Observation of a Triply Excited State in He^-

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A weak feature observed at 323.4 ± 0.2 Å in the foil-excited spectrum of a helium ion beam is ascribed to radiative autoionization from the triply excited $2p^3\,{}^4S$ state of the negative helium ion. The observation is consistent with recent calculations of the position and possible decay modes of the hitherto unobserved state.

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Triply excited states of three-electron systems provide sensitive tests of electron correlation, and as such are of interest in determining which theoretical approaches can best describe such effects. In addition to their fundamental interest, such states have also been proposed as a means of producing laser action at very short wavelengths (the radiative autoionization by which such states can decay can be considered analogous to the radiative dissociation which takes placed in excimer lasers).

In some three-electron systems, energies and transition rates for a number of $2p^2np\,{}^4S$ states have been predicted [1-3] and experimentally verified [4,5] in recent beam-foil experiments. Such states are elusive and appear to be difficult to excite by other than nonselective multiple-collision processes such as occur in beam-foil experiments. They have until now been seen only in Li I and Be II (now also in B III and C IV—see below), via decay to the *bound* $1s2p^2\,{}^4P$ states in those systems (this lower state is not bound in He^-) [6].

The hitherto unobserved $2p^3\,{}^4S$ state in the negative helium ion He^-, although very highly excited, cannot Coulomb autoionize into an adjacent continuum state, as no such state exists with the same parity and total orbital angular momentum L. The state *can*, however, radiate to lower states such as the $2s2p^2\,{}^4P$ resonance, or to a ${}^4P$ shape resonance near the $1s2p\,{}^3P$ threshold [1]. The lifetime of $2p^3\,{}^4S$ is expected to be typical of electric dipole transitions, i.e., 10^{-8} to 10^{-10} s.

A number of reviews have summarized the best available energy levels for *doubly* excited states of neutral helium (these are relevant here, as there is always a risk that an observed emission line could originate from such a state). The benchmark paper by Martin [7] reviews both theoretical and experimental work until 1973, and Lipsky, Anania, and Conneely [8] give an extensive tabulation using a uniform classification scheme for several members of the helium sequence, while the review by Shearer-Izumi [9] summarizes decay rates, both calculated and measured, in helium alone. Several compendia [10] of beam-foil spectroscopy results discuss multiply excited states, as the latter are known to be copiously populated by this technique.

Experimentally, doubly excited states in *neutral* helium were reported by Berry and co-workers [11], by Knystautas and Drouin [12], and by Ishii and Tomita [13], all using the beam-foil technique. A very thorough study of this spectrum in the far uv has recently been reported by Baltzer and Karlsson [14] using a new vacuum-uv-microwave source.

The position of the line emitted from $2p^3\,{}^4S$ has been predicted to be in the vicinity of the $1s2p\,{}^3P$-$2p^2\,{}^3P$ transition in neutral helium at 320.29 Å. No such line was observed during searches in previous beam-foil experiments [15]. The earlier calculations of Nicolaides and co-workers (see Ref. [3]) predict a line at 323.2 Å. Chung's earlier [1,4] and later [2] calculations give, respectively, −0.722546 a.u., −0.722898 Å, and −0.722957 a.u. (the differences among them are too small to be discernible in the present experiment) yielding a line position of about 323.1 Å.

The experiment involved He^+ ions produced in an arc discharge source and accelerated to 100 keV. The mass-analyzed ions then impinge on thin carbon foils prepared in our laboratory by carbon arc evaporation. The stopping power of the foils on alpha particles determined their thickness to be 12 ± 1 $\mu g/cm^2$. While the few-μA beams were stable, the foils were usually destroyed in about an hour under these conditions. This presented a problem, in that good statistics needed for the weak lines studied required slow wavelength scans, while foil longevity placed restrictions on the duration of each scan. A compromise was reached which allowed the spectrum to be scanned piecemeal, about 50 Å at a time, adequate for the present work.

Photons emitted by the excited beam particles exiting the foil were dispersed by a McPherson 2.2-m grazing-incidence monochromator and detected in first and second order by a Channeltron. Slit widths varied between 100 and 150 μm on most scans because of the very low intensity of the line studied, and were reduced to 50 μm for the final determination of the line position. The 600-line/mm grating blazed at 2°4′ was used at incidence angles of 82° and 86° Since the signal-to-background ratio is of the order of unity for the line of interest here, special care was taken to reduce noise in the detector and associated circuitry. In particular, a low-noise preamplifier was designed and built for such applications, which reduced the dark count rate to a few counts per minute. A relatively new Channeltron was used, as their dark count rate tends to increase gradually with time.

