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LETTER TO THE EDITOR

Enhancement of narrow resonances in photoabsorption from the He atom in metastable states

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Abstract. Photoionization cross sections from metastable (1s2s) $^1S^e$, $^3S^e$ states of He atom, for photon energies below the He$^+$ ($N = 2$) threshold are calculated using the hyperspherical close-coupling (HSCC) method. The results are compared with photoionization cross sections from the ground state He atom. By convoluting the calculated spectra with a resolution of 5.4 meV, we show that the narrow doubly excited states, which are weakly populated by photoabsorption from the ground state, are populated prominently in photoabsorption from the metastable (1s2s) $^1S^e$ state. The $^3P^o$ doubly excited states populated from the photoabsorption of metastable (1s2s) $^3S^e$ state are also studied.

Photoabsorption of helium atom from its ground state has been studied experimentally and theoretically over the years. It has been established that only a certain series of doubly excited states are prominently populated, and these doubly excited states are best described in terms of a set of approximate quantum numbers K, T, A (Lin 1986). For example, among the three series of doubly excited states below the $N = 2$ threshold of He$^+$, the prominent series is the $(K, T)^A = (0, 1)^+$ series (Domke *et al* 1991). The $(1, 0)^-$ series is barely visible in the spectrum and the third $(-1, 0)^0$ series was observed only very recently when the photon energy resolution of 4 meV was available (Domke *et al* 1992). This quasi-selection rule, or propensity rule, also applies to doubly excited states below the higher N thresholds of He$^+$. Since the ground state of helium has $(K, T)^A = (0, 0)^+$, this propensity rule has been formulated that the prominent series populated is the $A = +$ series with the quantum number $K = N - 2$. The other series are only weakly populated by photoabsorption from the ground state. This rule implies that a large class of doubly excited states which are predicted from theoretical studies cannot be easily confirmed by actual experiments using photoabsorption from the ground state of helium.

In this letter we show the calculated photoabsorption spectra from the metastable (1s2s) $^1S^e$ and (1s2s) $^3S^e$ states of He for energies below the He$^+$ ($N = 2$) threshold, using the hyperspherical close-coupling method (HSCC). These two states, with lifetimes of 0.02 and 8000 seconds respectively, can now be produced with enough quantity for performing electron–He (1s2s) $^1S^e$, $^3S^e$ collisions (Rall *et al* 1989). It is conceivable that experimental studies of photoabsorption from these metastable states will become feasible in the near

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future. Theoretical studies of photoionization from the He metastable states below the $N = 2$ threshold have been reported before (Norcross 1971, Jacob 1971, Doyle *et al* 1975, Chang 1993). Here we emphasize the comparison of the expected experimental photoabsorption spectra from the ground state and from the metastable (1s2s) ^{1}S^e state. Assuming an energy resolution of 5.4 meV, we show that the dominant doubly excited states populated in the two spectra are quite different and some doubly excited states which are difficult to observe in photoabsorption from the ground state are easily observed in photoabsorption from the metastable state.

The detailed account of the HSCC method has been given elsewhere (Tang *et al* 1992, Zhou *et al* 1993). In the following we shall only give a brief description. Atomic units are used throughout unless stated otherwise. Moreover, in the present paper we adopt the nomenclature $_N(K,T)_n^A$ or its simplified version K_n^A to designate a doubly excited state, all of which are associated with the $N = 2$ manifold of either ^{1}P^o or ^{3}P^o symmetry. Here n denotes the principal quantum number of the outer electron.

In hyperspherical coordinates, with the two-electron wavefunction of He expressed by $\psi(r_1, r_2) = \Psi(R, \alpha, \Omega)/(R^{5/2} \sin\alpha \cos\alpha)$, the Schrödinger equation can be written as

$$\left(-\frac{1}{2}\frac{\partial^2}{\partial R^2} + \frac{H_{\rm ad}}{R^2} - E\right)\Psi(R,\alpha,\Omega) = 0 \qquad (1)$$

where $R = (r_1^2+r_2^2)^{1/2}$ is the hyperradius, $\alpha = \tan^{-1}(r_1/r_2)$ is the hyperangle, and Ω denotes collectively the four angles $(\hat{r}_1, \hat{r}_2)$. $H_{\rm ad}$ is the adiabatic Hamiltonian with the hyperradius R being fixed.

