

## Photoionization of positive ions. I. Oxygen\*†

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Photoionization cross sections for all subshells occupied in the ground states of neutral oxygen and each positive ion  $O^{+n}$  ( $n = 1-6$ ) have been calculated using Hartree-Slater wave functions. The results show that removal of a  $2p$  or  $2s$  electron has no effect on the  $1s$  cross section other than shifting the threshold. The systematics of the cross section as a function of stage of ionization are analyzed, and the limits of applicability of the hydrogenic model are discussed.

### I. INTRODUCTION

A knowledge of the cross section for photoionization of positively charged atomic ions is necessary in connection with plasma physics and controlled thermonuclear fusion; in connection with upper atmospheric physics where solar radiation is absorbed by positive ions as well as neutral atoms and molecules; and in connection with space and astrophysics in the transport of radiation through stellar atmospheres and planetary nebulae. No laboratory measurements of the photoionization of multicharged positive ions have been performed owing to the temperatures of over  $10^5$  °K which are necessary to produce them in quantity and the intensity limitations of a crossed-beam experiment. On the theoretical side, the hydrogenic approximation<sup>1</sup> has been used fairly extensively to provide estimates of the photoionization cross section for positive ions, but the limits of validity of such a theoretical model are not known. Recently, however, a very few calculations have been carried out using more sophisticated wave functions.<sup>2-11</sup> Further theoretical work is, thus, desirable.

In this paper we report on the results of calculations using Hartree-Slater (HS) central-field wave functions for ions of oxygen from the neutral to  $O^{+6}$ . These calculations were performed with a threefold purpose in mind: first, to provide input data to other branches of physics, oxygen being chosen because of its abundance in planetary and stellar atmospheres; second, to obtain information on the systematics of the photoionization cross section as a function of both energy and ionicity (stage of ionization); third, to compare our results with the hydrogenic results and, thus, establish the limits of validity of the latter.

The next section gives a brief review of the theory of photoionization and the method of calculation along with some discussion of the accuracy of our

calculation. Section III presents and discusses our results for the  $1s$ ,  $2s$ , and  $2p$  subshells of our results with the hydrogenic. In Sec. IV, our conclusions are summarized and a prospectus for further work is given.

### II. THEORY AND METHOD OF CALCULATION

Within the framework of a central-potential model, the cross section for photoionization of an electron in the  $nl$ th subshell is given in the dipole approximation by<sup>12</sup>

$$\sigma_{nl}(\epsilon) = \frac{4}{3} \pi^2 \alpha a_0^2 N_{nl} \frac{\epsilon - \epsilon_{nl}}{2l+1} \times [lR_{l-1}(\epsilon)^2 + (l+1)R_{l+1}(\epsilon)^2]. \quad (1)$$

Here  $\epsilon_{nl}$  (in rydbergs) is the binding of an electron in the  $nl$ th subshell,  $\alpha$  is the fine-structure constant ( $1/137$ ),  $a_0$  is the Bohr radius ( $5.29 \times 10^{-9}$  cm),  $N_{nl}$  is the number of electrons in the subshell, and  $\epsilon$  (in rydbergs) is the energy of the ionized photoelectron, i.e.,  $h\nu = \epsilon - \epsilon_{nl}$ , where  $h\nu$  is the incident photon energy. The radial dipole matrix elements are

$$R_{l\pm 1}(\epsilon) = \int_0^\infty P_{nl}(r)rP_{\epsilon,l\pm 1}(r)dr, \quad (2)$$

where  $P_{nl}(r)/r$  and  $P_{\epsilon,l\pm 1}(r)/r$  are the radial parts of the single-particle wave functions of the initial (discrete) and final (continuum) states respectively, satisfying the normalization conditions

$$\int_0^\infty P_{nl}(r)^2 dr = 1, \quad (3)$$

$$P_{\epsilon l}(r) \xrightarrow{r \rightarrow \infty} \pi^{-1/2} \epsilon^{-1/4} \sin[\epsilon^{1/2} r + \epsilon^{-1/2} \ln 2\epsilon^{1/2} r - \frac{1}{2} l\pi + \sigma_l(\epsilon) + \delta_l(\epsilon)], \quad (4)$$

with  $\sigma_l(\epsilon) = \arg \Gamma(l+1 - i\epsilon^{-1/2})$ , and  $\delta_l(\epsilon)$  is the phase shift. This normalization of  $P_{\epsilon l}(r)$  is the usual normalization of continuum wave functions per

unit energy.

