Extensive Double-Excitation States in Atomic Helium

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High-resolution photoionization studies of He have revealed more than 50 states below the $N=2$–7 thresholds of He^+, including sixteen $(sp,2n+)$ and five $(sp,2n-)$ states in the $N=2$ series. With a resolving power of $E/\Delta E \simeq 10000$, states as narrow as 0.1 meV could be observed and linewidths were determined with an accuracy up to ± 0.5 meV. Interchannel interferences, evident through effects on positions, shapes, and intensities of Rydberg lines, were interpreted within the framework of the multichannel quantum-defect theory.

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Helium is the prototype neutral system for the study of electron-electron correlation. Of special interest is the excitation region from 60 to 80 eV, where double-excitation states couple to the continuum. The discovery of these autoionizing states by Madden and Codling,[1] and their explanation by Cooper, Fano, and Prats[2] and Fano,[3] led to the formulation of new correlation quantum numbers.[4,5] Since then, these weak double-excitation states have attracted considerable interest,[6–10] but the limitations of photon sources in the 60–80-eV range have severely restricted our experimental knowledge about them.

In this Letter, a study of autoionizing double-excitation resonances of He below the $N=2$–7 thresholds of He^+, measured at very high resolution ($\Delta E \simeq 6$ meV, FWHM) is presented. Some of these states are very narrow (≤ 1 meV), and thus ideally suited for determining the bandwidth of a monochromatized synchrotron-radiation beam. The double-excitation series, converging toward the $N=2$–6 thresholds, could be resolved up to rather high n values, and strong interferences between different channels were observed for the first time.

The measurements were performed with the SX700/II plane-grating monochromator operated by the Freie Universität Berlin at BESSY. With the small vertical beam size of BESSY, very high resolution is obtained with a 5-μm exit slit. The absolute energy scale was adjusted at the C K edge of gas-phase CO (287.400 eV), resulting in good agreement of the energy of the "23−" state of He at 62.766 eV with previous experimental[1] and theoretical[8,9] values. Photoionization was studied with an ionization chamber of 10-cm active length filled with typically 0.1 mbar He, separated from the monochromator by a 1500-Å Al (1% Si) or a 1000-Å Lexan window; the latter was used for the $N=3$–7 series. Saturation effects on the spectra could be excluded.

The photoionization profiles of states below the $N=2$ threshold are shown in Fig. 1, labeled by the "old" classification scheme of Madden and Codling.[1] Figure 1(a) gives an overview of the $1s^2\,{}^1S \rightarrow (sp,2n+)\,{}^1P^o$ region from the lowest 22+ state at $h\nu=60.15$ eV up to the $N=2$ threshold of He^+ (IP_2). Figure 1(b) shows a magnification of the near-threshold region starting with the 26+ resonance, with lines up to $n=16$ clearly resolved. The number of resolved peaks alone provides a good estimate of monochromator resolution. Simulations show that Rydberg states up to $n=13$, 16, or 20 can be resolved with instrumental linewidths of 10, 6, or 3 meV (FWHM), respectively.

The spectra in Fig. 1 represent the first observation of double-excitation Rydberg-like states up to such high quantum numbers in He. Up to 25+, the peaks were fitted by independent Fano profiles,[11] yielding a Fano parameter $q \simeq -2.6$ and Γ values varying from 42.3 ± 2.3 meV (22+), 10.0 ± 1.3 meV (23+), to 2.5 ± 0.6 meV (25+). The upper $2n+$ series ($n \geq 6$) was also fitted with Fano profiles, but with peak energies E_n given by a Rydberg formula with constant quantum defect μ_2, $E_n = IP_2 - R_{He}/(n-\mu_2)^2$; Γ was assumed to decrease with $(n^*)^{-3}$, where $n^* = n - \mu_2$.[9,10] The fit yielded $\mu_{2+} = 0.147$ and $IP_2 = 65.404$ eV, close to the theoretical value of 65.4012 eV, obtained from a quasihydrogenic Rydberg formula with $IP_\infty = 79.0052$ eV. The fits give a Gaussian linewidth of $\Delta E = 6.0$ meV (FWHM) at $h\nu \simeq 60$ eV (corresponding to a record resolving power of $E/\Delta E \simeq 10000$ in this energy region) and Fano linewidths Γ decreasing with n to less than 1 meV for $n \geq 8$. Within error bars, the present Γ values agree quite well with theoretical predictions[8,9] (see Fig. 3) and previous lower-resolution experimental work.[1,6]