To solve the Schrödinger equation in the HSCC method the configuration space is divided into two regions: the inner one ($R < R_M$) where electron–electron interaction is strong, and the outer or asymptotic one ($R > R_M$) where one electron is close to the nucleus and the other is far away. In the HSCC method, the range of the hyperradius in the inner region has been partitioned into many small sectors $[R_0, R_1, ..., R_M]$. Within each sector, $R \subset [R_{i-1}, R_i]$, $\Psi(R, \alpha, \Omega)$ is expressed in a close-coupling expansion

$$\Psi(R,\alpha,\Omega) = \sum_{\mu=1}^{N_{\rm ch}} F_\mu(R)\phi_\mu(R_i^m;\alpha,\Omega) \qquad (R_{i-1} < R < R_i) \qquad (2)$$

where R_i^m is chosen to be at the midpoint of the ith sector and $N_{\rm ch}$ is the number of channels included. Note that channel functions ϕ_μ are *independent* of R within the sector.

Substituting the expression (2) into the Schrödinger equation (1), one obtains the close-coupling equations for F_μ

$$\left(-\frac{\partial^2}{\partial R^2} - 2E\right)F_\mu(R) + \sum_\nu V_{\mu\nu}(R)F_\nu(R) = 0 \qquad (\mu = 1, ..., N_{\rm ch}) \qquad (3)$$

where $V_{\mu\nu}(R)$ is the coupling term between channels μ and ν. By making the channel functions ϕ_μ independent of R in (2) within each hyperradial sector, often referred as the diabatic-by-sector technique, the calculation of couplings $V_{\mu\nu}(R)$ among different channels are significantly simplified.

The calculation in the inner region is carried out in the following steps. Firstly, the diabatic channel functions ϕ_μ, thereby the channel couplings $V_{\mu\nu}(R)$ are calculated for each sector. Then starting from the innermost sector $i = 1$, the close-coupling equations (3) are integrated from R_{i-1} to R_i to obtain the radial functions F_μ, whose values at the end point R_i will serve as the initial boundary condition for the integration in the next sector. The integration propagates from inner sectors to outer ones, until the matching boundary $R = R_M$ is reached.

Beyond $R = R_M$, the two electrons are well separated and can be described as products of two functions in independent electron coordinates r_1, r_2,

$$\psi_E^{(\beta)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = \frac{1}{r_< r_>} \sum_{i=1}^{N_{\mathrm{ch}}} \Phi_i(r_<) Y_{l_1^i l_2^i}^{LM}(\Omega)[f_i^E(r_>)\delta_{i\beta} - g_i^E(r_>)K_{i\beta}(E)] \qquad (\beta = 1, \ldots, N_{\mathrm{ch}}). \tag{4}$$

where $Y_{l_1^i l_2^i}^{LM}(\Omega)$ is the coupled angular momentum wavefunction of the two electrons. Φ_i is the bound hydrogenic radial function of nuclear charge $Z = 2$ of the inner electron for channel i characterized by the binding energy $E_i = -2/N(i)^2$ with $N(i)$ as the inner electron's principal quantum number. The functions f_i, g_i are the energy normalized regular and irregular radial Coulomb functions of charge 1, respectively, of the outer electron if channel i is open ($E \geqslant E_i$), or exponentially increasing and decreasing functions if channel i is closed ($E < E_i$).

Similar to the R-matrix method, the reaction matrix $\boldsymbol{K}$ is obtained when the numerical solution and its derivative with respect to R in the inner region are matched with the asymptotic solutions at the boundary $R = R_M$. Since the inner and outer solutions are expressed in two different coordinates, a simple frame transformation has to be made in matching.

The above procedures are carried out separately for both the initial states as well as the final states of different energies. For both initial (1s2s) $^1S^e$ and $^3S^e$ states, 23 channels and 211 diabatic sectors with the matching distance $R_M = 22.8$ au are used in the present calculation. The binding energies for (1s2s) $^1S^e$ and (1s2s) $^3S^e$ obtained are −2.145 980 au and −2.175 268 au which are to be compared with the experimental values −2.146 074 au and −2.175 330 au (Kelly 1982) respectively. For the final state wavefunctions, 25 channels and 341 diabatic sectors with $R_M = 99.5$ au are used for both $^1P^o$ and $^3P^o$. The photoionization cross sections obtained in the dipole length form and in the dipole acceleration form agree to within about 2%.

