

tegrable solutions when the  $\lambda_3$  terms therein are dropped, corresponding to dropping the relative phase constraint terms in the starting expression (6). On the other hand, the reader easily can verify that even without the relative phase constraint our procedure leads quite directly to a (previously unreported) variational principle for  $F = |\phi_1^\dagger W \phi_2|^2$ , as is to be expected, because now the desired  $F(\phi^\dagger, \phi)$  is independent of the relative phase of  $\phi_1$  and  $\phi_2$ ; for  $|\phi_1^\dagger W \phi_2|^2$  the starting expression is the same as (6) except that the  $\lambda_{3f}$  term is dropped and the  $\phi_{1f}^\dagger W \phi_{2f}$  term is replaced by  $|\phi_{1f}^\dagger W \phi_{2f}|^2$ .

Many other classical and quantum-mechanical examples of variational-principle construction

(e.g., the Kohn and Schwinger variational principles, variational principles for the wave function itself, for a transition amplitude, and for the density matrix), together with a much fuller discussion of the role of constraints, including the consequences of introducing unnecessary constraints (e.g., the specification of the phase for a diagonal matrix element), are discussed in a broad review in progress.<sup>4</sup> We are reasonably certain that essentially all variational principles for quantities  $F$  given in the literature can be systematically and conveniently derived by the prescription we have presented. We recommend use of this prescription when seeking to derive new variational principles.

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## Autoionization from High-Lying $3p^5(^2P_{1/2})np'$ Levels in Argon\*

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A beam containing argon metastable atoms is crossed by the output beam of a pulsed tunable uv laser. The resulting ion production is measured as a function of wavelength within the range  $2945 < \lambda < 3075$  Å and displays several sharp resonances. These arise from excitation of  $\text{Ar}(^3P_0)$  metastable atoms to high-lying  $3p^5(^2P_{1/2})np'$  levels which subsequently undergo autoionization. The term values of these levels are measured to an accuracy of  $\pm 6$  cm<sup>-1</sup> and are in excellent agreement with values obtained from a quantum-defect extrapolation of the known lower terms of this series. An unambiguous assignment of principal quantum numbers to the observed levels is therefore possible. The lifetimes against autoionization of these levels are longer than  $2 \times 10^{-12}$  sec.

A study of autoionizing states of the type  $3p^5(^2P_{1/2})nd'$  and  $3p^5(^2P_{1/2})ns'$  in argon using optical excitation from the  $^1S_0$  ground state has been reported previously.<sup>1</sup> In the present work excitation from the  $\text{Ar}(^3P_0)$  metastable level has allowed study of the autoionization from the hitherto optically inaccessible  $3p^5(^2P_{1/2})np'$  levels.

The apparatus has been described in detail elsewhere<sup>2,3</sup> and only a brief description is included here. A beam of argon atoms in the metastable  $^3P_{0,2}$  states is produced by electron impact and is then irradiated by the output beam of a

pulsed laser. The ions so formed are detected with a particle multiplier.

To discriminate against ions resulting from collisions between the metastable atoms and background gas, the output of the multiplier is fed to two scalars. One of these is gated so as to count those ions produced during the laser pulse, while the other is gated for an equal time when no laser pulse is present and therefore counts only ions formed from background gas. The difference in the scalar count rates is then due solely to photo ions produced during the laser pulse. Care must

be taken to determine the small (<5%) contribution to the "laser-on" signal due to ions liberated at surfaces by scattered radiation. This contribution is obtained by switching off the electron gun in the metastable-atom source when surface ionization provides the only remaining source of ions.

The metastable-atom flux is determined by measuring the current of secondary electrons ejected from a surface whose secondary-electron ejection coefficient  $\gamma$  is determined *in situ* using a technique described elsewhere.<sup>4</sup> The total metastable-atom density may then be determined from a measurement of the velocity distribution of the metastable-atom beam.<sup>5</sup> Assuming that the two metastable levels are populated in amounts proportional to their statistical weights, the number density of  $\text{Ar}(^3P_0)$  at the interaction region is determined to be typically  $3 \times 10^9 \text{ cm}^{-3}$ .