Between the $2n+$ states, several very sharp and $\simeq 30$

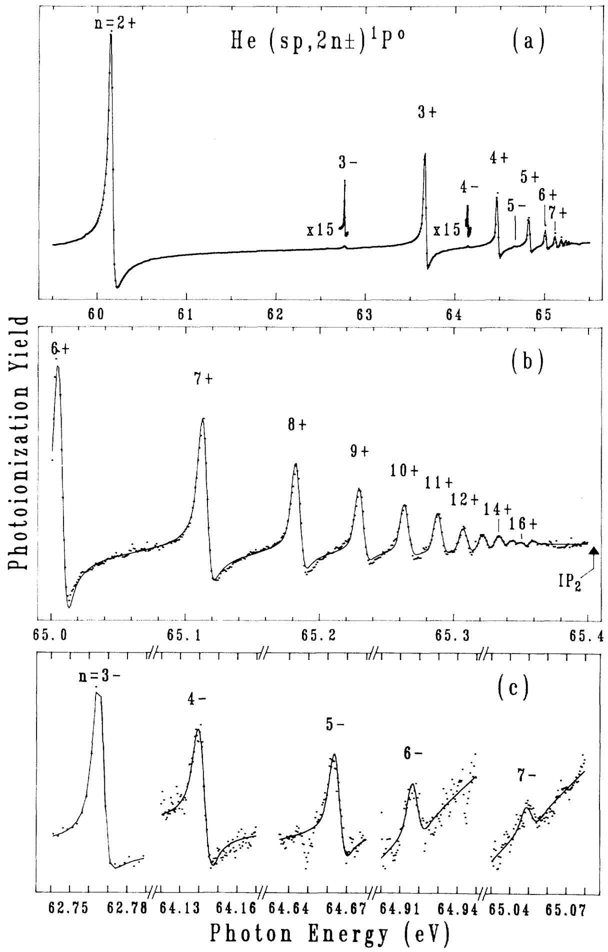

FIG. 1. Autoionizing states of double-excited He below the $N=2$ threshold (IP_2) of He: (a) overview, (b) magnification of the $n \geq 6$ region, and (c) "$2n-$" states.