Hartree-Slater (HS) central-field wave functions were used for the wave functions of the discrete orbitals of the initial ionic states and were calculated using the program of Herman and Skillman.<sup>13</sup> For the final state the wave function of the continuum orbital was taken to be the solution to the radial Schrödinger equation with the *same* central potential as the initial state. The orbitals of the passive electrons in the residual ion core were taken to be unchanged by the photoionization process, i.e., no core relaxation. The details of the calculation and normalization of the continuum wave function are given in Ref. 12.

Before proceeding to a discussion of our results, we note that the HS model of an atom or ion does not include multiplet splitting because of the inexact treatment of exchange as a central field.<sup>14</sup> This effect will only be of significance in the vicinity of the threshold of each subshell in an open-shell atom or ion. One can include the multiplet effects in an approximate way by introducing the different multiplet energy levels and relative multiplet strengths and use the HS dipole matrix elements. This procedure has been found to provide reasonably good results.<sup>15,16</sup>

### III. RESULTS AND DISCUSSION

Calculations have been performed for the photoionization of each subshell of the ground state of each stage of ionization of oxygen,  $O^{+n}$ , from  $n=0$  (neutral) to  $n=6$ .  $O^{+7}$  is a one-electron system and the hydrogenic treatment is thus essentially exact so it is omitted. Energies for each subshell from threshold to 30 Ry above threshold have been included.

#### A. 1s subshell

The calculated cross sections for photoionization of 1s electrons for neutral oxygen and its ions  $O^{+n}$  ( $n=1-6$ ), i.e., along the  $Z=8$  *isonuclear* sequence, are shown in Fig. 1 plotted against photon energy. Note that the cross sections lie essentially on the same curve, when plotted vs photon energy, with only minor variations (<3%). This shows that the removal of outer-shell electrons, 2s or 2p, affects only the 1s threshold ionization energy,  $\epsilon_{1s}$ , but leaves  $\sigma_{1s}(h\nu)$  constant as long as  $h\nu \geq \epsilon_{1s}$ . The removal does, however, move some oscillator strength into the discrete region when  $h\nu < \epsilon_{1s}$  for the given ion. This conforms to the conclusions of Barfield, Koontz, and Huebner.<sup>17</sup>

This result has several important implications. First it is clear that  $\sigma_{1s}$  will be essentially unaffected by excitation of outer-shell electrons inasmuch as the more drastic process of ionization

has such a negligible effect. Thus, although the calculation was performed for the ground state, of each ionic system we also have  $\sigma_{1s}$  for excited states of the atom or ions of oxygen where the excitation involves 2s and/or 2p electrons only. Secondly, we see that one need do the calculation for  $\sigma_{1s}$  for the neutral atom only and simply shift thresholds to obtain  $\sigma_{1s}$  for the various ions. Third, these conclusions should hold for the photoionization of 1s electrons in all higher- $Z$  atomic and ionic systems as well since removal of an outer electron there is a proportionally smaller change due to the larger number of electrons. Operationally, these points will save a great amount of calculation for  $\sigma_{1s}$  of the ions of other elements.

This behavior results from the fact that the spatial extent of the 1s wave function is concentrated very close to the nucleus ( $\langle r \rangle_{1s} \sim 0.18a_0$  for oxygen and its ions)<sup>19</sup> while the 2s and 2p lie predominantly much further from the nucleus, by about a factor of 5 ( $\langle r \rangle_{2s,2p} \sim 1.1a_0$  for oxygen and its ions).<sup>19</sup> This, of course, simply reflects the fact that  $\langle r \rangle$  is determined almost entirely by the principal quantum number. Thus, the 1s electrons "see" the 2s and 2p roughly as spherical shells of negative charge concentrated at  $\langle r \rangle_{2s,2p}$ . Then, since  $\langle r \rangle_{2s,2p}$  is well beyond the point where the 1s wave function is effectively zero, their removal only lowers the potential of the region of space  $r < \langle r \rangle_{2s,2p}$  by a constant without otherwise affecting the 1s wave function. This gives rise to the shift of the 1s threshold, with removal of 2s or 2p electrons, without affecting  $\sigma_{1s}$  in any other way.

