Theoretical photodetachment cross section for $He^-(^4P^o)$

A. U. Hazi and K. Reed
Lawrence Livermore National Laboratory, University of California, Livermore, California 94550
(Received 9 June 1981)

We report the first calculation of the photodetachment cross section for the metastable, $1s2s2p\,^4P^o$ state of He^-. Extensive configuration-interaction wave functions and the Stieltjes-moment-theory technique were used to determine the total cross section from threshold to 3.0 eV. The $1s2p^2\,^4P^e$ state of He^- gives rise to a very large ($\sim 24\times10^{-16}$ cm^2) and narrow peak 10 meV above the 2^3P^o threshold.

The $1s2s2p\,^4P^o$ state of He^- is metastable against both the autodetachment of electrons and radiative decay. Holøien and Midtdal[1] were the first to show theoretically that $He^-(^4P^o)$ is bound relative to $He(2^3S)$ and that it is metastable against autodetachment to the ^1S ground state of He because of spin selection rules. The experimental[2] and the most accurate theoretical[3] values for the binding energy of $He^-(^4P^o)$ are 79 and 77 meV, respectively. The energy separation and the lifetimes of the three fine-structure levels ($J=\frac{1}{2},\frac{3}{2}$, and $\frac{5}{2}$) have also been measured.[4,5]

Very recently two groups[6,7] have measured independently the absolute photodetachment cross sections of $He^-(^4P^o)$ at selected wavelengths. Compton, Alton, and Pegg[6] determined the cross sections at photon energies between 1.77 and 2.75 eV by detecting the photodetached electrons. In this energy region both the 2^3S and 2^3P^o states of He can be produced by photodetachment. Hodges, Coggiola, and Peterson[7] measured the cross sections between 1.6 and 4.0 eV by detecting the neutral product atoms. They also performed experiments near 0.11–0.13 eV and 1.17 eV, where $He(2^3S)$ is the only energetically accessible product. Hodges *et al.*[7] showed that the total photodetachment cross section of $He^-(^4P^o)$ is quite large above the 2^3S threshold (1.2×10^{-16} cm^2 at 0.12 eV) and that it increases again significantly at the 2^3P^o threshold at 1.22 eV. Both experiments[6,7] indicate some structure in the spectrum near 2.5–2.7 eV, a region where autodetaching states of He^- associated with the $n=3$ states of He are expected to occur.

From the theoretical point of view, photoabsorption by $He^-(^4P^o)$ is intrinsically interesting for several reasons. First, very little is known about the photodetachment of electrons from *unstable* negative ions. Second, photoexcitation of $He^-(^4P^o)$ may lead to higher, quartet, autodetaching states of He^-, which, in contrast to the doublet states, are not accessible in electron scattering experiments on the ^1S ground state of He. Finally, although the experimental cross sections of Compton *et al.*[6] and Hodges *et al.*[7] agree fairly well with each other, there remain large energy regions, e.g., 0.2–1.1 eV and 1.2–1.6 eV, where the magnitude of the cross section is not known.

In this Communication we report the first theoretical study of the process:

$$h\nu + He^-(1s2s2p\,^4P^o) \rightarrow He(1s2s^3S \text{ or } 1s2p\,^3P^o) + e^- . \quad (1)$$

We have used extensive configuration-interaction (CI) wave functions and the Stieltjes moment-theory technique[8,9] to calculate the total cross section for process (1) at photon energies between 0.08 and 3 eV. We also searched the region just below the $n=3$ thresholds to identify any possible even parity, quartet, Feshbach-type autodetaching states of He^-. The present calculations are noteworthy for several reasons. At the energies where experimental data are available, we find reasonably good agreement between the measured and calculated cross sections. We predict a very large ($\sim24\times10^{-16}$ cm^2) photodetachment cross section just above the 2^3P^o threshold at 1.23 eV due to a $1s2p^2\,^4P$ autodetaching shape resonance. An independent scattering calculation fixed the resonance position at $\sim$11 meV above $He(2^3P^o)$ and yielded a resonance width of 7 meV. In contrast, we found that the $1s3p^2\,^4P$ state is a Feshbach-type resonance lying $\sim$0.16 eV below $He(3^3P^o)$.

The Stieltjes-moment-theory technique[8,9] is a discrete-basis-set method in which only square-integrable (L^2) functions are used to approximate the electron scattering continuum. Since the method avoids the explicit construction of scattering wave functions, electron correlation and polarization effects are easily included in the calculation of photoionization or detachment cross sections via the configuration-interaction technique. The Stieltjes procedure was developed[9] primarily to treat molecular photoionization, but it has been also used successfully to determine the photodetachment cross sections of stable atomic negative ions.[10] Since the computa-

tional procedure is given in the literature, we discuss only those aspects relevant for $He^-(^4P^o)$.