Wavelengths were calibrated using the relatively strong lines of doubly excited neutral helium at 309.1 and 320.29 Å. A partial scan is presented in Fig. 1, which shows the series $1snp\,^3P$-$2p^2\,^3P$, beginning with the 320.29-Å line, the first member ($n=2$). The inset magnifies the region immediately to the right of this line, in a slow scan at maximum resolution with 50-μm slits. (It is in fact a smoothed sum of two successive runs.) There are two features, the first at 322.3 ± 0.1 Å, which was also seen (at 322.1 Å) by Baltzer and Karlsson [14], and which they assign to $1s2s\,^3S$-$2s2p\,^3P$. (Their discussion of uncertainty in line positions suggests one of ±0.05 Å for this line.) It should be pointed out that in scans with wider slits, this line showed up as an asymmetry at the base of the 320.29-Å line. The second feature appears somewhat wider than the first and is centered at 323.4 ± 0.2 Å, the larger error bar reflecting greater uncertainty in establishing the line center for this feature. It also shows up on a second-order scan taken in this region. This line is assigned to the radiative autoionization transition from the triply excited $2p^3\,^4S$ state, essentially on the basis of wavelength coincidence with recent calculations which seem to be reliable for the isoelectronic sequence (see below).

Although the transition from $2p^3\,^4S$ is very weak, it appears at the same position on several, though not all, spectra. This reproducibility lends credence to the identification. The fact that it is not on some spectra we attribute to gradual destruction of the foil target by the beam, with concomitant loss of intensity, which would make the weak lines disappear first into the background. This is in fact the case. It is unlikely to be a lifetime effect, as the 500 μm or so length of beam viewed by the detector is sufficient to see most of the decay of this state—its lifetime is expected [3] to be $\sim 10^{-10}$ s and the beam velocity about 2 mm/ns. Since even under our improved low-noise detection conditions, the signal-to-background ratio is still of the order of unity, this might explain why the line has escaped detection to date in other similar experiments [15]. The light source used by Baltzer and Karlsson [14] is much brighter than ours, and their resolution much higher (as an indication of the latter, they observe the Lyman series of hydrogenic He II down to $n=14$, while our spectra show resolved Lyman peaks only to $n=9$). Nevertheless, they do not observe the triply excited state reported here. Instead, they attribute a feature at 323.5 Å to an impurity line from N III. This is plausible in a microwave source where impurity gases are always present, albeit in small amounts. However, a foil-excited beam is known to be a particularly pure light source, and unique in populating multiply excited states to a significant extent. We have never seen impurity lines, even weak ones, from residual gas excitation. As a further confirmation of the fact that the observed line is not due to an N III impurity, we observed no other N III lines of comparable intensity in the same spectral range.

Nicolaides [3] suggests that the predicted transition from $2p^3\,^4S$ should take place at "∼317 Å"; however, the energy level given is the same as in his previous papers (59.33 eV). Although we do indeed see a weak feature at this wavelength (as do also Baltzer and Karlsson [14]), it is far more likely to be $1s5p\,^3P$-$2p3p\,^3D$, since we also see another member of the same series, $1s4p\,^3P$-$2p3p\,^3D$, at its expected value of ∼314.5 Å (see also Ref. [12]).

Other possibilities which might provide alternative explanations for the observed feature at 323.4 Å are (i) other transitions in the spectrum of helium or that of its ions,