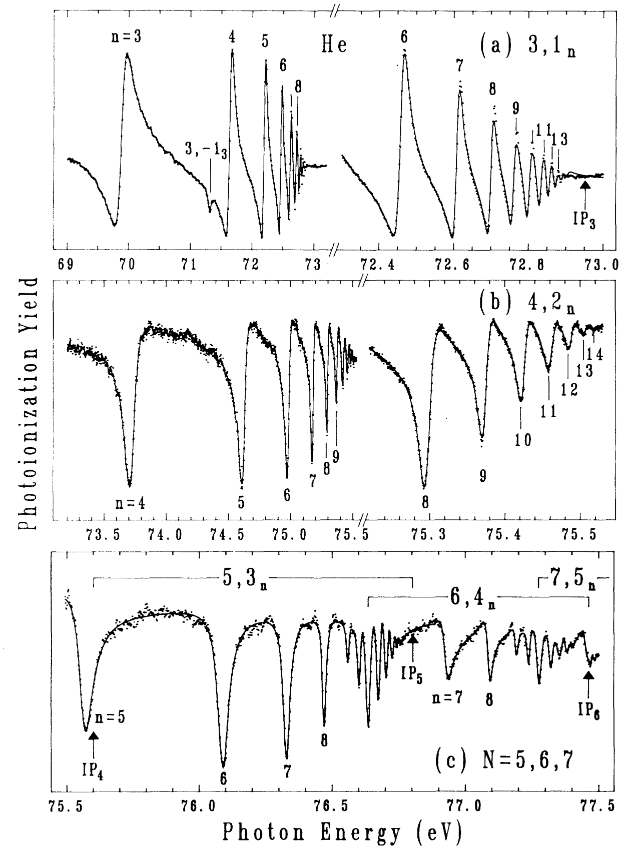

FIG. 2. Autoionizing states of He: (a) below the $N=3$ threshold (IP_3), (b) below the $N=4$ threshold (IP_4), and (c) below the $N=5$ and 6 thresholds (IP_5, IP_6). The high-n regions are shown magnified on the right-hand sides in (a) and (b). Note the overlapping of series in (c).

times weaker resonances are observed, which are identified as $2n-$ states[1] and displayed separately in Fig. 1(c). They are described by $\mu_{2-}=0.71$, $q=-3.5$ to -4.0, and Γ values decreasing from $\simeq 1$ meV $(23-)$ to $\simeq 0.1$ meV $(26-, 27-)$, with rather large error bars of ± 0.7 meV, reproducing the trend of theoretical linewidths.[9]

At higher photon energies, $^1P^{\circ}$ resonances below the $N=3$-7 thresholds of He^+ can be resolved (Fig. 2). These states are classified in the $N(K,T)_n^A$ scheme of Herrick and Sinanoglu[4] and Lin,[5] who introduced the correlation quantum numbers T and K to describe the strong electron-electron correlation. It is interesting to note that only states with $T=1$ and $A=$"+" are observed for $N \geq 3$; we have therefore adopted the simplified nomenclature N,K_n (see also Zubek *et al.*[10]). The spectra of the $N=3$ and 4 series are shown in Figs. 2(a) and 2(b). They constitute the first observation of such high states in these channels. The spectra were again fitted by Fano profiles employing a Rydberg formula with constant quantum defect and $\Gamma \propto (n^*)^{-3}$ (for $n \geq 5$ in the case of $N=3$, and $n \geq 7$ for $N=4$). For $N=3$ and 4, respectively, quantum defects of 0.796 and 1.351, Fano q values of $+1.6$ and $+0.45$, and series limits $IP_3=72.962$ eV and $IP_4=75.606$ eV were obtained (agreeing within 3 meV with theoretical quasihydrogenic values). The derived Γ values are again shown in Fig. 3, in comparison with the expected $(n^*)^{-3}$ dependence (anchored at $n=N+2$) and theoretical values.[12] Note for the Wannier ridge states $(n=N)$ the deviations of the experimental Γ values from the dashed $(n^*)^{-3}$ curve, and, on the other hand, the good agreement with theoretical Γ values.

With a single exception, all resonances in Fig. 2 correspond to autoionizing states in the lowest channel of the $N-1$ possible hyperspherical $A=+$ channels,[13] in close agreement with recent observations in H^-.[14] For a given N and $T=1$, the K selection rule allows values from $N-2$ to $-(N-2)$, with $\Delta K=2$;[5] this leads to $K=\pm 1$ for $N=3$. The dominant resonances (lowest +