The many-electron wave functions were built from orthonormal atomic orbitals which were linear combinations of Slater-type orbitals (STO). To construct the basis, we started with the $(4s, 4p, 2d)$ "critical" basis of Bunge and Bunge,[3] which was adequate to describe $He(2^3S)$, $He(2^3P^o)$, and $He^-(^4P^o)$, and we augmented it with $9s$, $7p$, and $9d$ diffuse STO's to approximate the ejected electron. The exponents of the augmenting functions were chosen in decreasing geometric sequences, i.e., $2s$:$0.244 \times 2^{-n/2}$ $n=0, \ldots, 8$; $2p$:$0.106 \times 2^{-n/2} n=0 \ldots, 6$; and $3d$:$0.2687 \times 2^{-n/2} n=0, \ldots, 8$. Complete CI calculations with the $(4s, 4p, 2d)$ core basis gave -2.1746 and -2.1325 hartree for the energies of $He(2^3S)$ and $He(2^3P^o)$, respectively. The calculated $^3S-^3P^o$ separation is 1.147 eV, in good accord with the exact value of 1.145 eV. To describe $He^-(^4P^o)$, we used all the configurations which could be constructed from the $(4s, 4p, 2d)$ basis plus 20 additional configurations which contained one diffuse s and three diffuse p STO's. The latter configurations were required to describe accurately the long-range tail of the wave function, and they were essential for obtaining good agreement between the length and the velocity forms of the dipole transition moments. Our 120-term wave function gave -2.1774 hartree for the energy of $He^-(^4P^o)$, compared to the accurate value of -2.17807 hartree.[3] Our calculated electron affinity of $He(2^3S)$ is 0.077 eV, which is identical to that obtained previously.[3]

For $h\nu < 4.85$ eV, there are five possible photodetachment channels: $He(2^3S) + e(ks)^4S$, $He(2^3S) + e(kd)^4D$, and $He(2^3P^o) + e(kp)^4S, ^4P, ^4D$. For each symmetry, the configurations representing the final states were formed by constructing all possible antisymmetrized Kronecker products of the He target configurations (15 for 2^3S and 24 for 2^3P^o) and the unoccupied orbitals in the $(13s, 11p, 11d)$ STO basis. We also included additional configurations to account for the contribution of the ^3D excited states to the polarizability of $He(2^3P^o)$. Thus, the final-state wave functions included both electron correlation and polarization effects to the full extent allowed by our orbital basis set.

Figure 1 shows the ^4S partial cross section representing the detachment of the $2p$ electron from $He^-(^4P^o)$ into the s-wave continuum. This cross section rises very rapidly from threshold, reaching its peak value $(1.2 \times 10^{-16}$ cm$^2)$ near 87 meV. Since the electron is ejected without orbital angular momentum $(l=0)$, no shape resonance is possible, and the rapid variation of the cross section with energy is due to the very diffuse nature of the weakly bound $2p$ orbital in $He^-(^4P^o)$.

Figure 2 shows the ^4P partial cross section representing the detachment of the $2s$ electron from

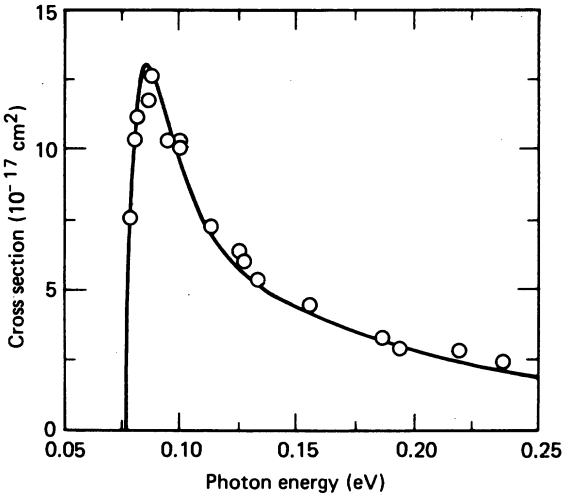

FIG. 1. ^4S partial cross section for $h\nu + He^-(^4P^o) \rightarrow He(2^3S) + e(ks)$. Circles denote Stieltjes data, while the smooth curve was obtained by fitting the calculated cumulative oscillator-strength distribution.