Table 1. Resonances of He $^1P^o$ states associated with the $N = 2$ manifold. The oscillator strength I is expressed in terms of number of electrons.

		$_N(K,T)_n^A$				
		$_2(0,1)_2^+$	$_2(1,0)_3^-$	$_2(0,1)_3^+$	$_2(-1,0)_3^0$	$_2(1,0)_4^-$
	E_r (au)	0.6930	0.5972	0.5642	0.5473	0.5467
	Γ (au)	1.39E−3	4.02E−6	3.01E−4	1.4E−7	1.97E-6
$(1s^2)\,^1S^e$	$\sigma_{\max}$ (Mb)	12.5	23.4	9.5	88.2	13.4
	I	6.76E−3	3.66E−5	1.11E−3	4.81E−6	1.03E−5
$(1s2s)\,^1S^e$	$\sigma_{\max}$ (Mb)	525	6.99E+4	8.93	2.28E+5	6468
	I	0.284	0.109	1.05E−3	0.012	0.005

Figure 1 shows the global spectrum, as a function of the total energy E, of the calculated photoionization cross section from the (1s2s) $^1S^e$ state of He below the He$^+$ ($N = 2$) threshold. To compare, the photoionization spectrum from the ground state ($1s^2$) $^1S^e$ of He is also shown. (Note the different scales in cross section between the two spectra.) The

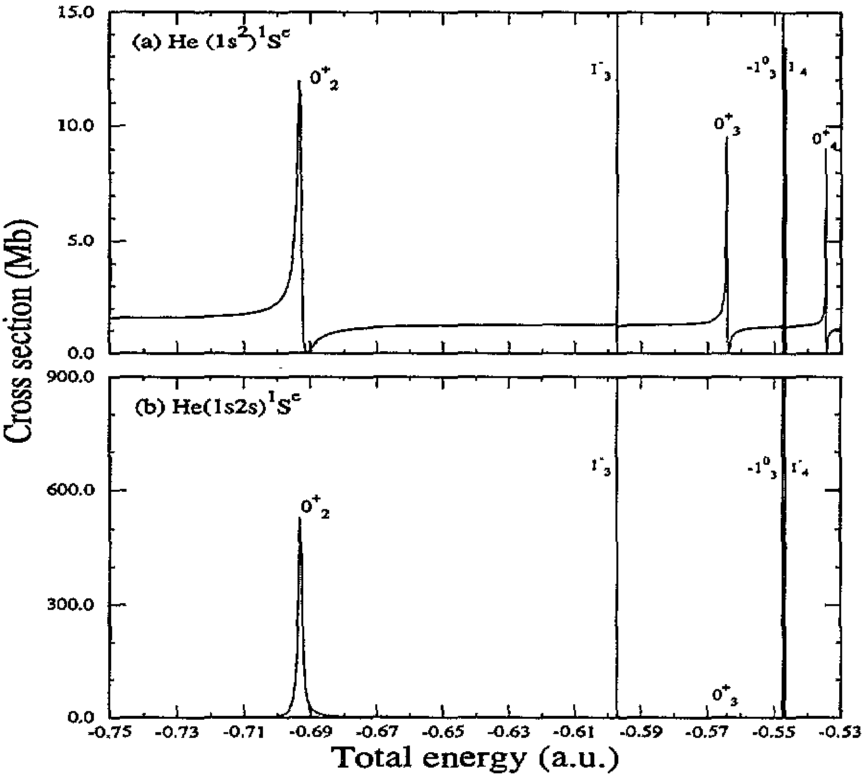

Figure 1. The calculated photoionization cross sections of He for energies below the He^+ $(N = 2)$ threshold: (*a*) from the ground state $(1s^2)$ $^1S^e$; (*b*) from the $(1s2s)$ $^1S^e$ state. The autoionizing doubly excited states are denoted with K_n^A.