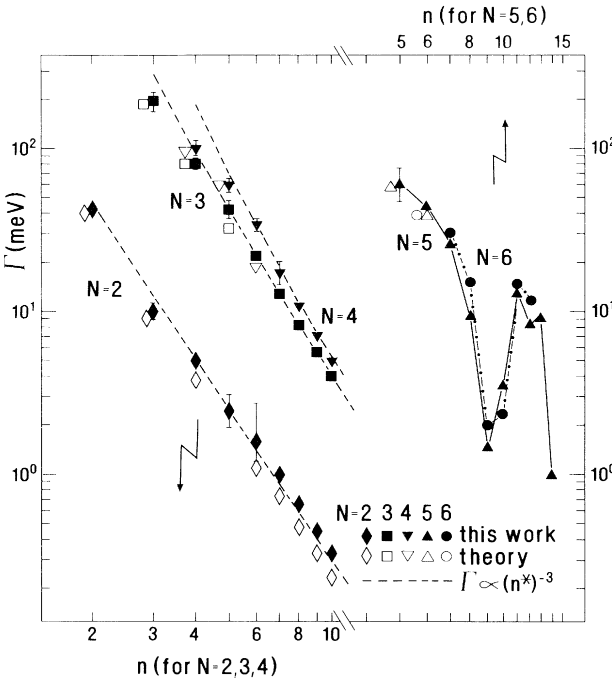

FIG. 3. Fit results for natural linewidths Γ as a function of n (solid symbols), shown for the different $N=2$–6 series in comparison with theoretical values (open symbols, for $N=2$ from Ref. 9; for $N=3$–6 from Ref. 12). For the $N=2$, 3, and 4 series, error bars are plotted up to $n=6$, 5, and 7, respectively, since from these values on $\Gamma \propto (n^*)^{-3}$ was assumed. For the $N=5,6$ series, a typical error bar of $\pm 20\%$ of Γ is given. In case of overlaps, the theoretical points were plotted slightly displaced to the left. Dashed lines describe a $(n^*)^{-3}$ dependence.

channel) all have quantum numbers $N,(N-2)_n$, i.e., $K=N-2$, corresponding to the lowest bending-vibrational state.[13] The single exception is observed between the $3,1_3$ and the $3,1_4$ states at 71.326 eV, which is identified as the $3,-1_3$ resonance (i.e., the first-excited bending-vibrational state in the second $N=3+$ channel). The observation of higher states in this channel is precluded by their expected low intensities and the fact that they sit on the wings of relatively broad $3,1_n$ resonances.

The $N=5$–7 range is shown in Fig. 2(c), with considerable overlap between the lowest resonances in series N and the highest members of series $N-1$. Because IP_4 coincides in energy with the $5,3_5$ state, interference with the (unresolved) highest-n members of the $N=4$ series is expected, but the $5,3_5$ state appears as a single broad resonance. In the $5,3_n$ Rydberg series, however, a novel perturbation is apparent in the energy range where the lowest resonance ($6,4_6$, Wannier ridge state) in the $N=6$ manifold is expected. Such a strong interference between the $N=6$ perturber and the $N=5$ Rydberg series has been anticipated,[13] but has not been observed until now. The $N=5$ and 6 series were least-squares fitted with independent Fano profiles [solid line in Fig.

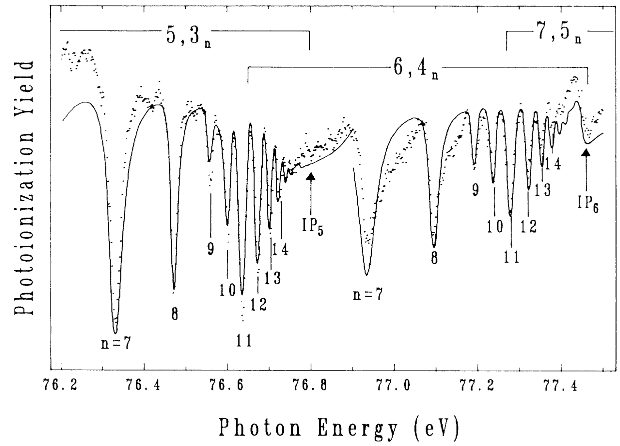

FIG. 4. Three-channel MQDT fit for the $N=5$ and 6 series of He.

