ was introduced by Herrick and Sinanoglu [9] and Lin [10], where the states are denoted by $N(K,T)^A_n$; here, N represents the threshold below which the state exists (the state of the inner electron), while n is the radial quantum number of the outer electron. In this scheme, the $(sp,2n+)$, $(sp,2n-)$, and $(2p,nd)$ series are denoted as $2(0,1)^+_n$, $2(1,0)^-_n$, and $2(-1,0)^0_n$, respectively. In a third scheme introduced by Lipsky and Conneely, the three series are just distinguished by a, b, and c, leading to the notations $(2,na)$, $(2,nb)$, and $(2,nc)$ [12].

The double-excitation spectra of He are dominated by the Rydberg series with $K=N-2$ and $T=1$ [8], i.e., by the $(sp,2n+)$ series for $N=2$. This is mainly a consequence of the much longer lifetimes of the other series. Since the lifetime of a state n in a given Rydberg series is $\propto n^{*3}$, with the effective quantum number $n^*=n-\mu$ (μ = quantum defect) [13], reduced widths ($\Gamma_n n^{*3}$) can be introduced. Theory predicts the reduced widths of the $(sp,2n-)$ and $(2p,nd)$ series to be smaller by factors of $\cong 10^2$ and up to $\cong 10^4$, respectively, than the one of the $(sp,2n+)$ series [6,12]. The extremely narrow widths of the $(2p,nd)$ states, with the theoretical predictions for the lowest $(2p,3d)$ state ranging from 4.2×10^{-5} meV [6] via $\cong 4.5\times10^{-4}$ meV [12,14,15] to 3.0×10^{-3} meV [5], make it difficult to observe these states.

The spectra in Fig. 2 were least-squares fitted by assuming Fano-type profiles for the $(sp,2n-)$ lines, convoluted with the monochromator function, while the profiles of the $(2p,nd)$ resonances were assumed to represent the monochromator function alone; in addition, a slanted background had to be added (dash-dotted line), which is caused by the neighboring $(sp,2n+)$ resonances not shown in Fig. 2. The solid lines through the data points represent the results of this analysis, while the dashed and solid components give the $(sp,2n-)$ and $(2p,nd)$ resonances, respectively. Note that the well-separated $(2p,3d)$ resonance line—due to its extremely narrow natural width—represents directly the monochromator function with a total width of $\cong 4.1$ meV (FWHM), corresponding to a resolving power of $E/\Delta E\cong 16000$ at $h\nu=64$ eV. The monochromator function can be well described by the weighted sum of a Gaussian (60%) and a Lorentzian (40%) profile.

A summary of the present results for the resonance energies of the $(sp,2n-)$ and $(2p,nd)$ states is given in the upper part of Table I (column 2); in the lower part, the energy separations, ΔE (in meV), between the $(sp,2(n+1)-)$ and the $(2p,nd)$ states are listed. They are all positive, amounting to 16.4 ± 0.4 meV for the $4-/3d$ pair, and decreasing to 4 ± 2 meV for the $7-/6d$ pair. Just as the other two $N=2$ series, the $(2p,nd)$ states converge to $IP_2=64.402$ eV. Since the $(2p,nd)$ states are so close in energy to the corresponding $(sp,2(n+1)-)$