$He^-(^4P^o)$ into the p-wave continuum. This channel exhibits an extremely large $(\sim 24 \times 10^{-16}$ cm$^2)$ and quite narrow peak about 10 meV above the 2^3P^o threshold. To identify the physical mechanism underlying this prominent feature of the $^4P^o \rightarrow ^4P$ spectrum, we calculated independently the ^4P scattering phase shift using the close-coupling code IMPACT.[11] We used the same orbitals and the same 24-term $He(2^3P^o)$ wave function as in the photodetachment calculations. Two $1snd\,^3D$ pseudostates were included as closed channels. Figure 3 shows that, starting from the 2^3P^o threshold, the calculated

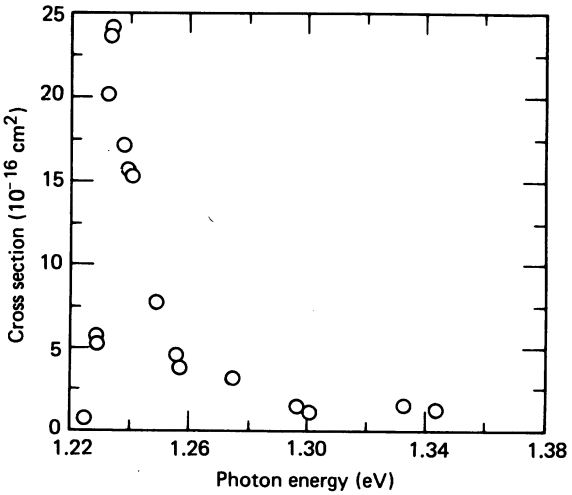

FIG. 2. ^4P partial cross section for $h\nu + He^-(^4P^o) \rightarrow He(2^3P^o) + e(kp)$. Circles denote Stieltjes data.

phase shift rises rapidly over a narrow energy region to 2.5 rad, a behavior which indicates a resonance. Inspection of the corresponding wave function shows that this enhancement should be assigned to a $1s2p^2\,{}^4P$ shape resonance. A Breit-Wigner analysis placed the resonance at 10.6 meV above He(2^3P^o) and gave 7.0 meV for the width. These values are consistent with the shape of the detachment cross section shown in Fig. 2.

Previously, Holøein and Geltman[12] calculated the $1s2p^2\,{}^4P$ state of He^- to be 0.2 eV below He(2^3P^o), contrary to the present results. With extensive CI wave functions containing 466 terms, we were not able to obtain a ${}^4P$ eigenvalue below He(2^3P^o), and the wave function associated with the lowest eigenvalue always represented a very low energy, ~0.001 eV, scattering solution (see Fig. 3). Unpublished calculations by Bunge and Bunge also place the $1s2p^2\,{}^4P$ state in the electron scattering continuum of He(2^3P^o). (See note added in proof.)

Figure 4 compares the total photodetachment cross sections calculated with the length and the velocity forms of the dipole transition moment to the experimental values. In the limited energy regions where measurements are currently avaliable, theory and the experiments[6,7] agree satisfactorily. Figure 4 also suggests that future experiments should be directed at the 0.1–1.5-eV region where the cross section is apparently large and varies rapidly with energy. The two narrow peaks at 0.08 and 1.22 eV are due to the previously mentioned $2^3S\,ks\,{}^4S$ and $2^3P\,kp\,{}^4P$ channels, respectively (see Figs. 1 and 2). The broad structure located near 0.3 eV, and, in fact, most of the total cross section in the 0.3–1.22- and 2.0–3.0-eV regions, are associated with the $2^3S\,kd\,{}^4D$ channel. The difference between the length and the velocity forms of the calculated cross sections apparent in Fig. 4 is due almost entirely to this channel and is possibly a consequence of the lack of f-type orbitals in the basis set.

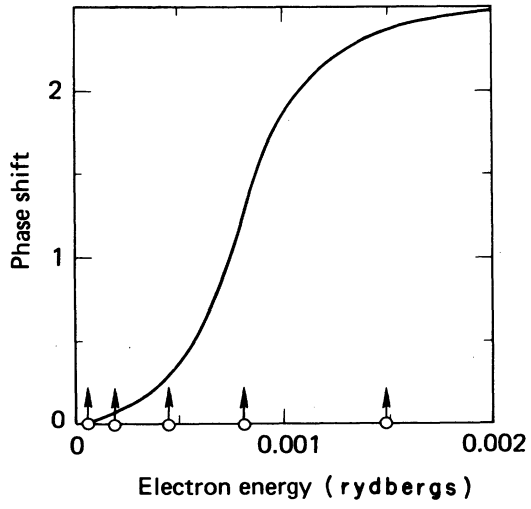

FIG. 3. ${}^4P$ phase shift for the He(2^3P^o) + e(kp) channel. The arrows indicate the energies of the discrete wave functions approximating the ${}^4P$ continuum in the Stieltjes calculations.