doubly excited states in this energy region fall into three series: ${}_2(0,1)_n^+$, $(n = 2, 3, ...)$, ${}_2(1,0)_n^-$ and ${}_2(-1,0)_n^0$, $(n = 3, 4, ...)$. Doubly excited states associated with $A = +$ series have the largest widths, while those associated with $A = 0$ have the smallest widths. It is difficult to tell which states have significant spectral intensities from figure 1 because of the narrow resonances ($A = -, 0$ states) usually have very sharp peaks. Since the spectral intensity is basically the area covered by the resonance, one can roughly estimate the local oscillator strength or the intensity of a resonance as $I \approx (c/4\pi)\sigma_{\max}\Gamma$. The information about the maximum height $\sigma_{\max}$, autoionization width Γ, and the estimated spectral intensity I are tabulated in table 1 for the resonances considered. From the table, one can clearly sees that for photoionization from the ground state intensities of the doubly excited states associated with the $A = +$ series are at least two orders of magnitude larger than those of the $A = -$ and 0 states. That is, only the + states are primarily populated by photoabsorption. However, for photoionization from the metastable $(1s2s)$ $^1S^e$ state one sees that the intensity of the first + resonance 0_2^+ (an intrashell state) is quite large, but the intershell 0_3^+ state is rather weak, especially if it is compared to the $A = -, 0$ resonances of the same n-manifold.

This change in spectral intensity can be illustrated in a better perspective if the spectra are displayed with an 'experimental' resolution of 0.0002 au or 5.4 meV, as shown in figure 2. The spectra in figure 2(*a*) have been observed in many experiments (Domke *et al* 1991, 1992), where the + series is distinctly visible, while the − series is barely seen. In contrast,

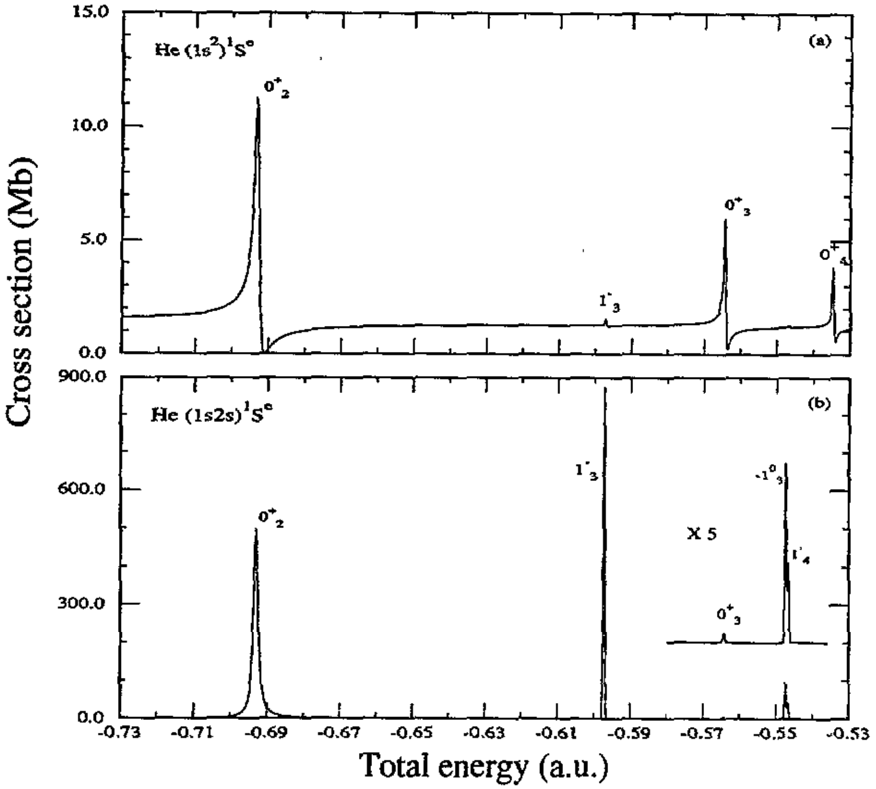

Figure 2. The convoluted photoionization cross sections of He with an energy resolution of 0.0002 au: (*a*) from the ground state ($1s^2$) $^1S^e$; (*b*) from the (1s2s) $^1S^e$ state. The inset in (*b*) shows the spectra that has been multiplied by five for clarity. Note that in (*a*) the $A = +$ series is predominantly populated and the resonances show asymmetric profiles. In (*b*), except for the first intrashell state 0_2^+, the $A = -$ and $A = 0$ series are more prominently populated than the $A = +$ series. The autoionizing doubly excited states are denoted with K_n^A.

for photoabsorption from the (1s2s) ^1S metastable state, except for the first member, the + series is not prominently seen, while the − and the 0 series are much more pronounced (see the inset of figure 2(*b*)). Furthermore, the narrow resonances populated by photoabsorption from the ground state and from the metastable state have quite different profiles, as shown in figure 3. For photoabsorption from the ground state, the calculated (without convolution) spectra always show asymmetric profiles, while from the metastable state, the resonances appear to be nearly Lorentzian. Figure 3 also shows the convoluted spectra with 5.4 meV resolution, indicating that the spectra are rather different even if the two states -1_3^0 and 1_4^- are not fully resolved.