Also shown in Fig. 1 is the hydrogenic result<sup>1</sup> with Slater inner screening<sup>14</sup> ( $Z_{\text{eff}} = Z - 0.31 = 7.69$ )

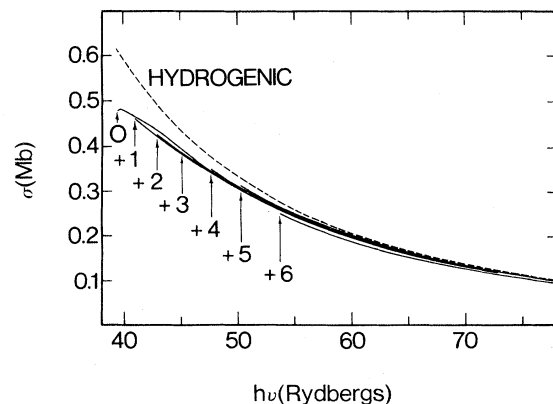


FIG. 1. Calculated 1s ( $K$ -shell) photoionization cross sections for the ground states of neutral atomic oxygen and each of its positive ions +1 to +6. The vertical lines are the theoretical 1s thresholds for each charge state and the dashed curve is the hydrogenic result.

and outer screening<sup>18</sup> to insure that the hydrogenic threshold energy equals the HS value. Note that the hydrogenic results as well lie along the same curve since the inner screening constant of the 1s subshell does not change with removal of outer electrons. The removal does, of course, change the outer screening,<sup>18</sup> for the reasons discussed above, so that the 1s threshold ionization energy increases in the hydrogenic model as well.

The agreement between HS and hydrogenic results is fairly good, as seen in Fig. 1. The hydrogenic  $\sigma_{1s}$  is about 30% too high at the threshold of neutral oxygen ( $h\nu \sim 40$  Ry) and by the 1s threshold of  $O^{+6}$  ( $h\nu \sim 55$  Ry) up to the limit of our calculation agreement is excellent. The hydrogenic result is somewhat high at threshold since the matrix element is determined primarily near the outer part of the 1s wave function for which the hydrogenic  $Z_{\text{eff}}$  is somewhat high. At higher photon energies, where the matrix element is determined mostly in the central region of the 1s function, agreement is excellent. At very large photon energies, the matrix element is determined quite close to the nucleus where the bare nuclear charge  $Z$  is operative, rather than the somewhat smaller  $Z_{\text{eff}}$ , so the hydrogenic result will drop below the HS.

#### B. 2s subshell

The photoionization cross sections for 2s electrons along the oxygen *isomuclear* sequence are

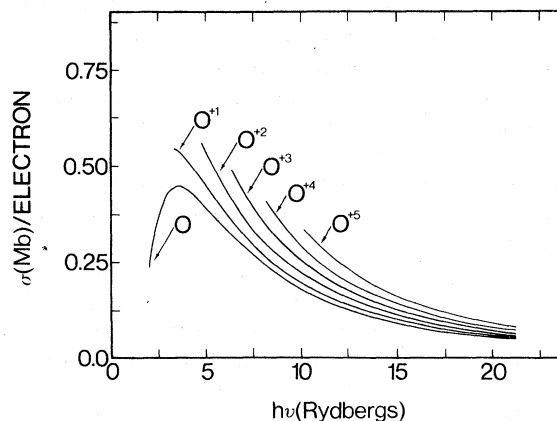


FIG. 2. Calculated 2s ( $L_1$ -shell) photoionization cross sections per 2s electron for the ground states of neutral atomic oxygen and each of its positive ions  $O^{+1}$  to  $O^{+5}$  in which the 2s appears.

shown in Fig. 2. The 2s results along the sequence *do not* lie along the same curve, even for stages of ionization for which only  $2p$  electrons are being removed. This is because  $\langle r \rangle$  for the 2s and  $2p$  wave functions are approximately the same.<sup>19</sup> Thus significant changes in the screening of the 2s electrons occur with the removal of a  $2p$  electron. The delayed maximum<sup>12,20,21</sup> which is present in the neutral is seen to have moved into the discrete transition region for  $O^{+1}$  and higher stages of ionization. The general behavior of the 2s cross