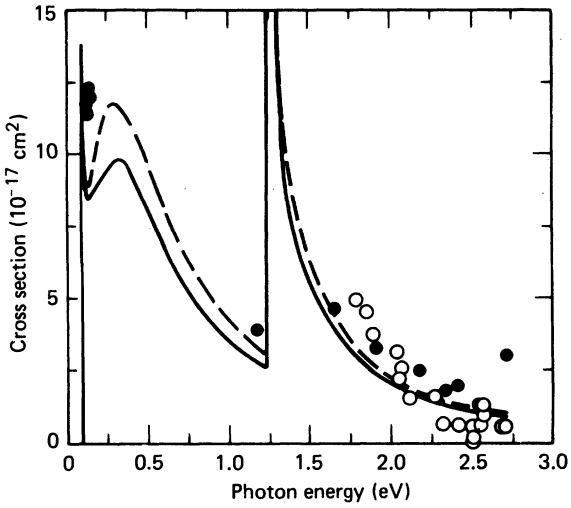

FIG. 4. Total photodetachment cross section of the $He^-(^4P^o)$. (– – –) calculated "length" form; (——) calculated "velocity" form; ○ Compton *et al.* (Ref. 6); ● Hodges *et al.* (Ref. 7).

At $h\nu = 2.41$ eV, Brehm *et al.*[2] measured the He(2^3S) to He(2^3P^o) branching ratio to be 7. From the calculated partial cross sections, we estimate this ratio to be 4. Considering the uncertainties which are usually associated with branching ratios calculated with the Stieltjes procedure, the disagreement between theory and experiment[2] is not serious. Because of the presence of ${}^4P$ shape resonance, the calculated ${}^3S$-${}^3P^o$ branching ratio varies quite rapidly with photon energy between 1.22 and 2.5 eV.[13]

In the 2.4–3.3-eV region we found only *one* even-parity, quartet, Feshbach resonance: $1s3p^2\,{}^4P$. Since the calculated oscillator strength for the $1s2s2p\,{}^4P^o \rightarrow 1s3p^2\,{}^4P$ transition was only 0.009, this resonance did not contribute significantly to the photodetachment spectrum. We did not find the $1s3s3d\,{}^4D$ resonance obtained by Oberoi and Nesbet[14] at 0.16 eV below He(3^3S). Clearly, more detailed measurements and additional calculations will be required to elucidate the energy dependence of the photodetachment cross section in the 2.6–3.5-eV region near the $n = 3$ thresholds.

Note added in proof: After this paper was accepted for publication, we became aware of two very recent calculations relating to the $1s2p^2\,{}^4P$ state of He^-. C. A. Nicolaides, Y. Komninos, and D. R. Beak [Phys. Rev. A 24, 1103 (1981)] analyzed electron correlations and found this state about 10 meV above He(2^3P^o). S. Watanabe [Phys. Rev. (in press)]

found the ^4P resonance 15–20 meV above He(2^3P^o) using hyperspherical coordinates.

One of us (A.U.H.) thanks Dr. R. Compton and Dr. J. Peterson for sending us their results prior to publication, and also for many useful discussions. This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

---

[1]E. Holøien and J. Midtdal, Proc. Phys. Soc. London A 68, 815 (1955).
[2]B. Brehm, M. A. Gusinow, and J. L. Hall, Phys. Rev. Lett. 19, 737 (1967).
[3]A. V. Bunge and C. F. Bunge, Phys. Rev. A 19, 452 (1979).
[4]R. Novick and D. Weinflash, Natl. Bur. Stand. (U.S.) Spec. Publ. 343, 403 (1971).
[5]D. L. Mader and R. Novick, Phys. Rev. Lett. 29, 199 (1972); 32, 185 (1974).
[6]R. N. Compton, G. D. Alton, and D. J. Pegg, J. Phys. B 13, L651 (1980).
[7]R. V. Hodges, M. J. Coggiola, and J. R. Peterson, Phys. Rev. A 23, 59 (1981).
[8]P. W. Langhoff, J. S. Sims, and C. T. Corcoran, Phys. Rev. A 10, 829 (1974).
[9]P. W. Langhoff, in *Electron-Molecule and Photon-Molecule Collisions,* edited by T. Rescigno, V. McKoy, and B. Schneider (Plenum, New York, 1979), p. 183.
[10]For references relating to H^-, Li^-, Na^-, and F^-, see pp. 212 and 213 in Ref. 9.
[11]M. A. Crees, M. J. Seaton, and P. M. H. Wilson, Comput. Phys. Commun. 15, 23 (1978).
[12]E. Holøien and S. Geltman, Phys. Rev. A 53, 81 (1967).
[13]We estimate the $^3S - {}^3P^o$ ratio to be 1/100 near 1.23 eV, and 4/1 near 2.4 eV.
[14]R. S. Oberoi and R. K. Nesbet, Phys. Rev. A 8, 2969 (1973).