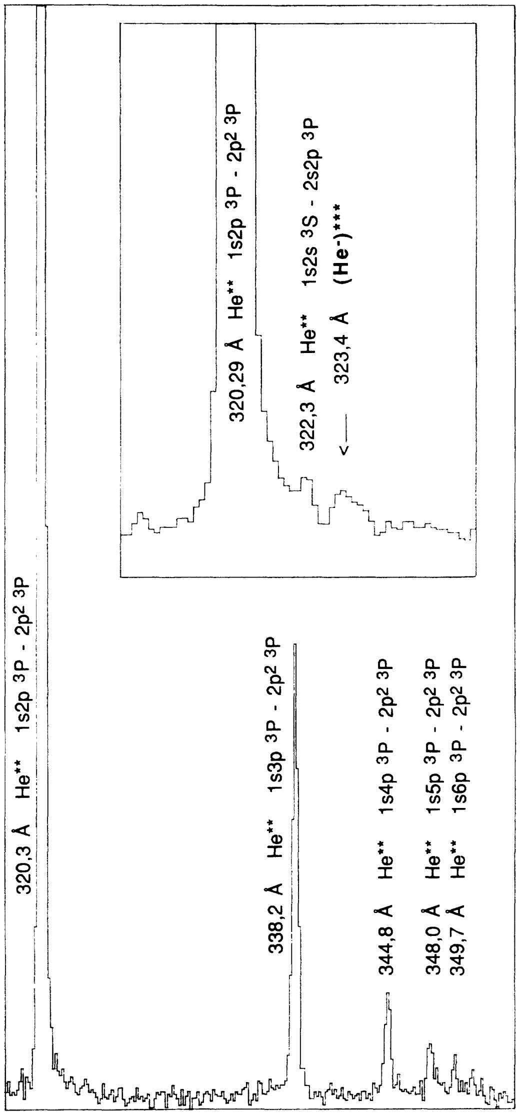

FIG. 1. Emission spectrum of a foil-excited 100-keV He^+ ion beam in the far uv showing several transitions from the doubly excited state $2p^2\,^3P$. The inset expands the region immediately to the right of the 320.29-Å line, showing the 323.4-Å line arising from radiative autoionization of the triply excited state $2p^3\,^4S$ of He^-.

TABLE I. Comparison of recent experimental and calculated values for transition wavelengths arising from the decay of triply excited $2p^3\,{}^4S$ in three-electron systems.

Ion	Wavelength (Å) Theory	Wavelength (Å) Experiment
He$^-$	323.1[a], 323.2[b]	323.4 ± 0.2[c]
Li I	145.019[a]	145.02 ± 0.05[d]
Be II	80.852[a]	80.85 ± 0.03[d]
B III	51.288[a]	51.4 ± 0.2[e]
C IV	35.359[a]	35.5 ± 0.2[e]

[a] Reference [2].
[b] Reference [3].
[c] This work.
[d] Reference [4].
[e] Our measurements (Ref. [16]).

or (ii) order mixing. The first seems unlikely in that recent calculated wavelengths cluster about the value measured. Furthermore, the transition *has* been observed [4] in isoelectronic Li I and Be II, albeit to a *bound* lower state. Since first submitting this manuscript, we have also found decay from $2p^3\,{}^4S$ in triply excited B III and C IV as well [16]. Table I compares experiment and theory for the entire isoelectronic sequence up to $Z=6$.

Helium has a relatively simple spectrum, and does not present the complex transition arrays observed in heavier atoms with large open shells. The possibilities that there is another origin for this line are thus very limited.

The second possibility mentioned above (order mixing) is excluded since the 323.4-Å line was also observed in second order, which would mean that if this feature were already in second order at 323.4 Å, the line positioned at 646.8 "Å" would have been in fourth order, not at all a plausible scenario. That scenario would imply a transition of 161.7 Å, which would place the upper level well above the $2p^2\,{}^3P$ bound-state threshold, thereby facilitating Coulomb autoionization.

A lifetime measurement would have allowed additional evidence for the $2p^3\,{}^4S$ state, as Nicolaides and Komninos (in Ref. [3]) have calculated the total radiative autoionization probability to be $1.14\times10^{10}\ \mathrm{s}^{-1}$. However, the observed line was far too weak to allow this further evidence to be obtained. The fact that the line seems broader than others in the helium spectrum might be due to the fact that, in the negative helium case, unlike in the other members of the isoelectronic sequence, the *lower* $1s2p^2\,{}^4P$ state is an unbound shape resonance. In an analogous case some years ago, broadening of lines in three-electron beam-foil spectra was attributed to a short-lived *lower* state which could Coulomb autoionize [17].

In conclusion, the triply excited spherically symmetric $2p^3\,{}^4S$ state of the negative helium ion has been observed for the first time, while undergoing radiative autoionization, as predicted by recent multiconfigurational calculations. The decay is accompanied by emission of a 323.4 ± 0.2 Å photon, in agreement with most theoretical estimates of the upper-level energy.

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