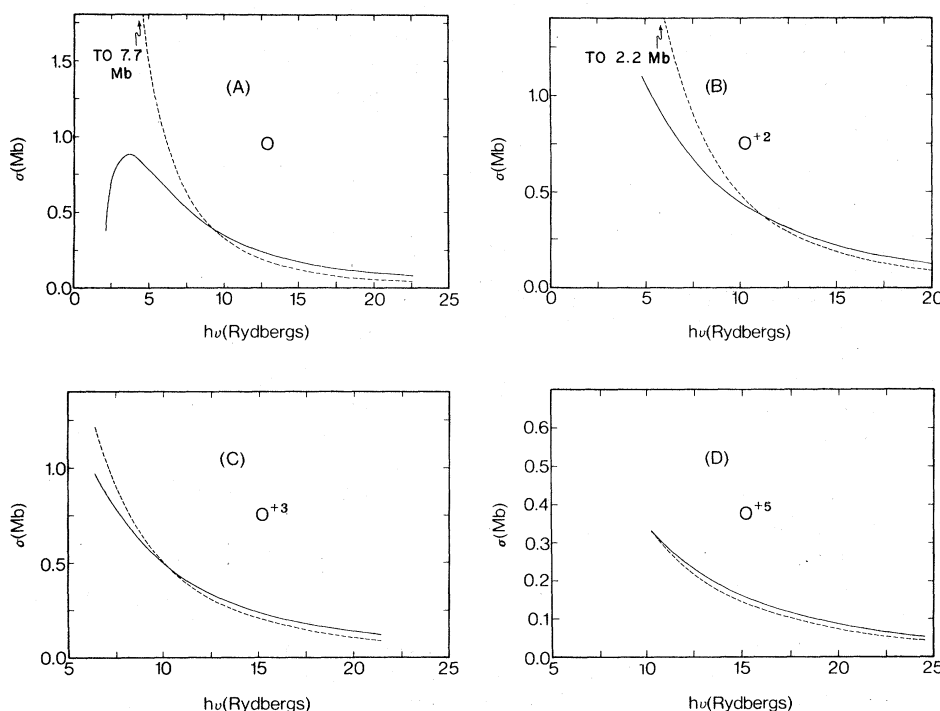


FIG. 3. Comparison between our results and the hydrogenic results for the photoionization of 2s electrons from neutral atomic oxygen,  $O^{+2}$ ,  $O^{+3}$ , and  $O^{+5}$ . The solid curve is our value, and the dashed curve is the hydrogenic result.

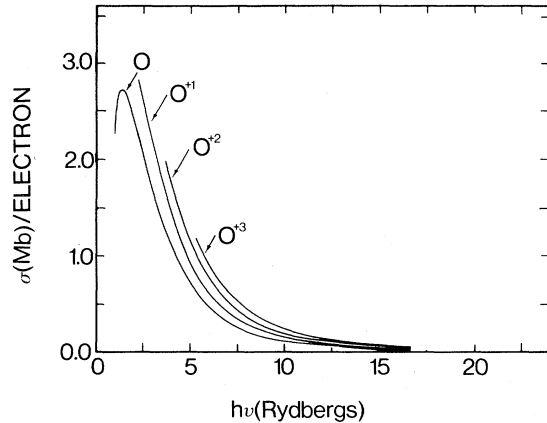


FIG. 4. Calculated  $2p$  ( $L_{2,3}$ -shell) photoionization cross sections *per*  $2p$  electron for the ground states of neutral atomic oxygen and each of its positive ions  $O^{+1}$  to  $O^{+3}$  in which the  $2p$  appears.

section for a given  $h\nu$  is to increase along the isonuclear sequence starting from the neutral, reflecting the contraction of the  $2s$  wave function.

Figure 3 shows the comparison of our HS results with the hydrogenic results which were calculated using Slater inner screening<sup>14</sup> and outer screening<sup>18</sup> to match with HS ionization potentials. The comparison shows that in all cases the hydrogenic results are much too large at low  $h\nu$  and too small at large  $h\nu$  for all stages of ionization. In addition, at  $h\nu \sim 10$  Ry the hydrogenic results cross over the HS for all stages of ionization. This is important

because it is just in this region that the hydrogenic results are good. Thus it would be very useful to be able to delineate the crossover point *a priori*.