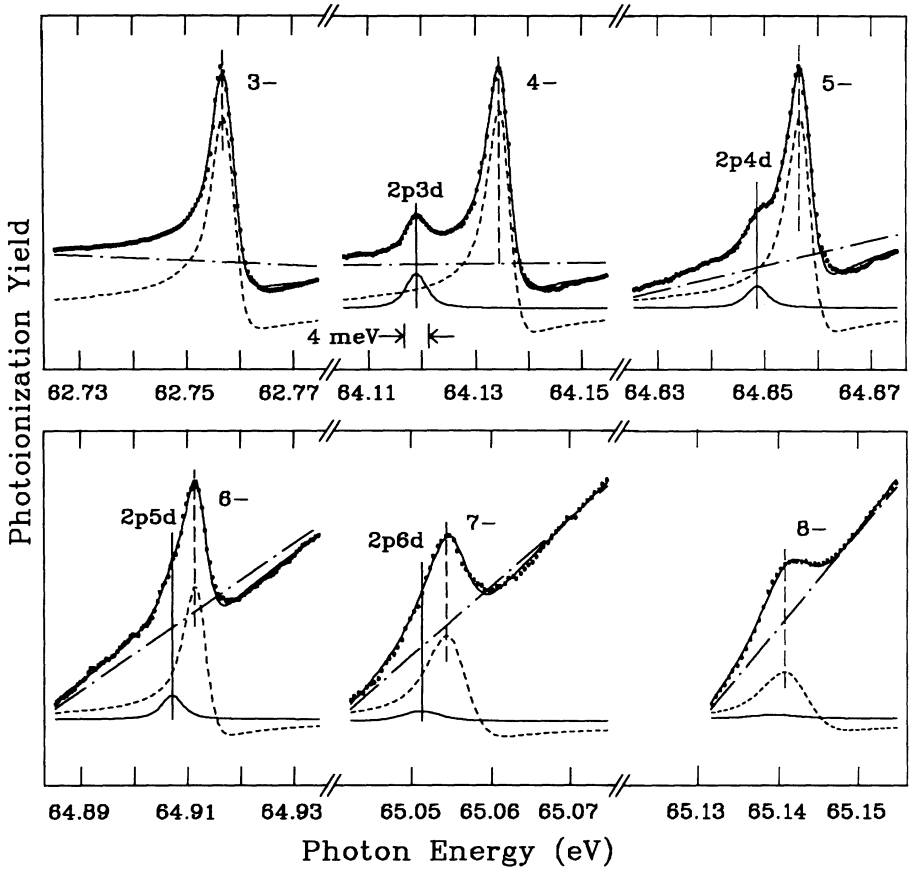

FIG. 2. $(sp,2n-)^1P^o$ and $(2p,nd)^1P^o$ resonances of doubly excited He.

TABLE I. Resonance energies of the $(sp,2n-)$ and $(2p,nd)$ states, and energy separations (present work: column 2; theory: columns 3–9). The numbers in parentheses are error bars in units of the last digit. Theoretical energies published in atomic units were converted to eV with 1 a.u. = 27.2106 eV and $IP_\infty = 79.0078$ eV.

State(s)	This work	Lipsky and Conneely (Ref. [12])	Ho (Ref. [14])	Moccia and Spizzo (Ref. [15])	Wu and Xi (Ref. [6])	Macias *et al.* (Ref. [5])	Chung and Chen (Ref. [11])	Burke and McVicar (Ref. [13])
				Resonance energy (eV)				
3−	62.7580(2)	62.7750	62.7611	62.7559	62.7616	62.7549	62.7606	62.7726
3*d*	64.1189(2)	64.1288	64.1211	64.1167	64.1272	64.1233	64.1396	64.1716
4−	64.1353(2)	64.1453	64.1374	64.1324	64.1383	64.1473	64.1232	64.1342
4*d*	64.6485(4)	64.6555	64.6512	64.6459	64.6530	64.6528	64.6618	64.6756
5−	64.6574(2)	64.6643	64.6598			64.6648	64.6545	64.6579
5*d*	64.9071(5)	64.9122	64.9096			64.9162	64.9208	
6−	64.9123(2)	64.9171	64.9145				64.9135	
6*d*	65.051(2)	65.0562	65.0545				65.0621	
7−	65.0552(2)	65.0592	65.0578				65.0584	
8−	65.1435(2)							
				Energy separation ΔE (meV)				
4−/3*d*	16.4(4)	16.5	16.3	15.7	11.1	24.0	−16.4	−37.1
5−/4*d*	8.9(6)	8.8	8.6			12.0	−7.3	−17.7
6−/5*d*	5.2(7)	4.9	4.9				−7.3	
7−/6*d*	4(2)	3.0	3.3				−3.7	

states, the quantum defect of the $(2p,nd)$ series is negative, $\mu_2^0 = -0.260 \pm 0.001$; the quantum defect of the $(sp,2n-)$ series is $\mu_2^- = 0.7205 \pm 0.0002$, in good agreement with a previous result [8], but of higher accuracy. While a negative quantum defect can be excluded for single excitations, it may occur for double excitations as observed here.