The above results can be understood qualitatively. Firstly, photoabsorption to doubly excited states below the $N = 2$ threshold of He$^+$ from the metastable state is close to an one-electron transition from the independent electron approximation point of view. Each doubly excited state is a linear combination of 2s*n*p, 2p*n*s and 2p*n*d configurations and the transition from 1s2s to 2s*n*p is essentially the one-electron 1s to *n*p transition. The propensity rule does not work well here since the K, T and A quantum numbers are not suitable for describing singly excited states such as the metastable state here. Thus it is not surprising that the − and 0 states are populated, meaning that the approximate quantum

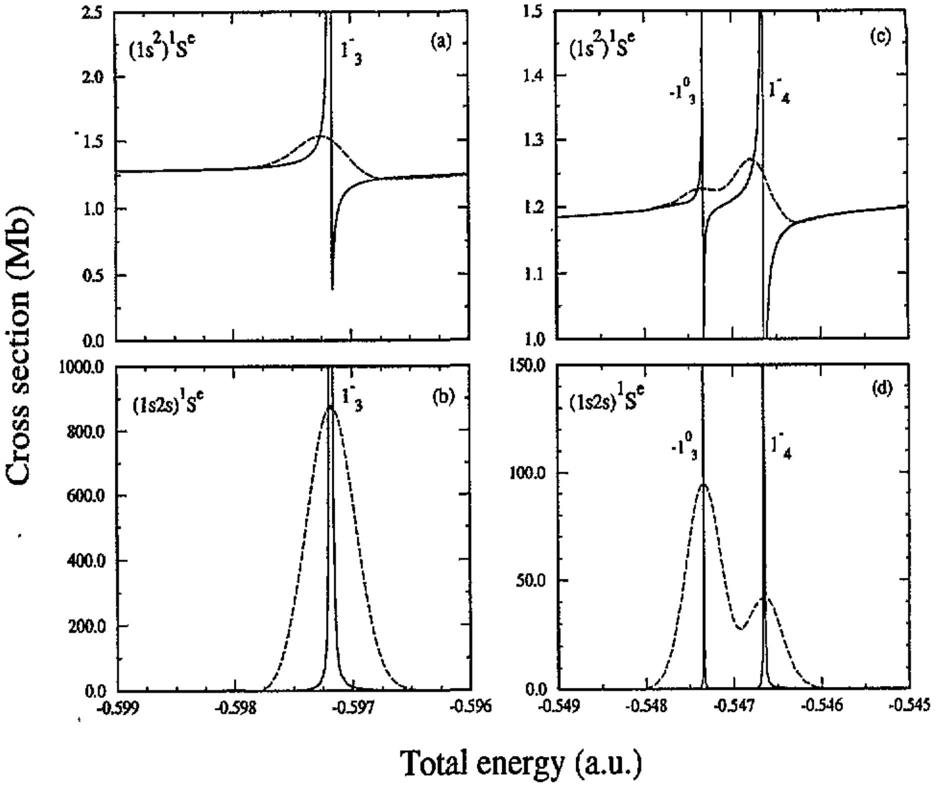

Figure 3. The detailed profiles of the three $^1P^o$ resonances appeared in photoionization cross sections of He from the ground state or from the metastable (1s2s) $^1S^e$ state. (*a*) 1_3^- resonance from the ground state; (*b*) 1_3^- resonance from the (1s2s) $^1S^e$ state; (*c*) -1_3^0 and 1_4^- resonances from the ground state; (*d*) -1_3^0 and 1_4^- resonances from the (1s2s) $^1S^e$ state. The full curves represent the calculated cross sections and the broken curves represent the convoluted cross sections with the energy resolution 0.0002 au.

number A is not preserved.