2(c)], revealing the following expected consequences of interferences: (i) a rise of the quantum defect from 1.7 for the $5,3_5$ and $5,3_6$ states to 2.75 for the $5,3_{14}$ state; (ii) maxima in intensity and width (see Figs. 2 and 3); (iii) a change in the sign of q (Fano q reversal),[15] which varies from -0.23 for $5,3_5$ to $+0.25$ for $5,3_{10}$, the latter state being close to the intensity maximum of the expected $6,4_6$ resonance.

Perturbation of the $N=5$ series by the $N=6$ Wannier ridge state is a characteristic form of channel interaction, describable by multichannel quantum-defect theory (MQDT).[16] This was verified by fitting a set of three-channel MQDT parameters to the interference region. Included in the fit are an open $N=4$ channel, a closed N $N=6$ channel, and an $N=5$ channel that is open above IP_5 and closed below; eight MQDT parameters were adjusted. An analogous fit was performed for the perturbations of the $N=6$ series by the $N=7$ Wannier ridge state. The fit results, convoluted by a Gaussian for experimental resolution, are shown in Fig. 4. While not perfect, these fits are sufficiently accurate to confirm the classification of the Rydberg channels. We also extracted global "perturber widths" from the MQDT fits. These are the expected widths of the $6,4_6$ and $7,5_7$ autoionizing resonances, if the $N=5$ and 6 channels, respectively, were open at all energies. The extracted values are $\Gamma=56$ meV for $6,4_6$ and $\Gamma=37$ meV for $7,5_7$, both fitting well in the trend of experimental linewidths plotted in Fig. 3 for the $N=3$–5 Wannier ridge states. The $N=6$ width, however, is slightly larger than the calculated value of 39 meV.[12]

A two-electron Rydberg formula[17] is known to describe the positions of Wannier ridge states, $N,(N-2)_{n=N}$, with good accuracy. If each such resonance is assumed to be the lowest member of an unperturbed one-electron Rydberg series converging to IP_N, one arrives at an approximate formula for all of the dominant resonances in He:

$$E(N,n) = \mathrm{IP}_\infty - R_{\mathrm{He}}[4/N^2 + 1/(n-\mu_N)^2]\,, \qquad (1)$$

with $R_{\mathrm{He}} = R_\infty(1 - m_e/m_{\mathrm{He}})$ and $\mu_N = N - [2(2-\sigma)^2/(N-\mu)^2 - 4/N^2]^{-1/2}$. Here μ is a phenomenological quantum defect and σ an effective screening factor. The one-electron quantum defect μ_N is obtained by equating Eq. (1) for $n=N$ to the energy of the Nth Wannier ridge state as given by Ref. 17, namely,

$$E(N,N) = \mathrm{IP}_\infty - R_{\mathrm{He}}[2(2-\sigma)^2/(N-\mu)^2]\,. \qquad (2)$$

Once μ_N is calculated in this way, it is assumed to be n independent, giving Eq. (1) for all levels in terms of μ and σ.

A fit of Eq. (1) to the experimental energies of the three Wannier ridge states with $N=3$–5 gives values of $\mu = -0.1815$ and $\sigma = 0.1587$. Except for the resonances below IP_2 and specific effects related to the interaction of states in different N manifolds, Eq. (1) predicts the energies of all the dominant + resonances with good accuracy. For the $3,1_4$ state, however, the measured and predicted energies differ by 90 meV, which presumably stems from a neglected energy dependence of the fit parameters. Note that Eq. (1) neglects the long-range charge-dipole attraction between the outermost electron and $\mathrm{He}^+(N)$, which plays a major role for the spectrum of H^-. The long-range Coulomb attraction diminishes the importance of this dipole interaction in double-excited He, but it should probably be incorporated to achieve a better quantitative description of the spectrum. In any case, Eq. (1) is sufficiently accurate to predict the global nature of the spectrum, particularly at high N, where observations and calculations both become difficult. At higher energies ($h\nu \geq 77.6$ eV), there are some hints in the spectra (not shown here) suggesting interference of the $7,5_n$ states with the $8,6_8$ intruder state. Work to improve the statistics of this spectrum is in progress.

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