From a mathematical point of view, the crossover point remains at (roughly) constant  $h\nu$  since in going along an *isonuclear* sequence, the HS and hydrogenic results increase by roughly the same amount. Physically, the crossover point occurs when the matrix element is generated primarily in the region of intermediate distance from the nucleus, as discussed previously. As the stage of ionization increases, the matrix element at the energy ( $h\nu$ ) of the crossover point seems to be still generated in the same region so that hydrogenic result remains close to the HS result at that  $h\nu$ , leading to the relative constancy of the crossover photon energy.

### C. $2p$ subshell

The photoionization cross sections for  $2p$  electrons along the oxygen *isonuclear* sequence are shown in Fig. 4. Note that the results are plotted *per electron* to isolate the changes in the atomic matrix elements by removing the effect of the decreasing number of  $2p$  electrons with increasing stage of ionization. As in the  $2s$  case, the neutral shows a delayed maximum which moves into the discrete by the first stage of ionization. In addition, the increase of the cross section, for a given  $h\nu$ , due to the contraction of the  $2p$  wave function is also seen, just as in the  $2s$  case.

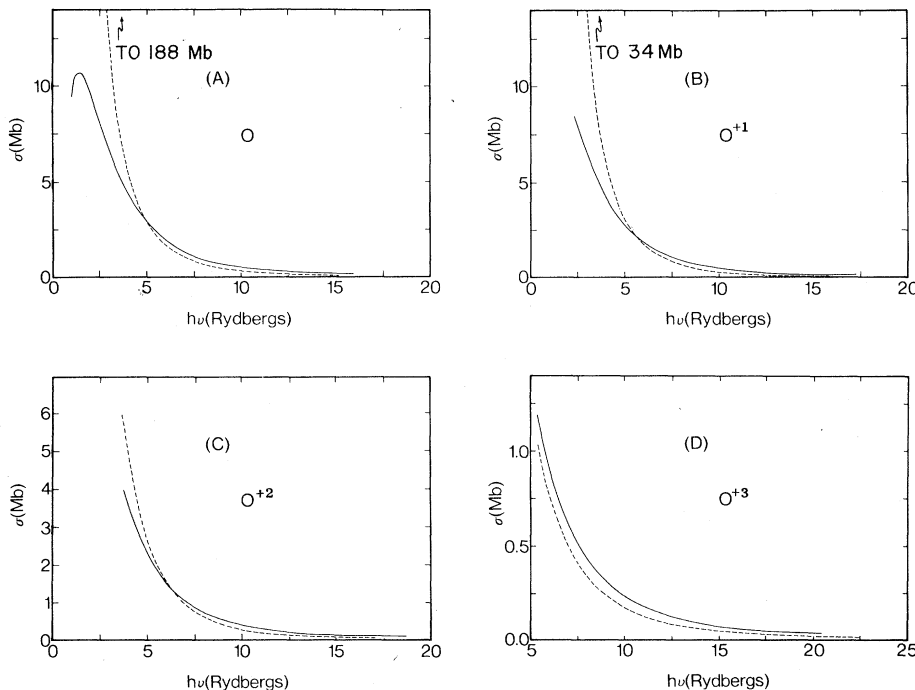


FIG. 5. Comparison between our results and the hydrogenic results for the photoionization of  $2p$  electrons from neutral atomic oxygen,  $O^{+1}$ ,  $O^{+2}$ , and  $O^{+3}$ . The solid curve is our value, and the dashed curve is the hydrogenic result.

The hydrogenic results are compared with our HS values in Fig. 5 where the same general trends as in the 2s case can be noted. In particular, the hydrogenic results are much too large for small  $h\nu$  and get progressively too small for large  $h\nu$  for reasons discussed previously. The crossover point again remains approximately constant, here at  $h\nu \sim 5$  Ry for the same reasons discussed above.

#### IV. FINAL REMARKS

We have found an approximate constancy (independent of stage of ionization) of the photon energy for which one obtains equality between HS and hydrogenic photoionization results for each of the 1s, 2s, and 2p subshell of oxygen. The crossover values for the 2p and 2s, approximately 5 and 10 Ry, respectively, are each roughly five times the neutral thresholds of 1.04 and 2.10 Ry, respectively. For the 1s, the crossover point is at about 90 Ry, as against a neutral 1s threshold of 39 Ry, or about a factor of 2.3. Further work is needed before an inference can be made reliably to predict *a priori* the crossover points and, thus, the regions of usefulness of the hydrogenic approximation.