The 'sudden' diminishing of higher members of 0_n^+ series from $n = 2$ to $n = 4$ in figure 1(*b*) and figure 2(*b*) reflects the existence of a Cooper minimum in the transitions from the (1s2s) state to the 0_n^+ series. This is more clearly seen by displaying the spectra including the higher members of the series, shown in figure 4. In figure 4, the height of 0_n^+ resonances decreases from 525 Mb at $n = 2$ to nearly zero at $n = 4$ and then increases ($n = 5, 6, 7$) with higher n. Another indication for the existence of the Cooper minimum is that the Fano shape parameter q, as seen from figure 4, changes from a negative value for 0_3^+ to a positive one for 0_5^+, 0_6^+ and 0_7^+. Since q is proportional to the dipole transition matrix element from the initial state to the doubly excited state, this implies that there exists a sign change in the dipole transition matrix element between $n = 3$ and 5 of the 0_n^+ series.

Another important feature in the resonance spectra for photoabsorption from the metastable state is that each resonance is more or less Lorentzian, implying that the background continuum is very weak. This can also be understood from the 'independent' electron model. The continuum p electron in the background channel 1sϵp results from the direct ionization of the 2s electron in the (1s2s) initial state. Since the photon energies considered (about 40 eV) are about ten times higher than the 2s threshold energy (about 4 eV), this single ionization cross section is quite small, as compared to the 'single' photon

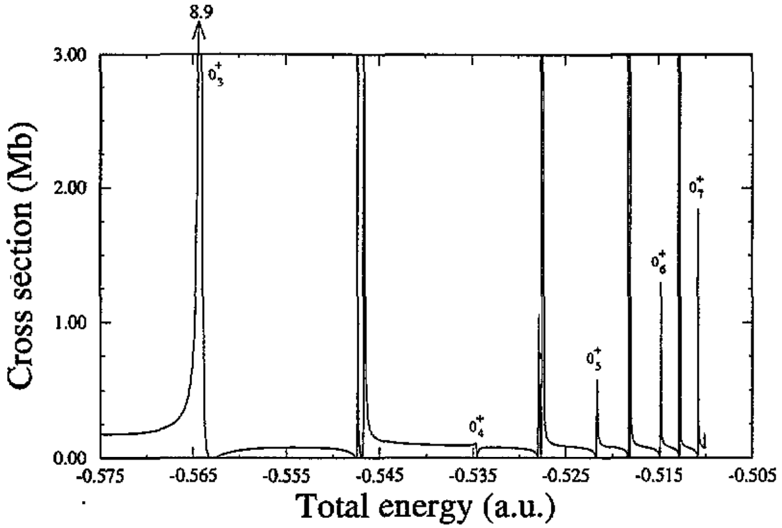

Figure 4. The calculated photoionization cross sections from the metastable (1s2s) $^1S^e$ state of He near the 0_4^+ resonance. The peak heights of 0_n^+ resonances decrease from $n = 2$ to 4 then increase from 4 to 5, 6 and 7, indicating the existence of a Cooper minimum near the 0_4^+ resonance.

transition of the 1s electron in the ground state, where the corresponding photon energies (about 60 eV) are much closer to the threshold if measured with the 1s binding energy (about 24.6 eV).

Table 2. Resonances of He $^3P^o$ states associated with the $N = 2$ manifold. The oscillator strength f is expressed in terms of number of electrons.

		${}_N(K,T)_n^A$					
		${}_2(1,0)_2^+$	${}_2(1,0)_3^+$	${}_2(0,1)_3^-$	${}_2(-1,0)_3^0$	${}_2(1,0)_4^+$	${}_2(0,1)_4^-$
	E_r (au)[a]	0.7605	0.5848	0.5791	0.5490	0.5431	0.5397
	Γ (au)[a]	3.06E−4	7.77E−5	1.60E−6	1.41E−9	3.14E−5	6.37E−7
	Γ (au)[b]	3.00E−4	8.40E−5	2.06E−6	9.20E−9	3.04E−5	4.80E−7
	Γ (au)[c]	2.90E−4	7.90E−5	1.98E−6	∼3E−7	3.10E−5	8.35E−7
(1s2s) $^3S^e$	σ_{max} (Mb)	2491.0	42.0	9.6E+4	3.54E+6	153.0	5.86E+4
	f	0.297	1.27E−3	0.060	1.94E−3	1.87E−3	0.037

[a] Present work.
[b] Moccia and Spizzo (1987).
[c] Chang (1993).