Table I also contains the available theoretical results for the energies of the lowest $(2p,nd)$ states as well as the neighboring $(sp,2n-)$ states. As is obvious from the listed energy separations ΔE, two of the calculations predict even the wrong sequence (Refs. [13] and [11]); this is also the case for Ref. [7]. The best agreement with experiment is found for the relatively old calculation with the truncated diagonalization method by Lipsky and Conneely (with 83 configurations included) [12], and the recent calculations with the complex rotation method by Ho [14]. The results in Refs. [5] and [6] define the right sequence result, however, in quite different energy separations; this is also the case for Ref. [17], with $\Delta E(4-/3d) = 23.2$ meV.

The narrow natural widths of the $(2p,nd)$ states cannot be derived in a direct way by curve fitting. This is also the case for the highest resolved lines of the $(sp,2n+)$ series, where the natural widths are known to be ≤ 0.05 meV for $n \geq 16$ [8,12]. From the observed line form, we can thus give an upper limit of 0.05 meV for the width of the $(2p,3d)$ state. A second way of estimating the width of this state is based on the ratio of intensities of the $(2p,3d)$ and $(sp,24-)$ resonance lines in the spectrum of Fig. 2, which amounts to $\cong 0.1$. Simulations show that this intensity ratio scales approximately with the ratio of widths, if equal excitation cross sections are assumed. This suggests a width of $\cong 0.01$ meV for the $(2p,3d)$ state, considering a width of $\cong 0.1$ meV for the $(sp,24-)$ state [12], in agreement with the analysis of the spectrum in Fig. 2. The uncertainty of this procedure is determined by the unknown Fano profile of the $(2p,nd)$ states as well as by the relative excitation cross sections to states in the two series [7].

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[1] R. P. Madden and K. Codling, Phys. Rev. Lett. **10**, 516 (1963); Astrophys. J. **141**, 364 (1965).
[2] J. W. Cooper, U. Fano, and F. Prats, Phys. Rev. Lett. **10**, 518 (1963).
[3] U. Fano, Rep. Prog. Phys. **46**, 97 (1983).
[4] H. R. Sadeghpour and C. H. Greene, Phys. Rev. Lett. **65**, 313 (1990).
[5] A. Macias, T. Martin, A. Riera, and M. Yunez, Phys. Rev. A **36**, 4187 (1987).
[6] L. Wu and J. Xi, J. Phys. B **23**, 727 (1990).
[7] P. Hamacher and J. Hinze, J. Phys. B **22**, 3397 (1989).
[8] M. Domke *et al.*, Phys. Rev. Lett. **66**, 1306 (1991).
[9] D. R. Herrick and O. Sinanoglu, Phys. Rev. A **11**, 97 (1975).
[10] C. D. Lin, Phys. Rev. A **29**, 1019 (1984).
[11] K. T. Chung and I. Chen, Phys. Rev. Lett. **28**, 783 (1972).
[12] L. Lipsky and M. J. Conneely, Phys. Rev. A **14**, 2193 (1976).
[13] P. G. Burke and D. D. McVicar, Proc. Phys. Soc. **86**, 989 (1965).
[14] Y. K. Ho, Z. Phys. D **21**, 191 (1991).
[15] R. Moccia and P. Spizzo, J. Phys. B **20**, 1423 (1987).
[16] M. Domke *et al.*, Rev. Sci. Instrum. **63**, 80 (1992).
[17] H. Fukuda, N. Koyama, and M. Matsuzawa, J. Phys. B **20**, 2959 (1987).