We have also verified that in going along an *isomuclear* sequence, removal of an electron with principal quantum number  $n$  does not affect the photoionization of electrons with principal quantum number  $n-1$ , except to shift the threshold, which

has been pointed out previously.<sup>17</sup> This should be generally true, not only for 1s electrons, since it rests on the fact that  $\langle r \rangle$  is determined almost entirely by principal quantum number. For this reason, removal of an  $nl$  electron affects all electrons with the same  $n$  whether or not they are in the same subshell. In addition, it is expected that other inner-shell properties will remain largely unaffected by removal of outer shell electrons, but this point still needs verification. In any case, it is clear that a considerable simplification results from this observation both computationally and from the point of view of understanding the systematics of photoabsorption of positive atomic ions.

Note further that this observation was made possible by looking at various stages of ionization of a given atom, i.e., an *isomuclear* sequence, and plotting vs photon energy rather than photoelectron energy. If *isoelectronic* sequences were considered, the simplification would not have been evident, nor would it have shown up if the cross sections were plotted vs electron energy. This points up, clearly, the notion that various ways of looking at ionic data reveals different aspects of the systematics.<sup>22</sup>

Finally we note that this paper is part of a larger study in which photoionization calculations have been performed on the *isomuclear* sequences of N, Fe, and Hg as well as the *isoelectronic* sequences of Ne, Ar, Kr, Xe, and Hg. These results will be reported shortly.

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<sup>1</sup>H. Hall, Rev. Mod. Phys. **8**, 358 (1936).

<sup>2</sup>R. H. W. Henry, J. Chem. Phys. **48**, 3635 (1968).

<sup>3</sup>M. B. Hidalgo, Astrophys. J. **153**, 981 (1968).

<sup>4</sup>R. J. W. Henry, Astrophys. J. **161**, 1153 (1970).

<sup>5</sup>K. L. Bell and A. E. Kingston, J. Phys. B **4**, 1308 (1971).

<sup>6</sup>D. W. Missavage and S. T. Manson, Phys. Lett. **38A**, 85 (1972).

<sup>7</sup>R. D. Chapman and R. J. W. Henry, Astrophys. J. **173**, 243 (1972).

<sup>8</sup>F. Combet Farnoux and M. Lamoureux, Phys. Lett. **43A**, 183 (1973).

<sup>9</sup>R. L. John and D. J. Morgan, Phys. Lett. **45A**, 135 (1973).

<sup>10</sup>M. Lamoureux and F. Combet Farnoux, J. Phys. (Paris) **35**, 205 (1974); J. Phys. B **6**, 897 (1976).

<sup>11</sup>G. R. Daum and H. P. Kelly, Phys. Rev. A **13**, 715 (1976).

<sup>12</sup>S. T. Manson and J. W. Cooper, Phys. Rev. **165**, 126 (1968).

<sup>13</sup>F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

<sup>14</sup>J. L. Slater, Phys. Rev. **81**, 385 (1951).

<sup>15</sup>S. T. Manson, D. J. Kennedy, A. F. Starace, and D. Dill, Planet. Space Sci. **22**, 1535 (1974).

<sup>16</sup>A. F. Starace, S. T. Manson, and D. J. Kennedy, Phys. Rev. A **9**, 2453 (1974).

<sup>17</sup>W. D. Barfield, G. D. Koontz, and W. F. Huebner, J. Quant. Spectrosc. Radiat. Transfer **12**, 1409 (1972).

<sup>18</sup>J. L. Slater, Phys. Rev. **36**, 57 (1930).

<sup>19</sup>J. B. Mann, Atomic Structure Calculations II. Hartree-Fock Wave Functions and Radial Expectation Values: Hydrogen to Lawrencium, Los Alamos Scientific Report LA-3691, 1968 (unpublished).

<sup>20</sup>J. W. Cooper, Phys. Rev. **128**, 681 (1962).

<sup>21</sup>U. Fano and J. W. Cooper, Rev. Mod. Phys. **40**, 441 (1968).

<sup>22</sup>K. D. Chao, J. L. Dehmer, U. Fano, M. Inokuti, S. T. Manson, A. Msezane, R. F. Reilman, and C. E. Theodosiou, *Proceedings of the Fourth International Conference on Beam-Foil Spectroscopy and Heavy Ion Symposium*, edited by D. Pegg and I. A. Sellin (Plenum, New York, 1976), p. 637.