The ultraviolet radiation required to excite the transitions is obtained by frequency doubling<sup>3</sup> the output of a tunable pulsed dye laser operating at 10 pps in the visible.<sup>6</sup> The resultant uv beam has a linewidth of  $0.5 \text{ \AA}$ , a peak pulse power of several kilowatts, and a pulse length of 5 nsec. The wavelength determinations are made using a Jarrell-Ash  $\frac{1}{2}$ -m spectrometer and are considered accurate to  $\pm 0.25 \text{ \AA}$ . The mean power, and hence the mean photon flux, in the laser beam is determined using an Eppley thermopile.

The experimental results, which display a number of sharp resonances, are shown in Fig. 1. The ion count rate, typically  $0.1\text{--}1.0 \text{ sec}^{-1}$ , is normalized both to unit photon flux and to unit metastable-atom density. The error bars represent one standard deviation of the mean of the

observed count rate. The results may be interpreted with the aid of Fig. 2, an abbreviated argon term diagram, which includes, in addition to the metastable levels and ionization limits, the series of terms  $3p^5(^2P_{1/2})np'[\frac{1}{2}] J=1$  which are optically coupled with the  $\text{Ar}(^3P_0)$  state. These term values are known for  $n \leq 8$  from spectroscopic data, and extrapolation using a quantum-defect method is used to obtain the term values for  $n > 8$ . These results agree with those obtained experimentally to within the experimental error of  $\pm 6 \text{ cm}^{-1}$  and the assignment of principal quantum numbers to the measured terms is therefore unambiguous. Terms of the type  $3p^5(^2P_{1/2})np'[1\frac{1}{2}] J=1$  are also optically coupled to the  $\text{Ar}(^3P_0)$  metastable state. However, the term values derived from the spectroscopic data differ from those of the corresponding terms in the  $np'[\frac{1}{2}]$  series by less than  $1 \text{ cm}^{-1}$ ; as a result the two series are not resolved in the present work. The experimental and theoretical results are summarized in Table I.

Also shown in Fig. 1 are  $\lambda_1$ ,  $\lambda_2$ , and  $\lambda_3$ , the wavelengths appropriate to the energy intervals indicated in Fig. 2. It is evident from energy considerations that the  $\text{Ar}(^3P_2)$  metastable atoms cannot contribute to the ion signal within the wavelength range of the present experiment.

It was not possible to determine the shapes or heights of the resonances because of their narrow widths. However, the major peaks have widths less than  $1.5 \text{ \AA}$ , which may be considered as an upper bound because of the  $0.5\text{-}\text{\AA}$  linewidth of the laser. The lifetime against autoionization of the upper states must therefore be longer than

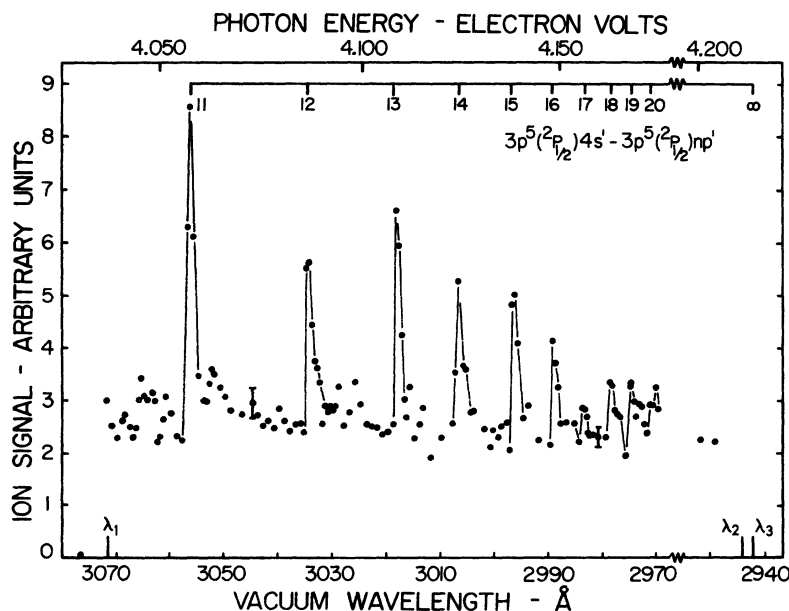


FIG. 1. Ion production in the  $\text{Ar}(^3P_0)$  autoionization region.