We have also calculated the photoionization cross section of He from the (1s2s) $^3S^e$ state. There are three series of doubly excited states associated with the manifold $^3P^o$ ($N = 2$): ${}_2(1,0)_n^+$, ($n = 2, 3, \ldots$), ${}_2(0,1)_n^-$, ($n = 3, 4, \ldots$) and ${}_2(-1,0)_n^0$, ($n = 3, 4, \ldots$). Note the quantum number K, T of the + and − states of $^3P^o$ are opposite to those of $^1P^o$. The convoluted spectrum with an energy resolution 0.0002 au is depicted in figure 5. The information of energy position, autoionization width, maximum peak height, and the spectral intensity for autoionizing doubly excited states up to $n = 4$ are listed in table 2. As seen from both figure 5 and table 2, except for the first + resonance 1_2^+, an intrashell state which is populated predominantly by the single electron 1s to 2p transition, for the

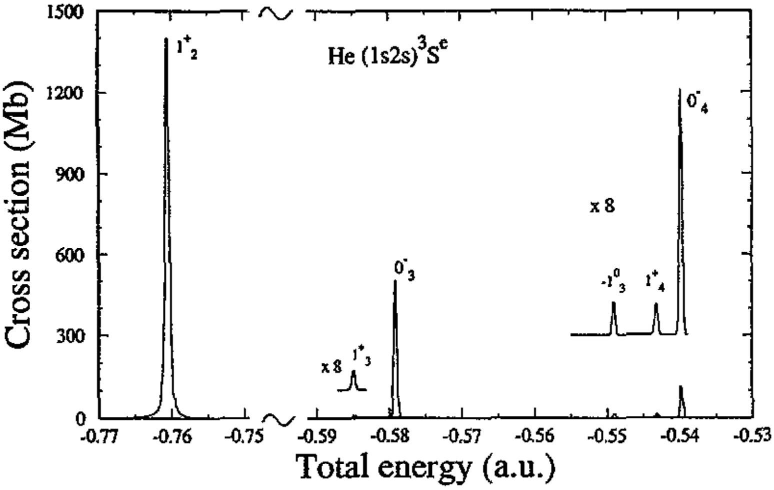

Figure 5. Photoionization spectrum from the metastable state (1s2s) ^{3}S^e of He for energies below the He$^+$ ($N = 2$) threshold convoluted with energy resolution 0.0002 au The autoionizing doubly excited states of ^{3}P^o are denoted with K_n^A.

intershell states the $A = -$ series is stronger than the $A = +$ series in the photoionization spectra despite that the $A = +$ states have much broader widths. Note that the intensity of the $A = 0$ resonance, -1_3^0, despite of its extremely narrow width, as can be seen from table 2, has an intensity comparable to those of the $A = +$ resonances 1_3^+ and 1_4^+. From table 2 and figure 5, it seems that there is a Cooper minimum near the $n = 3$ resonance for the 1_n^+ series, similar to the singlet state case described above. In table 2 we also compare our calculated widths with two representative results among the numerous other calculations (Moccia and Spizzo 1987, Chang 1993, Ho 1986, Wu and Xi 1990, Oza 1986, Norcross 1971). The resonance positions predicted by various theories converge within four significant digits but conspicuous discrepancies exist for autoionization widths. In particular, the present calculation predicts a much narrower width for the -1_3^0 state.

To summarize, we have calculated photoionization cross sections of He from metastable excited states, (1s2s) ^{1}S^e and (1s2s) ^{3}S^e, for energies below the He$^+$(N=2) threshold. It is found that the spectra of doubly excited states populated by photoabsorption from the ground state and the metastable (1s2s) ^{1}S^e state are drastically different. The $A = +$ series, which is predominately populated by photoabsorption from the ground state, is no longer the dominant series for photoabsorption from the metastable (1s2s) ^{1}S^e state. In the latter, the $A = -$ and $A = 0$ series become more prominent. We have also calculated the photoabsorption spectra from the metastable (1s2s) ^{3}S^e state and identified a number of doubly excited states below the $N = 2$ threshold of He$^+$. The calculated spectra have been convoluted with an energy resolution of 5.4 meV to show the expected experimental spectra. It would be desirable to check if such experiments can be carried out with the density of metastable helium atoms that is achievable today.

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