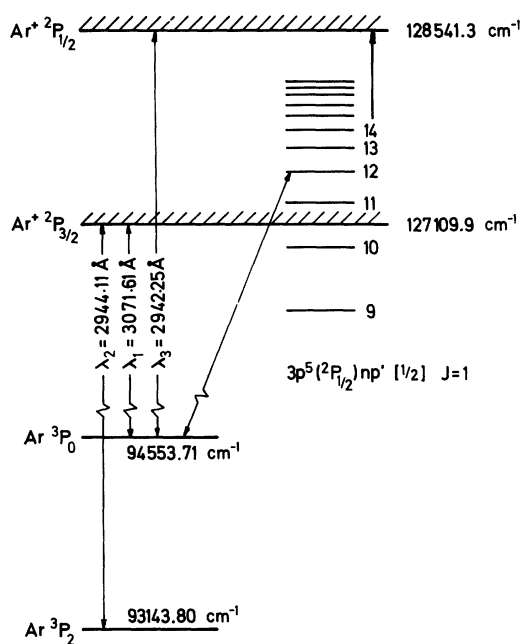


FIG. 2. Abbreviated term diagram for argon.

$2 \times 10^{-12}$  sec. The observation of ion production at wavelengths below  $\lambda_1$  in regions remote from autoionizing peaks is thought to result from direct transitions into the  $P_{3/2}$  continuum. No ion production was observed at wavelengths greater than  $\lambda_1$ .

The results demonstrate that a two-step process, namely, electron-impact excitation to a metastable level followed by optical excitation to a higher level, may be employed to produce significant numbers of atoms or molecules in a selected high Rydberg state. The generation of useful quantities of many such species by photoexcitation from the ground state is not possible because intense tunable narrow linewidth sources, such

TABLE I.  $\text{Ar}(^3P_0)3p^5(^2P_{1/2})4S' - 3p^5(^2P_{1/2})np'$  transition wavelengths.

$n$	Calculated wavelength $np' [1/2] J=1$	Calculated term value $\text{cm}^{-1}$	Measured wavelength $\text{\AA} \pm 0.5 \text{\AA}$	Measured term value $\text{cm}^{-1} \pm 6 \text{cm}^{-1}$
9	3131.49	126487.4		
10	3086.55	126952.3		
11	3056.08	127275.4	3056.3	127273
12	3034.41	127509.0	3034.5	127508
13	3018.43	127683.5	3018.2	127686
14	3006.30	127817.2	3006.8	127812
15	2996.87	127921.9	2996.5	127926
16	2989.38	128005.5	2989.0	128010
17	2983.34	128073.2	2983.8	128068
18	2978.40	128128.8	2978.5	128128
19	2974.30	128175.1	2974.8	128169
20	2970.86	128214.0	2971.0	128212
21	2967.95	128247.0		
22	2965.46	128275.3		

as pulse lasers, are not available at wavelengths below  $2300 \text{\AA}$ . High Rydberg states may be produced by electron-impact excitation from the ground state but the energy resolution is such that, in general, individual upper states may not be selected.

It is hoped that the resolution and precision of the data may be improved by the use of a frequency-doubled mode-locked cw dye laser currently under development. In this connection it is important to remember that the use of a well-collimated beam of atoms traveling perpendicularly to the photon beam greatly reduces effects due to Doppler broadening, thereby permitting high-resolution work to be undertaken.

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